DEVELOPMENT AND EVALUATION OF AN IRRITANT GAS PLUME DISPERSION MODEL FOR EPIDEMIOLOGIC STUDY

A DISSERTATION

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Dev D. Jani, MPH

APPROVED BY COMMITTEE:

Roy Rando, ScD
Erik Svendsen, PhD
Jeffrey Wickliffe, PhD
Jeffrey Shaffer, PhD
Mark Wilson, PhD
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ABSTRACT

Atmospheric transport and dispersion modeling systems are often used in assessing human exposures to chemical hazards. Models validated through quantitative and qualitative evaluation can be applied to epidemiologic study. Here, we modeled the 2005 Graniteville, South Carolina, USA railcar release of chlorine using dense gas plume dispersion models including the Hazard Prediction and Assessment Capability (HPAC) and Areal Locations of Hazardous Atmospheres (ALOHA). The release volume (54,915 kg) and rate was estimated by an engineering analysis combining semi-quantitative observations and fundamental physical principles. The use of regional meteorological conditions was validated by statistically (correlation, mean bias, root mean square deviation) comparing 1,024 HPAC concentration and surface dosage point estimates generated by two source-location weather data sets. An improved HPAC model was then statistically (correlation, root mean square deviation) compared to the earlier HPAC model using up to 9,446 surface dosage sampling points paired in time and space. The older HPAC model consistently overpredicted compared to the newer, refined model. When compared to HPAC, the ALOHA model significantly overpredicted downwind, centerline concentrations (up to 55 times that of HPAC). The refined HPAC model was then evaluated against post-incident environmental indicators of exposure such as phytotoxicity, corrosion events, deposition benchmarks, casualty data and exposed animal health outcome. A further sub-analysis was performed by comparing observed dog health outcome-derived exposure estimations versus model-predicted exposure.
This statistical sub-analysis showed good agreement between observed and estimated, particularly when a sub-cohort of indoor dogs was excluded to determine the impact of structural shielding. Although the model was favorably evaluated based on literature-established standards, further assessment should be performed before the model can be fully validated and applied in human epidemiologic study to estimate acute exposures.
BACKGROUND AND SIGNIFICANCE

The principles of public health, a field defined by the emphasis on population-level wellbeing and vitality as it relates to morbidity and mortality, has dramatic influences on political, socioeconomic and legislative processes. A large portion of public health resources are often devoted to identifying, analyzing and mitigating potential adverse impacts of environmental exposure to contaminants. Indeed, advances in technologies ranging from body-substance isolation (i.e. personal protective equipment) to water purification systems have served as important interventions in ensuring that human, animals and ecosystems are not adversely impacted due to exposure to toxic substances. Particularly, the fields of toxicology and exposure assessment seek to examine these impacts and implement data-driven protective actions such as regulations that limit exposure to industrial chemicals. Toxic industrial chemicals (TICs), particularly pulmonary irritant gases or toxic inhalation hazards (TIHs), are used widely in science, industry and warfare. The increasing volume of industrial chemicals transported via railroad, highway, pipeline, air, and marine traffic presents unique consequence management implications, particularly in terms of public health and safety. Of these modes, rail transportation represents the second largest by volume (after road) and is often the primary mode of choice for TICs and TIHs (US DOT, 2015).

Chemical commodities are transported by rail between manufacturers, consumers and transfer locations such as ports, intermodal yards and terminals. Many communities - particularly those which host major chemical and/or
transportation industries - have invested considerable resources in commodity flow studies and other means to better understand the risks associated with potential exposure to these chemicals. The efficiencies of rail transportation (each tank railcar can potentially transport chemicals equivalent to three truckloads) has resulted in particular emphasis on the chemicals transported via this mode such as chlorine. Chlorine, a dense gas and potent pulmonary irritant, is among the top five most common toxic inhalation hazards (TIH) transported by the U.S. railroad system and used extensively in many major manufacturing areas (Jones et al, 2010). Because the elemental form of chlorine does not exist naturally in high concentrations (due to high reactivity), most human exposures to chlorine gas occur occupationally, purposely or accidentally (ATSDR, 2010). While chlorine, a dense gas, was used as a warfare agent in the early to mid-20th century, the number of malicious incidents involving chlorine gas has decreased extensively since ratification of the Chemical Weapons Convention (CWC). Yet, the frequency of accidental releases has remained fairly constant (i.e. Macedonia, Texas [2004], Graniteville, South Carolina [2005], Tacoma, Washington [2007]), among others (see literature review). The important nature of chlorine as an industrial chemical and ease of weaponizing as a terrorist agent supports the notion that releases will continue to occur (CDC, 2005; Jones et al, 2010). As such, there is an urgent need to assess the public health implications - particularly the toxicological, ecological and socioeconomic effects - of these releases for effective population health interventions.
The catastrophic, large-scale release of a chemical such as chlorine can have profound political and socioeconomic impacts. The 2005 railcar release of chlorine in Graniteville, South Carolina resulted in major changes to the small industrial community including the shutting of several major milling companies which had continuously operated for over a century. Immediately following a release, the immediate priority is always the protection of life. The processes and methodologies utilized during emergency and disaster response are constantly modified as best practices informed by public health research and practice are established. The United States, through a variety of intramural and extramural research, has long studied the mechanisms and effects of catastrophic chemical releases. Even during the development of this project, a multidisciplinary consortium led by the U.S. Department of Homeland Security is well into the planning for the second phase of the Jack Rabbit II field trials. These trials, conducted at the Dugway Proving Grounds in Utah, will release large quantities of chlorine and other TICs for purposes of studying transport, dispersion and interaction of these chemical gases with environmental features such as diverse topography, vegetation and manmade structures. Yet, the largest of these releases do not accurately replicate the amount of chemical gas that may be, or has been, released when a fully loaded tanker railcar or other storage/transport vessel is ruptured. This gap is where atmospheric transport and dispersion (or plume) models are immeasurably valuable.

Plume dispersion modeling has progressed considerably from the simple gaussian models of the 20th century to advanced algorithmic and integrated
software systems which can simulate micro-meteorology, randomness, terrain effects, and dynamic spread. This increasing level of sophistication has allowed for the application of these technologies to public health; in 2009, Zou and colleagues concluded that modeling systems are becoming primary tools in epidemiologic study (Zou et al, 2009). Atmospheric dispersion models, as a minimum, require two sets of input parameters: source term, which is the physical description of the release itself, and meteorology. The latter is often considered the largest influencing factor in gas transport and dispersion, although the physical characteristics of gases such as density are highly important (Hanna et al, 1982). For dense gases such as chlorine, topography will have a larger impact although many widely distributed modeling systems do not take into account this influence. As a result, the variability in sophistication results in widespread variance in predictive accuracy, particularly for events involving a dense gas. Plume dispersion software will often over or under-predict the exposure limit isopleths, forcing emergency responders to implement highly conservative public safety interventions and rendering accurate use in public health studies all but null. This presents a critical gap because of the aforementioned need to study these impacts. Although numerous studies concerning the health effects of chlorine exposure have been published, most are limited by the lack of prior knowledge of the respiratory physiology of the exposed, small sample sizes and the lack of well-characterized data such as duration, extent and concentration (Jani et al, 2015). The field of atmospheric dispersion modeling is well suited as a valuable tool in public health studies and
a method to move this sub-field of exposure science into the proactive realm (BASC, 2003; Farago et al, 2005). But, these models must first be evaluated for predictive accuracy before they can be utilized for human toxicology and epidemiology applications.

The process of refining modeling systems to improve predictive accuracy involves, among other approaches, analysis of agreement with post-release environmental indicators of exposure. While field exposure indicators from field trials (such as Jack Rabbit I and II and Joint Urban 2003) can provide useful eco-toxicological data to which estimations of exposure can be compared, the best comparative opportunities generally derive from actual releases. But, the unpredictable nature and frequency of releases makes continuous, real-time monitoring nearly impossible to attain outside of industrial facilities. The majority of these facilities are not located in areas of high population and vulnerability where the catastrophic release of toxic gas would have the highest consequence. As such, data is usually limited to that collected post-release but can still be used in the evaluation of atmospheric transport and dispersion modeling systems. Ultimately, based upon the assessment, the modeling system can be improved by re-engineering the algorithmic basis or incorporating newer calculation methodologies so the output is in better agreement with what would be the observed environmental impact. These validated models can then be used to generate accurate and precise estimations of personal exposure, which in turn can be used with confidence in epidemiologic studies. The focus of this project is the development and evaluation of a chlorine plume dispersion model that may
be used to estimate exposure in subsequent epidemiologic studies of the Graniteville, South Carolina, USA 2005 accidental tanker railcar release of chlorine.

On January 6th, 2005 at 2:39 AM Eastern, a train (Norfolk Southern Railway Company NS 192) traveling at approximately 76 km/h collided with a parked train (NS P22) when an improperly aligned switch resulted in the train being diverted away from the main track. As per the official accident report, the outgoing crew mistakenly left the switch turned towards the industrial mill spur. The collision resulted in the derailment of three locomotives, 17 railcars of which three tank cars contained chlorine; of these, one ruptured and released nearly ⅔ of the total commodity volume (NTSB, 2005). The railcars were of the DOT 105J500W type, which typically hold up to 81,646 kg of pressurized liquid chlorine. The rapid release and phase change of liquid chlorine to gas (Cl2) yielded a large, dense plume of chlorine inundating the surrounding community with transport and dispersion observed several kilometers downwind. The collision and release resulted in nine fatalities (train engineer and eight civilians), over 550 hospitalizations and the evacuation of nearly 5,400 from the surrounding area (NTSB 2005a).

Situated in a small valley formed by Horse Creek, Graniteville is an unincorporated community located in South Carolina, United States of America about 4.5 miles west of Aiken and 10 miles northeast of Augusta, Georgia. While it is predominantly a mixed rural and suburban area, population activity was centered on a complex of textile mills which had continuously operated for over a
century prior to the 2005 accident. Of these, the Avondale Mills company was the most prominent and site of the accident. The rail track runs in a north to south direction through Graniteville, separating the residential (east) neighborhoods from primarily industrial (west) complexes. The industrial spur on which NS P22 was stationary diverges from the aforementioned main line and proceeds into the Avondale Mills complex. The release resulted in widespread human and animal mortality/morbidity and current research work to identify the pulmonary health effects (notably within the Graniteville Recovery and Chlorine Epidemiology [GRACE] consortium) will be advanced by the application of an evaluated atmospheric dispersion model which can estimate personal dosage/exposure with high predictive accuracy.

Although the primary focus of this project is the evaluation of an irritant gas plume dispersion model specific to the Graniteville incident, the analytic methodologies, research strategy and limitations can be extrapolated to represent any similar evaluation process. It builds upon established literature by utilizing many of the techniques that have been developed as it relates to the evaluation of atmospheric transport and dispersion modeling. Lastly, this project has significant implications for a growing yet fairly modest field that emphasizes the use of validated irritant gas plume dispersion models for specific public health and epidemiology applications. Large-scale, longitudinal etiologic and toxicology studies are difficult and costly to conduct; considerable efficiency can result from using validated models as a research methodology.
LITERATURE REVIEW

The literature review conducted throughout the development of this study and summarized here focuses on the physical characteristics and toxicity of chlorine (as our toxic inhalational chemical [TIC] of interest), the history and science of atmospheric transport and dispersion modeling, and the established literature as it relates to the Graniteville incident.

Chlorine (Cl$_2$), under normal temperature and atmospheric pressure, is a greenish gas with a uniquely identifiable odor (Turner et al, 1990; ATSDR, 2010). The chemical has a molecular weight of 70.906, density of 3.214 and a relatively low boiling point of 238.4 K (Turner et al, 1990). When chlorine reacts with water, it dissociates into hypochlorous and hydrochloric acids and results in the release of oxygen free radicals. Discovered over 200 years ago, the chemical has become one of the top industry-consumed and transported commodities due to its high reactivity and weak bonding characteristics; it is used in nearly every sector spanning transportation, public health, agriculture and petrochemical manufacturing (Chlorine Institute, 2016). Due to the high volume of production, consumption and transport, chlorine has been the primary hazard in a large percentage of TIC releases starting with its application as a war gas in the 1920s. During World War I, over 150 tons of chlorine was released across the European battlefront, resulting in 1,843 casualties in the American Expeditionary Forces (Das, 1993). In 2005, the railcar release of chlorine in Graniteville, South Carolina released an estimated 54,915 kg in less than two minutes, resulting in nine fatalities, over 500 hospitalizations and the evacuation of over 5,400
residents (Jani et al, 2015). The 2004 industrial release of approximately 41,000 kg in Macdona, Texas resulted in two fatalities (Hanna et al, 2008). A railcar release in 1978 in Florida resulted in eight fatalities (Jones et al, 1986). Similarly, a railcar release in San Luis Potosi, Mexico (1981) resulted in 14 fatalities and an infant was killed in La Barre, Louisiana (1961) following exposure to liquid chlorine from a freight train (Costero, 1983; Joyner, 1962). Other releases in the past century include Morganza, Louisiana (1969), Alberton, Montana (1998) and twice in Springdale, Arkansas (2010). Upon release, the dense physical nature of chlorine gas emphasizes gravitational slumping and the chemical tends to disperse close to ground level, hugging geographical contours and sinking into valleys. Due to this heavier-than-air characteristic, chlorine releases will often exhibit greater spread at the release (source) site, often in an upwind and uphill direction when large quantities are released.

**Human, Animal and Vegetation Toxicity**

Regarding chlorine exposure and toxicology, although accidental releases have resulted in deaths within the past century, there is a somewhat limited literature set in which measurements of acute lethal exposure concentrations in humans were made. A series of studies which exposed volunteers to chlorine for up to 15 minutes were performed between 1980 and 2000 and contributed to the human toxicity profile (Anglen, 1981; Rotman et al, 1983; Schins et al, 2000). There is considerable literature on the acute effects of exposure in animals such as horses, primates, dogs and rodents (a comprehensive database of over 100
manuscripts has been collected). In fact, most chlorine literature today still references or gives homage to the 1920s work of Underhill and Winternitz of Yale University who studied the effects of chlorine exposure during the World War I (Underhill, 1913; Winternitz, 1920; Winternitz et al, 1920). This body of produced literature effectively paved the toxicological foundation for all war gas studies in subsequent decades. Much of the literature which focuses on human health effects is extrapolated from animal studies, cognizant of the similarities between humans and other animals in terms of respiratory function and structure and that effects are often similar. In both humans and animals, the primary exposure targets of chlorine gas are the respiratory airways and other mucous membranes (ATSDR, 2010). Exposure generally occurs only by inhalation as the surface layers of the skin lack high levels of mucous and watery membranes. Based upon studies of high-dose exposures from its use as a chemical weapon (World War I and more recently the Syrian conflict) and accidents such as Macdona (Texas), Tulare (California) and Graniteville (South Carolina), a series of benchmark exposure levels have been established in toxicology literature and used by governmental agencies such as the Centers for Disease Control and Prevention (CDC), Environmental Protection Agency (EPA) and Agency for Toxic Substances and Diseases Registry (ATSDR) for regulatory purposes.

These studies indicate that exposure to as little as 1-3 ppm for one hour may result in tolerable irritation of the mucous membranes; 5-15 ppm produces greater respiratory tract and eye irritation. Humans have developed a remarkable ability to detect (via olfactory sense) chlorine at very low concentrations (0.2 - 3.5
ppm) and the pungent odor generally deters prolonged exposure (Ellenhorn and Barceloux, 1998). At around 30 ppm, humans begin to experience chest pain, dyspnea and slight hemoptysis as the chemical reacts with water to form hydrochloric acid (HCL). Exposures to 40-60 ppm results in noticeable pulmonary edema and death generally occurs at 430 ppm exposure for 30 minutes, or less than five minutes exposure at 1,000 ppm (ATSDR, 2010). It is important to note that in the large-scale, catastrophic release scenarios such as Graniteville, concentrations quickly exceed 1,000 ppm in large distances from the release site and asphyxiation due to displacement of oxygen is often the cause of death as opposed to the actual toxicity of chlorine gas itself (Van Sickle et al, 2009). In regards to carcinogenicity, the EPA, International Agency for Research on Cancer (IARC), other health authorities have not highlighted any particular cancer risk of chlorine as of 2016. Based upon the established toxicity literature, ATSDR has defined the minimal risk levels (MRLs) for inhalation exposure to chlorine as 0.06 ppm for 14 days or less, 0.002 ppm for 15-364 days and 0.00005 ppm for 365 days or more (ATSDR, 2010). In regards to more acute exposures, the aforementioned human exposure studies coupled with data from animal studies has established LC50, or the lethal concentration at which 50% of an exposed human individual would be killed, at approximately 364 ppm for ten minutes and 210 ppm for 30 minutes (Withers and Lee, 1985; Prater, 1990). While these values have been established for the average population, the 10-min LC50 can be estimated as low as 173 ppm and 30-min LC50 as 100 ppm for individuals with pulmonary or other physical health susceptibility. In a 1947 study,
Chasis and colleagues reported tracheobronchitis in 33 patients 24-48 hours post exposure to a 100 pound liquid chlorine release in a Brooklyn subway station (Chasis et al, 1947). This particular study, like many others, is limited due to sample size and the lack of specific demographic information and possible confounders. The first study to utilize pulmonary function test (PFT) measurements was conducted in 1967, where 59 longshoremen exposed to a chlorine tank leak during removal from a cargo transfer operations showed significantly abnormal vital capacity, increased elastic work and decreased diffusing capacity (Kowitz et al, 1967). In this study, exposure concentration was not recorded so health outcomes could not be compared to exposure. The use of PFT was further expanded by Kaufman and colleagues in 1971, when 18 individuals exposed to a leak in a liquid chlorine storage tank were examined within 48 hours post-incident; airway obstruction was found in the most heavily exposed but resolved within 30 days (Kaufman et al, 1971).

The Morganza, Louisiana derailment of a chlorine tank car was studied by Weill and colleagues in 1969, where 12 subjects were longitudinally studied but exhibited no respiratory symptoms at the time of examination (Weill et al, 1986). The Morganza incident had residual concentrations up to 400 ppm recorded seven hours after the release. Two sisters studied in 1977 after indoor exposure to chlorine gas resulting from an external accident showed reduced pulmonary function 55 months post-incident in one sister, but resolved function within 12 months for the second sister (Chester et al, 1977). In this study, both sisters were smokers which was recorded as a possible major confounder. A 1983
longitudinal study followed 18 students who were exposed to chlorine that leaked into their dormitory ventilation system; although the majority symptomatically recovered within a week, airway obstruction was recorded with 18 hrs and resolved after a few weeks (Hasan et al, 1983). Charan and colleagues followed 19 construction workers exposed to chlorine at a pulp mill in 1985, in which ten showed obstruction in the days following and all 19 were asymptomatic after two years (Charan et al, 1985). In this study, it was concluded that while acute exposure may cause immediate pulmonary changes, the small sample size created difficulty when attempting to discern residual health effects. The Youngstown, Florida train derailment and release of approximately 45,000 kg of chlorine was studied in a longitudinal cohort of 116 exposed individuals (Jones et al, 1986). Here, it was shown that PFT changes were not associated with distance from spill or severity of initial injury, in contradiction to similar studies. Ploysongsang and colleagues followed four men exposed to chlorine due to a container leak at a swimming pool who showed slight pulmonary restriction up to one month post-incident, but resolved all pulmonary health issues after this time (Ploysongsang et al, 1982). A cohort of 14 industrial workers exposed to chlorine leaking from an factory unit were studied for six months in 1989, after which it was found that those with chronic obstructive airway diseases (COAD) had greater obstruction compared to the non-COAD group (Abhyanker, 1989). Given and colleagues published a case report in 1989 which followed a female infant for two years after being exposed to chlorine gas fumes from an industrial accident; here, obstruction was recorded for several months afterwards, possibly
leading to the conclusion that infants are predispositioned to greater pulmonary health effects (Given et al, 1989). However, in this study, maternal smoking exposure may have served as a confounder. Donnelly and Fitzgerald also produced a case report which showed that a 33 year old male exposed to chlorine gas from an industrial accident had persistent obstruction up to six years post-exposure (Donnelly and Fitzgerald, 1990). A longitudinal study of 20 millworkers exposed to an approximate 1,000 ppm concentration of chlorine following a loading accident showed high airway obstruction and stiffening of airways after 12 years (Schwartz et al, 1990).

Moulick and colleagues reported 82 factory workers who exhibited throat irritation, diminished PFT and other pulmonary issues for up to one year after being exposed to chlorine leaking from a storage tank (Moulick et al, 1992). In this study, a concentration of 66 ppm was measured two hours after the leak. Moore and Sherman published another case report in 1991 which showed that a 25 year old male exposed to chlorine gas in a sewer system suffered from recurrent bouts of asthma and severe persistent obstruction over four year period (Moore and Sherman, 1991). A chlorine plume released from a factory in Georgia exposed three police officers who showed bronchial hyperresponsiveness at 2.5 years post-incident (Schonhofer et al., 1996). Lemiere and colleagues followed a 36 year old non-smoker male exposed to chlorine dioxide mixed with water and reported that this type of exposure can result in acute, marked but partially reversible pulmonary abnormalities (Lemiere et al, 1997). Kilburn followed 13 female nursing home employees exposed to approximately 5-50 ppm of chlorine
(based upon observations) with flu-like symptoms that sustained for months (Kilburn, 2003). A 23 year old non-smoking male exposed to chlorine gas at a fitness center exhibited diminished PFT 96 hours post-exposure and full clinical recovery within five months (Parimon et al, 2004). Bonetto and colleagues followed ten children for 15 months after being exposed to chlorine gas during a swimming lesson; all cases exhibited respiratory distress and diminished function with certain inflammatory biomarkers present for several months (Bonetto et al, 2006). A nine year old female was followed for four months following a similar exposure and dyspnea and pneumonitis was apparent after 12 hours, with the child exhibited mild obstruction up to four months post-exposure (Vohra and Clark, 2006). A common limitation in many of the above described studies in addition to small sample sizes is the lack of definitive concentration measurements at the time of incident, thereby creating difficulty to perform a complete epidemiologic analysis.

As briefly mentioned above, far more significant literature exists on the effects of exposure in animals. Following the initial work of Eulenberg in the 1860s, K.B. Lehmann performed a series of experiment on animals (mainly dogs, rabbits, cats and rodents) to study the effects of repeated exposure, simulating that which a factory worker may experience. Dr. Lehmann found that some dogs could tolerate up to 40 ppm of constant chlorine exposure for 4-6 hours, mainly due to behavioral instincts such as using the paws to filter and absorption by the fur and skin. Underhill and Winternitz propelled this work forward in 1919 mainly due to the use of chlorine during World War I; their studies utilized dogs exposed
to acute and chronic levels of chlorine gas (Underhill, 1919; Winternitz, 1919). In an initial study using 112 dogs exposed to chlorine gas for 30 minutes, the colleagues found that the approximate LC50 was 650 ppm. As exposure concentrations increased, the ability of the animal to tolerate and/or recover diminished rapidly and pulmonary edema was readily observable. Lehman studied the effect of both continuous and interval exposure to single dogs and concluded that exposure time may not be correlated to health effects and outcomes (Lehman, 1899). Further, he observed that dogs because acclimated to low levels of exposure and built up tolerance. In a similar study with cats, it was noted that the ability to build tolerance was not as profound as dogs.

Other animals have also been used as models in exposure studies. A 1996 study concluded that in terms of exposure, physiology and response, rodents and the Rhesus monkey were the most valid models for translation to assessment of human risk (Ibanes et al, 1996). Withers and Lee have compiled a substantial review of this data beginning with U.S. Army research on dogs and other war service animals (Withers and Lee, 1985). The military research showed that while exposures above 870 ppm acutely were fatal in military working dogs, those below 650 ppm often produced non-lethal morbidity. A 1940 study in rodents, namely rats and mice, showed that exposure of rats to 1,000 ppm resulted in death within 1.7 hours, with the majority expiring within 20 minutes (Weedon et al, 1940). Further studies with rodents have produced 10, 30 and 60-min LC50 estimations of 1,032, 516 and 447 ppm, respectively (Zwart and Woutersen, 1988; Alarie, 1981). The German researcher Fritz Haber (of Haber’s
Law and the Haber-Bosch Process) utilized cats and other animals to show military commanders that chlorine and similar gases such as phosgene are effective chemical warfare agents.

The literature base in regards to chlorine phytotoxicity is somewhat limited. Griffiths and Smith concluded that the extent of plant damage due to chlorine exposure is not a linear correlation (Griffiths and Smith, 1990). Most of the post-incident vegetation studies are almost exclusively visual inspections only; however, a number of experiments in the controlled laboratory environment have been performed to determine exposure thresholds. Due to the variety of flora species present in any given area of exposure and inter-species differences in physiology, it is difficult to derive specific exposure thresholds. Several studies have shown that the sensitivity range of plants to chlorine exposure varies dramatically depending upon species (Brennan et al, 1965; Brennan et al, 1966). In the case of Graniteville, the predominant vegetation was mature pine trees. A 2001 publication by Schreuder and Brewer, researchers at the University of Montana, studied the effects on transpiration, growth and mortality on pine trees following an acute chlorine exposure event (Schreuder and Brewer, 2001). Over the span of three years, both species of pine studied showed foliar injury, decreased photosynthetic efficiency and increased rates of cuticular transpiration until the affected needles defoliated. In laboratory studies where different types of vegetation was exposed to chlorine gas, damage thresholds of less than 5 ppm for two hours were apparent (Sikora and Chappelka, 1996; Buckley et al, 2007). Brennan and colleagues studied three species of pine and found that three hours
of exposure to 1.0 ppm of chlorine was sufficient to cause visible effects
(Brennan et al, 1966). Phytotoxicity has been used to evaluate dispersion models
when data is available (Buckley et al, 2007; Griffiths et al, 1990; Shreuder and
Brewer, 2001; among others). It has been also been concluded that vegetation
can significantly attenuate the transport and dispersion of large-scale releases,
particularly during stable atmospheric conditions (Khan and Abbasi, 2001).

**Estimating Chlorine Transport and Dispersion**

Chlorine is generally stored and transported in pressurized containers as a
liquid, or transported over large lengths of pipeline as a gas (Chlorine Institute,
2016). Due to its importance in industrial processes, annual domestic production
exceeds 13,000,000 metric tons, in addition to approximately 1,000,000 metric
tons of import (ATSDR, 2010). This large volume of production and transport, it is
one of the most common released TICs (examples of releases within the past
century are highlighted earlier in this literature review). Indeed, approximately
88% of the total environmental air releases reported to the Toxic Release
Inventory (TRI) in 2006 was chlorine (ATSDR, 2010). Between 1993 and 2000,
over 950 chlorine release events were reported to ATSDR, with over half
involving release into the air (ATSDR, 2010; Horton et al, 2002). Upon release
from a pressurized tank, the chemical tends to phase change back into its normal
gaseous form; however, a rapidly occurring release will often be composed of
both liquid and gas chlorine. The dense nature of the gas hinders immediate
transport and dispersion out of the affected area (depending upon meteorological
conditions) compared to many chemicals, but the high reactivity tends to limit the
time in which it remains in the environment. In addition to removal mechanisms such as dry deposition into soils, photolysis in the air and conversions in water reduce the half-life to the order of minutes, if not seconds. Due to the risks posed by chlorine exposure, it has been the focus of many studies and applications using atmospheric transport and dispersion models.

In its basic form, an atmospheric transport and dispersion model is a software or toolkit which utilizes information from a potential or actual release - such as the source terms, meteorological conditions and topographical features - to predict the transport and dispersion of a toxic chemical away from the release site. Most dispersion models have a basic chemical library which includes the most common hazardous commodities and their physical characteristics such as density, reactivity and half-life. The modeling of air dispersants using mathematical formulas dates back to the early 1930s, when Sutton, Taylor and colleagues researched methods by which to model the movement of air in the atmosphere. This work was greatly propelled forward in the mid-1940s and 1950s by Stewart, Gifford, Hewson and colleagues who focused on the need to model pollutants released from elevated sources such as smoke stacks. In the 1960s, Gifford, Pasquill, Turner and Briggs developed many of the Gaussian principles that are the basis for common dispersion models used today (i.e. Areal Locations of Hazardous Atmospheres [ALOHA], PUFF-PLUME). These models assume that the air pollutant distribution has a normal probability distribution and are most useful for continuous, buoyant plumes. Models such as Hazard Prediction and Assessment Capability (HPAC) and the National Atmospheric
Release Advisory Center (NARAC), which are significantly more advanced, utilize the Lagrangian approach as opposed to just Gaussian principles. In these models, a moving frame of reference is used to follow particles and compute their trajectories as they disperse and transport away from the source point. These models often also incorporate topography and dynamic micro-meteorological data - multiple locations and surface/upper observations - in their calculations. Additionally, these Lagrangian models often have the ability to track moving receptors and provide dosage estimations, which is particularly important for purposes of post-incident exposure assessment and/or epidemiologic application.

While there is a body of literature which utilizes dispersion modeling to crudely assess human exposure, the number of studies which utilize models for purposes of epidemiologic study, particularly following an acute, high-dose exposure such as Graniteville, is severely limited. Due to the increased scrutiny that error in dispersion modeling has gained, there has been particular emphasis in validating established modeling systems against environmental indicators of exposure collected post-release (i.e. one of the key focuses of this project). Simply put, this involves comparing model predictions with observations produced by instruments, other models or analyses. There is a large body of established literature in the area of evaluating atmospheric transport and dispersion models ranging from government-owned models such as the ALOHA and HPAC to proprietary models such as TRACE and PHAST. The primary goal of these evaluation studies is not only to determine predictive accuracy, but to
also identify which models are best suited for planning, response and other types of applications. As an example, several models, including HPAC, were compared to field experiment-derived mesoscale datasets of sulfur hexafluoride tracer gas by Chang and colleagues (Chang et al, 2003). This study found that only around 50% of HPAC predictions were within a factor of two of the observations. In URBAN 2000, the same tracer gas was again used in urban (Salt Lake City, Utah) trials and compared to HPAC predictions (Warner et al, 2004). Here, HPAC overpredicted the observed concentrations and dosages. Similarly, Hanna and colleagues compared HPAC to the Joint Urban 2003 field trials in Oklahoma City and found that while overprediction was common, there was relatively good agreement between the predicted and observed plumes (Hanna et al, 2007).

Beyond those noted above, there have been several other experiments with the focus of identifying agreement between estimated and observed plumes (Hanna et al, 2008; Warner et al, 2006a; Warner et al, 2006b; Warner et al, 2005; Warner et al, 2004; Pullen et al, 2005; among others). The Jack Rabbit trials (I and II, which is currently in the execution phase) at the Dugway Proving Grounds in Utah are one example of the large-scale experiments being performed to study gas behavior and to validate existing modeling systems.

The role of deposition, especially dry deposition and reactions with soil-based acids for dense gases such as Cl2, is an emerging area of research and large focus of the Jack Rabbit experiments (see Hearn et al, 2012; Hearn et al, 2013; Hanna et al, 2012; Bauer et al, 2013 among others). A multitude of sensors and prepared deposition matrices surrounding the release site are
utilized to analyze the dispersion, transport and interaction of Cl₂ and other gases post-release. For soils, a large influencer is soil moisture and organic species with which the chlorine can quickly react (Hearn et al, 2013). Many dispersion models overestimate the plume impact area because a wide range of removal mechanisms are not accounted for by the models. Dillon reported that based upon atmospheric stability, environmental surroundings (such as greenbelts and structures) may highly influence deposition and can attenuate a highly reactive dense gas plume by 50% within 150 meters of the source point under stable conditions. Even under unstable conditions, this number only doubles to approximately 300 meters. The distance at which deposition reduces the cloud concentration is significantly higher for moderately or non-reactive gases (Dillon, 2009). Jonsson and colleagues performed a model-based study of lighter gases (SO₂ and nerve agents) and found a 50% reduction in total airborne concentration within 500 meters with stable atmospheric conditions and low wind velocity (Jonsson et al, 2005).

A 2010 study commissioned by the U.S. Department of Homeland Security (DHS) Chemical Security Analysis Center (CSAC) and developed by the Institute for Defense Analyses compared HPAC to three proprietary models (CHARM, PHAST and TRACE) (Urban et al, 2010). These models were evaluated against both passive, long-distance (Project Prairie Grass) and dense-gas (Thorney Island) experiments. The Prairie Grass comparison, which utilized two metrics (maximum atmospheric dosage and estimated width of dosage footprint), showed that HPAC, PHAST and TRACE accurately predicted the
phenomenon of reduced dosages near ground level as atmospheric stability increased. Yet, all three of these modeling systems under-predicted dosage near the ground by up to a factor of five, with HPAC under-predicting slightly more than the other two. CHARM tended to not predict properly compared to the other three, especially in the context of dynamic atmospheric stability. In regards to this dense-gas evaluation, the two metrics utilized were dosage and toxic load. All four of the models predicted the gravity-induced slumping effect characteristic of dense gases, but similar to the previous evaluation underprediction was common at centerline receptor points. HPAC and TRACE had higher predictive accuracy with dense gases compared to PHAST and CHARM.

Graniteville Incident

The 2005 Graniteville, South Carolina accidental release of chlorine gas is to-date the largest TIC incident in a populated area within the United States. As such, this incident provides a prime opportunity to examine the reliability and accuracy of plume dispersion models. Buckley and colleagues at the Savannah River National Laboratory (SRNL) studied the effects of deposition into nearby surfaces, including water bodies (Buckley et al, 2012). The SRNL team utilized the SCIPUFF module, part of HPAC, in conjunction with the Regional Atmospheric Modeling System (RAMS) to output a model of the Graniteville release. Then, they compared the model to published data on human health and environmental effects such as vegetation bleaching, fish mortality and estimated deposition. The Buckley study found reasonably good agreement between the
model and indicator data when a deposition velocity of 1 cm/s was observed. It is important to note that Buckley and the SRNL were among the first governmental entities to provide modeling support post-release (Hunter et al, 2005; Buckley et al, 2007; Hunter et al, 2005). Hanna and colleagues compared six common dense gas dispersion models using three incidents, one of which as Graniteville (Hanna et al, 2008). In this study, there was relatively good agreement between the models; however, unlike the Buckley study, the Hanna experiment did not take into account removal mechanisms. Further studies have analyzed the Graniteville release, but largely for purposes of describing existing modeling systems or response provided during the crisis (Buckley, 2005; Meris, 2014; Koffman et al, 2008). A large number of studies have also analyzed the post-incident evacuation process, behavioral processes and health outcomes (Mitchell et al, 2005; Mitchell et al, 2007; Ginsberg et al, 2012; Wenck et al, 2007; Duncan et al, 2011; Dunning and Oswalt, 2007; Clark et al, 2013; Runkle et al, 2013; Mackie et al, 2014; Craig et al, 2013; Abara et al, 2014; Chanda et al, 2010; Culley et al, 2014; Pollock, 2013; among others).

**Statistical Evaluation of Models**

The evaluation of atmospheric transport and dispersion models generally falls into three categories: operational, which examines the user interface and other user-facing capabilities; scientific, which focuses on the actual physics and algorithms; and statistical, which quantifies the degree of accuracy between predictions and observations (Chang and Hanna, 2004). The statistical evaluation of dispersion modeling systems presents a unique challenge due to
the profound differences between simulated/predicted and observed systems. Notably, as described by Oreskes et al (1994), Irwin (2014) among others, the exact validation of a model predicting a natural system is impossible. Dispersion models generally predict ensemble means, in contrast to field observations which are single instances out of infinite possible scenarios. Further, the uncertainties present in models and natural systems result from different sources (stochastic). Indeed, it has been observed that small variations in wind direction often predict plumes that do not overlap the observed plumes at all (Weil et al, 1992). There is large room for bias during the input process (source term etc); however, even with an unbiased input, bias may occur due to the differences between model algorithms. As summarized by Irwin, variance is generally due to four factors: input uncertainty, errors in concentration measurements, software errors, and the intrinsic natural variability (Irwin, 2014; Weil et al, 1992; Venkatram, 1979; Fox, 1984).

As such, there has been much attention directed towards the development of suitable statistical methods for evaluation of plume modeling systems. As a first step, it is often suggested to perform exploratory data analysis, including the development of scatter, quantile-quantile and residual plots to visually examine the data (Chang and Hanna, 2004). After this initial step, further analysis can be performed using a number of established performance measures. In a summary of suitable measures, Chang and Hanna (1991) identified six primary metrics: fractional bias (FB), geometric mean bias (MG), normalized mean square error (NMSE), geometric variance (VG), correlation coefficient (R), and the fraction of
predictions within a factor of two of observations (FAC2). These performance measures (equations below) have been recommended for and utilized by similar studies in evaluating plume models (see Hanna et al 1991, Hanna et al 1993, among others). In these equations, $C_0$ and $C_p$ refer to the observed and predicted concentrations, respectively.

$$FB = 2 \times \left( \frac{C_0 - C_p}{C_0 + C_p} \right)$$

$$MG = \exp \left( \ln C_0 - \ln C_p \right)$$

$$NMSE = \frac{(C_0 - C_p)^2}{C_0 \times C_p}$$

$$VG = \exp \left[ \ln C_0 - \ln C_p \right]^2$$

$$r = \frac{(C_o - \bar{C}_o)(C_p - \bar{C}_p)}{\sigma_o \sigma_{C_o}}$$

Based upon the above criteria, complete unity between the model prediction and observed values would have MG, VG, R and FAC2 equal to 1.0, and FB and NMSE equal to 0.0. These metrics have been consolidated into the BOOT software, originally developed by Hanna et al (1991, 1993), which has been used by many larger model validation/evaluation studies such as those by Ichikawa et al (2002), Nappo et al (2001) and Mosca et al (1998). Further, it has been included as part of the larger Model Validation Kit, which was first developed as part of the Harmonisation within Atmospheric Dispersion Modeling for Regulatory Purposes international conferences.

There are several other approaches in the literature as well. Although not as widely used as the above metrics, the Taylor’s single nomogram method utilizes three performance measures: the normalized mean standard deviation
(NSD), the normalized root mean square error (NRMSE) and the correlation coefficient (R) (Taylor, 2001; Gates et al, 1999). In the Taylor approach, a perfect model would have R and NSD equal to 1.0 and the NRMSE equal to 0.0. A far more subjective and qualitative method is the Merit in Space (FMS), which depends far less on the detailed distribution and is not particularly utilized for short-term releases with high life safety implications (Mosca et al, 1998; Klug et al, 1992; Wilks, 2011). Both the FMS and similar measure of effectiveness (MOE) approaches are better for long-range releases where the fields can be contoured. The cumulative distribution function (CDF) is primarily used to verify the consistency between model residuals and expectations of uncertainty and while it takes a different approach than the deterministic evaluation, it is usually combined with another quantitative methodology (Lewellen et al, 1985; Weil et al, 1992; Lewellan, 1989). Similar to the CFD approach, the American Society for Testing and Materials (ASTM), an international standards organization, has published the Standard Guide for the Statistical Evaluation of Atmospheric Dispersion Model Performance, originally developed in 2000 and reapproved in April 2015 (ASTM, 2015). The ASTM method, like the BOOT approach, is well suited for short-term releases and was developed primarily as an effort to account for the limitations of directly comparing observations to predictions. As such, the predictions are compared to a grouping of observations by similar conditions and the performance measures are calculated based upon condition averages. This approach represents an alternative method to statistically evaluating model performance, but has many similarities with the BOOT
approach and the latter software has incorporated some of the peripheral ASTM approaches into its calculations. Particularly, the calculation of FB, use of the bootstrap resampling technique to estimate confidence level, paired sampling between observed/predicted, and grouping of data in blocks are all part of the BOOT approach (Chang et al, 2004).

After statistical evaluation, the results must be analyzed to determine usability of the model. Based upon the data produced by the aforementioned statistical measures, Chang and Hanna (2004) have developed three basic guidelines:

- The fraction of predictions within a factor of two of observations is about 50% or greater (i.e., FAC2 ≥ 0.5)
- The mean bias is within ± 30% of the mean (i.e., roughly |FB| < 0.3 or 0.7 < MG < 1.3).
- The random scatter is about a factor of two to three of the mean (i.e., roughly NMSE < 1.5 or VG < 4).

Similarly, Olesen and colleagues (2001) noted that for better modeling systems such as HPAC, the relative mean bias is ±40% and the random scatter is about a factor of two of the mean. This determination involved studies of relatively short-range dispersion, similar to the Graniteville incident. As such, our project utilized some of the above standards to determine if our model is in good agreement with observed indicator data. If so, the model may be suitable for epidemiologic application. Although the model would be specific to the Graniteville incident, the
themes and evaluation methodologies are transferrable to the larger sub-fields within environmental health and environmental epidemiology.
HYPOTHESES AND SPECIFIC AIMS

H1: Generated (modeled) exposure data using HPAC versions 4.04, 5.3 and ALOHA version 5.4.3 will be different.

SA1: Assess improvements in predictive accuracy between Hazard Prediction and Assessment Capability (HPAC) versions 4.04, 5.3 and ALOHA 5.4.3 models of the Graniteville, South Carolina, USA 2005 rail-car release of chlorine.

   SA1.1: Identify the release source term, meteorological data and terrain inputs that will be utilized in the models.
   SA1.2: Model the release using HPAC 4.04, HPAC 5.3, and ALOHA version 5.4.3
   SA1.3: Determine accuracy between the HPAC 4.04 and 5.3 models at +15, +30, +60, +120, +180 and +240 minutes post release.
   SA1.4: Determine agreement between both HPAC models and ALOHA model.

H2: Generated (modeled) exposure data using HPAC 5.3 will differ from observed exposure indicator data.

SA2: Evaluate the Hazard Prediction and Assessment Capability (HPAC) 5.3 model of the Graniteville, South Carolina, USA 2005 rail-car release of chlorine using best available exposure indicator data.

   SA2.1: Identify the best available indicator data.
   SA2.2: Determine accuracy between the HPAC 5.3 model and best available indicator data.
METHODS AND MATERIALS

Specific Aim #1

The overall purpose of this project is to develop and evaluate a suitable atmospheric dispersion model for the possibility of future epidemiologic application. The focus of specific aim #1 was to develop a novel source term, meteorological and other model inputs for the Graniteville incident. These developed inputs have then been used in both the Hazard Prediction and Assessment Capability (HPAC) and Areal Locations of Hazardous Atmospheres (ALOHA) models to generate dispersion plumes. Because only HPAC 4.04 was available at the beginning of this project, phase one of this project also includes a statistical comparison between the 4.04 and newer 5.3 versions of HPAC. Both models will be compared to the ALOHA 5.4.3 model, primarily to emphasize the differences in government-owned atmospheric transport and dispersion models and implications for public health response.

Sub-Aim 1.1 (source term): The essential first element of developing a dispersion model is the identification of the source term. Using established literature and official accident reports, it was identified that the transported commodity was chlorine (Cl₂ - in liquid form due to pressurization) in a U.S. Department of Transportation (DOT) classified 105J500W tanker railcar. An engineering analysis performed in association with Dr. Charles Feigley of the University of South Carolina - Arnold School of Public Health (South Carolina, USA) developed the source term as follows (and reported in Jani et al. 2015):
The progression of events that characterize release of a compressed gas, such as Cl\textsubscript{2}, stored at a temperature less than or equal to its saturation temperature was described by Britter et al. (2011). Release from a rupture initially well below the liquid/gas interface and well above the bottom of the tank can take place in three consecutive stages. Stage 1 begins with the release of liquid Cl\textsubscript{2}. Inside the tank near the interface, Cl\textsubscript{2} starts to boil and a two-phase, foamy layer consisting of bubbles of vapor/aerosol in the liquid forms. This two-phase layer swells, deepens, and descends. Stage 2 begins as the two-phase layer nears the rupture from above, and the release through the rupture becomes two-phase as well. The exact behavior as this material approaches and flows through the rupture is not very well understood as acknowledged by Britter et al. (2011), but some sophisticated models of this phenomenon have been developed such as the w-model (Leung J.C. 1986; Leung J.C. 1990) and the Homogeneous Equilibrium model (HEM) (Richardson S.M. et al. 2006).

Stage 3 occurs if release continues long enough to completely deplete the two-phase layer such that the release from the tank becomes all vapor. The mass flow rate decreases from Stage 1 to Stage 3 (Britter et al. 2011). Note that the transitions from stage to stage are often not distinct. Further complicating this is the formation of an aerosol phase.

For escape of a saturated liquid through a rupture in a container with a wall thickness equal to or less than 0.1 m, the flow approximates that of flow through a sharp-edged orifice. The flow is said to be “non-equilibrium” because the time required for the liquid to pass through the rupture is too short to allow
equilibration to the new pressure condition until it is well outside the vessel; this is often referred to as “choked” flow. Here, the thickness of the tank wall at the site of the tear measured approximately 0.020 m (range= 0.000034 m) (NTSB, 2005b), indicating that thermodynamic equilibrium was not achieved upstream of the rupture during the initial phase of release.

Thus, the earliest release from the tank should have been liquid-phase Cl₂. After release (outside the tank), this liquid jet would have abruptly approached an equilibrium condition at atmospheric pressure, causing “flashing” flow. This complex phenomenon results from the combined effects of rapid evaporation of Cl₂, warming of the Cl₂ jet due to the entrainment of ambient air, and cooling of the jet and the surrounding air through uptake of latent heat of evaporation. Condensed and frozen water was noted on the outside of the tank car near the rupture in photographs.

The methods used here to estimate the rate of Cl₂ emission and the cumulative loss from the tank car were chosen to be appropriate for the ultimate goals of this research: to provide estimates of Cl₂ exposure in Graniteville for participants in health effects studies, not to develop generally applicable approaches for determining pollutant emission, dispersion and transport. This analysis began by calculating the depth of liquid Cl₂ in the car using a tilt angle of 10° reported by a SC Department of Health and Environmental Control (DHEC) responder, which agreed with the approximate angle given as 5-10° reported by the NTSB (2005a), the approximate orientation of the car shown in numerous pictures, and the volume of Cl₂ initially present. Based upon NTSB (2005a)
pictures, the tear on the side of car was a jagged gash very nearly perpendicular to the ground and 4.88 meters from the higher end of the car (the “A” end). The depth of liquid Cl\textsubscript{2} was calculated as a function of the liquid-filled tank volume using a web-based program supplied by LMNO Engineering (2009). Then, to simplify computation further, a cubic equation was derived by regression (R\textsuperscript{2}=0.9989) for directly computing the volume of Cl\textsubscript{2} in the tank from its depth and vice versa. The next step was to compute the combined pressure resulting from the average head pressure of liquid along the tear and the vapor pressure in the enclosed space above the liquid. Using an equation for flow through a submerged opening (Perry and Green, 1984), we estimated that the time required for the liquid Cl\textsubscript{2} level to reach the top of the vertical tear, using the approximation that the two-phase portion of the fluid does not have a significant effect on the mass release rate.

At the beginning of this stage one, the pressure in the Cl\textsubscript{2} gas equaled the vapor pressure of chlorine at the tank temperature, estimated to be -3.3 degrees Celsius (26 F) (NTSB, 2005a), corresponding to a vapor pressure of 317 kPa (46 psia) (Occidental Chemical Corporation, 2000). An overview of the source term information we have used as inputs is shown in Appendix 1.1.

*Sub-Aim 1.1 (meteorology):* The meteorological validation, presented as follows, is necessary to utilize the available weather data sets. At the time of the incident, there was no onsite meteorological station in Graniteville to provide the most accurate weather data for input into the plume modeling software. Conventionally, in lieu of onsite observations, data from the National Weather
Service (NWS) and National Climatic Data Center is often used for planning, response, and investigative modeling. NWS stations are generally located at airports or areas that serve as population centers. Alternatively, the US Forest Service operates Remote Automated Weather Stations (RAWS) which are generally self-sufficient stations located in national forests and similar areas for monitoring forest fires. Information from these mobile stations is transmitted electronically (often via satellite) every hour to the National Interagency Fire Center in Boise, Idaho. We have used archived meteorological surface observations recorded at 13 different RAWS sites collected during the night (and time of incident) on 6 January 2005.

A portable weather station was setup at the incident site late in the morning of 6 January and remained there throughout the duration of cleanup activities. For purposes of validation, we compared archived observational data from the 13 different RAWS sites for five nights beginning on 7 January and ending on 12 January (10 January was excluded due to missing data) with data from this portable site. We modeled the incident in HPAC 4.04 using both the RAWS and portable weather station data (micro-environmental) collected on the aforementioned nights. Concentration (5, 15, 30, 45 and 60-minute) and surface dosage (60-minute) were calculated at 1,024 points (see Appendix 1.2) across a three by three mile grid with identical source terms and correlation, mean bias, and root mean square error between the two models were calculated using IBM SPSS Statistics (Version 20, IBM, Armonk, NY). The goal of this validation was to support the notion that RAWS data collected during the night of 6 January
provided an accurate representation of the incident site micro-environment in Graniteville. Although this meteorological validation was performed using HPAC 4.04, the results and methodology support the use of the RAWS meteorological data with HPAC 5.3 as well.

*Sub-Aim 1.1 (topography)*: The final input parameter is the terrain resolution field. Within HPAC 4.04 and 5.3, both models utilized the “native resolution” function due to the hilly terrain in Graniteville. This setting, coupled with the small 1-km resolution and domain, will emphasize topographical accuracy to the highest ability in lieu of customized terrain maps (which are unavailable for the 2005 Graniteville area).

*Sub-Aim 1.2 (modeling)*: Using the Industrial Transportation (iTRANS) model in HPAC 4.04 and 5.3, the Graniteville release was modeled for up to eight hours post start of release using the source term, meteorological data and terrain settings identified in sub-aim 1.1. The iTRANS model is the de facto HPAC engine used to model the release of a toxic industrial chemical, such as chlorine, from a transportation vehicle. Using the same source term identified in specific aim #1.1 to the greatest extent possible, the Graniteville incident was also modeled in the ALOHA version 5.4.3 software. The plumes from HPAC 4.04 and 5.3 were then plotted either using the intrinsic mapper or ArcMap (ArcGIS, Redlands, CA) as necessary. Several different types of plumes were generated:

- HPAC 4.04 8-hour AEGL (Appendix 1.3)
- HPAC 5.3 8-hour AEGL (Appendix 1.5)
- HPAC 5.3 4-hour AEGL (Appendix 2.1)
The ALOHA plume was also plotted using the intrinsic MARPLOT software, part of the Computer Aided Management of Emergency Operations (CAMEO) software suite. This plume is referenced within manuscript #1. For HPAC 4.04, a comparative graph of 30-minute and 60-minute maximum estimated concentration of chlorine at centerline distances (0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 kilometers) was also developed.

Sub-Aim 1.3 (HPAC 4.04 to 5.3 comparisons): The purpose of sub-aim 1.3 was to quantify the differences between the HPAC 4.04 and 5.3 models. Although the 4.04 model was our initial model of choice, the 5.3 model incorporates several algorithmic improvements which will increase the predictive accuracy of the model itself. Because the evaluation of this model is for possible human epidemiology application, the surface dosage output was determined to be the best parameter to compare. The surface dosage was outputted in both models at a 1.5 meter breathing height in 30-minute post-release intervals for a maximum of four hours: 3:09 AM, 3:39 AM, 4:09 AM, 4:39 AM, 5:09 AM, 5:39 AM, 6:09 AM and 6:39 AM. For purposes of identifying surface dosage sampling points at the aforementioned time intervals, the SCIPUFF Adaptive Grid (SAG) sampling methodology was utilized in HPAC 4.04. This intrinsic approach automatically
identifies sampling locations that best represent the data field and are time-dependent. As such, the density of sampling locations increases as geographic proximity to the source point increases and the number of sampling points differs between the different output times. The same time-dependent sampling locations were utilized in both versions of HPAC when comparing at a certain output time.

The time-dependent data for both models was then grouped into eight bins based upon the standard output categories in HPAC 5.3. The data was consolidated further by collapsing the bins under 1.0 kg-s/m³ into one bin, reducing our 2x8 table into a 2x4 configuration, based upon which frequencies were calculated. These ranges identified were utilized because these are the natural, intrinsic differentiating points within the HPAC software. Further, given that the Graniteville incident was a relatively acute exposure scenario (< 4 hrs until plume dissipation) and in the context of an evacuating human, surface dosage of less than 1.0 kg-s/m³ for a relatively short exposure period are not likely to result in severe health impacts such as incapacitation and/or lethality. Utilizing a mathematical conversion and 30 minute model output timestep, 1.0 kg-s/m³ is roughly approximate to 200 ppm, less than half of the lethality exposure concentration for 40 minutes. Similar to the maximum plume run time, we have elected to use a conservative approach for this. The D2 bin was also expanded into five ranges: 100-199, 200-299, 300-399, 400-499 and 500-599 kg-s/m³ and frequencies calculated. Subsequently, as our focus here is to statistically compare the two model data sets, the median, correlation coefficient r (p = 0.01) and root mean square error (RMSE) were calculated using IBM SPSS.
Statistics (Version 20, IBM, Armonk, NY). Scatter plots comparing HPAC 5.3 (x-axis) and HPAC 4.04 (y-axis) were also developed for each of the eight surface dosage output times, with predictions for both models paired in space and time on a logarithmic scale. A Loess line of best fit was applied as a visualization tool. 

Sub-Aim 1.4 (HPAC 4.04 and 5.3 to ALOHA 5.4.3 comparison): Both HPAC models were compared to the ALOHA output based upon a more simplistic approach using concentration (ppm) due to the inability of the ALOHA software to quantify surface dosage. In manuscript #1, both 30-min and 60-min HPAC 4.04 outputs was compared to ALOHA using three parameters:

- Concentration (ppm) at downwind distances (km): 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0 and 25.0
- Downwind distance (km) to concentrations (ppm): 2000, 400 and 20
- Maximum width (km) to concentrations (ppm): 2000, 400 and 20

In manuscript #2, the HPAC 4.04 and 5.3 60-min concentrations were compared to the 60-min ALOHA concentrations at the downwind distances identified above.

Specific Aim 2

In specific aim one, we identified the best available model for evaluation. In the second specific aim, this model will be evaluated against available environmental indicator data collected in the aftermath of the Graniteville release or defined elsewhere in existing literature and databases.

Sub-Aim 2.1 / 2.2: A wide variety of environmental indicator data was examined for suitability in the evaluation. The first was corrosion data, which was collected several months post-release under the direction of Dr. Lisa Detter-Hoskin of the
Georgia Tech Research Institute’s (GTRI) Materials Analysis Center under contract with several entities involved in the Graniteville incident. This data includes sulfur/chloride concentrations (using x-ray fluorescence [XRF] among other techniques) on common metallurgical surfaces both in the environment (i.e. telephone poles) and the household. There are limited benchmarks in existing materials science research against which this corrosion data may be compared, but it is unclear whether the predicted and observed values can be correlated without performing additional exposure chamber studies of the types of metal surfaces in Graniteville. For this reason, this current project did not utilize the corrosion data fully for purposes of evaluating the model, although this indicator is highlighted as a future direction. A spatial comparison of the plume footprint and corrosion event locations on mill buildings was performed as part of manuscript #3.

Environmental remediation companies immediately contracted by the rail carrier and other entities post-release collected a limited amount of both air and soil samples. The air samples are not usable for this evaluation because they were largely collected in the days and weeks after the incident, which does not temporally match our four hour HPAC 5.3 plume. The soil samples were collected several weeks and months post-release while remediation and resettlement was occurring. The data collected represents over 50 samples from a variety of locations throughout the affected area at depths ranging from surface to 2.4 meters below the surface. This data was also not used because it is unclear of the impacts that environmental degradation would have on the soil
chloride content. Due to the high reactivity of chlorine and numerous elements and organics present in native soil, it is likely difficult to estimate the original deposition concentration in the aforementioned sample locations. This analysis is not impossible to perform though with on-site sampling and chemistry to assess for residual chloride. Due to these reasons, this project did not utilize the soil or air data for purposes of evaluating the model, although the soil indicator is highlighted as a future direction.

There are also a number of databases such as calls placed to public safety answering points (PSAP) and similar human-derived reports. This data was not utilized for this project because of possibly large amounts of bias but could prove useful after further, extensive analysis. But, it should be noted that the eventual goal here is to develop a model that may be suitable for epidemiologic application such as comparing model exposure predictions to the actual health outcomes reported by humans and animals exposed in the plume. For this reason, individuals who were hospitalized and/or received medical care due to chlorine exposure were not utilized for spatial analysis due to the circular nature of that comparison. But, a cursory overview of those within the SCDHEC acute exposure registry and the GRACE study cohort was performed using de-identified databases.

As highlighted in the literature review, there is an existing body of research regarding the phyto-toxicological effects of chlorine exposure. Particularly, a small number of studies have determined approximate exposure thresholds in a variety of plant species including pine. The majority of native forests surrounding
the Graniteville release site were mature pines, so this research may be applied here. Researchers from the Savannah River National Laboratory (SRNL), part of the U.S. Department of Energy (DOE) Savannah River Site (SRS) conducted a spatial vegetation damage survey approximately one month after the release and mapped the extent of visible injury. The researchers also noted that the bleaching effect was limited to a height of approximately 10 meters. For purposes of comparison, the HPAC 5.3 model was adjusted to predict surface dosages and concentrations at a height (z) of 10 meters. Based upon existing phytotoxicity research, a plume was developed which depicted the predicted area at which an exposure of at least 5 ppm was sustained for two hours or more. This plume was plotted in ArcMap and compared to the imported vegetation damage survey shapefile.

The role of deposition in attenuating plume dispersion and transport, particularly due to dry deposition, interactions with vegetation and manmade structures, is an emerging area of research. As highlighted in the literature review, a body of research exists which has examined the deposition rates (or deposition velocity, Vd) in a number of controlled experiments. Based upon these experiments and mathematical extrapolation, approximate benchmarks for deposition have been developed. As presented by Dillon (2005), highly reactive gases such as chlorine may deposit 50% of the total airborne concentration within 150 meters of the release site. As such, a 60-min concentration plume was generated in HPAC and centerline concentration predicted at 100 points in 30 meter intervals starting at the source point to the edge of plume. These values,
originally reported in kg/m3, were converted to ppm and subsequently graphed using Microsoft Excel. The model predicted deposition was then compared with the approximate deposition standards in literature. HPAC includes the ability to estimate unprotected (personal protective equipment) human casualties. For purposes of comparison, the model predicted casualties for a nighttime 2005 population dataset was compared to the actual observed human health outcomes.

There are limited datasets available on animals exposed during the Graniteville release due to the immediate priority of protecting human life. The animal secondary data set utilized for this study was sourced from three different sub-sets: a survey of eight veterinary practices within the Graniteville area who treated exposed pets, the South Carolina Department of Health and Environmental Control (DHEC) Acute Epidemiological Survey which was administered within 48 hours post-release, and the Norfolk Southern/DHEC Housing Inspection Survey (HIS). The majority of the usable animal data was from the first two sub-sets; the HIS focused heavily on the status of the physical residence itself and included minimal information on pet morbidity. The initial larger database, which numbered 303 animals, was reviewed and any animals without reported location information were omitted. With the assistance of a public health veterinarian working as part of the Graniteville Recovery and Chlorine Epidemiology (GRACE) Study, each animal was then classified into one of seven outcome categories based upon reported outcome: died, euthanized due to unrelated reason, missing, injured/ill, no apparent effect, assume no
apparent effect and unknown outcome. The data was trimmed further by removing those animals classified as euthanized (due to an unrelated reason), missing, assume no apparent effect, and unknown outcome. This reduced the overall dataset to 117 animals, comprised of birds (3), cats (32), chickens (6), dogs (63), ducks (2), a ferret (1), fish (5), a frog (1), goats (2), a lizard (1) and a possum (1). These animals were reclassified into three consolidated categories based upon reported health outcome: no health effect, injured, or killed. For spatial comparative purposes, the locations of all animals were plotted in ArcMap along with the plume model.

A further analysis was performed utilizing the dog data (n = 63). Based upon existing toxicology profiles (Underhill 1919), each dog was assigned to experimentally derived 30-min acute exposure ranges by observed health outcome: low exposure/no health effect (\(\leq 250\) ppm), medium exposure/injured (251 - 649 ppm) and high exposure/killed (\(\geq 650\) ppm). Each reported location was geocoded into the HPAC model and peak 30-min predicted exposure was generated for each dog. To identify the role of shielding (i.e. indoor vs outdoor location) and improve sensitivity and specificity, a sub-cohort which omitted all dogs that were reported to be indoors was created (n = 56). For both groups, a comparison of the observed health outcomes and model-predicted exposure was performed by first conducting exploratory data analysis such as frequencies, scatterplots and box plots. Then, chi square analysis (goodness of fit) performed using IBM SPSS Statistics (Version 20, IBM, Armonk, NY).
Final Compilation

The overall methodology, findings and conclusions were compiled in the three manuscript dissertation format that is specified by the Tulane University - School of Public Health and Tropical Medicine. The first manuscript was submitted and accepted for publication; the remaining two are in the process of being submitted to journals for consideration.
MODELING AN IRRITANT GAS PLUME FOR EPIDEMIOLOGIC STUDY
Dev D. Jani\(^1\), David Reed\(^2\), Charles E. Feigley\(^3\), Erik R. Svendsen\(^1\)

\(^1\)Department of Global Environmental Health Sciences, Tulane University School of Public Health and Tropical Medicine, New Orleans, LA, USA
\(^2\)Department of Epidemiology and Biostatistics, University of South Carolina Arnold School of Public Health, Columbia, South Carolina, USA
\(^3\)Department of Environmental Health Sciences, University of South Carolina Arnold School of Public Health, Columbia, South Carolina, USA


Abstract

Plume dispersion modeling systems are often used in assessing human exposures to chemical hazards for epidemiologic study. We modeled the 2005 Graniteville, South Carolina, 54,915 kg railcar chlorine release using both the Areal Locations of Hazardous Atmospheres (ALOHA) and Hazard Prediction and Assessment Capability (HPAC) plume modeling systems. We estimated the release rate by an engineering analysis combining semi-quantitative observations and fundamental physical principles. The use of regional meteorological conditions was validated by comparing concentration estimates generated by two source-location weather data sets. The HPAC model estimated a chlorine plume with 20 ppm outdoor concentrations up to 7 km downwind and 0.25 km upwind/downgrade. A comparative analysis of our two models showed that HPAC was the best candidate for use as a model system on which epidemiologic studies could be based after further model validation. Further validation studies are needed before individual exposure estimates can be reliable and the chlorine plume more definitively modeled.
Introduction

Chlorine gas (Cl₂) is used widely in science, industry and warfare. Today, chlorine is among the top ten industrial chemicals produced in the United States and is used in many major manufacturing areas such as production of automobiles and pharmaceuticals (Jones et al, 2010). The Association of American Railroads (AAR) noted in 2007 that railroads typically transport over 100,000 tank car loads of toxic inhalation hazard (TIH) chemicals annually, such as chlorine and anhydrous ammonia (AAR, 2007). Many of these transportation routes pass through or in close proximity to population centers and other areas in which an accidental release could have detrimental impact on human health. The elemental form of chlorine is highly reactive and, therefore, does not exist naturally in high concentrations. The majority of human exposures occur only occupationally, purposely or accidently (ATSDR, 2010). Indeed, there have been numerous incidents involving chlorine within the past decade such as the intentional releases in Iraq (2007) and Syria (2011, 2014), and accidental releases from railcars in Macedona, Texas (2004), Graniteville, South Carolina (2005) and Tacoma, Washington (2007). The integral nature of chlorine in manufacturing industries and its ease of use and effectiveness as a terrorist agent supports the notion that releases will continue to occur (Jones et al, 2010; CDC, 2005). Accordingly, there is a continuing need to comprehensively assess the toxicological, ecological and socioeconomic effects of these events for purposes of both planning and response.
Currently, large inhalation events involving toxic irritant gases are assessed using a combination of onsite monitoring and comparing injuries to known health effects. The methodology and instrumentation to detect atmospheric concentrations of toxic gases such as chlorine has existed for many years. Yet, the use of continuous monitoring apparatus in settings such as the occupational workplace represents significant investment and preplanned placement, luxuries that are nearly impossible to attain during emergencies due to their unpredictable nature. The initial focus during response to a TIH incident is always the protection of life and property. Therefore, environmental testing is usually only conducted after the initial release has dissipated and it is safe to deploy monitoring equipment.

Many epidemiologic studies concerning the residual effects of chlorine exposure are limited by the lack of prior knowledge of the respiratory physiology of the exposed, small sample sizes, and, perhaps most importantly (and most relevant to this paper), the lack of well-characterized exposure data such as duration, extent and concentration. It is in bridging this gap where the modern science of atmospheric detection and plume modeling is highly valuable (Farago et al, 2005; BASC, 2003).

These algorithmic simulations of pollutant dispersion are important in managing environmental quality and protecting human health. There is considerable variability in the predictive accuracy and robustness of currently available dispersion modeling systems. All models require two basic inputs: source term (physical descriptors of the release itself) and meteorology. It is
commonly believed that meteorology (such as atmospheric stability, wind speed and ambient conditions) have some of the most profound implications on dispersion (Hanna et al., 1982). As an example, a highly stable/less turbulent atmosphere, such as night, will likely result in diminished dispersion. Topography also greatly influences dispersion; however, many mainstream software packages, particularly those targeted towards the first responder and optimized for rapid usability, do not take into account terrain influences during dispersion. Our study focuses on different models with varying sophistication.

The use of air pollution modeling technologies in epidemiologic studies of irritant gas exposure events is an emerging area of research. A review of exposure assessment techniques by Zou and colleagues noted that modeling systems are becoming primary tools in environmental epidemiology studies as robustness increases (Zou et al., 2009). Historically, particularly for incidents involving dense chlorine gas, dispersion models have either over-predicted or under-predicted the exposure limits forcing emergency decisions to be highly conservative. Applications to determine individual exposure estimates for etiologic studies have been largely unsuccessful. Increasing processing power and incorporation of algorithms addressing randomness, variability and the effects of physical and chemical reactions, particularly for dense gases such as chlorine, have yielded increasingly robust model systems. Unlike earlier modeling software, these newer systems are often able to account for dry deposition, ambient reactions and dynamic weather conditions, such as anti-cyclonic phenomena, but with varying accuracy. Simulations of high concentration events
emphasizing the collection of plume migration and eco-toxicological data via field experiments have been performed in studies such as the Joint Urban 2003 (Oklahoma City, Oklahoma) and Jack Rabbit (Dugway Proving Ground, Utah) (NOAA FRD, 2013; ). Such field trials provide markers against which existing models can be validated (Hanna et al, 2008a). These experiments have produced valuable contributions, and further validation against known exposure thresholds and other markers collected in the aftermath of an incident are useful to ensure these computerized models generate accurate and precise point estimates of personal exposure, which are particularly useful for subsequent epidemiologic study. The purpose here is to describe the first step in developing a validated chlorine plume dispersion model that can be used to adequately estimate exposure in subsequent etiologic epidemiologic studies.

**Methods**

*2.1 Description of the exposure event*

On January 6th, 2005 at 2:39 AM eastern standard time a freight train traveling through Graniteville, South Carolina at a speed of 76 km/hr was inadvertently diverted off the main line onto an industrial spur where it collided with a parked train. An incorrectly aligned switch was later determined by the National Transportation Safety Board (NTSB) as the culprit. Both locomotives and several railcars were derailed, including three railcars containing approximately 81,646 kg of pressurized liquid chlorine (Cl₂) each (NTSB, 2005a). While all three railcars were damaged, the integrity of one of these cars was
compromised, resulting in the release of approximately 55,000 kg of chlorine gas into the surrounding community (NTSB, 2005a; NTSB 2005b). Emergency personnel, including hundreds of volunteer firefighters from local and mutual aid departments along with state and federal hazardous materials and investigative assets, responded to Graniteville during the emergency period.

Graniteville is a textile mill town situated within a small river valley. The 2000 census population, most relevant to this paper, was 7,112 (U.S Census, 2000). The collision and release occurred on the industrial track of Avondale Mills, which was a major manufacturer of textiles and employer at the time. The chlorine release resulted in nine fatalities, over 550 people sought medical care in regional hospitals due to respiratory distress, and the evacuation of nearly 5,400 people living and working nearby during the 3-week clean-up period (NTSB, 2005a).

The 2005 Graniteville, South Carolina accidental release of chlorine following a railroad accident is a prime example of the devastating public health impacts that an incident of this magnitude can have on a community. The large-scale exposure to chlorine gas resulted in widespread human and animal fatality and morbidity. Current research projects studying the health implications of this exposure could be strongly advanced by using a validated model to estimate individual dosage. Here, as a first step in producing a validated model, we have modeled the Graniteville accidental release using two atmospheric dispersion models. The selection of these models is explained further in section 2.4.
2.2 Estimation of the Source Term

An essential first step in implementing such a model is to estimate the contaminant release rate and duration. Here, “release rate” is considered to be the flux of Cl\textsubscript{2} through the plane defined as the open gash in the side of the tank car. Initially, the amount of Cl\textsubscript{2} released as a function of time after the accident was estimated using an engineering analysis that combined semi-quantitative observations and fundamental principles. Our results were then compared with the findings of other investigators. Both this study and the comparison studies focused on the period of the highest Cl\textsubscript{2} emission rate, beginning immediately after the accident occurred.

The rate of Cl\textsubscript{2} loss from the tank car was a function of several constants, as well as time-varying, factors. The constants included: the location and orientation of the tank car after coming to rest, the location of the tear on the car, and the size and shape of the tear. The most fundamental time-varying factors were the amount of liquid Cl\textsubscript{2} remaining in the tank and the temperature of the Cl\textsubscript{2}—knowing that these two allows determination of the fluids’ physical properties including vapor pressure, density, viscosity and heat capacity of both liquid-phase and gas-phase Cl\textsubscript{2}.

Information concerning the orientation of the car and of the size and shape of the tear in its side were obtained from measurements, pictures (NTSB, 2005a and 2005b) and interviews with emergency response personnel. These documents contain pictures and descriptions of the leaking tank car and the
jagged, roughly vertical tear in the side of the car, and estimate of the amount of chlorine in the car at several times, and its temperature immediately after the accident. While many of these documents are publicly available, we were able to obtain the maximal amount of documentation using a Freedom of Information Act (FOIA) request. Taking into account the volume of Cl$_2$ in the tank, the tank dimensions, and the angle of repose of the car after the accident, the upper end of the rupture was approximately 1.55 m below the initial vapor/liquid phase.

2.2.1 Background

The progression of events that characterize release of a compressed gas, such as Cl$_2$, stored at a temperature less than or equal to its saturation temperature was described by Britter et al. (2011). Release from a rupture initially well below the liquid/gas interface and well above the bottom of the tank can take place in three consecutive stages. Stage 1 begins with the release of liquid Cl$_2$. Inside the tank near the interface, Cl$_2$ starts to boil and a two-phase, foamy layer consisting of bubbles of vapor/aerosol in the liquid forms. This two-phase layer swells, deepens, and descends. Stage 2 begins as the two-phase layer nears the rupture from above, and the release through the rupture becomes two-phase as well. The exact behavior as this material approaches and flows through the rupture is not very well understood as acknowledged by Britter et al. (2011), but some sophisticated models of this phenomenon have been developed such as the w-model (Leung J.C. 1986; Leung J.C. 1990) and the Homogeneous Equilibrium model (HEM) (Richardson S.M. et al. 2006).
Stage 3 occurs if release continues long enough to completely deplete the two-phase layer such that the release from the tank becomes all vapor. The mass flow rate decreases from Stage 1 to Stage 3 (Britter et al. 2011). Note that the transitions from stage to stage are often not distinct. Further complicating this is the formation of an aerosol phase.

For escape of a saturated liquid through a rupture in a container with a wall thickness equal to or less than 0.1 m, the flow approximates that of flow through a sharp-edged orifice. The flow is said to be “non-equilibrium” because the time required for the liquid to pass through the rupture is too short to allow equilibration to the new pressure condition until it is well outside the vessel; this is often referred to as “choked” flow. Here, the thickness of the tank wall at the site of the tear measured from 0.020 m (range= 0.000034 m) (NTSB, 2005b), indicating that thermodynamic equilibrium was not achieved upstream of the rupture during the initial phase of release.

Thus, the earliest release from the tank should have been liquid-phase Cl₂. After release (outside the tank), this liquid jet would have abruptly approached an equilibrium condition at atmospheric pressure, causing “flashing” flow. This complex phenomenon results from the combined effects of rapid evaporation of Cl₂, warming of the Cl₂ jet due to the entrainment of ambient air, and cooling of the jet and the surrounding air through uptake of latent heat of evaporation. Condensed and frozen water was noted on the outside of the tank car near the rupture in photographs.
2.2.2 Estimation Methods

The methods used here to estimate the rate of Cl\textsubscript{2} emission and the cumulative loss from the tank car were chosen to be appropriate for the ultimate goals of this research: to provide estimates of Cl\textsubscript{2} exposure in Graniteville for participants in health effects studies, not to develop generally applicable approaches for determining pollutant emission, dispersion and transport. This analysis began by calculating the depth of liquid Cl\textsubscript{2} in the car using a tilt angle of 10° reported by a SC Department of Health and Environmental Control (DHEC) responder, which agreed with the approximate angle given as 5-10° reported by the NTSB (2005a), the approximate orientation of the car shown in numerous pictures, and the volume of Cl\textsubscript{2} initially present. Based upon NTSB (2005a) pictures, the tear on the side of car was a jagged gash very nearly perpendicular to the ground and 4.88 meters from the higher end of the car (the “A” end). The depth of liquid Cl\textsubscript{2} was calculated as a function of the liquid-filled tank volume using a web-based program supplied by LMNO Engineering (2009). Then, to simplify computation further, a cubic equation was derived by regression (R\textsuperscript{2}=0.9989) for directly computing the volume of Cl\textsubscript{2} in the tank from its depth and vice versa. The next step was to compute the combined pressure resulting from the average head pressure of liquid along the tear and the vapor pressure in the enclosed space above the liquid. Using an equation for flow through a submerged opening (Perry and Green, 1984), we estimated that the time required for the liquid Cl\textsubscript{2} level to reach the top of the vertical tear, using the
approximation that the two-phase portion of the fluid does not have a significant effect on the mass release rate.

At the beginning of this stage one, the pressure in the Cl₂ gas equaled the vapor pressure of chlorine at the tank temperature, estimated to be -3.3 degrees Celsius (26 F) (NTSB, 2005a), corresponding to a vapor pressure of 317 kPa (46 psia) (Occidental Chemical Corporation, 2000). An overview of the source term information we have used as inputs is shown in Table 1.

2.3 Weather Validation Methods

At the time of the incident, there was no on-site meteorological station in Graniteville to provide the most accurate weather data for input into the plume modeling software. Conventionally, in lieu of onsite observations, data from the National Weather Service (NWS) National Climatic Data Center (NCDC) is often used for planning, response and investigative modeling. NWS stations are generally located at airports or areas that serve as population centers. Alternatively, the U.S. Forest Service (USFS) operates Remote Automated Weather Stations (RAWS) which are generally self-sufficient stations located in national forests and similar areas for monitoring forest fires. Information from these mobile stations is transmitted electronically (often via satellite) every hour to the National Interagency Fire Center in Boise, Idaho. We have used archived meteorological surface observations recorded at 13 different RAWS sites collected during the night (and time of incident) on January 6th, 2005 (Figure 1).
A portable weather station was setup at the incident site late in the morning of January 6\textsuperscript{th} and remained there throughout the duration of cleanup activities. For purposes of validation, we compared archived observational data from the 13 different RAWS sites for five nights beginning on January 7\textsuperscript{th} and ending on January 12\textsuperscript{th} (January 10\textsuperscript{th} was excluded due to missing data) with data from this portable site. We modeled the incident in HPAC using both the RAWS and portable weather station data (micro-environmental) collected on the aforementioned nights. Concentration and surface dosage were calculated at 1,024 points across a three by three mile grid with identical source terms and correlation, mean bias and root mean square error between the two models were calculated using IBM SPSS Statistics (Version 20, IBM, Armonk, NY). The goal of this validation was to support the notion that RAWS data collected during the night of January 6\textsuperscript{TH} provided an accurate representation of the incident site micro-environment in Graniteville. It has been previously reported than an inversion layer may have been present during the morning of the accident which exaggerated the spread of chlorine gas (Buckley et. al, 2012). This inversion would have exasperated the spread of the gas over the surrounding terrain.

2.4 \textit{Description of the Models and Usage}

The Graniteville incident was modeled in two un-classified versions of standard software packages using the above mentioned source term and meteorological data. First, we used the commonly available Areal Locations of Hazardous Atmospheres (ALOHA) model, which was jointly developed by the National Oceanic and Atmospheric Administration (NOAA) and U.S.
Environmental Protection Agency (EPA). Second, we used the Hazard Prediction and Assessment Capability (HPAC, 5.2 Service Pack, DTRA, Ft. Belvoir, VA), developed by the Defense Threat Reduction Agency (DTRA), to incorporate increasingly accurate topographical and meteorological data in an effort to improve the predictive accuracy of our model before proceeding to validation studies. There were several reasons why we selected ALOHA and HPAC instead of other available plume modeling software. Due to its widespread distribution and ease of use, ALOHA may be the most common model in general use by initial responders, such as local fire departments. HPAC has been widely used in studies regarding both the Graniteville and other chlorine releases, and was also utilized by authorized emergency management entities during the response (Hannah et. al, 2008a, 2008b; Buckley et. al, 2007, 2012). We have avoided use of proprietary software because these models may not be in widespread use among those with critical public health and safety decision-making responsibility.

An updated and localized 30 km topographical file of the Graniteville area using the ArcMap geographical information system software (ArcMAP 10, ESRI, Redlands, CA) was utilized with HPAC while simulating the release. No terrain input was used with ALOHA because the standard (and most commonly available) version of the software assumes flat topography and does not accommodate the incorporation of diverse terrain (NOAA, 2013). All models estimated the outdoor atmospheric concentrations of Cl₂.

The ALOHA system, part of the Computer-Aided Management of Emergency Operations (CAMEO) suite, is likely the most widely used
atmospheric dispersion modeling program at the local level. We used ALOHA version 5.4.3 to model the Graniteville release. The software uses the Dense Gas Dispersion Model (DEGADIS) system to model Gaussian puff and plumes including dispersion of dense gas such as chlorine (NOAA, 1992). Outputs including threat zones can be displayed using the intrinsic CAMEO plotter (MARPLOT) or exported to ArcMap via extensions. The intrinsic CAMEO mapping software, MARPLOT, was used to illustrate the ALOHA output as 60-min Acute Exposure Guideline Level (AEGL) isopleths. Confidence lines were, also, shown on the map.

The HPAC system has several advantages over ALOHA, including the consideration of deposition and depleting effects such as terrain-induced gravity slumping. HPAC consists of several different modules that work together to determine source term, incorporate weather and topographical data, and calculate theoretical migration to develop a dispersion model. Although originally designed for use by the military, the HPAC system is now available to the authorized municipal and research community members and serves as a valuable tool for predicting the effects of hazardous materials releases into the atmosphere and its subsequent impact on a proximal population. The HPAC system uses a second-order closure transport/dispersion model, SCIPUFF, which is a Langrangian model utilizing multi-dimensional Gaussian distributions (DTRA, 2005). In association with a wind field model (SWIFT), the system can describe diffusion processes while allowing variances in concentration fields for purposes of measuring uncertainty. The transport/dispersion and wind field
components of HPAC have been validated in the laboratory as well as field trials for short and long-range dispersion over various types of terrain and urban environments (Hanna et al, 2008; Warner et al, 2006; Warner et al, 2008).

Results

3.1 Source Term Calculation Results

Cl₂ emission began immediately after the accident and continued at a high rate: 523 kg/s. The vapor pressure of Cl₂ trapped above the liquid was the dominant force pushing the liquid out of the tank car. We calculated that the liquid level would have reached the top of the tear opening with release of 54,915 kg in about 105 seconds with gas alone slowly escaping afterwards. This represents a loss of nearly 2/3 of the original Cl₂ in the tank car, in relatively good agreement with estimates based on the Cl₂ remaining in the car at 4:00 PM on the day of the accident from SC DHEC and Norfolk Southern cleanup contractors (NTSB 2005c). The nearest National Weather Service monitoring station in Augusta, Georgia reported an initial ambient temperature of 55° F. Nevertheless, the condensation and ice on the surface of the tank shown in pictures taken on the morning of January 6, 2005 was to be expected given the high rate of Cl₂ evaporation and resulting cooling due to the uptake of latent heat.

3.2 Comparison of RAWS and micro-environmental data

For the initial 60 minutes after the accident, cumulative surface dosage results from the HPAC models using RAWS surface observation data were similar to results using observations from a single portable meteorological station.
positioned near the leaking tank car. Concentration and surface dosage data from the RAWS HPAC plume dispersion model without measured micro-environmental weather data was significantly correlated with the model that included measured micro-environmental data (Table 2). There was overall good agreement between the two models with the exception being as we neared the 60-min averages for certain days. Yet, after calculating an overall strong correlation between the RAWS data and portable weather station, and, therefore, making the assumption that these data were representative of the microenvironment during the incident itself, we are confident that our usage of the RAWS data is suitable for our modeling purposes.

3.3 ALOHA and HPAC Model Results

The ALOHA predicted 60-min average concentrations (Figure 2), as shown in Table 3, ranged from 156,000 ppm at a receptor 0.1 km downwind (x) to 10 ppm at a receptor 10 km downwind. We report these values in conservative 60-min averages as this is the standard in ALOHA. Unlike HPAC, the ALOHA system does not report values past 10 km downwind; however, manual calculation of very approximate concentrations is possible using the relevant mathematical modeling equations.

The HPAC output is shown as 30-min AEGL isopleths on an ArcMap GIS layer of the Graniteville incident area (Figure 3). On Table 3, we reported averaged centerline maximum concentrations in both 30-min and 60-min averages. For 30-min averages, these values ranged from 14,900 ppm at 0.1 km
downwind to 0 ppm at 25 km downwind. 60-min averages ranged from 11,642 ppm at 0.1 km downwind to 0 ppm at 25.0 km downwind. These maximum 30-min and 60-min concentrations are also shown versus downwind distance graphically (Figure 4). Upwind dispersion up to 0.7 km due to gravitational slumping and maximum width to specific concentrations (2,000, 400, and 20 ppm) were reported for the HPAC model. Although it is possible to show variance in times shorter than 30 minutes, we opted to model 30 and 60-min outputs for comparative purposes to the more output-restricted ALOHA model.

**Discussion**

Our purpose here has been to identify an atmospheric dispersion modeling system that is suitable for epidemiologic application to etiologic study of toxic inhalation hazard releases. ALOHA lacked the precision required to use it within epidemiological studies. Because it is designed to be used by a wide range of emergency management personnel, ALOHA has limited functionality compared to more “robust” systems such as HPAC. The ALOHA program is intended for use during the immediate response phase of a release and, therefore, sacrifices accuracy for increased speed and ease of use (NOAA, 2011). We opted to compare HPAC with ALOHA, as opposed to other dispersion modeling systems, because ALOHA may be the most widely known and utilized gas dispersion model. Our purpose here is to compare two “tiers” of modeling systems with the aforementioned input parameters, and to identify HPAC as the model of choice to continue our study with. However, a wide variety of models,
many of which have been previously compared by Hanna and others, are in use throughout public applications, industry and academia.

The behavior of a dense gas is highly influenced by the geography surrounding the release site, and the failure to account for this terrain leads to concentration estimates which are skewed from reality. Indeed, flat terrain models have been shown to overestimate the range of hazard by nearly a factor of five and direction of migration by up to 90 degrees (McBride et al, 2001). Further, most models like ALOHA which are available freely in the public domain do not consider major removal mechanisms, such as deposition and depletion. These factors are particularly important for a dense gas like chlorine which tends to hug the ground. Furthermore, the flat terrain models tend to incorporate linear removal which is not particularly representative of reality. As a consequence, near-fatal exposures are often approximated beyond distances at which human health impacts are reported. The ALOHA output is suitable for its primary intention, that is, the immediate modeling of an incident by emergency responders for purposes of response. Yet, it is unsuitable as a model for us to base future epidemiologic study on due the relative “fixed” nature of the system as input type and variability is concerned and highly conservative estimated concentration outputs. For this, HPAC is far more suitable because of its ability to incorporate mesoscale wind variations with more advanced algorithms among other improvements. It is for these reasons that we have chosen to proceed with the HPAC system model as a basis for our future epidemiologic studies.
Although HPAC represents a significant advantage over models such as ALOHA, other robust options exist. As an example, the National Atmospheric Release Advisory Center (NARAC) at the Lawrence Livermore National Laboratory (LLNL) in California provides national support to emergency managers for purposes of planning and real-time assessment of chemical, radiological, biological and other similar events. NARAC utilizes the ADAPT/LODI system, which consists of a robust meteorological data assimilation component (ADAPT) and dispersion modeling component (LODI) which considers turbulence, chemical reactions, wet and dry ground deposition, settling due to density and plume rise (NARAC, 2013). Coupled with extensive databases on the properties of agents such as chlorine, accurate topographical data and real-time meteorological observations, NARAC is a critical resource for emergency planning and response. However, unlike HPAC, the advanced methodologies of the NARAC group are available by request only and cannot be performed by unauthorized independent agencies and organizations for research purposes. A 2001 study by LLNL researchers concluded that HPAC and NARAC predictions for a series of simulated scenarios had overall favorable agreement (Warner et al. 2001). We have chosen to proceed with HPAC because it is the most accurate modeling system available to authorized academic researchers. Further, DTRA provides Interagency Modeling & Atmospheric Assessment Center (IMAAC) support through its Technical Reachback unit.

A few papers have been published estimating the Graniteville release rates for purposes different from those of this study. Buckley et al. (2007)
described the results of analyses performed by the Savannah River National Laboratory (SRNL) provided in support of the Graniteville emergency response efforts, as well as some more detailed atmospheric transport calculations including HPAC model results in the first 2-3 hours after the accident. They assumed that >62,000 kg of Cl\textsubscript{2} was released instantaneously as vapor and aerosol phases. A more comprehensive follow-up analysis on the Graniteville Cl\textsubscript{2} release by SRNL covering the same 3-hour time period has also been published (Buckley et al. 2012); it included the estimated emission rate, meteorology, dispersion, as well as the fate and the effects of the chlorine released. In their research, the tear was represented by a 0.8 m long by 0.08 m wide opening extending "just above the mid-point of the tank." This does agree with our findings. The emission rate was determined using ALOHA code, and the Industrial Transportation (ITRANS) component of the HPAC program. This resulted in a total estimated emission of 59,000 kg, most occurring in the first minute after the accident with the total discharge requiring 5 minutes. They pointed out that ITRANS will not accept a detailed specification of the damage to the tank. The time required for discharge was adjusted using SCIPUFF to achieve better agreement with a short release duration implied by Hanna et al (2008) and Britter (2010). Thus, Buckley et al (2012) concluded that vapor and aerosol release, 59% of the total, was essentially complete after the 3 minutes, while the remaining 41%, a subcooled liquid release, was assumed to have pooled on the ground and then evaporated.
Hanna et al (2008) compared three dense gas dispersion models for several chlorine railcar accidents, including the Graniteville accident. For Graniteville, the duration of source emissions was determined using the PHAST and TRACE models along with a thermodynamic analysis, and the vertical slash in the side of the rail car was represented by a 4-5 inch hole. Based upon the Cl$_2$ release of rate of 1,565 kg/s, they estimated that a two-phase release of liquid and vapor lasted for 34 s, for a discharge of 53,210 kg; the vapor phase release was estimated to continue at the rate of 0.2 kg/s for 3,600 s for an additional discharge of 720 kg. One major reason our results are different is because the Hanna paper, for purposes of comparison between SCIPUFF and other models, assumed flat terrain and utilize a slightly different source term. This was primarily due to the inability of some of the models being compared to incorporate topography (such as ALOHA). The variability between our model and that aforementioned is a prime example of the impact that migration of a heavy gas through complex terrain has on predicted upwind concentrations.

This study also demonstrates the limits of using dispersion modeling for guiding emergency response to accidental releases of compressed, acutely toxic dense gases. Here, 2/3 of a railroad tank car of chlorine was emitted in about 105 s. This is insufficient time to prevent exposure and, in many cases, to prevent death and disabling injury, even when a community is extremely well-prepared. The approach employed here can be of significant value for post-event evaluation, or for response in scenarios with a slower release or for less acutely toxic contaminants. Many modeling systems are incapable of producing
exposure estimates in time intervals less than 30 or 60 minutes, or incorporating estimate variability. For purposes of epidemiology, this is highly problematic for the reason mentioned above: many rapid relief incidents occur in minutes. The ability of HPAC to output estimates in short intervals – minutes – is another advantage over ALOHA for our purposes.

**Conclusion & Future Directions**

Out of our two selected models studied, HPAC is likely the best candidate for use as a model system on which future human epidemiologic studies could be based. HPAC was selected over ALOHA because the system accounts for dynamic plume rise and to a greater degree the dense gas effects, time and space-dependent boundary layers, and mesoscale wind variations over complex terrain. Although the focus of our model development is entirely emergency response, the HPAC modeling system does represent significant improvement over the common ALOHA system. This increased predictive accuracy can have profound impacts during response to hazardous chemical releases. It is recommendable for jurisdictions without access or training on software such as HPAC to fortify mutual aid collaborations with agencies who utilize higher modeling systems.

Yet, there is intrinsic bias in any simulation and performance can be improved (or confirmed) by field studies. Further verification of our model is necessary before epidemiologic application. In other words, to ensure predictive accuracy, a model must be validated using observed indicators of exposure. The
next step in improving plume model accuracy is to compare the model to exposure indicator data collected in the aftermath of the incident. Eventually, the resulting validated plume dispersion model could be used to estimate personal exposures for etiologic environmental epidemiology studies. The resulting models presented herein provide preliminary estimates only of outdoor exposure concentrations and should not be interpreted to represent the exact chlorine plume model after the Graniteville exposure event. Further validation studies are needed before individual exposure estimates can be reliably made and the chlorine plume more definitively modeled.
ACKNOWLEDGEMENTS

We acknowledge Ronald G. Meris, Chief of the Reachback Analysis Branch of the Defense Threat Reduction Agency (DTRA), for his scientific review and helpful commentary on this manuscript.

WORKS CITED


LMNO. “Inclined Cylinder Volume Calculation.”


National Transportation Safety Board. Material Laboratory Division. Washington, DC (September 8, 2005).


Table 1. Modeling Inputs for Graniteville, SC Chlorine Release

<table>
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<tr>
<th>Release Parameters</th>
<th>Graniteville, SC, USA</th>
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<td>Location</td>
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<td>Date and time</td>
<td>Longitude: 81° 48’ 29.99” W</td>
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<td>Upstream pressure in tank (psig)</td>
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<td>Total release (liquid + vapor) (kg)</td>
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### Table 2: Comparison between HPAC models with RAWS and Portable Station Data

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<tr>
<td><strong>R²</strong></td>
<td><strong>Mean Bias</strong></td>
<td><strong>RMSE</strong></td>
<td><strong>R²</strong></td>
<td><strong>Mean Bias</strong></td>
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<td></td>
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<tr>
<td>January 7</td>
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<td>0.677 x 10^{-7}</td>
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<tr>
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<td>0.997</td>
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**Note:** Statistical analyses shown above include correlation (R²), mean bias and root mean square deviation (RMSE).

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**Concentration:**

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<td><strong>R²</strong></td>
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<td><strong>RMSE</strong></td>
<td><strong>R²</strong></td>
<td><strong>Mean Bias</strong></td>
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<tr>
<td>January 7</td>
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**Surface Dosage:**

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<td><strong>R²</strong></td>
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<td><strong>RMSE</strong></td>
<td><strong>R²</strong></td>
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Table 2: Comparison between HPAC models with RAWS and Portable Station Data
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<tr>
<th>Downwind distance (km)</th>
<th>HPAC (30-min) ppm</th>
<th>HPAC (60-min) ppm</th>
<th>ALOHA (60-min) ppm</th>
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<tr>
<td>0.1</td>
<td>14,900</td>
<td>11,642</td>
<td>156,000</td>
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<td>0.2</td>
<td>6,868</td>
<td>5,860</td>
<td>81,100</td>
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<td>0.5</td>
<td>837</td>
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<td>10.0</td>
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<td>25.0</td>
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<th>Downwind distance to concentration</th>
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<tr>
<td>2,000 ppm</td>
<td>0.45</td>
<td>0.4</td>
<td>1.31</td>
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<tr>
<td>(0.22 upwind)</td>
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<tr>
<td>400 ppm</td>
<td>0.69</td>
<td>0.6</td>
<td>2.43</td>
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<tr>
<td>(0.39 upwind)</td>
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<tr>
<td>20 ppm</td>
<td>2.6</td>
<td>2.6</td>
<td>7.57</td>
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<tr>
<td>(0.66 upwind)</td>
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<th>Maximum width to concentration</th>
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<tr>
<td>2,000 ppm</td>
<td>0.54</td>
<td>0.4</td>
<td>-</td>
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<tr>
<td>400 ppm</td>
<td>0.8</td>
<td>0.7</td>
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</tr>
<tr>
<td>20 ppm</td>
<td>1.44</td>
<td>1.32</td>
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COMPARISON OF THREE IRRITANT GAS PLUME MODELS FOR EPIDEMIOLOGIC STUDY
Dev D. Jani¹, Mark Wilson¹, Jeffery Wickliffe¹, Jeffrey Shaffer², Roy Rando¹, Erik R. Svendsen³

¹ Department of Global Environmental Health Sciences, Tulane University School of Public Health and Tropical Medicine, New Orleans, LA, USA
² Department of Biostatistics and Bioinformatics, Tulane University School of Public Health and Tropical Medicine, New Orleans, LA, USA
³ Department of Public Health Sciences, Medical University of South Carolina, Charleston, SC, USA

Abstract

Atmospheric transport and dispersion models are used in predicting exposure to toxic irritant gas plumes. Previously, we reported the development of a Hazard Prediction and Assessment Capability (HPAC) plume model of the 2005 Graniteville, South Carolina, 54,915 kg railcar chlorine release. Here, this existing model is compared to both an updated HPAC and Areal Locations of Hazardous Atmospheres (ALOHA) plume model. A dynamic, time-dependent grid sampling methodology (HPAC versus HPAC) and downwind concentration receptor points (HPAC versus ALOHA) was utilized to assess agreement. Exploratory data analysis including log-log scatterplots and boxplots were developed. Visual and statistical (correlation, RMSE) differences were observed between the three models. The refined HPAC model was selected to be evaluated against environmental indicators of exposure in subsequent studies.
Introduction

Atmospheric dispersion and transport models, commonly known as plume models, are widely used to estimate the transport, dispersion and more recently the health impacts of toxic gas and particulate releases. In the most basic sense, these models seek to identify the concentration of an air pollutant at a given point in time and space, mathematically accounting for transport, diffusion and, in the most advanced models - which generally require supercomputers - basic chemical transformation and ground deposition (Daly et al, 2007). The modeling of air dispersants using mathematical formulas dates back to the early 1930s, when Sutton, Taylor and colleagues researched methods by which to model the movement of air in the atmosphere (Sutton, 1932; Taylor, 1915; Taylor, 1921). This work was propelled forward in the mid-1940s and 1950s by Stewart, Gifford, Hewson and colleagues who focused on the need to model pollutants released from elevated sources such as smokestacks (Stewart et al, 1958; Gifford, 1957a; Gifford, 1957b). In the 1960s, Gifford, Pasquill, Turner and Briggs developed many of the Gaussian principles that are the basis for common dispersion models used today (i.e. Areal Locations of Hazardous Atmospheres [ALOHA] and PUFF-PLUME) (Gifford, 1959; Gifford, 1960a; Gifford, 1960b; Gifford et al, 1973; Briggs, 1965). Many of these models assume that the air pollutant has a normal probability distribution and are most useful for continuous, buoyant plumes, but certain software like ALOHA have dense gas modeling capabilities as well. Over the past few decades, momentum to improve the predictive...
accuracy of existing model systems - and to develop new ones - has accelerated due to concerns over air pollution, industrial accidents and climate change.

A newer generation of models employing the Langrangian algorithms represents a significant advancement over earlier systems. In these models, a moving frame of reference is used to follow particles and compute their trajectories as they disperse and transport away from the source point. These models often also incorporate topography and dynamic micro-meteorological data such as multiple locations and surface/upper observations in their calculations. As an example, the federal government and other entities have built virtual models of several large cities in the United States, which are then imported into modeling systems and used to simulate dispersion and transport around buildings and through urban canyons (DTRA, 2015). Additionally, these Lagrangian models often have the ability to track moving receptors and provide dosage estimations, which is particularly important for purposes of post-incident exposure assessment and other public health application. Currently, focus has also been on integrating the transport and dispersion models with health effect models, effectively creating a full-scope consequence assessment platform which can be utilized for both planning, response and research (i.e. epidemiology) focuses.

Given the wide range of software that is developed by governmental, academic and corporate entities, studies are often conducted to compare the outputs of different models. A 2008 analysis by Hanna and colleagues of six dense gas dispersion models showed that when utilizing uniform source
emission inputs for three different scenarios, all models agreed within a factor of plus and minus two (Hanna et al, 2008). Although this factor of two is considered a standard in dispersion modeling development and analysis, additional evaluation must be conducted to ensure this deviation is further minimized before application in human public health studies. These evaluation analyses often involve the comparison of model-predicted data to environmental observations or other models. The comparison of different models to each other is our focus here.

Previously, we reported the development of a Hazard Prediction and Assessment Capability (HPAC) plume dispersion model of the 2005 Graniteville, South Carolina, USA railcar release of chlorine gas (Jani et al, 2015). We developed a source term using independent engineering analysis, validated the microenvironmental weather data and produced a plume model using the 4.04 version of HPAC. In order to develop a model with the highest feasible predictive accuracy, we identified the need to replicate this process using a newly released version of HPAC. This study represents the second of three steps in the development and evaluation of an irritant gas plume model for epidemiologic study. Here, we provide a comparative assessment of three models before choosing one for subsequent evaluation against environmental indicators of exposure.

**Methods**

*Description of the exposure event*
A more thorough description of the Graniteville incident is presented in Jani et al, 2015. Graniteville is a small town (2000 U.S. Census Population - 7,112) in South Carolina, United States of America. In brief, approximately 54,915 kg of chlorine gas was released when a traveling freight train collided with a stationary train due to an improperly aligned switch at 2:39 AM Eastern Standard Time (EST) on January 6, 2005. The accident occurred in the vicinity of a large mill complex and of three derailed railcars of chlorine, one ruptured and inundated the surrounding community with approximately 2/3 of the total commodity volume in the tank car (NTSB, 2005). The incident resulted in the evacuation of nearly 5,400 people, hospital treatment of over 550 and nine fatalities (the train crew and individuals in the immediate vicinity of the release) (NTSB, 2005). It is important to note that the evacuation itself was due to the cleanup process and occurred several hours after the release; immediately afterwards, a shelter-in-place order as issued via reverse 911 from the local public safety answering point (PSAP) (NTSB, 2005). In the months following the release, the prominent Avondale Mills and several surrounding manufacturing businesses were shuttered directly due to the economic impact of this incident.

**Description of the models and usage**

We have modeled the Graniteville incident in unclassified versions of both the HPAC (Defense Threat Reduction Agency, Ft. Belvoir, VA) and ALOHA (National Oceanic and Atmospheric Administration, Silver Springs, MD) softwares. Collectively, these software packages represent the two most widely used dense gas dispersion modeling systems developed by the U.S. federal
government. Although equivalent proprietary software exists, we have avoided
the use of these programs because they are not commonly accessible by
governmental and academic entities. Building upon the previously developed
HPAC 4.04 and ALOHA 5.4.3 models, the Graniteville release was modeled in
the newer HPAC 5.3 version utilizing the same inputs. These source term,
meteorological and topographical inputs are detailed further in Jani et al, 2015.

ALOHA is one of several programs in the Computer Aided Management of
Emergency Operations (CAMEO) software suite and is the most widely used
plume modeling programs by the government first responder/public safety sector
(NOAA, 2015). The software is geared towards the common first responder and
provides quick estimation of plume dispersion based upon minimal inputs; as
such, it sacrifices predictive accuracy for ease of use. ALOHA utilizes the Dense
Gas Dispersion Model (DEGADIS) to model Gaussian puffs and plumes and is
one the best mainstream models suited for dense gases such as chlorine
(NOAA, 2013). It includes an infiltration model for indoor exposure predictions.
The plume model itself can be outputted onto the intrinsic CAMEO plotter
MARPLOT, or exported to geographic information systems (GIS) software such
as ArcMap or Google Earth.

In contrast to ALOHA, HPAC utilizes the Langrangian Second-Order
Closure Integrated Puff (SCIPUFF) transport/dispersion model and the Stationary
Wind Field and Turbulence (SWIFT) wind field model. HPAC 4.04 was previously
described extensively (Jani et al, 2015). HPAC 5.3 represents a major update
from 4.04 with definite implications for the eventual epidemiologic application of
our model. Particularly, there have been significant updates to the SCIPUFF transport and dispersion code, iTRANS source term model, material file data properties, health effects data, plot display, and visual improvements to the graphical user interface (DTRA, 2015). The newer version also allows for 64-bit computing which facilitates larger problem resolution with complex releases such as Graniteville. Other improvements include a new high resolution climatology data set and daughter products and updates to the population data sets; however, these latter upgrades do not impact our experiment. Due to security concerns, the full and detailed extent of improvements is not available to those outside of the classified community. Like ALOHA, the plume model and isopleths can be exported to GIS software for visualization and further analysis. Here, we have plotted both HPAC 4.04 and 5.3 models onto a publically available ArcMap topographic base map (ArcMap 10, Esri, Redlands, CA).

Existing literature on the Graniteville incident has shown that the plume likely dispersed within a three hour period; for this reason, we have conservatively run 4-hour models in both versions of HPAC (Buckeley et al, 2012). In contrast to the previous study (Jani et al, 2015) in which we solely compared concentration (ppm) between the HPAC and ALOHA plumes, here we compare surface dosage (kg-s/m3) between the two versions of HPAC. Because the eventual evaluation is for human epidemiology and exposure assessment, the surface dosage parameter is highly relevant. The surface dosage was predicted in both models at a 1.5 meter breathing height in 30-minute post-release intervals for a maximum of four hours: 3:09 AM, 3:39 AM, 4:09 AM, 4:39
AM, 5:09 AM, 5:39 AM, 6:09 AM and 6:39 AM. For purposes of identifying surface dosage sampling points at the aforementioned time intervals, the SCIPUFF Adaptive Grid (SAG) sampling methodology was utilized. This dynamic approach automatically selects a large number of sampling locations with increased density around the source location itself. From a human exposure and epidemiologic standpoint, this approach best represents the data field, particularly in the areas with highest potential exposure threat. The sampling field is time-dependent and number of sampling points increases as the plume itself grows due to dispersion and transport away from the source location.

**Description of the HPAC 4.04 to 5.3 comparison and statistical methodology**

The time-dependent surface dosage data for both models was then grouped into eight bins based upon the standard output categories in HPAC. The ranges identified in Table 1 were utilized because these are the natural, intrinsic differentiating points within the HPAC software. The data was consolidated further by collapsing the bins under 1.0 kg-s/m³ into one bin, reducing our 2x8 table into a 2x4 configuration (Table 1), based upon which frequencies and median were calculated. Further, given that the Graniteville incident was a relatively acute exposure scenario (< 4-hours until plume dissipation) and in the context of an evacuating human, surface dosage of less than 1.0 kg-s/m³ for a relatively short exposure period are not likely to result in severe health impacts such as incapacitation and/or lethality. It has been reported in existing literature that 400 ppm of constant inhalational exposure to chlorine can be lethal to
humans after 40 minutes and exposure of over 1,000 ppm can result in immediate death (ATSDR, 2010; Prater et al, 1990). Utilizing a mathematical conversion and 30 minute model output timestep, 1.0 kg-s/m³ is approximately half of the lethal exposure concentration for 40 minutes, which like the 4-hour model run time is a conservative approach. A preliminary exploratory data analysis was performed by creating scatter plots with both sets of surface dosage observations paired in space and time on a logarithmic scale. Subsequently, as our focus here is to statistically compare the two model data sets, the Pearson correlation coefficient $r (p = 0.01)$ and root mean square error (RMSE) were calculated using IBM SPSS Statistics (Version 20, IBM, Armonk, NY). These metrics were chosen because they are among the established evaluation criteria in dispersion modeling and were used previously in our research (Jani et al, 2015; Duijm and Carissimo, 2001; ASTM International, 2015; Irwin, 1999; among others). A further analysis was performed on the highest exposure/threat category (D2) by dividing into five equally spaced exposure ranges to assess differences in frequency. A chi-square analysis was performed between the frequency ranges in this sub-analysis.

**Description of the HPAC 4.04 and 5.3 to ALOHA 5.4.3 comparison**

Both HPAC models were compared to the ALOHA model based upon a more simplistic approach using concentration (ppm) due to the inability of the ALOHA software to estimate surface dosage. The three models were compared using pre-identified downwind receptor points at 60-min post-release. For downwind distance, the receptor locations were 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0.
and 25.0 km from the source location (directly downwind on centerline). These receptor points have been chosen based on similar comparisons in established literature (Hanna et al, 2008; Jani et al, 2015).

Results

Comparison of HPAC 4.04 to 5.3

The full extent of 4-hour surface dosage plumes were plotted in ArcMap for HPAC 4.04 (Figure 1), HPAC 5.3 (Figure 2), HPAC 4.04 vs 5.3 (Figure 3) and HPAC 4.04 vs 5.3 with the SAG sampling points (Figure 4). The full range of plotted plumes can be found referenced as appendices: version 4.04 (Appendix 1.4), version 5.3 (Appendix 1.6) and as two comparable layers without (Appendix 1.7) and with (Appendix 1.8) the SAG sampling points. Visually, the 5.3 plume model is far narrower and hugs the topographic contour (creek valley) tightly compared to 4.04. In terms of downwind transport/dispersion, the 4.04 model is nearly double in length at specific time-steps post-release. Further, at 4 hours post-release - the end of our modeling period - the 5.3 model is shorter than the 4.04 model. Software generated SAG sampling points ranged from 7,835 at 3:09 AM (+30 min post-release) to 9,446 at 6:39 AM (+4 hours post-release).

Frequency values (Table 2) in the A2 and B2 bins differed by up to 500 between the two HPAC versions. The differences were much larger in the C2 and D2 bins, with frequency values in the C2 HPAC 4.04 bin generally smaller than the respective HPAC 5.3 bin; yet exhibiting an opposite effect in the D2 bin, where differences of up to 2,000 occurred within 60 minutes post-release. A further analysis of the highest threat category (D2, or \geq 100) showed higher frequency of
HPAC 4.04 predictions in the 100-199 kg-s/m³ and 200-299 kg-s/m³ ranges, but an opposite effect beyond 300 kg-s/m³ (Table 3). Chi-square analysis showed there was significant difference. Median values were consistently higher for HPAC 4.04 compared to 5.3 (Table 4). Scatter plots with Loess fit lines were generated for each timestep with surface dosages paired in space (Figures 6A-H). There was greater variability between the two data sets at lower dosages within the first 30 minutes post-release. After this time-step, agreement increased as the post-release time increased. For all output times, both models were positively correlated. Correlation values (r) ranged from 0.847 (p = 0.01) at 3:09 AM to 0.894 (p = 0.01) at 6:39 AM (Table 4). The RMSE ranged from 60.608 at 3:09 AM to 53.938 at 6:39 AM (Table 4).

**Comparison of HPAC 4.04 and 5.3 to ALOHA 5.4.3**

The HPAC 4.04 predicted 60-min averaged concentrations of 11,642 ppm at 0.1 km downwind to 0 ppm at 25.0 km downwind (Table 5). For HPAC 5.3, these downwind distances corresponded to 2,831 ppm and 0 ppm, respectively. While 4.04 estimates a linear decrease in concentration as downwind distance increases, 5.3 interestingly predicted slightly higher concentrations at 0.2 km compared to 0.1 km. Further, the 5.3 predicted concentrations at 0.5 km and 1.0 km downwind exceeded that of 4.04. The ALOHA (Figure 5) estimated the concentration at 0.1 km downwind to be 156,000 ppm and 10.0 ppm at 10.0 km downwind, which are manyfold increases over the HPAC concentrations respective to downwind location. Unlike HPAC, ALOHA does not report estimated values beyond the 10 km threshold.
Discussion

Building upon previously reported research, our purpose here has been primarily to compare the established HPAC 4.04 model to the newer HPAC 5.3 model. We chose to include the ALOHA comparison not because it is possibly suitable for public health or epidemiologic application, but rather to show the major differences in estimation that these two “tiers” of modeling systems can produce. The comparative analysis between ALOHA and HPAC showed drastic differences: at 0.1 km downwind, the 60-min average for ALOHA was approximately 13 times that of HPAC 4.04, and nearly 55 times that of HPAC 5.3. While overestimation is universal in all dispersion models, clearly, the ALOHA model has significantly overpredicted.

The primary two drivers behind our study, applications for emergency response and public health, both support the need for a model to be accurate. Within emergency response, accuracy can strongly influence critical decisions such as evacuation, shelter-in-place and other protective actions. Evacuating, sheltering and providing disaster welfare for large amount of affected populations is costly and reliable models can increase the efficiency of response. In Graniteville, the initial decision to shelter-in-place likely saved countless lives due to the shielding effect that buildings provide. Additionally, a model that may eventually be used to estimate or validate human exposures in pre or post-exposure epidemiologic studies must assure a high level of predictive accuracy. With HPAC 5.3, the enhanced ability of the dispersion and transport model compared to 4.04 is a step in the right direction towards this goal. As mentioned,
the newer 5.3 model incorporates several algorithmic changes which increases the predictive accuracy of the model.

The visual analysis between the HPAC 4.04 and 5.3 models shows that there are significant spatial differences between the two versions. The older model tends to spread more in the crosswind direction and although a large amount of chlorine gas was released in a relatively short time, the dense physical nature of chlorine would attenuate extensive uphill transport out of the valley. This supports the general belief that older models tend to be increasingly conservative and often estimate transport, dispersion and exposure far beyond what is observed. The differences in downwind concentration are likely due to the ability of 5.3 to better predict terrain-effects and acutely geofence transport; as such, a higher concentration is downwind (0.2 km) than in proximity to the release site (0.1 km) within 60-minutes post-release. In contrast, 4.04 estimated a nearly linear decrease in concentration as centerline, downwind distance from the release site increased. For the same aforementioned reason, HPAC 5.3 predicted a longer footprint of higher concentration beyond 1.0 km downwind. HPAC 4.04 also predicted consistently higher median values for all time steps, supporting the notion that the older model is likely overpredicting compared to the newer. Although the correlation values would be considered favorable in many areas of science, it supports disagreement between the two HPAC models in this context.

Although there are a large number of studies which compare different model systems such as HPAC and ALOHA, very few compare different versions
of the same system, particularly in the context of a large-scale release with human exposure implications such as Graniteville. A 2010 report commissioned by the U.S. Department of Homeland Security (DHS) Chemical Security and Analysis Center (CSAC), produced by the Institute for Defense Analyses, compared HPAC to three proprietary atmospheric transport and modeling systems (CHARM, PHAST and TRACE) in both near-field (i.e. dense gases) and far-field (i.e. neutrally buoyant gases) scenarios (Urban et al, 2010). With respect to a dense gas scenario such as Graniteville, all four models accurately modeled gravity-induced dense gas slumping. In particular, the TRACE model seemed to produce the best predictions; however, the authors noted that only HPAC was able to produce high resolution outputs appropriate for risk assessment (or possible epidemiologic application). The study also noted that HPAC, as a government modeling system, has distinct advantages in terms of breadth, transparency, technical support structures, and distribution to other governmental and academic organizations.

Our goal here has been to compare the established 4.04 model to the newer 5.3 model, and both to ALOHA. As a limitation, it is important to note that the estimations provided here are largely preliminary and may not be fully representative of individual human exposures during the Graniteville incident. Namely, many of the exposures were indoors and transient, so additional calculation must be performed before applying this model to acutely exposed indoor populations after evaluation against environmental observations. In addition, a universal limitation in dispersion modeling is applicable: that a model
itself is never truly representative of the actual release as the latter is one iteration of infinite possibilities, while a model generates an averaged prediction based on many possible ensembles.

**Conclusion and Future Direction**

The process of refining modeling systems to improve predictive accuracy involves, among other approaches, analysis of agreement with post-release environmental indicators of exposure. Having selected the HPAC 5.3 model as our best candidate and an improvement upon the earlier established model (4.04), the next step will be to evaluate the model against available incident-specific observed exposure data sets. Field exposure indicators from accidental releases and field trials (such as Jack Rabbit I and II and Joint Urban 2003) can provide useful eco-toxicological data to which estimations of exposure can be compared (Hanna et al, 1993; Hanna et al, 2003; Warner et al, 2004). Ultimately, the modeling system can be improved by re-engineering the algorithmic engine, adjusting for bias or incorporating newer calculation methodologies so the output is in better agreement with the observed environmental impact. These validated models can then be used to generate more accurate and precise estimations of personal exposure as part of epidemiologic studies.
References


**Table 1**: Original and collapsed bins and associated ranges for both HPAC 4.04 and 5.3 models.

<table>
<thead>
<tr>
<th>Bins (original and collapsed)</th>
<th>Range (kg-s/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>x ≤ 1E-30</td>
</tr>
<tr>
<td>B1</td>
<td>1E-30 &lt; x &lt; .001</td>
</tr>
<tr>
<td>C1</td>
<td>.001 ≤ x &lt; .01</td>
</tr>
<tr>
<td>D1</td>
<td>.01 ≤ x &lt; .1</td>
</tr>
<tr>
<td>E1</td>
<td>.1 ≤ x &lt; 1.0</td>
</tr>
<tr>
<td>F1</td>
<td>1.0 ≤ x &lt; 10.0</td>
</tr>
<tr>
<td>G1</td>
<td>10.0 ≤ x &lt; 100.0</td>
</tr>
<tr>
<td>H1</td>
<td>100.0 ≤ x</td>
</tr>
</tbody>
</table>
Table 2: Number of sampling points per output time and frequency of surface dosage values for HPAC 4.04 and 5.3 by collapsed bin.

<table>
<thead>
<tr>
<th>Output Time (EST)</th>
<th>Model</th>
<th>A2</th>
<th>B2</th>
<th>C2</th>
<th>D2</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:09 AM (+30 min post-release)</td>
<td>HPAC 4.04</td>
<td>1,423 (18%)</td>
<td>486 (6%)</td>
<td>1,506 (19%)</td>
<td>4,420 (56%)</td>
<td>7,835</td>
</tr>
<tr>
<td></td>
<td>HPAC 5.3</td>
<td>1,916 (24%)</td>
<td>426 (5%)</td>
<td>3,262 (41%)</td>
<td>2,231 (28%)</td>
<td>7,835</td>
</tr>
<tr>
<td>3:39 AM (+60 min post-release)</td>
<td>HPAC 4.04</td>
<td>1,823 (22%)</td>
<td>547 (6%)</td>
<td>1,496 (18%)</td>
<td>4,458 (54%)</td>
<td>8,324</td>
</tr>
<tr>
<td></td>
<td>HPAC 5.3</td>
<td>1,886 (23%)</td>
<td>552 (7%)</td>
<td>3,097 (18%)</td>
<td>2,789 (54%)</td>
<td>8,324</td>
</tr>
<tr>
<td>4:09 AM (+90 min post-release)</td>
<td>HPAC 4.04</td>
<td>2,105 (24%)</td>
<td>547 (6%)</td>
<td>1,496 (17%)</td>
<td>4,458 (52%)</td>
<td>8,606</td>
</tr>
<tr>
<td></td>
<td>HPAC 5.3</td>
<td>1,973 (23%)</td>
<td>600 (7%)</td>
<td>2,610 (30%)</td>
<td>3,423 (40%)</td>
<td>8,606</td>
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<td>4:39 AM (+120 min post-release)</td>
<td>HPAC 4.04</td>
<td>2,306 (26%)</td>
<td>547 (6%)</td>
<td>1,496 (17%)</td>
<td>4,458 (51%)</td>
<td>8,807</td>
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<td>HPAC 5.3</td>
<td>2,093 (24%)</td>
<td>658 (7%)</td>
<td>2,595 (29%)</td>
<td>3,461 (39%)</td>
<td>8,807</td>
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<td>HPAC 4.04</td>
<td>2,438 (27%)</td>
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<td>1,496 (17%)</td>
<td>4,458 (50%)</td>
<td>8,939</td>
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<td>HPAC 5.3</td>
<td>2,225 (25%)</td>
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<td>2,595 (29%)</td>
<td>3,461 (39%)</td>
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</tr>
<tr>
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<td>HPAC 4.04</td>
<td>2,648 (29%)</td>
<td>547 (6%)</td>
<td>1,496 (16%)</td>
<td>4,458 (49%)</td>
<td>9,149</td>
</tr>
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<td>HPAC 5.3</td>
<td>2,435 (27%)</td>
<td>658 (7%)</td>
<td>2,595 (28%)</td>
<td>3,461 (38%)</td>
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</tr>
<tr>
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<td>HPAC 4.04</td>
<td>2,801 (30%)</td>
<td>547 (6%)</td>
<td>1,496 (16%)</td>
<td>4,458 (48%)</td>
<td>9,302</td>
</tr>
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<td>2,588 (28%)</td>
<td>658 (7%)</td>
<td>2,595 (28%)</td>
<td>3,461 (27%)</td>
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<td>1,496 (16%)</td>
<td>4,458 (47%)</td>
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<td>658 (7%)</td>
<td>2,595 (27%)</td>
<td>3,461 (27%)</td>
<td>9,446</td>
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</tbody>
</table>

A2 = < 1.0 kg-s/m3; B2 = 1.0 ≤ x < 10.0 kg-s/m3; C2 = 10.0 ≤ x < 100.0 kg-s/m3; D2 = 100.0 ≤ x kg-s/m3
Table 3: Frequency of surface dosage values for HPAC 4.04 and 5.3 when D2 bin is expanded.

<table>
<thead>
<tr>
<th>Output Time (EST)</th>
<th>Model</th>
<th>100 - 199 kg·s/m³</th>
<th>200 - 299 kg·s/m³</th>
<th>300 - 399 kg·s/m³</th>
<th>400 - 499 kg·s/m³</th>
<th>500 - 599 kg·s/m³</th>
<th>Chi-Square sig = 0.05</th>
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<td>3:09 AM (+30 min post-release)</td>
<td>HPAC 4.04</td>
<td>2997</td>
<td>1375</td>
<td>48</td>
<td>0</td>
<td>0</td>
<td>1047.27</td>
</tr>
<tr>
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<td>1171</td>
<td>497</td>
<td>344</td>
<td>106</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>p &lt; 0.00001 significant</td>
</tr>
<tr>
<td>3:39 AM (+60 min post-release)</td>
<td>HPAC 4.04</td>
<td>2990</td>
<td>1417</td>
<td>51</td>
<td>0</td>
<td>0</td>
<td>984.55</td>
</tr>
<tr>
<td></td>
<td>HPAC 5.3</td>
<td>1496</td>
<td>639</td>
<td>387</td>
<td>154</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>p &lt; 0.00001 significant</td>
</tr>
<tr>
<td>4:09 AM (+90 min post-release)</td>
<td>HPAC 4.04</td>
<td>2990</td>
<td>1417</td>
<td>51</td>
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<td>0</td>
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<td>p &lt; 0.00001 significant</td>
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<tr>
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<td>2990</td>
<td>1417</td>
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<td></td>
<td>HPAC 5.3</td>
<td>2130</td>
<td>604</td>
<td>384</td>
<td>210</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>p &lt; 0.00001 significant</td>
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<tr>
<td>5:09 AM (+150 min post-release)</td>
<td>HPAC 4.04</td>
<td>2990</td>
<td>1417</td>
<td>51</td>
<td>0</td>
<td>0</td>
<td>959.67</td>
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<tr>
<td></td>
<td>HPAC 5.3</td>
<td>2130</td>
<td>604</td>
<td>374</td>
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<td>p &lt; 0.00001 significant</td>
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<tr>
<td>5:39 AM (+180 min post-release)</td>
<td>HPAC 4.04</td>
<td>2990</td>
<td>1417</td>
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<td>0</td>
<td>959.67</td>
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<tr>
<td></td>
<td>HPAC 5.3</td>
<td>2130</td>
<td>604</td>
<td>374</td>
<td>210</td>
<td>143</td>
<td></td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>p &lt; 0.00001 significant</td>
</tr>
<tr>
<td>6:09 AM (+210 min post-release)</td>
<td>HPAC 4.04</td>
<td>2990</td>
<td>1417</td>
<td>51</td>
<td>0</td>
<td>0</td>
<td>959.67</td>
</tr>
<tr>
<td></td>
<td>HPAC 5.3</td>
<td>2130</td>
<td>604</td>
<td>374</td>
<td>174</td>
<td>179</td>
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<td></td>
<td></td>
<td>p &lt; 0.00001 significant</td>
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<tr>
<td>6:39 AM (+240 min post-release)</td>
<td>HPAC 4.04</td>
<td>2990</td>
<td>1417</td>
<td>51</td>
<td>0</td>
<td>0</td>
<td>959.67</td>
</tr>
<tr>
<td></td>
<td>HPAC 5.3</td>
<td>2130</td>
<td>604</td>
<td>374</td>
<td>174</td>
<td>179</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>p &lt; 0.00001 significant</td>
</tr>
<tr>
<td>Output Time (EST)</td>
<td>Median (kg-s/m³)</td>
<td>Correlation</td>
<td>RMSE</td>
<td></td>
<td></td>
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<tr>
<td><strong>3:09 AM (+30 min post-release)</strong></td>
<td>HPAC 4.04 111.331</td>
<td>( r = 0.847 ) sig (2-tailed) = 0.000</td>
<td>60.608</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>HPAC 5.3 52.841</td>
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<tr>
<td><strong>3:39 AM (+60 min post-release)</strong></td>
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<td>( r = 0.883 ) sig (2-tailed) = 0.000</td>
<td>56.087</td>
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<tr>
<td></td>
<td>HPAC 5.3 75.189</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td><strong>4:09 AM (+90 min post-release)</strong></td>
<td>HPAC 4.04 105.909</td>
<td>( r = 0.891 ) sig (2-tailed) = 0.000</td>
<td>54.959</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HPAC 5.3 78.601</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td><strong>4:39 AM (+120 min post-release)</strong></td>
<td>HPAC 4.04 102.522</td>
<td>( r = 0.892 ) sig (2-tailed) = 0.000</td>
<td>54.697</td>
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<td></td>
<td>HPAC 5.3 75.971</td>
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<td></td>
</tr>
<tr>
<td><strong>5:09 AM (+150 min post-release)</strong></td>
<td>HPAC 4.04 99.605</td>
<td>( r = 0.893 ) sig (2-tailed) = 0.000</td>
<td>54.608</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HPAC 5.3 73.225</td>
<td></td>
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<td>HPAC 4.04 93.948</td>
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<td>54.283</td>
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<td></td>
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<tr>
<td></td>
<td>HPAC 5.3 70.397</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td><strong>6:09 AM (+210 min post-release)</strong></td>
<td>HPAC 4.04 89.116</td>
<td>( r = 0.894 ) sig (2-tailed) = 0.000</td>
<td>54.097</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>HPAC 5.3 68.307</td>
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<tr>
<td><strong>6:39 AM (+240 min post-release)</strong></td>
<td>HPAC 4.04 85.375</td>
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<td>53.938</td>
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<tr>
<td></td>
<td>HPAC 5.3 66.831</td>
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<td></td>
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</tr>
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</table>
Table 5: HPAC 4.04, 5.3 and ALOHA model results (concentration) for Graniteville, SC chlorine release.

<table>
<thead>
<tr>
<th>Downwind distance (km)</th>
<th>HPAC 4.04 ppm (60-min)</th>
<th>HPAC 5.3 ppm (60-min)</th>
<th>ALOHA 5.4.3 ppm (60-min)</th>
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<tr>
<td>0.1</td>
<td>11,642</td>
<td>2,831</td>
<td>156,000</td>
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<tr>
<td>0.2</td>
<td>5,860</td>
<td>2,971</td>
<td>81,100</td>
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<tr>
<td>0.5</td>
<td>553</td>
<td>2,652</td>
<td>17,200</td>
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<tr>
<td>1.0</td>
<td>51</td>
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<td>3,830</td>
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<tr>
<td>2.0</td>
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<td>7</td>
<td>672</td>
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<tr>
<td>5.0</td>
<td>13</td>
<td>0</td>
<td>58.3</td>
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<tr>
<td>10.0</td>
<td>0.32</td>
<td>0</td>
<td>10</td>
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<tr>
<td>25.0</td>
<td>0</td>
<td>0</td>
<td>N/A</td>
</tr>
</tbody>
</table>
EVALUATION OF AN IRRITANT GAS PLUME MODEL FOR EPIDEMIOLOGIC STUDY
Dev D. Jani¹, Mark Wilson¹, Jeffery Wickliffe¹, Jeffrey Shaffer², Roy Rando¹, Erik R. Svendsen³

¹ Department of Global Environmental Health Sciences, Tulane University School of Public Health and Tropical Medicine, New Orleans, LA, USA
² Department of Biostatistics and Bioinformatics, Tulane University School of Public Health and Tropical Medicine, New Orleans, LA, USA
³ Department of Public Health Sciences, Medical University of South Carolina, Charleston, SC, USA

Abstract

Previously, we reported the development of a Hazard Prediction and Assessment Capability (HPAC) plume dispersion model of the 2005 Graniteville, South Carolina, USA accidental release of chlorine. Here, we evaluate this model by spatial and statistical comparison with post-incident observed environmental indicators of exposure. Moderate agreement was found when the model was spatially compared to phytotoxic bleaching and corrosion events observed in 2 km radius around the release site. Acceptable agreement (< 30% deviation) was found when model estimations of centerline, downwind concentration was compared to deposition benchmarks derived from the existing literature base. When spatially compared to locations of injured or killed animals, model predictions of the plume footprint were in relatively good agreement. Model-predicted human casualties differed from observed casualty counts primarily due to the shielding effect of buildings. A statistical comparison of observed dog health outcome-derived exposure versus model predicted exposure showed relatively good agreement, particularly when a sub-cohort of indoor dogs was excluded. Although the model has been favorably evaluated, further evaluation
and assessment of the building infiltration effect is necessary before the model can be validated and applied in human epidemiologic study.

**Introduction**

The use of atmospheric transport and dispersion (AT&D) models in predicting the environmental and health impacts of toxic inhalational gas releases has been widely studied since the use of war gases during the 1920s (Hanna et al, 1982; Zou et al, 2009). Ensuring predictive accuracy has been a formidable challenge: these systems produce an ensemble of possible scenarios while the actual release is one iteration of an infinite number of scenarios. Although this limitation is unavoidable, emphasis on improving the algorithmic capabilities of this software includes the evaluation of AT&D models against post-release environmental indicators in both the experimental and natural setting. Numerous experiments have been performed in which inert and toxic gases are released, exposure observations collected and then compared to the model predicted dispersion and transport of the gas (Hanna et al, 2008; Warner et al, 2006a; Warner et al, 2006b; Warner et al, 2005; Warner et al, 2004; Pullen et al, 2005; among others).

As an example, several models, including the Hazard Prediction and Assessment Capability (HPAC), were compared to field experiment-derived mesoscale datasets of sulfur hexafluoride tracer gas by Chang and colleagues (Chang et al, 2003). This study found that only around 50% of HPAC predictions were within a factor of two of the observations. In URBAN 2000, the same tracer gas was again used in Salt Lake City, Utah trials and compared to HPAC
predictions (Warner et al, 2004). Here, HPAC overpredicted the observed concentrations and dosages in 19 out of 20 model configurations. Similarly, Hanna and colleagues compared HPAC to the Joint Urban 2003 field trials in Oklahoma City and found that overprediction was common (Hanna et al, 2007). A 2010 study produced for the U.S. Department of Homeland Security (DHS) Chemical Security Analysis Center (CSAC) by the Institute for Defense Analyses compared HPAC and three proprietary models using data from the 1982-1984 Thorney Island field experiments (Urban et al, 2010). The CSAC study, which was designed to assess model ability to predict gravity-induced dense gas slumping, showed that while all of the models captured the slumping effect, they underpredicted and overpredicted dosage by up to a factor of five. Of the four models, HPAC tended to perform better and predicted dosages usually within a factor of two.

Beyond those noted above, there have been several other experiments with the focus of identifying agreement between estimated and observed plumes (Hanna et al, 2008; Warner et al, 2006a; Warner et al, 2006b; Warner et al, 2005; Warner et al, 2004; Pullen et al, 2005; among others). The Jack Rabbit trials by CSAC (phase I in 2010 and phase II, which began in 2013) at the Dugway Proving Grounds in Utah are one example of the large-scale experiments being performed to study gas behavior and to validate existing modeling systems. The role of deposition as a removal mechanism, especially dry deposition and reactions with soil-based acids for highly reactive dense gases such as Cl₂, is an emerging area of research and large focus of the Jack Rabbit experiments (see
Hearn et al, 2012; Hearn et al, 2013; Hanna et al, 2012; Bauer et al, 2013 among others). A multitude of sensors and prepared deposition matrices surrounding the release site are utilized to analyze the dispersion, transport and interaction of Cl₂ and other gases post-release. This area of research has also expanded to account for deposition beyond greenbelts, such as on structures and other manmade objects (Dillon, 2009; Jonsson et al, 2005).

In regards to greenbelts (areas of vegetation in and around urban development), there has been some research performed in the area of phytotoxic injury as a result of chlorine exposure, including the use of phytotoxic indicators during post-accident investigation (Griffiths and Smith, 1989; Khan and Abbasi, 2001). While the body of literature is limited, two seminal studies have shown that the sensitivity range of plants to chlorine exposure varies dramatically depending upon species (Brennan et al, 1965; Brennan et al, 1966). In the case of Graniteville, a large portion of the greenbelt vegetation consists of mature pine trees. A 2001 publication by Schreuder and Brewer, researchers at the University of Montana, studied the effects on transpiration, growth and mortality on pine trees following an acute daytime chlorine exposure event (Schreuder and Brewer, 2001). In these studies among others, a noticeable injury and bleaching effect occurred when the species was exposed to 5 ppm or greater concentration of chlorine gas for over 2 hours. Further, both species of pine studied showed foliar injury, decreased photosynthetic efficiency and increased rates of cuticular transpiration until the affected needles defoliated. In laboratory studies with other vegetation species, damage thresholds of less than 5 ppm for two hours were
apparent (Sikora and Chappelka, 1996; Buckley et al, 2012). Clearly, both acute and chronic health effects in living organisms result from short-term exposure to chlorine gas.

A body of literature spanning back to the late 1800s does exist regarding animal toxicity to chlorine. Particularly, a seminal and foundational series of experiments on dogs has shown that 30-min acute exposures of below 250 ppm tend to have no health effects, while exposures between 251-649 ppm may cause immediate or delayed injuries and those above 650 ppm generally results in mortality (Underhill, 1919). Similar experiments have been also performed on primates, rabbits, cats and rodents, but dogs are employed far more often in occupational and recreational settings (Coppinger et al, 1995). As performed here, the observed health effects in dogs is an innovative comparative method to evaluate in-silico models when data exists. Animal health effects data, when combined with other environmental indicators of exposure such as the aforementioned phytotoxicity, corrosion or deposition benchmark data, can be utilized as important evaluation criteria when assessing model predictive accuracy and informing potential toxicity in humans.

Of the aforementioned experimental releases, even the largest have not exceeded 20,000 kg, less than half of the total multiphase volume expelled in the 2005 Graniteville, South Carolina, USA railcar release of chlorine (DHS CSAC, 2016). Large-scale releases, particularly those in urban or settled areas, generally utilize inert tracer gases for public health and safety. Although experiments such as the Jack Rabbit trials are performed at military proving
grounds, safety concerns, environmental regulations and financial constraints often prevent scientists from releasing large quantities such as the 80,000 kg that an average chlorine tanker railcar carries. The comparison of model predictions to exposure observations collected following an actual release is difficult due to the lack of data. Indeed, the immediate priority post-release is emergency response and life safety. Although the data set is somewhat limited, the Graniteville incident presents a unique opportunity to evaluate a model prediction with actual environmental and health effects exposure data collected post-incident.

**Methods**

*Description of the exposure event*

A detailed description of the Graniteville incident is presented in Jani et al, 2015 and summarized here. On January 6, 2005, a freight train traveling at approximately 76 km/h was diverted onto an industrial spur at the Avondale Mills complex in Graniteville, South Carolina, United States of America. Due to an improperly configured switch, the traveling train collided with a stationary train at approximately 2:39 AM Eastern Standard Time (EST). Three railcars containing chlorine were among the 14 that derailed and one of these railcars was ruptured, releasing an estimated 54,915 kg of chlorine (both in gaseous and liquid form) into the surrounding community (Jani et al, 2015; NTSB, 2005a). As a result of this accidental release of toxic dense gas, 5,400 (76% of total impacted population) were evacuated, over 550 were treated at the hospital and nine were killed. It is important to note that the evacuation occurred at approximately 4:00
PM EST on the day of release due to the cleanup process and was not an immediate incident response. Rather, the local public safety answering point (PSAP) issued a shelter-in-place order for all residents using reverse 911 within 30-minutes post-release (NTSB, 2005). Graniteville is a small industrial town located within a shallow creek valley. This terrain likely contributed to limiting the crosswind dispersion and enhancing the downwind dispersion, as our HPAC 5.3 plume model illustrates (Figure 1). The ambient weather conditions prevented the plume from dispersing towards Aiken, with an estimated 28,000 residents in 2005 (U.S. Census Bureau).

**Description of the models and usage**

Previously, we modeled the Graniteville incident in unclassified versions of both the Hazard Prediction and Assessment Capability versions 4.04 and 5.3 General Distribution (HPAC, Defense Threat Reduction Agency [DTRA]) and ALOHA (National Oceanic and Atmospheric Administration/US Environmental Protection Agency). As a software system, HPAC consists of several integrated modules which develop the source term based upon input parameters and then estimates transport and dispersion of the chemical away from the source location. The iTRANS source term model, developed by Science Applications International Corporation (SAIC), allows estimation of release quantity based upon the physical characteristics of the chemical and release mechanism such as mode of transport. HPAC utilizes Second-order Closure Integrated Puff (SCIPUFF), developed by Sage Management, for estimating transport and dispersion. SCIPUFF is a Langrangian model which simulates the released
chemical as Gaussian puffs and is particularly well-suited for dense gas releases. For purposes of predicting the concentration variance due to meteorological conditions, HPAC utilizes the Stationary Wind Field and Turbulence (SWIFT) wind model which creates multi-dimensional wind fields based upon basic knowledge of localized topographical features and contours. In addition to direct input using observational weather data, HPAC can also import data from DTRA’s Meteorological Data Service (MDS) (Urban et al, 2010). HPAC also contains several urban models; however, this function was not utilized in this study due to the lack of building databases for the Graniteville area. The plume model and isopleths can be exported to GIS software for visualization and further analysis. Here, we have plotted onto a ArcMap topographic base map (Figure 1) (ArcMap 10, Esri, Redlands, CA). Our HPAC 5.3 model was previously selected for evaluation over other software due to these capabilities.

**Comparison to environmental exposure indicator and other evaluation data**

A range of available environmental data was evaluated for both comprehensiveness and feasibility of use within our comparative analysis. Eventually, we settled upon the use of phytotoxicity, corrosion location, literature-established deposition benchmark, casualty estimation and animal toxicity data. While no formal vegetation damage assessment was performed immediately following the incident, researchers from the Savannah River National Laboratory (SRNL) visually recorded the spatial extent of vegetation damage approximately one month post-release (Buckley et al, 2007). The researchers also noted that the bleaching effect was limited to a height of approximately 10 m in a 2 km
radius around the release site. Based upon this observation, the HPAC 5.3 model was adjusted to estimate concentration at a height (z) of 10 meters. Based upon existing phytotoxicity research, a plume was developed which depicted the predicted area at which an exposure of at least 5 ppm was sustained for two hours or more. This plume was plotted in ArcMap and compared to the imported vegetation damage survey shapefile. Similarly, observed episodes of corrosion by on-site responders and environmental remediation personnel due to surface reactions with chlorine gas were plotted as a layer and compared.

The role of deposition in attenuating plume dispersion and transport, particularly due to dry deposition, interactions with greenbelt vegetation and manmade structures, is an emerging area of research. A body of research exists which has examined the deposition rates (or deposition velocity, Vd) in a number of controlled experiments. Based upon these experiments and mathematical extrapolation, approximate benchmarks for deposition have been developed. As presented by Dillon (2005), highly reactive gases such as chlorine may deposit 50% of the total airborne concentration within 150 meters of the release site under stable atmospheric conditions over 60 minutes. Likewise, a 60-min averaged concentration plume was generated in HPAC and centerline airborne concentration predicted at 100 points in 30 meter intervals starting at the source point to the edge of plume. These values were subsequently graphed using Microsoft Excel (Microsoft, Redmond, WA). The model predicted deposition was then compared with this approximate deposition standard described above. Additionally, because HPAC is designed to support critical decision-making
including protective actions, population databases and other statistical data are incorporated into the software suite. The casualty estimation tool within HPAC was utilized to predict both fatality and injury (using estimated 2005 nighttime population statistics) and subsequently compared with the actual observed health outcomes.

There are limited datasets available on animals exposed during the Graniteville release due to the immediate priority of protecting human life. The animal secondary data set utilized for this study was sourced from three different sub-sets: a survey of eight veterinary practices within the Graniteville area who treated exposed pets, the South Carolina Department of Health and Environmental Control (DHEC) Acute Epidemiological Survey which was administered within 48 hours post-release, and the Norfolk Southern/DHEC Housing Inspection Survey (HIS). The majority of the usable animal data was from the first two sub-sets; the HIS focused heavily on the status of the physical residence itself and included minimal information on pet status. The initial larger database, which numbered 303 animals, was reviewed and any animals without reported location information were omitted. With the assistance of a public health veterinarian working as part of the Graniteville Recovery and Chlorine Epidemiology (GRACE) Study, each animal was then classified into one of seven outcome categories based upon reported outcome: died, euthanized due to unrelated reason, missing, injured/ill, no apparent effect, assume no apparent effect and unknown outcome. The data was trimmed further by removing those animals classified as euthanized (due to an unrelated reason), missing, assume
no apparent effect, and unknown outcome. This reduced the overall dataset to 117 animals, comprised of birds (3), cats (32), chickens (6), dogs (63), ducks (2), a ferret (1), fish (5), a frog (1), goats (2), a lizard (1) and a possum (1). These animals were reclassified into three consolidated categories based upon reported health outcome: no health effect, injured, or killed (Figure 2). For spatial comparison, the locations of all animals were plotted in ArcMap along with the plume model (Figure 3).

**Description of the dog comparative evaluation criteria**

A further analysis was performed utilizing the dog data (n = 63). Based upon existing toxicology profiles (Underhill 1919), each dog was assigned to experimentally derived 30-min acute exposure ranges by observed health outcome: low exposure/no health effect (≦ 250 ppm), medium exposure/injured (251 - 649 ppm) and high exposure/killed (≧ 650 ppm). Each reported dog location was geocoded into the HPAC model and peak 30-min predicted exposure was generated for each dog. To identify the role of shielding (i.e. indoor vs outdoor location) and improve sensitivity and specificity, a sub-cohort which omitted all dogs that were reported to be indoors was created (n = 56). For both groups, a comparison of the observed health outcomes and model-predicted exposure was performed by first conducting exploratory data analysis such as descriptive statistics, scatterplots and box plots. Then, chi square analysis (goodness of fit) was performed using IBM SPSS Statistics (Version 20, IBM, Armonk, NY). For the latter analysis, our null hypothesis states that the predicted exposures (by category) match the observed exposures.
Results

Phytotoxicity and Corrosion Analysis

When the visible vegetation bleaching effect was spatially compared to the model predicted area at which > 5 ppm exposure was sustained for two hours or more, there was noticeable overprediction by the model (Figure 4). The bleaching of pine largely was confined to an elongated downwind shape that widened as distance from the source point increased. The model predicted area was largely circular, indicative of the gravity slumping effect of dense gas but not particularly fully representative of Graniteville’s topographic contours. However, an important observation here is that the vast majority of the extent of vegetation bleaching was within the predicted isopleth. All of the observed corrosion on mill and other buildings were within the plume footprint in proximity to the source point (Figure 4).

Deposition Benchmark Data Analysis

In the deposition benchmark analysis, 60-min averaged centerline airborne concentrations ranged from 4,088 ppm at the release site to 0.06 ppm at 2.9 km directly downwind (Figure 5). There was a noticeably sharp decrease in concentration within the first 200 meters, followed by a slight increase and then gradual decrease. At 150 meters downwind, the predicted concentration was 2,882 ppm, or 70% of the concentration at the source point. Although this varies from the 50% benchmark, it is well within the up to 40% deviation expected between model predictions and observations, including quantitatively derived benchmarks (Chang and Hanna, 2004; Venkatram, 1979; Olesen et al, 2001).
Animal Health Outcome Analysis

The locations of animals with health outcomes of “injured” (Figure 6) and “killed” (Figure 7) was plotted against the HPAC plume. Of the total animal cohort (n = 117), 24 were reported injured and 31 killed. The remainder had no observed health effect. For injured animals, all but two (dogs) were located within the plume footprint, although both exhibited adverse health effects. The locations of all 31 animal fatalities were within the plume itself, largely centered around the source point and highest exposure threat zones. For dogs specifically, 14 of 63 were located outside of the plume footprint, but only two of those exhibited injuries (Figure 8). The remaining 49 were within the plume, largely centered around a 1.5 km radius from the release point. The remaining had no observed health outcome, in agreement with the model predicted lack of exposure.

For all dogs (n = 63) and outdoor dogs only (n = 56), classification by health outcome (observed) and model exposure estimation (predicted) was reported (Table 1). The results were then stratified by whether or not the model prediction and field observation matched by exposure category (Table 2). Following the established standards in dispersion model evaluation exploratory data analysis, a scatter plot visualization (Figure 9) and box plot (Figure 10) comparing the model predicted exposure to the classification by health outcome (observed) suggested overall good agreement but a number of outliers in all three categories. To account for these outliers, dogs reported to be indoors were removed from the cohort. All dogs removed were mismatched between field observed health outcome versus model predicted exposure, with each predicted
exposure far higher than what the observed health outcome supported. The results for this sub-cohort were also stratified by whether or not the predictions and observations matched (Table 1). A scatter plot (Figure 11) and box plot (Figure 12) was generated which suggested better agreement for all three categories, with fewer outliers. Chi square analysis for both dog cohorts was significant (Table 3).

**Casualty Estimation Analysis**

HPAC 5.3 model estimated casualties based upon night-time population differed significantly from the observed casualty statistics when differentiated between fatality and injury. Interestingly, total numbers were similar (Table 4). The model estimated 575 total casualties compared to the observed number of 563. Fatality numbers differed greatly, with the model estimating 500 fatalities compared to 9 observed. Similarly, the model predicted 75 injuries, compared to the 554 who were treated at local hospitals with respiratory distress and other symptoms (NTSB, 2005).

**Discussion**

Building upon our previous work, we have evaluated a Hazard Prediction and Assessment Capability (HPAC) version 5.3 irritant gas plume model against upon applicable data (phytotoxicity, corrosion, deposition benchmark, casualty and animal toxicity) selected from a larger survey of available environmental exposure indicator data. An analysis of the severe phytotoxic bleaching effect clearly shows the limited horizontal dispersion due to terrain-induced dense gas effects such as gravitational slumping. As also shown in similar studies by
Buckley and others, the observed vegetation is clearly shorter and narrower than the exposure area predicted by our model. The significant overprediction is likely due to an inability to fully account for the terrain effects, particularly in Graniteville where the valley extended and turned the plume direction within the creek valley. However, one consideration that may have limited the bleaching effect is that vegetation respiration rates are typically much lower at night compared to the day. The aforementioned studies which describe the response of pine trees to chlorine exposure were conducted in the laboratory and/or daytime setting, which is not fully representative of the Graniteville environmental conditions (including temperature and humidity) and time of release. Further, the rate of deposition will typically decrease when the surrounding environment is warmer than the releasing gas due to heat transfer-induced loss of gas stability. Although all of the corrosion episodes were located within the plume, further work analyzing the actual exposure at each of these locations should be performed to better quantify model bias.

As noted previously, the impact of dense gas deposition into dry soils, greenbelts and environmental objects is an emerging area of research. The rate of deposition is highly incident-specific. The immediate area around the Graniteville release contained semi-rural surfaces for deposition and consists mainly of low buildings and industrial parks before opening to predominantly pine forest and residential neighborhoods. Additionally, a large-volume release will typically rapidly surpass the deposition capacity (i.e. dry deposition into soils) of the immediate surrounding environment, limiting the attenuation of a dispersing
plume. Our model predicted that 30% of the airborne concentration was deposited within the first 150 meters. While this is within the up to 40% deviation expected between predictions and benchmark/observation data, it is below the 50% deposition rate suggested in the literature. The majority of models utilize a linear deposition velocity (Vd) and while HPAC utilizes a more dynamic approach, the model may be underestimating deposition rate. The slight increase in concentration observed beyond 120 m downwind on the centerline may be due to a dispersion and terrain effect (i.e. gravity slumping) over the 60-min output period. The fairly rapid and linear decrease in concentration after this is indicative of decreasing gas stability and increasing behavior similar to a neutrally buoyant gas as mixing occurs.

The majority of injured and killed animals were within the plume model footprint, which positively evaluates our model. Those that were reported ill or killed but were outside of the plume footprint may have been exposed and then attempted to escape the plume before succumbing to the effects of exposure. When dogs were further investigated, it was apparent that a shielding effect protected dogs that were reported to be indoors. Particularly, each of the 7 dogs reported to be indoors had very high model predicted exposures, but no or low-level observed health outcomes. The differentiation between indoor and outdoor exposure is a critically important component of accurately estimating human exposures. In Graniteville, the majority of human exposures were indoors due to the time of day. The differences between model estimated casualties and actual observed casualties further supports this because the number of predicted
fatalities far exceeded that which was observed. The HPAC estimations are for unprotected night-time population, which does not accurately reflect the reality due to the majority of human exposures being indoors. Similar to the dogs, this shielding effect likely prevented the greater number of casualties the HPAC model predicted. The infiltration of dense toxic gas into buildings is difficult to study due to the numerous regional differences in construction and individual behavior such as leaving windows open for ventilation. Given that the month of release was January, it is assumed that the majority of homes had most direct ventilation pathways closed due to colder weather. This likely prevented major infiltration of buildings, particularly for those residing within the high threat areas of the plume.

There are several limitations which may influence the results presented here. Particularly, although nearly all injured and killed animals were within the plume footprint, those locations may not necessarily represent exposures that result in illness or death for species other than dogs. The chlorine exposure toxicology is not known for many of the reported species, so this location bias is unverifiable. However, the general notion that the dose-response outcome for smaller animals is generally more severe compared to larger animals may support the belief that once exposed to high concentrations, the majority of smaller species within our sample likely did not travel great distances prior to being killed. For the dog analysis, it is important to note that several factors could have led to the existing mismatches between the model predicted exposure and observed health outcome derived exposure. For example, the existing physiology
and/or existing illness in the identified dogs may have exacerbated the health
effects of chlorine exposure. Some of the dogs were not located and treated until
days after the release and the lack of nourishment may have contributed to
health outcomes more severe than the original exposure (or model predicted
exposure) may have caused. Further, a reporting bias may be present in some
dogs because while all dogs were examined and treated by certified
veterinarians, owners were asked to recall the location of the dogs at time of
release and probable exposure. Many were located within a fenced in yard or
compound and therefore could not escape or travel far distances. Individuals
dogs also tend to exhibit different behavior to exposure (i.e. some experiments
have found more intelligent breeds utilize their paws to filter breath).

Beyond the limitations described above, the analysis here did not take into
consideration several factors which may accelerate the removal process. For
example, reactions that occur between chlorine, other ambient chemicals and
surfaces (such as metallurgic corrosion) may significantly contribute to limit the
hazard extent of the plume. Nearly all tracer gas studies, including those
described here, evaluate the agreement between observed and predicted
dispersion, but usually do not study further the influence of ambient reactions on
bias. This is a very dynamic factor which is difficult to properly account for and
requires further study. Chlorine also rapidly reacts with water to form hydrochloric
acid and the ambient atmosphere during the time of release was highly humid
and foggy, which likely increased the removal rate and attenuated the dispersion
and transport of the gas. The model itself does not fully account for this.
Additionally, while the surrounding area was not densely packed with buildings, the effects of the urban canyon (or similar air-flow effects) are not accounted for by the HPAC model outside of areas which have specific urban model datasets built within the software package.

**Conclusion and Future Direction**

While we have concluded that our HPAC model of the Graniteville incident is favorably evaluated, further work is needed before it can be assumed to be fully validated. Plume models often significantly overpredict the exposure isopleths, fatalities and environmental effects of a dense gas release. The primary cause of this overprediction is the inability for even the most sophisticated models to account for all removal mechanisms and variability between individual toxic gases. The implications for health effects is profound and this work illustrates the need for further research in evaluation methodologies, particularly using observed indicator data from actual, not necessarily experimental, large-scale releases. Further, additional research should be performed to examine building infiltration and dynamic removal mechanisms such as dry deposition and ambient chemical reactions with the atmosphere and surfaces.
References


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UNDERHILL, F. P. (1919). The physiology and experimental treatment of poisoning with the lethal war gases. *Archives of Internal Medicine, 23*(6), 753.


Table 1: Frequency values for both dog cohorts (all and outdoor only) differentiated by health outcome category.

<table>
<thead>
<tr>
<th>Cohort</th>
<th>No Health Effects (≦ 250 ppm)</th>
<th>Injured (251-649 ppm)</th>
<th>Killed (≧ 650 ppm)</th>
<th>Kruskal-Wallis Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Dogs (n = 63) Health Outcome (Observed)</td>
<td>37 (58.7%)</td>
<td>19 (30.2%)</td>
<td>7 (11.1%)</td>
<td>p = 0.002 significant difference</td>
</tr>
<tr>
<td>All Dogs (n = 63) Model Exposure (Predicted)</td>
<td>44 (69.8%)</td>
<td>5 (7.9%)</td>
<td>14 (22.2%)</td>
<td></td>
</tr>
<tr>
<td>Outdoor Dogs (n = 56) Health Outcome (Observed)</td>
<td>33 (58.9%)</td>
<td>16 (28.6%)</td>
<td>7 (12.5%)</td>
<td>p = 0.00 significant difference</td>
</tr>
<tr>
<td>Outdoor Dogs (n = 56) Model Exposure (Predicted)</td>
<td>44 (78.6%)</td>
<td>3 (5.4%)</td>
<td>9 (16.1%)</td>
<td></td>
</tr>
</tbody>
</table>
Table 2: Dog cohorts stratified by matched and unmatched pairs between model predicted and field observed.

<table>
<thead>
<tr>
<th>Exposure Category (ppm)</th>
<th>No Health Effects</th>
<th>Injured</th>
<th>Killed</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Match</td>
<td>31</td>
<td>3</td>
<td>6</td>
<td>40</td>
</tr>
<tr>
<td>Mismatch</td>
<td>6</td>
<td>16</td>
<td>1</td>
<td>23</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exposure Category (ppm)</th>
<th>No Health Effects</th>
<th>Injured</th>
<th>Killed</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Match</td>
<td>31</td>
<td>3</td>
<td>6</td>
<td>40</td>
</tr>
<tr>
<td>Mismatch</td>
<td>2</td>
<td>13</td>
<td>1</td>
<td>16</td>
</tr>
</tbody>
</table>

Note: all omitted dogs between full and outdoor cohorts were mismatched.
Table 3: Chi square (goodness of fit) analysis for both dog cohorts

<table>
<thead>
<tr>
<th>Cohort</th>
<th>Chi-Square (p-value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Dogs (n = 63)</td>
<td>21.454 (.000)</td>
</tr>
<tr>
<td>All Dogs (matched pred vs obs)</td>
<td>80.000 (.000)</td>
</tr>
<tr>
<td>All Dogs (mismatched pred vs obs)</td>
<td>12.901 (.012)</td>
</tr>
<tr>
<td>Outdoor Dogs (n = 56)</td>
<td>36.343 (.000)</td>
</tr>
<tr>
<td>Outdoor Dogs (matched pred vs obs)</td>
<td>80.000 (.000)</td>
</tr>
<tr>
<td>Outdoor Dogs (mismatched pred vs obs)</td>
<td>9.941 (.007)</td>
</tr>
</tbody>
</table>
Table 4: Model estimated vs actual observed casualties from the Graniteville incident.

<table>
<thead>
<tr>
<th>Casualty</th>
<th>Model Estimation</th>
<th>Actual Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatalities</td>
<td>500</td>
<td>9</td>
</tr>
<tr>
<td>Injuries</td>
<td>75</td>
<td>554</td>
</tr>
<tr>
<td>Total Casualties</td>
<td>575</td>
<td>563</td>
</tr>
</tbody>
</table>
DISCUSSION

The focus of this project has been to (1) develop an atmospheric transport and dispersion model that accurately estimates the 2005 Graniteville, South Carolina, USA railcar release of chlorine and (2) evaluate this model against post-release environmental indicators of exposure. The ultimate purpose is to apply this model in human exposure assessment and epidemiologic study, particularly for those who were acutely exposed during the Graniteville incident.

In manuscript #1, titled “Modeling an Irritant Gas Plume for Epidemiologic Study”, we independently derived a source term, validated microenvironmental meteorology observations and developed an initial Hazard Prediction and Assessment Capability (HPAC) 4.04 plume model. Our estimated multiphase release volume of 54,915 kg is similar to that reported elsewhere in the literature. Of note, the National Transportation Safety Board (NTSB) official report estimated a release volume of 54,431 kg (NTSB, 2005). Hanna and colleagues derived a discharge volume of 53,210 kg (Hanna et al, 2008). Using preserved source term inputs, the incident was also modeled in the Areal Locations of Hazardous Atmospheres (ALOHA). The ALOHA model significantly overpredicted the plume compared to HPAC, although we note that the ALOHA model is well suited for its primary application of emergency response. The HPAC 4.04 plume was identified as the best candidate for further study at the time of development.

In manuscript #2, titled “Comparison of Three Irritant Gas Plume Models for Epidemiologic Study”, we compared the HPAC 4.04 model to a newer HPAC
5.3 model. When using the preserved inputs described in manuscript #1 (source term, meteorology and terrain), the HPAC 4.04 model tended to overpredict compared to the HPAC 5.3 model. Again, ALOHA overpredicted when compared to both HPAC models. Based upon our analysis, the HPAC 5.3 model was identified as the best candidate (comparably to HPAC 4.04 and ALOHA) to evaluate using indicator data. We avoided the use of proprietary model systems due to accessibility and other issues that would be faced by government and academic researchers. In manuscript #3, titled “Evaluation of an Irritant Gas Plume Model for Epidemiologic Study”, we compared the HPAC 5.3 model to several sets of exposure indicator data collected in the aftermath of the Graniteville incident: phytotoxicity bleaching effect, episodes of metallurgical corrosion, approximate deposition benchmark standards established in literature, casualty estimations, and animal health exposure data. A further sub-study was performed using observed dog health outcome data paired with model estimated exposure estimations. The evaluation of a plume model with the above indicators, particularly animal health effects data, represents a relatively novel approach as most model evaluation studies compare computer-predicted simulations with tightly controlled experimental releases of inert tracer and/or toxic industrial gases.

Although our ultimate focus here was not necessarily to advance the field of emergency response, it is important to consider the public safety implications of our work. Specific to the Graniteville incident, a combination of time of day, ambient atmospheric conditions and population density surrounding the release...
site minimized the number of casualties. A survey of similar accidents produced an average of 0.3 - 0.9 fatalities per 1,000 kg of toxic industrial gas released (Marshal, 1977; Khan and Abbasi, 1999). When extrapolated to the Graniteville incident, this would yield approximately 168 to 504 fatalities (compared to the 9 that occurred). Successful response to a catastrophic, large-scale chemical incident is contingent upon rapid assessment of the situation, including but not limited to detection, classification of the toxic agent and dissemination of situational awareness so the necessary assets (personnel and materiel) may be dispatched to the scene. The Graniteville incident also exemplified the importance of rapid protective actions such as evacuation or shelter-in-place.

Recognizing that the major inundation of the surrounding area with dense toxic gas would prevent successful evacuation measures, the local public safety answering point (PSAP) issued a shelter-in-place order post-release. This action likely saved countless lives. The evacuation itself was ordered until several hours later when the cleanup process began and the gas had dispersed from the area. In the context of chlorine, the dense nature of the gas may prevent rapid dispersion and transport out of the area, so responders must be prepared for a prolonged event with decontamination needs, large implications for hospital capacity and surge, and sustained mass evacuations. Plume dispersion models generally overpredict the downwind hazard. Although the priority of life safety is foremost, the use of properly evaluated - or perhaps validated - atmospheric dispersion modeling technologies with increased predictive accuracy can add efficiency and effectiveness to a public health emergency response. Yet, the
need for high predictive accuracy within atmospheric transport and dispersion modeling systems is critically higher when using the predicted data to assess health effects or within an environmental epidemiology study.

Models that overpredict the downwind extent of hazard - whether it is due to inadequate inclusion of removal mechanisms, insufficient knowledge of atmospheric chemistry or other factors - can significantly overestimate human exposure at specific or moving receptor points. For purposes of applying dispersion models to exposure assessment and/or environmental epidemiology study, this is inadequate. Therefore, as demonstrated here, it is critical that this model bias be analyzed by comparing the in silico model estimation with observations following experimental or actual releases. The extensive literature review mentioned within this dissertation of experimental studies shows that while tracer gases are widely used to assess model dispersion capability, these experiments do not adequately account for the wide range of removal mechanisms (such as dry deposition and ambient chemical reactions). The use of dense toxic gases in field trials is rare and difficult to conduct and the few experiments that have been performed may not be representative of many planning scenarios due to location and climatology variations.

There are a number of limitations within this study that are described in further detail in each of the three manuscripts. Although the comparison of model predictions with observations currently represents the primary means of evaluating dispersion model accuracy, this direct comparison method is limited because of two predominant reasons: (1) as aforementioned, plume models
estimate ensemble means while an observation is one realization out of an infinite possible scenarios under the same conditions, and (2) most uncertainties in model predictions and field observations arise from different sources. In regards to the secondary survey data we utilized (particularly within the animal health effects evaluation), the locations of animals were generally self-reported by owners and/or reported by the extraction teams sent to retrieve the animal. There is possibility of location bias here; however, a thorough review of the available data was performed to eliminate any questionable entries prior to settling on the cohort of 117 animals. For dogs specifically, the exhibited health outcomes may have been more exacerbated due to pre-existing medical condition and the effects of lack of nourishment between the time of release and when the dog was treated. A major limitation of current dispersion modeling technology is the ability to fully account for removal mechanisms. In addition to deposition into soils and on surfaces, additional removal occurs due to ambient chemical reactions, atmospheric turbulence and other microenvironmental factors. Photolytic reactions also influence removal but was not considered a major factor with this particular study as the release occurred at night. As such, the stochastic nature of plume modeling can produce variations of up to 40% between predictions and observations (Venkatram, 1979). Similarly, it is commonly accepted that a model can be favorably evaluated if the fraction of predictions is within a factor of two of observations (Chang and Hanna, 2004).
CONCLUSION & RECOMMENDATIONS

The HPAC 5.3 model of the Graniteville incident has been favorably evaluated in this study. Particularly, although bias was identified between the model prediction and observed indicators, there was overall good agreement. Yet, further work is needed before the model can be fully validated and applied to human exposure assessment and epidemiologic study. The shielding effect that buildings afford - or differentiating between indoor versus outdoor exposure - is critical in understanding the actual exposure to humans. In Graniteville, the time of release (2:39 AM) meant that the majority of those exposed were indoors. The model itself estimates outdoor exposures, so further calculation must be performed before accurately identifying the individual exposures. The highest fidelity of this analysis can be obtained by analyzing the regional construction and building-specific infiltration rates. Additional evaluation work should be performed using other data sets (such as soil and air quality samples) or expansion of data sets that were utilized in this study (such as corrosion). With further work, model bias can be quantified, adjusted and the model itself corrected to ensure high predictive accuracy when estimating individual exposure and dosages.
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## Dissertation Study Estimation:

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<tbody>
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</tr>
<tr>
<td>Time</td>
<td>02:39 AM Eastern</td>
</tr>
<tr>
<td>Location</td>
<td>33 degrees, 33’ 43.02” N 81 degrees, 48’ 29.99” W</td>
</tr>
<tr>
<td>Upstream pressure in tank</td>
<td>46 psig</td>
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<tr>
<td>Temperature in tank</td>
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<tr>
<td>Release height</td>
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<td>Area of opening</td>
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<tr>
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<tr>
<td>(NOTE: actual conditions will be</td>
<td>from RAWS analysis)</td>
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<tr>
<td>Atmospheric stability</td>
<td>E</td>
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<td>Wind speed</td>
<td>RAWS Stations</td>
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<td>Duration</td>
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<td>Sum of releases</td>
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</tr>
<tr>
<td>Elevation of Car # 9</td>
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### NTSB Official Report (Nov 29, 2005)

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<tr>
<td>Time</td>
<td>02:39 AM (Eastern)</td>
</tr>
<tr>
<td>Speed of NS 192 (collided into NS P22)</td>
<td>47 MPH</td>
</tr>
<tr>
<td>Time/Length until NS 192 came to rest post-collision</td>
<td>20 seconds / 145 feet for lead locomotive</td>
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<tr>
<td>Extent of cloud based upon responder/fatality observations</td>
<td>2,500 feet to N, 1,000 feet to E, 900 feet to S, 1,000 feet to W</td>
</tr>
<tr>
<td>Ruptured tank car (UTLX 900270) full load</td>
<td>90 tons of chlorine (180,000 lbs or 13,830 gallons) DOT 105J500W</td>
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<tr>
<td>Release amount</td>
<td>120,000 lbs (most in two phase jet within first minute)</td>
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<td>Rupture characteristics</td>
<td>Right side near middle and slightly towards the A-end; 34 inches long and 5 inches wide at widest point</td>
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<tr>
<td>Temp of Cl(_2) at derailment</td>
<td>26 F</td>
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<tr>
<td>Ruptured tank car remaining load</td>
<td>30 tons (4,609 gallons)</td>
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<tr>
<td>Wx based upon Augusta, GA NWS station (17 miles away)</td>
<td>02:32 AM (Eastern) Winds: 7 MPH from SSW Visibility: 5 miles Clear skies Temperature: 55 F Dew Point: 54 F No precipitation</td>
</tr>
</tbody>
</table>
APPENDIX 1.2

WEATHER VALIDATION – SAMPLING POINTS
Weather Validation - Location of Sampling Points

n = 1,024
Green dot = release site
DEVELOPMENT AND EVALUATION OF AN IRRITANT GAS PLUME DISPERSION MODEL FOR EPIDEMIOLOGIC STUDY

APPENDIX 1.3

HPAC 4.04 Plume (8 hour AEGL)
APPENDIX 1.4

HPAC 4.04 Plume (Surface Dosage)

4 Hours Maximum in 30 Minute Timesteps
DEVELOPMENT AND EVALUATION OF AN IRRITANT GAS PLUME DISPERSION MODEL FOR EPIDEMIOLOGIC STUDY

APPENDIX 1.5

HPAC 5.3 Plume (8 hour AEGL)
DEVELOPMENT AND EVALUATION OF AN IRRITANT GAS PLUME DISPERSION MODEL FOR EPIDEMIOLOGIC STUDY

APPENDIX 1.6

HPAC 5.3 Plume (Surface Dosage)

4 Hours Maximum in 30 Minute Timesteps
HPAC 5.3 Surface Dosage - 0339 EST

Sources: Esri, HERE, DeLorme, TomTom, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community
HPAC 5.3 Surface Dosage - 0639 EST
DEVELOPMENT AND EVALUATION OF AN IRRITANT GAS PLUME DISPERSION MODEL FOR EPIDEMIOLOGIC STUDY

APPENDIX 1.7

HPAC 4.04 vs 5.3 (Surface Dosage)

4 Hours Maximum in 30 Minute Timesteps
HPAC 4.04 vs 5.3 Surface Dosage - 0309 EST
HPAC 4.04 vs 5.3 Surface Dosage - 0409 EST
DEVELOPMENT AND EVALUATION OF AN IRRITANT GAS PLUME DISPERSION MODEL FOR EPIDEMIOLOGIC STUDY

APPENDIX 1.8

HPAC 4.04 vs 5.3 (Surface Dosage) with Sampling Points

4 Hours Maximum in 30 Minute Timesteps
HPAC 4.04 vs 5.3 Surface Dosage - 0309 EST
SAG Sampling Points (n=7,835).

Sources: Esri, HERE, DeLorme, TomTom, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community
HPAC 4.04 vs 5.3 Surface Dosage - 0439 EST
SAG Sampling Points (n=8,807)
HPAC 4.04 vs 5.3 Surface Dosage - 0509 EST
SAG Sampling Points (n=8,939)
HPAC 4.04 vs 5.3 Surface Dosage - 0609 EST
SAG Sampling Points (n=9,302)
HPAC 4:04 vs 5.3 Surface Dosage - 0639 EST
SAG Sampling Points (n=9,446)
DEVELOPMENT AND EVALUATION OF AN IRRITANT GAS PLUME DISPERSION MODEL FOR EPIDEMIOLOGIC STUDY

APPENDIX 1.9

Manuscript #1 – Published Version
Modeling an irritant gas plume for epidemiologic study

Dev D. Jani\textsuperscript{a}, David Reed\textsuperscript{b}, Charles E. Feigley\textsuperscript{c} & Erik R. Svendsen\textsuperscript{a}

\textsuperscript{a} Department of Global Environmental Health Sciences, Tulane University School of Public Health and Tropical Medicine, New Orleans, LA, USA

\textsuperscript{b} Department of Epidemiology and Biostatistics, University of South Carolina Arnold School of Public Health, Columbia, SC, USA

\textsuperscript{c} Department of Environmental Health Sciences, University of South Carolina Arnold School of Public Health, Columbia, SC, USA

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Modeling an irritant gas plume for epidemiologic study

Dev D. Jania, David Reedd, Charles E. Feigleye and Erik R. Svendse*a*

aDepartment of Global Environmental Health Sciences, Tulane University School of Public Health and Tropical Medicine, New Orleans, LA, USA; bDepartment of Epidemiology and Biostatistics, University of South Carolina Arnold School of Public Health, Columbia, SC, USA; cDepartment of Environmental Health Sciences, University of South Carolina Arnold School of Public Health, Columbia, SC, USA

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Plume dispersion modeling systems are often used in assessing human exposures to chemical hazards for epidemiologic study. We modeled the 2005 Graniteville, South Carolina, 54,915 kg railcar chlorine release using both the Areal Locations of Hazardous Atmospheres and Hazard Prediction and Assessment Capability (HPAC) plume modeling systems. We estimated the release rate by an engineering analysis combining semi-quantitative observations and fundamental physical principles. The use of regional meteorological conditions was validated by comparing concentration estimates generated by two source-location weather data-sets. The HPAC model estimated a chlorine plume with 20 ppm outdoor concentrations up to 7 km downwind and 0.25 km upwind/downgrade. A comparative analysis of our two models showed that HPAC was the best candidate for use as a model system on which epidemiologic studies could be based after further model validation. Further validation studies are needed before individual exposure estimates can be reliable and the chlorine plume more definitively modeled.

Keywords: atmospheric; agriculture; risk; epidemiology

Introduction

Chlorine gas (Cl₂) is used widely in science, industry, and warfare. Today, chlorine is among the top 10 industrial chemicals produced in the United States, and is used in many major manufacturing areas such as production of automobiles and pharmaceuticals (Jones et al. 2010). The Association of American Railroads (AAR) noted in 2007 that railroads typically transport over 100,000 tank car loads of toxic inhalation hazard (TIH) chemicals annually, such as chlorine and anhydrous ammonia (AAR 2007). Many of these transportation routes pass through or in close proximity to population centers and other areas in which an accidental release could have detrimental impact on human health. The elemental form of chlorine is highly reactive and, therefore, does not exist naturally in high concentrations. The majority of human exposures occur only occupationally, purposely, or accidently (ATSDR 2010). Indeed, there have been numerous incidents involving chlorine within the past decade such as the intentional releases in Iraq (2007) and Syria (2011, 2014), and accidental releases from railcars in Macedonia, Texas (2004), Graniteville, South Carolina (2005), and Tacoma, Washington (2007). The integral nature of chlorine in manufacturing industries and its ease of use and

*Corresponding author. Email: esvendse@tulane.edu

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effectiveness as a terrorist agent supports the notion that releases will continue to occur (CDC 2005; Jones et al. 2010). Accordingly, there is a continuing need to comprehensively assess the toxicological, ecological, and socioeconomic effects of these events for purposes of both planning and response.

Currently, large inhalation events involving toxic irritant gases are assessed using a combination of onsite monitoring and comparing injuries to known health effects. The methodology and instrumentation to detect atmospheric concentrations of toxic gases such as chlorine has existed for many years. Yet, the use of continuous monitoring apparatus in settings such as the occupational workplace represents significant investment and preplanned placement, luxuries that are nearly impossible to attain during emergencies due to their unpredictable nature. The initial focus during response to a TIH incident is always the protection of life and property. Therefore, environmental testing is usually only conducted after the initial release has dissipated and it is safe to deploy monitoring equipment.

Many epidemiologic studies concerning the residual effects of chlorine exposure are limited by the lack of prior knowledge of the respiratory physiology of the exposed, small sample sizes, and, perhaps most importantly (and most relevant to this paper), the lack of well-characterized exposure data such as duration, extent, and concentration. It is in bridging this gap where the modern science of atmospheric detection and plume modeling is highly valuable (BASC 2003; Farago et al. 2005).

These algorithmic simulations of pollutant dispersion are important in managing environmental quality and protecting human health. There is considerable variability in the predictive accuracy and robustness of currently available dispersion modeling systems. All models require two basic inputs: source term (physical descriptors of the release itself) and meteorology. It is commonly believed that meteorology (such as atmospheric stability, wind speed, and ambient conditions) have some of the most profound implications on dispersion (Hanna et al. 1982). As an example, a highly stable/less turbulent atmosphere, such as night, will likely result in diminished dispersion. Topography also greatly influences dispersion; however, many mainstream software packages, particularly those targeted toward the first responder and optimized for rapid usability, do not take into account terrain influences during dispersion. Our study focuses on different models with varying sophistication.

The use of air pollution modeling technologies in epidemiologic studies of irritant gas exposure events is an emerging area of research. A review of exposure assessment techniques by Zou and colleagues noted that modeling systems are becoming primary tools in environmental epidemiology studies as robustness increases (Zou et al. 2009). Historically, particularly for incidents involving dense chlorine gas, dispersion models have either over-predicted or under-predicted the exposure limits forcing emergency decisions to be highly conservative. Applications to determine individual exposure estimates for etiologic studies have been largely unsuccessful. Increasing processing power and incorporation of algorithms addressing randomness, variability, and the effects of physical and chemical reactions, particularly for dense gases such as chlorine, have yielded increasingly robust model systems. Unlike earlier modeling software, these newer systems are often able to account for dry deposition, ambient reactions, and dynamic weather conditions, such as anti-cyclonic phenomena, but with varying accuracy. Simulations of high concentration events emphasizing the collection of plume migration and eco-toxicological data via field experiments have been performed in studies such as the Joint Urban 2003 (Oklahoma City, Oklahoma) and Jack Rabbit (Dugway Proving Ground, Utah) (NOAA FRD 2013). Such field trials provide markers against
which existing models can be validated (Hanna, Chang, et al. 2008). These experiments have produced valuable contributions, and further validation against known exposure thresholds and other markers collected in the aftermath of an incident are useful to ensure these computerized models generate accurate and precise point estimates of personal exposure, which are particularly useful for subsequent epidemiologic study. The purpose here is to describe the first step in developing a validated chlorine plume dispersion model that can be used to adequately estimate exposure in subsequent etiologic epidemiologic studies.

**Methods**

*Description of the exposure event*

On 6 January 2005 at 2:39 AM, Eastern Standard Time, a freight train traveling through Graniteville, South Carolina, at a speed of 76 km/h was inadvertently diverted off the main line onto an industrial spur where it collided with a parked train. An incorrectly aligned switch was later determined by the National Transportation Safety Board (NTSB) as the culprit. Both locomotives and several railcars were derailed, including three railcars containing approximately 81,646 kg of pressurized liquid chlorine (Cl₂) each (NTSB 2005a). While all three railcars were damaged, the integrity of one of these cars was compromised, resulting in the release of approximately 55,000 kg of chlorine gas into the surrounding community (NTSB 2005a, 2005b). Emergency personnel, including hundreds of volunteer firefighters from local and mutual aid departments along with state and federal hazardous materials and investigative assets, responded to Graniteville during the emergency period.

Graniteville is a textile mill town situated within a small river valley. The 2000 census population, most relevant to this paper, was 7112 (U.S Census, 2000). The collision and release occurred on the industrial track of Avondale Mills, which was a major manufacturer of textiles and employer at the time. The chlorine release resulted in nine fatalities, over 550 people sought medical care in regional hospitals due to respiratory distress, and the evacuation of nearly 5400 people living and working nearby during the three-week clean-up period (NTSB 2005a).

The 2005 Graniteville, South Carolina, accidental release of chlorine following a railroad accident is a prime example of the devastating public health impacts that an incident of this magnitude can have on a community. The large-scale exposure to chlorine gas resulted in widespread human and animal fatality and morbidity. Current research projects studying the health implications of this exposure could be strongly advanced by using a validated model to estimate individual dosage. Here, as a first step in producing a validated model, we have modeled the Graniteville accidental release using two atmospheric dispersion models. The selection of these models is explained further in section “Description of the models and usage”.

*Estimation of the source term*

An essential first step in implementing such a model is to estimate the contaminant release rate and duration. Here, “release rate” is considered to be the flux of Cl₂ through the plane defined as the open gash in the side of the tank car. Initially, the amount of Cl₂ released as a function of time after the accident was estimated using an engineering analysis that combined semi-quantitative observations and fundamental principles. Our
results were then compared with the findings of other investigators. Both this study and the comparison studies focused on the period of the highest Cl₂ emission rate, beginning immediately after the accident occurred.

The rate of Cl₂ loss from the tank car was a function of several constants, as well as time-varying factors. The constants included: the location and orientation of the tank car after coming to rest, the location of the tear on the car, and the size and shape of the tear. The most fundamental time-varying factors were the amount of liquid Cl₂ remaining in the tank and the temperature of the Cl₂- knowing that these two allows determination of the fluids’ physical properties including vapor pressure, density, viscosity, and heat capacity of both liquid-phase and gas-phase Cl₂.

Information concerning the orientation of the car and of the size and shape of the tear in its side were obtained from measurements, pictures (NTSB 2005a, 2005b), and interviews with emergency response personnel. These documents contain pictures and descriptions of the leaking tank car and the jagged, roughly vertical tear in the side of the car, and estimate of the amount of chlorine in the car at several times, and its temperature immediately after the accident. While many of these documents are publicly available, we were able to obtain the maximal amount of documentation using a Freedom of Information Act request. Taking into account the volume of Cl₂ in the tank, the tank dimensions, and the angle of repose of the car after the accident, the upper end of the rupture was approximately 1.55 m below the initial vapor/liquid phase.

Background

The progression of events that characterize the release of a compressed gas, such as Cl₂, stored at a temperature less than or equal to its saturation temperature was described by Britter et al. (2011). Release from a rupture initially well below the liquid/gas interface and well above the bottom of the tank can take place in three consecutive stages. Stage 1 begins with the release of liquid Cl₂. Inside the tank near the interface, Cl₂ starts to boil and a two-phase foamy layer consisting of bubbles of vapor/aerosol in the liquid forms. This two-phase layer swells, deepens, and descends. Stage 2 begins as the two-phase layer nears the rupture from above, and the release through the rupture becomes two-phase as well. The exact behaviour as this material approaches and flows through the rupture is not very well understood as acknowledged by Britter et al. (2011), but some sophisticated models of this phenomenon have been developed such as the w-model (Leung 1986, 1990) and the homogeneous equilibrium model (HEM) (Richardson et al. 2006).

Stage 3 occurs if release continues long enough to completely deplete the two-phase layer such that the release from the tank becomes vapor. The mass flow rate decreases from Stage 1 to Stage 3 (Bwitter et al. 2011). Note that the transitions from stage to stage are often not distinct. Further complicating this is the formation of an aerosol phase.

For escape of a saturated liquid through a rupture in a container with a wall thickness equal to or less than 0.1 m, the flow approximates that of flow through a sharp-edged orifice. The flow is said to be “non-equilibrium” because the time required for the liquid to pass through the rupture is too short to allow equilibration to the new pressure condition until it is well outside the vessel; this is often referred to as “choked” flow. Here, the thickness of the tank wall at the site of the tear measured from 0.020 m (range = 0.000034 m) (NTSB 2005b), indicating that thermodynamic equilibrium was not achieved upstream of the rupture during the initial phase of release.
Thus, the earliest release from the tank should have been liquid-phase Cl\textsubscript{2}. After release (outside the tank), this liquid jet would have abruptly approached an equilibrium condition at atmospheric pressure, causing “flushing” flow. This complex phenomenon results from the combined effects of rapid evaporation of Cl\textsubscript{2}, warming of the Cl\textsubscript{2} jet due to the entrainment of ambient air, and cooling of the jet and the surrounding air through uptake of latent heat of evaporation. Condensed and frozen water was noted on the outside of the tank car near the rupture in photographs.

**Estimation methods**

The methods used here to estimate the rate of Cl\textsubscript{2} emission and the cumulative loss from the tank car were chosen to be appropriate for the ultimate goals of this research: to provide estimates of Cl\textsubscript{2} exposure in Graniteville for participants in health effects studies, not to develop generally applicable approaches for determining pollutant emission, dispersion, and transport. This analysis began by calculating the depth of liquid Cl\textsubscript{2} in the car using a tilt angle of 10° reported by a SC Department of Health and Environmental Control (DHEC) responder, which agreed with the approximate angle given as 5–10° reported by the NTSB (2005a), the approximate orientation of the car shown in numerous pictures, and the volume of Cl\textsubscript{2} initially present. Based upon NTSB (2005a) pictures, the tear on the side of car was a jagged gash very nearly perpendicular to the ground and 4.88 meters from the higher end of the car (the “A” end). The depth of liquid Cl\textsubscript{2} was calculated as a function of the liquid-filled tank volume using a web-based program supplied by LMNO Engineering (2009). Then, to simplify computation further, a cubic equation was derived by regression ($R^2 = 0.9989$) for directly computing the volume of Cl\textsubscript{2} in the tank from its depth and vice versa. The next step was to compute the combined pressure resulting from the average head pressure of liquid along the tear and the vapor pressure in the enclosed space above the liquid. Using an equation for flow through a submerged opening (Perry & Green 1984), we estimated that the time required for the liquid Cl\textsubscript{2} level to reach the top of the vertical tear, using the approximation that the two-phase portion of the fluid does not have a significant effect on the mass release rate.

At the beginning of this stage one, the pressure in the Cl\textsubscript{2} gas equaled the vapor pressure of chlorine at the tank temperature, estimated to be $-3.3^\circ C$ (26 F) (NTSB 2005a), corresponding to a vapor pressure of 317 kPa (46 psia) (Occidental Chemical Corporation 2000). An overview of the source term information we have used as inputs is shown in Table 1.

**Weather validation methods**

At the time of the incident, there was no onsite meteorological station in Graniteville to provide the most accurate weather data for input into the plume modeling software. Conventionally, in lieu of onsite observations, data from the National Weather Service (NWS) and National Climatic Data Center is often used for planning, response, and investigative modeling. NWS stations are generally located at airports or areas that serve as population centers. Alternatively, the US Forest Service operates Remote Automated Weather Stations (RAWS) which are generally self-sufficient stations located in national forests and similar areas for monitoring forest fires. Information from these mobile stations is transmitted electronically (often via satellite) every hour to the National Interagency Fire Center in Boise, Idaho. We have used archived meteorological surface...
observations recorded at 13 different RAWS sites collected during the night (and time of incident) on 6 January 2005 (Figure 1).

A portable weather station was setup at the incident site late in the morning of 6 January and remained there throughout the duration of cleanup activities. For purposes of validation, we compared archived observational data from the 13 different RAWS sites for five nights beginning on 7 January and ending on 12 January (10 January was excluded due to missing data) with data from this portable site. We modeled the incident in HPAC using both the RAWS and portable weather station data (micro-environmental) collected on the aforementioned nights. Concentration and surface dosage were calculated at 1024 points across a three by three mile grid with identical source terms and correlation, mean bias, and root mean square error between the two models were calculated using IBM SPSS Statistics (Version 20, IBM, Armonk, NY). The goal of this validation was to support the notion that RAWS data collected during the night of 6 January provided an accurate representation of the incident site micro-environment in Graniteville. It has been previously reported that an inversion layer may have been present during the morning of the accident which exaggerated the spread of chlorine gas (Buckley et al. 2012). This inversion would have exasperated the spread of the gas over the surrounding terrain.

**Description of the models and usage**

The Graniteville incident was modeled in two unclassified versions of standard software packages using the above-mentioned source term and meteorological data. First, we used the commonly available Areal Locations of Hazardous Atmospheres (ALOHA) model, which was jointly developed by the National Oceanic and Atmospheric Administration (NOAA) and US Environmental Protection Agency (EPA). Second, we used the Hazard Prediction and Assessment Capability (HPAC, 5.2 Service Pack, DTRA, Ft. Belvoir, VA), developed by the Defense Threat Reduction Agency (DTRA), to incorporate increasingly accurate topographical and meteorological data in an effort to improve the predictive accuracy of our model before proceeding to validation studies. There were
several reasons why we selected ALOHA and HPAC instead of other available plume modeling software. Due to its widespread distribution and ease of use, ALOHA may be the most common model in general use by initial responders, such as local fire departments. HPAC has been widely used in studies regarding both the Graniteville and other chlorine releases, and was also utilized by authorized emergency management entities during the response (Buckley et al. 2007, 2012; Hanna, Chang, et al. 2008; Hanna, Dharmavaram, et al. 2008). We have avoided the use of proprietary software because

Figure 1. (Color online) Locations of 13 RAWS sites utilized in weather validation study. Map was developed using ArcGIS ArcMap Version 10.0, Esri, Redlands, CA.
these models may not be in widespread use among those with critical public health and safety decision-making responsibility.

An updated and localized 30 km topographical file of the Graniteville area using the ArcMap geographical information system software (ArcMAP 10, ESRI, Redlands, CA) was utilized with HPAC while simulating the release. No terrain input was used with ALOHA because the standard (and most commonly available) version of the software assumes flat topography and does not accommodate the incorporation of diverse terrain (NOAA 2013). All models estimated the outdoor atmospheric concentrations of Cl₂.

The ALOHA system, part of the Computer-Aided Management of Emergency Operations (CAMEO) suite, is likely the most widely used atmospheric dispersion modeling program at the local level. We used ALOHA Version 5.4.3 to model the Graniteville release. The software uses the Dense Gas Dispersion Model (DEGADIS) system to model Gaussian puff and plumes including dispersion of dense gas such as chlorine (NOAA 1992). Outputs including threat zones can be displayed using the intrinsic CAMEO plotter (MARPLOT) or exported to ArcMap via extensions. The intrinsic CAMEO mapping software, MARPLOT, was used to illustrate the ALOHA output as 60-min Acute Exposure Guideline Level (AEGL) isopleths. Confidence lines were, also, shown on the map.

The HPAC system has several advantages over ALOHA, including the consideration of deposition and depleting effects such as terrain-induced gravity slumping. HPAC consists of several different modules that work together to determine source term, incorporate weather and topographical data, and calculate theoretical migration to develop a dispersion model. Although originally designed for use by the military, the HPAC system is now available to the authorized municipal and research community members, and serves as a valuable tool for predicting the effects of hazardous material releases into the atmosphere and its subsequent impact on a proximal population. The HPAC system uses a second-order closure transport/dispersion model, SCIPUFF, which is a Langrangian model utilizing multi-dimensional Gaussian distributions (DTRA 2005). In association with a wind field model (SWIFT), the system can describe diffusion processes while allowing variances in concentration fields for purposes of measuring uncertainty. The transport/dispersion and wind field components of HPAC have been validated in the laboratory as well as field trials for short- and long-range dispersion over various types of terrain and urban environments (Warner et al. 2006, 2008; Hanna, Chang et al. 2008).

Results

Source term calculation results

Cl₂ emission began immediately after the accident and continued at a high rate: 523 kg/s. The vapor pressure of Cl₂ trapped above the liquid was the dominant force pushing the liquid out of the tank car. We calculated that the liquid level would have reached the top of the tear opening with release of 54,915 kg in about 105 s with gas alone slowly escaping afterwards. This represents a loss of nearly 2/3 of the original Cl₂ in the tank car, in relatively good agreement with estimates based on the Cl₂ remaining in the car at 4:00 PM on the day of the accident from SC DHEC and Norfolk Southern cleanup contractors (NTSB 2005c). The nearest NWS monitoring station in Augusta, Georgia, reported an initial ambient temperature of 12.8 °C. Nevertheless, the condensation and ice on the surface of the tank shown in pictures taken on the morning
of 6 January 2005 was to be expected given the high rate of Cl₂ evaporation and resulting cooling due to the uptake of latent heat.

**Comparison of RAWS and micro-environmental data**

For the initial 60 min after the accident, cumulative surface dosage results from the HPAC models using RAWS surface observation data were similar to results using observations from a single portable meteorological station positioned near the leaking tank car. Concentration and surface dosage data from the RAWS HPAC plume dispersion model without measured micro-environmental weather data were significantly correlated with the model that included measured micro-environmental data (Table 2). There was overall good agreement between the two models with the exception being as we neared the 60-min averages for certain days. Yet, after calculating an overall strong correlation between the RAWS data and portable weather station, and, therefore, making the assumption that these data were representative of the micro-environment during the incident itself, we are confident that our usage of the RAWS data is suitable for our modeling purposes.

**ALOHA and HPAC model results**

The ALOHA predicted 60-min average concentrations (Figure 2), as shown in Table 3, ranged from 156,000 ppm at a receptor 0.1 km downwind (x) to 10 ppm at a receptor 10 km downwind. We report these values in conservative 60-min averages as this is the standard in ALOHA. Unlike HPAC, the ALOHA system does not report values past 10 km downwind; however, manual calculation of very approximate concentrations is possible using the relevant mathematical modeling equations.

The HPAC output is shown as 30-min AEGL isopleths on an ArcMap GIS layer of the Graniteville incident area (Figure 3). On Table 3, we reported averaged centerline maximum concentrations in both 30-min and 60-min averages. For 30-min averages, these values ranged from 14,900 ppm at 0.1 km downwind to 0 ppm at 25 km downwind. About 60-min averages ranged from 11,642 ppm at 0.1 km downwind to 0 ppm at 25.0 km downwind. These maximum 30-min and 60-min concentrations are also shown vs. downwind distance graphically (Figure 4). Upwind dispersion up to 0.7 km due to gravitational slumping and maximum width to specific concentrations (2000, 400, and 20 ppm) were reported for the HPAC model. Although it is possible to show variance in times shorter than 30 min, we opted to model 30 and 60-min outputs for comparative purposes to the more output-restricted ALOHA model.

**Discussion**

Our purpose here has been to identify an atmospheric dispersion modeling system that is suitable for epidemiologic application to etiologic study of TIH releases. ALOHA lacked the precision required to use it within epidemiological studies. Because it is designed to be used by a wide range of emergency management personnel, ALOHA has limited functionality compared to more “robust” systems such as HPAC. The ALOHA program is intended for use during the immediate response phase of a release and, therefore, sacrifices accuracy for increased speed and ease of use. We opted to compare HPAC with ALOHA, as opposed to other dispersion modeling systems, because ALOHA may be the most widely known and utilized gas dispersion model.
Table 2. Comparison between HPAC models with RAWS and portable station data.

<table>
<thead>
<tr>
<th></th>
<th>7 January</th>
<th>8 January</th>
<th>9 January</th>
<th>11 January</th>
<th>12 January</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>Mean bias</td>
<td>RMSE</td>
<td>$R^2$</td>
<td>Mean bias</td>
</tr>
<tr>
<td>Surface dosage</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 min</td>
<td>0.990</td>
<td>1.995</td>
<td>1.412</td>
<td>0.987</td>
<td>2.021</td>
</tr>
<tr>
<td>Concentration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 min</td>
<td>0.997</td>
<td>.000</td>
<td>.000</td>
<td>0.971</td>
<td>.000</td>
</tr>
<tr>
<td>15 min</td>
<td>0.974</td>
<td>.000</td>
<td>.001</td>
<td>0.965</td>
<td>.000</td>
</tr>
<tr>
<td>30 min</td>
<td>0.975</td>
<td>.000</td>
<td>.001</td>
<td>0.973</td>
<td>.000</td>
</tr>
<tr>
<td>45 min</td>
<td>0.946</td>
<td>.000</td>
<td>.001</td>
<td>0.888</td>
<td>.000</td>
</tr>
<tr>
<td>60 min</td>
<td>−0.136</td>
<td>.000</td>
<td>$7.1 \times 10^{-7}$</td>
<td>0.677</td>
<td>.000</td>
</tr>
</tbody>
</table>

Note: Statistical analyses shown above include correlation ($R^2$), mean bias, and root mean square deviation (RMSE).
Our purpose here is to compare two “tiers” of modeling systems with the aforementioned input parameters, and to identify HPAC as the model of choice to continue our study with. However, a wide variety of models, many of which have been previously compared by Hanna and others, are in use throughout public applications, industry, and academia.

The behaviour of a dense gas is highly influenced by the geography surrounding the release site, and the failure to account for this terrain leads to concentration estimates which are skewed from reality. Indeed, flat-terrain models have been shown to overestimate the range of hazard by nearly a factor of five and direction of migration by up to \(90^\circ\) (Mcbride et al. 2001). Further, most models like ALOHA which are available freely in the public domain do not consider major removal mechanisms, such as deposition and depletion. These factors are particularly important for a dense gas like chlorine which tends to hug the ground. Furthermore, the flat-terrain models tend to incorporate linear removal which is not particularly representative of reality. As a consequence, near-fatal exposures are often approximated beyond distances at which human health impacts are reported. The ALOHA output is suitable for its primary intention, that is, the immediate modeling of an incident by emergency responders for purposes of

Figure 2. (Color online) ALOHA Model of Graniteville, SC chlorine release. Estimated 60-min AEGL isopleths and confidence lines are shown up to a maximum distance of 10 km downwind. AEGL-3 (red), 2 (yellow), and 1 (green) correspond to 20, 2, and 0.5 ppm, respectively.
response. Yet, it is unsuitable as a model for us to base future epidemiologic study on due the relative “fixed” nature of the system as input type and variability is concerned and highly conservative estimated concentration outputs. For this, HPAC is far more suitable because of its ability to incorporate mesoscale wind variations with more advanced algorithms among other improvements. It is for these reasons that we have chosen to proceed with the HPAC system model as a basis for our future epidemiologic studies.

Although HPAC represents a significant advantage over models such as ALOHA, other robust options exist. As an example, the National Atmospheric Release Advisory Center (NARAC) at the Lawrence Livermore National Laboratory (LLNL) in California provides national support to emergency managers for purposes of planning and real-time assessment of chemical, radiological, biological, and other similar events. NARAC utilizes the ADAPT/LODI system, which consists of a robust meteorological data assimilation component (ADAPT) and dispersion modeling component (LODI) which considers turbulence, chemical reactions, wet and dry ground deposition, settling due to density and plume rise (NARAC 2011). Coupled with extensive databases on the properties of agents such as chlorine, accurate topographical data, and real-time meteorological observations, NARAC is a critical resource for emergency planning and response. However, unlike HPAC, the advanced methodologies of the NARAC group are available by request only and cannot be performed by unauthorized independent agencies and organizations for research purposes. A 2001 study by LLNL researchers concluded that HPAC and NARAC predictions for a series of simulated scenarios had overall favorable agreement (Warner et al. 2001). We have chosen to proceed with HPAC because it is the most accurate modeling system available to authorized academic researchers. Further, DTRA provides Interagency Modeling & Atmospheric Assessment Center (IMAAC) support through its Technical Reachback unit.

Table 3. HPAC and ALOHA model results for Graniteville, SC chlorine release.

<table>
<thead>
<tr>
<th>Downwind distance (km)</th>
<th>HPAC (30-min) ppm</th>
<th>HPAC (60-min) ppm</th>
<th>ALOHA (60-min) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>14,900</td>
<td>11,642</td>
<td>156,000</td>
</tr>
<tr>
<td>0.2</td>
<td>6868</td>
<td>5860</td>
<td>81,100</td>
</tr>
<tr>
<td>0.5</td>
<td>837</td>
<td>553</td>
<td>17,200</td>
</tr>
<tr>
<td>1.0</td>
<td>89</td>
<td>51</td>
<td>3830</td>
</tr>
<tr>
<td>2.0</td>
<td>47</td>
<td>36</td>
<td>672</td>
</tr>
<tr>
<td>5.0</td>
<td>0</td>
<td>13</td>
<td>58.3</td>
</tr>
<tr>
<td>10.0</td>
<td>0</td>
<td>0.32</td>
<td>10</td>
</tr>
<tr>
<td>25.0</td>
<td>0</td>
<td>0</td>
<td>N/A</td>
</tr>
<tr>
<td>Downwind distance to concentration km</td>
<td>km</td>
<td>km</td>
<td></td>
</tr>
<tr>
<td>2000 ppm</td>
<td>0.45</td>
<td>0.4</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td>(0.22 upwind)</td>
<td>(0.18 upwind)</td>
<td>–</td>
</tr>
<tr>
<td>400 ppm</td>
<td>0.69</td>
<td>0.6</td>
<td>2.43</td>
</tr>
<tr>
<td></td>
<td>(0.39 upwind)</td>
<td>(0.28 upwind)</td>
<td>–</td>
</tr>
<tr>
<td>20 ppm</td>
<td>2.6</td>
<td>2.6</td>
<td>7.57</td>
</tr>
<tr>
<td></td>
<td>(0.66 upwind)</td>
<td>(0.5 upwind)</td>
<td>–</td>
</tr>
<tr>
<td>Maximum width to concentration km</td>
<td>km</td>
<td>km</td>
<td></td>
</tr>
<tr>
<td>2000 ppm</td>
<td>0.54</td>
<td>0.4</td>
<td>–</td>
</tr>
<tr>
<td>400 ppm</td>
<td>0.8</td>
<td>0.7</td>
<td>–</td>
</tr>
<tr>
<td>20 ppm</td>
<td>1.44</td>
<td>1.32</td>
<td>–</td>
</tr>
</tbody>
</table>
A few papers have been published estimating the Graniteville release rates for purposes different from those of this study. Buckley et al. (2007) described the results of analyses performed by the Savannah River National Laboratory (SRNL) provided in support of the Graniteville emergency response efforts, as well as some more detailed

Figure 3. (Color online) HPAC Model of Graniteville, SC chlorine release. Estimated 30-min AEGL isopleths are shown. AEGL-3 (red), 2 (yellow), and 1 (green) correspond to 28, 2.8, and 0.5 ppm, respectively.

A few papers have been published estimating the Graniteville release rates for purposes different from those of this study. Buckley et al. (2007) described the results of analyses performed by the Savannah River National Laboratory (SRNL) provided in support of the Graniteville emergency response efforts, as well as some more detailed
atmospheric transport calculations including HPAC model results in the first 2–3 h after
the accident. They assumed that > 62,000 kg of Cl₂ was released instantaneously as vapor
and aerosol phases. A more comprehensive follow-up analysis on the Graniteville Cl₂
release by SRNL covering the same 3-h time period has also been published (Buckley
et al. 2012); it included the estimated emission rate, meteorology, dispersion, as well as
the fate and the effects of the chlorine released. In their research, the tear was represented
by a 0.8 m long and by 0.08 m wide opening extending “just above the mid-point of the
tank.” This does agree with our findings. The emission rate was determined using
ALOHA code, and the Industrial Transportation (ITRANS) component of the HPAC pro-
gram. This resulted in a total estimated emission of 59,000 kg, most occurring in the
first minute after the accident with the total discharge requiring 5 min. They pointed out that
ITRANS will not accept a detailed specification of the damage to the tank. The time
required for discharge was adjusted using SCIPUFF to achieve better agreement with a
Thus, Buckley et al. (2012) concluded that vapor and aerosol release, 59 % of the total,
was essentially complete after the 3 min, while the remaining 41 %, a subcooled liquid
release, was assumed to have pooled on the ground and then evaporated.

Hanna, Dharmavaram, et al. (2008) compared three dense gas dispersion models for
several chlorine railcar accidents, including the Graniteville accident. For Graniteville,
the duration of source emissions was determined using the PHAST and TRACE models
along with a thermodynamic analysis, and the vertical slash in the side of the rail car
was represented by a 4–5 inch hole. Based upon the Cl₂ release of rate of 1565 kg/s,
they estimated that a two-phase release of liquid and vapor lasted for 34 s, for a dis-
charge of 53,210 kg; the vapor phase release was estimated to continue at the rate of
0.2 kg/s for 3600 s for an additional discharge of 720 kg. One major reason our results
are different is because the Hanna paper, for purposes of comparison between SCIPUFF
and other models, assumed flat terrain and utilize a slightly different source term. This
was primarily due to the inability of some of the models being compared to incorporate
topography (such as ALOHA). The variability between our model and that aforementioned
is a prime example of the impact that migration of a heavy gas through complex
terrain has on predicted upwind concentrations.
This study also demonstrates the limits of using dispersion modeling for guiding emergency response to accidental releases of compressed, acutely toxic dense gases. Here, 2/3 of a railroad tank car of chlorine was emitted in about 105 s. This is insufficient time to prevent exposure and, in many cases, to prevent death and disabling injury, even when a community is extremely well prepared. The approach employed here can be of significant value for post-event evaluation, or for response in scenarios with a slower release or for less acutely toxic contaminants. Many modeling systems are incapable of producing exposure estimates in time intervals less than 30 or 60 min, or incorporating estimate variability. For purposes of epidemiology, this is highly problematic for the reason mentioned above: many rapid relief incidents occur in minutes. The ability of HPAC to output estimates in short intervals – minutes – is another advantage over ALOHA for our purposes.

Conclusion and future directions
Out of our two selected models studied, HPAC is likely the best candidate for use as a model system on which future human epidemiologic studies could be based. HPAC was selected over ALOHA because the system accounts for dynamic plume rise and to a greater degree the dense gas effects, time- and space-dependent boundary layers, and mesoscale wind variations over complex terrain. Although the focus of our model development is entirely emergency response, the HPAC modeling system does represent significant improvement over the common ALOHA system. This increased predictive accuracy can have profound impacts during response to hazardous chemical releases. It is recommendable for jurisdictions without access or training on software such as HPAC to fortify mutual aid collaborations with agencies who utilize higher modeling systems.

Yet, there is intrinsic bias in any simulation and performance can be improved (or confirmed) by field studies. Further verification of our model is necessary before epidemiologic application. In other words, to ensure predictive accuracy, a model must be validated using observed indicators of exposure. The next step in improving plume model accuracy is to compare the model to exposure indicator data collected in the aftermath of the incident. Eventually, the resulting validated plume dispersion model could be used to estimate personal exposures for etiologic environmental epidemiology studies. The resulting models presented herein provide preliminary estimates only of outdoor exposure concentrations and should not be interpreted to represent the exact chlorine plume model after the Graniteville exposure event. Further validation studies are needed before individual exposure estimates can be reliably made and the chlorine plume more definitively modeled.

Acknowledgements
We acknowledge Ronald G. Meris, Chief of the Reachback Analysis Branch of the Defense Threat Reduction Agency (DTRA), for his scientific review and helpful commentary on this manuscript.

Funding
This work was supported by the National Institute of Environmental Health Sciences [5R01ES015532-05].
References


DEVELOPMENT AND EVALUATION OF AN IRRITANT GAS PLUME DISPERSION MODEL FOR EPIDEMIOLOGIC STUDY

APPENDIX 1.10

Manuscript #1 – Figures

Figure Captions:

Figure 1: Locations of 13 RAWS sites utilized in weather validation study. Map was developed using ArcGIS ArcMap Version 10.0, Esri, Redlands, CA).

Figure 2: ALOHA Model of Graniteville, SC chlorine release. Estimated 60-min AEGL isopleths and confidence lines are shown up to a maximum distance of 10 km downwind. AEGL-3 (red), 2(yellow) and 1 (green) correspond to 20, 2 and 0.5 ppm, respectively.

Figure 3: HPAC Model of Graniteville, SC chlorine release. Estimated 30-min AEGL isopleths are shown. AEGL-3 (red), 2 (yellow) and 1 (green) correspond to 28, 2.8 and 0.5 ppm, respectively.

Figure 4: Concentration vs Downwind Distance for HPAC mode. Both 30-min and 60-min curves are shown for the maximum estimated concentration of chlorine at specific centerline distances downwind.
FIGURE 2
FIGURE 3

[Map showing the spread of a chemical plume from a tank car release in Aiken County, South Carolina, with the areas of different concentration levels indicated by colors.]
FIGURE 4

Concentration vs. Downwind Distance, HPAC Model

Chlorine concentration (ppm)

Downwind Distance (km)

HPAC 30 min

HPAC 60-min
DEVELOPMENT AND EVALUATION OF AN IRRITANT GAS PLUME DISPERSION MODEL FOR EPIDEMIOLOGIC STUDY

APPENDIX 1.10

Manuscript #2 – Figures

Figure Captions:

Figure 1: HPAC 4.04 surface dosage plume model at 6:39 EST (+4 hours post-release).

Figure 2: HPAC 5.3 surface dosage plume model at 6:39 EST (+4 hours post-release).

Figure 3: HPAC 4.04 versus 5.3 surface dosage plume models at 6:39 EST (+4 hours post-release).

Figure 4: HPAC 4.04 versus 5.3 surface dosage plume models at 6:39 EST (+4 hours post-release) with sampling points (n = 9,446).

Figure 5: ALOHA Model of Graniteville, SC chlorine release. Estimated 60-min AEGL isopleths and confidence lines are shown up to a maximum distance of 10 km downwind.

Figures 6A-H: Log-log scatter plots comparing HPAC 4.04 versus 5.3 surface dosage estimations at sampling points for each output time-step.
FIGURE 5
FIGURE 6C
HPAC 4.04 vs 5.3 Surface Dosage
04:09 EST

FIGURE 6D
HPAC 4.04 vs 5.3 Surface Dosage
04:39 EST
FIGURE 6E

HPAC 4.04 vs 5.3 Surface Dosage
05:09 EST

FIGURE 6F

HPAC 4.04 vs 5.3 Surface Dosage
05:39 EST
DEVELOPMENT AND EVALUATION OF AN IRRITANT GAS PLUME DISPERSION MODEL FOR EPIDEMIOLOGIC STUDY

APPENDIX 2.1

HPAC 5.3 Plume (4 hour AEGL)
APPENDIX 2.2

HPAC 5.3 Plume (Concentration)

4 Hours Maximum in 30 Minute Timesteps
APPENDIX 2.3

HPAC 5.3 Concentration (Centerline Graphs)

30, 60 and 90 Minute Timestep
HPAC 5.3 - Centerline Concentration (60 min)
DEVELOPMENT AND EVALUATION OF AN IRRITANT GAS PLUME
DISPERSION MODEL FOR EPIDEMIOLOGIC STUDY

APPENDIX 2.4

Manuscript #3 – Figures

Figure Captions:

Figure 1: HPAC 5.3 surface dosage plume model at 6:39 EST (+4 hours post-release).

Figure 2: Reported health outcome classification for all animals (n=117) based upon a review of survey data. The majority of animals exhibited no health effect.

Figure 3: Locations of all animals (n=117) plotted on the HPAC 5.3 surface dosage plume map.

Figure 4: HPAC 5.3 estimated exposure area of 5 ppm or greater for 2 or more hours with extent of visible vegetation bleaching and corrosion episodes plotted.

Figure 5: HPAC 5.3 centerline concentration (60-min) every 30 meters from the release point to extent of plume.

Figure 6: Locations of all injured animals plotted on the HPAC 5.3 surface dosage plume map.

Figure 7: Locations of all killed animals plotted on the HPAC 5.3 surface dosage plume map.

Figure 8: Locations of all dogs (n=63) plotted on the HPAC 5.3 surface dosage plume map.

Figure 9: Scatter plot of all dogs (n=63) binned by observed health outcome classification.

Figure 10: Box plot of all dogs (n=63) binned by observed health outcome classification.

Figure 11: Scatter plot of outdoor dogs (n=56) binned by observed health outcome classification.

Figure 12: Box plot of outdoor dogs (n=56) binned by observed health outcome classification.
FIGURE 2

Reported Health Outcome Classifications, Animals
(n = 117)
HPAC 5.3 - Phytotoxicity and Corrosion Events

> 5 PPM for 2 hrs or greater at z = 10 meters

Extent of visible vegetation bleaching

Corrosion event (green dots)
HPAC 5.3 Surface Dosage
Injured Animal Locations

Sources: Esri, HERE, DeLorme, TomTom, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCan, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community
HPAC 5.3 Surface Dosage with Dog Locations

Sources: Esri, HERE, DeLorme, TomTom, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community
FIGURE 9
All Dogs Cohort - Predicted vs Observed

n = 53

FIGURE 10
All Dogs Cohort - Predicted vs Observed
DEVELOPMENT AND EVALUATION OF AN IRRITANT GAS PLUME DISPERSION MODEL FOR EPIDEMIOLOGIC STUDY

APPENDIX 3.1

Prospectus
Development and Evaluation of an Irritant Gas Plume Dispersion Model for Epidemiologic Study

PROSPECTUS

Dev Jani
Department of Global Environmental Health Sciences
School of Public Health and Tropical Medicine
Tulane University

Dissertation Committee

Dr. Roy Rando, Co-Chair (Tulane University)
Dr. Erik Svendsen, Co-Chair (Medical University of South Carolina)
Dr. Jeffrey Wickliffe (Tulane University)
Dr. Mark Wilson (Tulane University)
Dr. Jeffrey Shaffer (Tulane University)

ACCEPTED BY COMMITTEE
August 24, 2015
Abstract

Incidents involving toxic industrial chemicals have detrimental impact on human and ecological health. The transport and dispersion of an irritant dense gas such as chlorine can be predicted by atmospheric dispersion modeling software, which are often used to make critical public safety and protective health decisions. Beyond this, the application of these software for epidemiologic and public health study is an emerging area of research. Here, we seek to evaluate the Hazard Prediction and Assessment Capability (HPAC) model of the Graniteville, South Carolina 2005 rail-car release of chlorine. First, an improved HPAC 5.2 model will be compared to an older model previously published by our study group. This improved model will then be evaluated against best available environmental indicator data using a variety of exploratory data analyses and statistical evaluation techniques. Finally, the model will be compared to the commonly available Areal Locations of Hazardous Atmospheres (ALOHA) and other published models of the incident. The ultimate goal here is to show how an evaluated model may be suitable for epidemiologic application as part of post-disaster public health studies.
**Background and Significance**

Toxic industrial chemicals (TICs), particularly pulmonary irritant gases, are used widely in science, industry and warfare. The increasing volume of industrial chemicals transported via railroad, highway and marine traffic presents unique consequence management implications, particularly in terms of public health and safety. Chlorine, a dense gas and potent pulmonary irritant, is among the top five most common toxic inhalation hazards (TIH) transported by the U.S. railroad system and used extensively in many major manufacturing areas (Jones et al, 2010). Because the elemental form of chlorine does not exist naturally in high concentrations (due to high reactivity), most human exposures to chlorine gas occur occupationally, purposely or accidentally (ATSDR, 2010). While chlorine, a dense gas, was commonly used as a warfare agent in the early to mid-20th century, the number of malicious incidents involving chlorine gas has decreased extensively since ratification of the Chemical Weapons Convention (CWC). Yet, the frequency of accidental releases has remained fairly constant (i.e. Macedonia, Texas [2004], Graniteville, South Carolina [2005], and Tacoma, Washington [2007]). The important nature of chlorine as an industrial chemical and ease of weaponizing as a terrorist agent supports the notion that releases will continue to occur (CDC, 2005; Jones et al, 2010). As such, there is an urgent need to assess the public health implications - particularly the toxicological, ecological and socioeconomic effects - of these releases for effective population health interventions.

In terms of rail transportation, chlorine is one of the top two TIH products by volume (the other being anhydrous ammonia) (Branscomb et al, 2010). Chlorine gas (Cl2) is used in water purification systems and as an important industrial chemical
intermediary in a wide variety of processes ranging from the manufacturing of plastics and paper to cosmetics (American Chemistry Council, 2009; ATSDR, 2010). The most common method of transporting chlorine gas (Cl2) is as a pressurized liquid in railcars due to efficiency: a single railcar can transport up to four tanker-trucks loads of the chemical. In general, rail transportation is considered safer than road transportation; however, accidental releases from railcars pose greater risk due to the vastly higher volumes being transported. The gaseous form of chlorine exists at room temperature and normal atmospheric pressure as a green-yellow noncombustible gas (ATSDR, 2010). As a dense gas (density 3.2 g/L), chlorine hugs topographical contours and sinks into low-lying areas when released into the open environment. This physical characteristic also increases the gravity slumping effect at the release site and in terms of human exposure, poses greater threat as dispersion and transport away from the release site can be attenuated.

Exposure to chlorine gas can result in significant morbidity and mortality at moderately high concentrations. As little as 3.5 ppm can be detected as an odor and 15 ppm in short periods of time can cause throat irritation. At high concentrations, pulmonary exposure to chlorine gas creates hydrochloric acid that damages throat and lung tissue, resulting in massive pulmonary edema and death. Although numerous variables such as exposure time, quantity and pulmonary medical predispositions and moisture content of the pulmonary membranes determines the extent of toxicity, previous studies have produced approximate concentrations at which certain health effects are observed (Table 1; summarized from ATSDR, 2010).

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Observed Health Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>271</td>
<td></td>
</tr>
<tr>
<td>Concentration</td>
<td>Health Effect</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------</td>
</tr>
<tr>
<td>1 - 3 ppm</td>
<td>Mild irritation of nose (tolerable for up to one hour)</td>
</tr>
<tr>
<td>5 ppm</td>
<td>Eye irritation</td>
</tr>
<tr>
<td>5 - 15 ppm</td>
<td>Headache and throat irritation</td>
</tr>
<tr>
<td>30 ppm</td>
<td>Immediate chest pain, nausea, vomiting, dyspnea and cough</td>
</tr>
<tr>
<td>40 - 60 ppm</td>
<td>Toxic pneumonitis and pulmonary edema</td>
</tr>
<tr>
<td>430 ppm</td>
<td>Death within 30 minutes due to pneumonitis and pulmonary edema</td>
</tr>
<tr>
<td>1,000 ppm</td>
<td>Fatal within a few minutes due to the above health effects</td>
</tr>
</tbody>
</table>

**Table 1:** Concentration and observed health effect of chlorine gas.

The environmental air limit set by the U.S. Environmental Protection Agency (US EPA) is 0.5 ppm, although the health effects of acute exposures at this level are usually reversible. The Occupational Safety and Health Administration (OSHA) legal limit is 1.0 ppm (ATSDR, 2010). Individuals with previously identified pulmonary conditions and/or children will likely be more susceptible to the effects of exposure. The Agency for Toxic Substances and Disease Registry (ATSDR) has determined the exposure level posing minimal risk to humans (MRL) as 0.06 ppm for acute-duration inhalation exposure (< 14 days), 0.002 ppm for intermediate-duration exposure (15-364 days) and 0.000005 ppm for chronic-duration exposure (> 365 days). The gas is not classified as a carcinogen by the US EPA, International Agency for Research on Cancer (IARC) and U.S. Department of Health and Human Services (US DHHS). Upon release from a pressurized tank, the chlorine liquid will rapidly phase change into a gas which is then transported by ambient weather conditions. The gas is highly unstable and will react with other chemicals and water; however, this project will not consider the impact of environmental reactions...
and/or photoreactions as the science of dispersion modeling has not advanced to the level at which these removal mechanisms are fully accounted for.

The science of assessing large-scale releases of toxic irritant gases has progressed extensively over the past few decades; however, the unpredictable nature and frequency of releases makes continuous, real-time monitoring nearly impossible to attain. As such, data is usually limited to that collected post-release and not adaptable for epidemiologic application. Although numerous studies concerning the residual effects of chlorine exposure have been published, most are limited by the lack of prior knowledge of the respiratory physiology of the exposed, small sample sizes and the lack of well-characterized data such as duration, extent and concentration (Jani et al, 2015). The field of atmospheric dispersion modeling is well suited as a valuable tool in public health studies and a method to move this sub-field of exposure science into the proactive realm (BASC, 2003; Farago et al, 2005). Plume dispersion modeling has progressed considerably from the simple Gaussian models of the 20th century to advanced algorithmic and integrated software systems which can simulate micro-meteorology, randomness, terrain effects, and dynamic spread. This increasing level of sophistication has allowed for the application of these technologies to epidemiology; in 2009, Zou and colleagues concluded that modeling systems are becoming primary tools in etiologic study (Zou et al, 2009).

Atmospheric dispersion models, as a minimum, require two sets of input parameters: source term, which is the physical description of the release itself, and meteorology. The latter is often considered the largest influencing factor in gas transport and dispersion, although the physical characteristics of gases such as density are highly
important (Hanna et al, 1982). For dense gases such as chlorine, topography will have a larger impact although many widely distributed modeling systems such as the Areal Locations of Hazardous Atmospheres (ALOHA) do not take into account this influence. As a result, the variability in sophistication results in widespread variance in predictive accuracy, particularly for events involving a dense gas. Plume dispersion software will often over or under-predict the exposure limit isopleths, forcing emergency responders to implement highly conservative public safety interventions and rendering accurate use in public health studies all but null.

The process of refining modeling systems to improve predictive accuracy involves, among other approaches, analysis of agreement with post-release environmental indicators of exposure. Field exposure indicators from accidental releases and field trials (such as Jack Rabbit I and II and Joint Urban 2003) can provide useful eco-toxicological data to which estimations of exposure can be compared. Ultimately, the modeling system can be improved by re-engineering the algorithmic basis or incorporating newer calculation methodologies so the output is in better agreement with the observed environmental impact. These validated models can then be used to generate accurate and precise estimations of personal exposure, which in turn can be used with confidence in epidemiologic studies. The focus of this project is the development and evaluation chlorine plume dispersion model that may be used to adequately estimate exposure in subsequent etiologic studies of the Graniteville, South Carolina, USA 2005 accidental railcar release of chlorine.

On January 6th, 2005 at 2:39 AM Eastern, a train traveling at approximately 76 km/h collided with a parked train when an improperly aligned switch resulted in the train
being diverted away from the main track. The collision resulted in the derailment of both locomotives and three tank cars containing chlorine; of these, one ruptured and released nearly $\frac{2}{3}$ of the total commodity volume (NTSB 2005a, 2005b). The railcars were of the DOT 105J500W type, which typically hold up to 81,646 kg of pressurized liquid chlorine. The rapid release and phase change of liquid chlorine to gas (Cl2) yielded a large, dense plume of chlorine inundating the surrounding community with transport and dispersion observed several kilometers downwind. The collision and release resulted in nine fatalities, over 550 hospitalizations and the evacuation of nearly 5,400 from the surrounding area (NTSB 2005a). Situated in a small river valley, Graniteville was predominantly an industrial town centered on a complex of textile mills, notably the Avondale Mills, which was one of oldest continuously operating mill facilities in the United States. The release resulted in widespread human and animal mortality/morbidity and current research work to identify the pulmonary health effects (notably within the Graniteville Recovery and Chlorine Epidemiology [GRACE] consortium) will be advanced by the application of a validated atmospheric dispersion model which can estimate personal dosage/exposure with high predictive accuracy. An expanded background is available in Jani et al, 2015.

For purposes of this project, two atmospheric dispersion modeling systems will be utilized: the Hazard Prediction and Assessment Capability (HPAC) developed by the U.S. Department of Defense (DOD) Defense Threat Reduction Agency (DTRA) and ALOHA, jointly developed by the U.S. National Oceanic and Atmospheric Administration (NOAA) and US EPA. HPAC consists of several integrated modules which determine the remaining source term parameters, simulate advanced micro-meteorological
phenomena and outputs a plume model which incorporates advanced deposition and depleting effects (particularly important for a dense gas such as chlorine). The model was originally developed by the military for use during the first Gulf war, but improvements and distribution to authorized civilian authorities and researchers as increased the application of HPAC in public safety planning, public health and exposure assessment studies. HPAC includes a Lagrangian second-order closure transport/dispersion model, SCIPUFF, which utilizes multi-dimensional Gaussian puff distributions (DTRA 2005). The vast majority of common dispersion models are Gaussian models, which assume that the pollutant has a normal probability distribution. While often used for continuous releases, Gaussian puff models can be used to model non-continuous releases such as Graniteville. In contrast, Lagrangian models simulate dispersion as a random walk process and calculate transport and dispersion based upon the statistical trajectory of many individual particles. In HPAC, the associated wind model SWIFT predicts weather-induced diffusion processes while incorporating robust measurements of variance and uncertainty. The SWIFT model is a better choice for the Graniteville incident because it is better suited for releases under 1,000 km. HPAC has been tested in many of the field trials described earlier and remains the de facto model of choice for federal commodity/warfare gas release experiments.

The development of a Graniteville chlorine plume dispersion model using HPAC version 4.04 was previously published (see Jani et al, 2015); however, considerable software improvements have been made with the release of version 5.2. A focus of this study will be to identify how these capability improvements, such as increased emphasis on micro-meteorology, will impact the dispersion model and agreement
between models generated by versions 4.04 and 5.2. Further, it is widely assumed and
established that HPAC is superior to ALOHA; however, the latter is the most commonly
used and widely distributed plume modeling software in the U.S., particularly among
public safety and local health authorities. ALOHA is part of the Computer-Aided
Management of Emergency Operations (CAMEO) suite, which also includes the
CAMEO Chemicals library and MARPLOT plotting software. Therefore, another focus of
this project will be to compare the validated HPAC 5.2 model and the ALOHA output
and identify implications for public health study and homeland security. It has been
previously determined that ALOHA lacks the accuracy required for epidemiologic study
(see Jani et al, 2015); hence, this project will mainly focus on the development and
evaluation of an HPAC model. However, we will compare the newly developed model to
the ALOHA output for purposes of explaining the intricacies of community-level
response.
Literature Review

Regarding chlorine exposure and toxicology, although accidental releases have resulted in deaths within the past century, there is a somewhat limited literature set in which measurements of acute lethal exposure concentrations in humans were made. There is considerable literature on the acute effects of exposure in animals such as horses, primates, dogs and rodents (Sommerville et al, 2009; a comprehensive database of over 100 manuscripts has been collected). In fact, most chlorine literature today still references or gives homage to the 1920s work of Underhill and Winternitz of Yale University who studied the effects of chlorine exposure during the World War I. This body of produced literature effectively paved the toxicological foundation for all war gas studies in subsequent decades.

The modeling of air dispersants using mathematical formulas dates back to the early 1930s, when Sutton, Taylor and colleagues researched methods by which to model the movement of air in the atmosphere. This work was greatly propelled forward in the mid-1940s and 1950s by Stewart, Gifford, Hewson and colleagues who focused on the need to model pollutants released from elevated sources such as smoke stacks. In the 1960s, Gifford, Pasquill, Turner and Briggs developed many of the Gaussian principles that are the basis for common dispersion models used today (i.e. ALOHA, PUFF-PLUME). These models assume that the air pollutant distribution has a normal probability distribution and are most useful for continuous, buoyant plumes. Models such as HPAC and NARAC, which are significantly more advanced, utilize the Lagrangian approach as opposed to just Gaussian principles. In these models, a moving frame of reference is used to follow particles and compute their trajectories as
they disperse and transport away from the source point. These models often also incorporate topography and dynamic micro-meteorological data - multiple locations and surface/upper observations - in their calculations. Additionally, these Lagrangian models often have the ability to track moving receptors and provide dosage estimations, which is particularly important for purposes of post-incident exposure assessment and/or epidemiologic application.

While there is a body of literature which utilizes dispersion modeling to crudely assess human exposure, the number of studies which utilize models for purposes of epidemiologic study, particularly following an acute, high-dose exposure such as Graniteville, is severely limited. Due to the increased scrutiny that error in dispersion modeling has gained, there has been an particular emphasis in validating established modeling systems against environmental indicators of exposure collected post-release (i.e. one of the key focuses of this project). Simply put, this involves comparing model predictions with observations produced by instruments, other models or analyses. As an example, several models, including HPAC, were compared to field experiment-derived mesoscale datasets of sulfur hexafluoride tracer gas by Chang and colleagues (Chang et al, 2003). This study found that only around 50% of HPAC predictions were within a factor of two of the observations. In URBAN 2000, the same tracer gas was again used in urban (Salt Lake City, Utah) trials and compared to HPAC predictions (Warner et al, 2004). Here, HPAC over predicted the observed concentrations and dosages. Similarly, Hanna and colleagues compared HPAC to the Joint Urban 2003 field trials in Oklahoma City and found that while over prediction was common, there was relatively good agreement between the predicted and observed plumes (Hanna et al, 2007). Beyond
those noted above, there have been several other experiments with the focus of identifying agreement between estimated and observed plumes (Hanna et al, 2008; Warner et al, 2006a; Warner et al, 2006b; Warner et al, 2005; Warner et al, 2004; Pullen et al, 2005; among others). The Jack Rabbit trials (I and II, which is currently in the execution phase) at the Dugway Proving Grounds in Utah are one example of the large-scale experiments being performed to study gas behavior and to validate existing modeling systems. The role of deposition, especially dry deposition and reactions with soil-based acids for dense gases such as Cl2, is an emerging area of research and large focus of the Jack Rabbit experiments (see Hearn et al, 2012; Hearn et al, 2013; Hanna et al, 2012; Bauer et al, 2013 among others). A multitude of sensors and prepared deposition matrices surrounding the release site are utilized to analyze the dispersion, transport and interaction of Cl2 and other gases post-release.

Specific to the Graniteville incident, Buckley and colleagues at the Savannah River National Laboratory (SRNL) studied the effects of deposition into nearby surfaces, including water bodies (Buckley et al, 2012). The SRNL team utilized the SCIPUFF module, part of HPAC, in conjunction with the Regional Atmospheric Modeling System (RAMS) to output a model of the Graniteville release. Then, they compared the model to published data on human health and environmental effects such as vegetation bleaching, fish mortality and estimated deposition. The Buckley study found reasonably good agreement between the model and indicator data when a deposition velocity of 1 cm/s was observed. Although we will be utilizing different indicator data for purposes of evaluation, our project will also, for purposes of comparison, qualitatively assess and discuss the differences between our and the Buckley model. It is important to note that
Buckley and the SRNL were among the first governmental entities to provide modeling support post-release (Buckley et al, 2007; Hunter et al, 2005).

The evaluation of dispersion modeling systems presents a unique challenge due to the profound differences between simulated/predicted and observed systems. Notably, as described by Oreskes et al (1994), Irwin (2014) among others, the exact validation of a model predicting a natural system is impossible. Dispersion models generally predict ensemble means, in contrast to field observations which are single instances out of an infinite possible scenarios. Further, the uncertainties present in models and natural systems result from different sources (stochastic). As such, there has been much attention directed towards the development of suitable statistical methods for evaluation of plume modeling systems. In a summary of available methodologies, Chang and Hanna (2004) described several approaches for purposes of statistically analyzing models. Of these, the BOOT software, originally developed by Hanna et al (1991, 1993), has been used by many larger model validation/evaluation studies such as those by Ichikawa et al (2002), Nappo et al (2001) and Mosca et al (1998). Further, it has been included as part of the larger Model Validation Kit, which was first developed as part of the Harmonisation within Atmospheric Dispersion Modeling for Regulatory Purposes international conferences. The BOOT software utilizes the following statistical performance measures to evaluate predictions with observations: fractional bias (FB), geometric mean bias (MG), normalized mean square error (NMSE), geometric variance (VG), correlation coefficient (R), and the fraction of predictions within a factor of two of observations (FAC2). These performance measures
have been recommended for and utilized by similar studies in evaluating plume models (see Hanna et al. 1991, Hanna et al. 1993, among others).

The American Society for Testing and Materials (ASTM), an international standards organization, has published the Standard Guide for the Statistical Evaluation of Atmospheric Dispersion Model Performance, originally developed in 2000 and reapproved in April 2015 (ASTM, 2015). This approach represents an alternative method to statistically evaluating model performance; however, the ASTM methodology has many similarities with the BOOT approach and the latter software has incorporated some of the peripheral ASTM approaches into its calculations. Particularly, the calculation of FB, use of the bootstrap resampling technique to estimate confidence level, paired sampling between observed/predicted, and grouping of data in blocks are all part of the BOOT approach (Chang et al., 2004). While the ASTM approach is promising, further investigation and refining is recommended by several researchers (Chang et al., 2004). Because BOOT incorporates many of the ASTM procedures and has been previously applied in a variety of studies, this project will likely utilize BOOT for purposes of statistical evaluation.

After statistical evaluation, the results must be analyzed to determine usability of the model. Based upon the data produced by the aforementioned statistical measures, Chang and Hanna (2004) have developed three basic guidelines:

- The fraction of predictions within a factor of two of observations is about 50% or greater (i.e., FAC2 > 0.5)
- The mean bias is within ± 30% of the mean (i.e., roughly |FB| < 0.3 or 0.7 < MG < 1.3).
• The random scatter is about a factor of two to three of the mean (i.e., roughly NMSE < 1.5 or VG < 4).

Similarly, Olesen and colleagues (2001) noted that for better modeling systems such as HPAC, the relative mean bias is ±40% and the random scatter is about a factor of two of the mean. This determination involved studies of relatively short-range dispersion, similar to the Graniteville incident. As such, our project will likely utilize the above standards to determine if our model is in good agreement with observed indicator data. If so, the model may be suitable for epidemiologic application. Although the model would be specific to the Graniteville incident, the themes and evaluation methodologies are transferrable to the larger sub-fields within environmental health and environmental epidemiology.
Hypothesis, Research Question and Specific Aims

H1: Generated (modeled) exposure data using HPAC versions 4.04, 5.2 and ALOHA version 5.4.3 will be different.

SA1: Assess improvements in predictive accuracy between Hazard Prediction and Assessment Capability (HPAC) versions 4.04, 5.2 and ALOHA 5.4.3 models of the Graniteville, South Carolina, USA 2005 rail-car release of chlorine.

   SA1.1: Identify the release source term, meteorological data and terrain inputs that will be utilized in the models.
   SA1.2: Model the release using HPAC 4.04, HPAC 5.2, and ALOHA version 5.4.3
   SA1.3: Determine accuracy between the HPAC 4.04 and 5.2 models at +15, +30, +60, +120, +180 and +240 minutes post release.
   SA1.4: Determine agreement between both HPAC models and ALOHA model.

H2: Generated (modeled) exposure data using HPAC 5.2 will differ from observed exposure indicator data.

SA2: Evaluate the Hazard Prediction and Assessment Capability (HPAC) 5.2 model of the Graniteville, South Carolina, USA 2005 rail-car release of chlorine using best available exposure indicator data.

   SA2.1: Identify the best available indicator data.
   SA2.2: Determine accuracy between the HPAC 5.2 model and best available indicator data.
**Methodology**

The overall purpose of this project is to evaluate a suitable atmospheric dispersion model for the possibility of epidemiologic application. We have chosen to utilize the HPAC software because it is the most advanced model which is freely available to authorized recipients. Therefore, it may be the most commonly used software for exposure assessment, epidemiology and public health impact studies. Because we have previously developed and published a model utilizing an earlier version of HPAC, our first step is to assess possible differences between the incumbent and newer model. Specific aim one seeks to identify the source term and other model inputs, produce plume models, and assess both models, ultimately choose the best one for evaluation.

**Specific Aim 1**

Sub-Aim 1.1: This sub-aim will seek to quantitatively identify the accidental release source term and meteorological data that will be used in modeling the release. The source term is the accurate determination of the time behavior of the release. Of this, the chlorine release rate is the most integral component. The source term has been estimated by study team members using an engineering analysis that combined official National Transportation Safety Board (NTSB) publications, semi-quantitative observations and fundamental principles (as published in Jani et al, 2015 and shown in Table 2 below). The methods used here to estimate the rate of Cl2 emission and the cumulative loss from the tank car were chosen to be appropriate for the ultimate goals of this research: to provide estimates of Cl2 exposure in Graniteville for participants in
health effects studies, not to develop generally applicable approaches for determining pollutant emission, dispersion, and transport. This analysis began by calculating the depth of liquid Cl₂ in the car using a tilt angle of 10° reported by a SC Department of Health and Environmental Control (DHEC) responder, which agreed with the approximate angle given as 5–10° reported by the NTSB, the approximate orientation of the car shown in numerous pictures, and the volume of Cl₂ initially present. Based upon NTSB pictures, the tear on the side of car was a jagged gash very nearly perpendicular to the ground and 4.88 meters from the higher end of the car (the “A” end). The depth of liquid Cl₂ was calculated as a function of the liquid-filled tank volume using a web based program supplied by LMNO Engineering (2009). Then, to simplify computation further, a cubic equation was derived by regression ($R^2 = 0.9989$) for directly computing the volume of Cl₂ in the tank from its depth and vice versa. The next step was to compute the combined pressure resulting from the average head pressure of liquid along the tear and the vapor pressure in the enclosed space above the liquid. Using an equation for flow through a submerged opening (Perry & Green 1984), we estimated that the time required for the liquid Cl₂ level to reach the top of the vertical tear, using the approximation that the two-phase portion of the fluid does not have a significant effect on the mass release rate. At the beginning of this stage one, the pressure in the Cl₂ gas equaled the vapor pressure of chlorine at the tank temperature, estimated to be −3.3 °C (26 F), corresponding to a vapor pressure of 317 kPa (46 psia) (Occidental Chemical Corporation 2000). An overview of the source term information we have used as inputs is shown in Table 2.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Value</th>
</tr>
</thead>
</table>

286
<table>
<thead>
<tr>
<th>Date</th>
<th>January 6, 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>02:39 AM Eastern</td>
</tr>
</tbody>
</table>
| Location     | 33 degrees, 33’ 43.02” N  
               81 degrees, 48’ 29.99” W |
| Upstream pressure in tank | 46 psig |
| Temperature in tank | -3.3 C |
| Release height | 1.0 m |
| Area of opening | 294 cm² |
| Weather conditions (NOTE: actual conditions will be from RAWS analysis) | Partly cloudy |
| Atmospheric stability | E |
| Wind speed | 1 - 3 m/s from SSW |
| Surface roughness | 100 |
| Discharge rate | 523 kg/s |
| Duration | 105 seconds |
| Sum of releases | 54,915 kg |

**Table 2:** Source term of the Graniteville, SC, USA 2005 rail-car release of chlorine as estimated by the study team.

The meteorological validation, presented as follows, is necessary to utilize the available weather data sets. At the time of the incident, there was no onsite meteorological station in Graniteville to provide the most accurate weather data for input into the plume modeling software. Conventionally, in lieu of onsite observations, data from the National Weather Service (NWS) and National Climatic Data Center is often used for planning, response, and investigative modeling. NWS stations are generally located at airports or areas that serve as population centers. Alternatively, the US Forest Service operates Remote Automated Weather Stations (RAWS) which are
generally self-sufficient stations located in national forests and similar areas for monitoring forest fires. Information from these mobile stations is transmitted electronically (often via satellite) every hour to the National Interagency Fire Center in Boise, Idaho. We have used archived meteorological surface observations recorded at 13 different RAWS sites collected during the night (and time of incident) on 6 January 2005. A portable weather station was setup at the incident site late in the morning of 6 January and remained there throughout the duration of cleanup activities. For purposes of validation, we compared archived observational data from the 13 different RAWS sites for five nights beginning on 7 January and ending on 12 January (10 January was excluded due to missing data) with data from this portable site. We modeled the incident in HPAC 4.04 using both the RAWS and portable weather station data (micro-environmental) collected on the aforementioned nights. Concentration and surface dosage were calculated at 1024 points across a three by three mile grid with identical source terms and correlation, mean bias, and root mean square error between the two models were calculated using IBM SPSS Statistics (Version 20, IBM, Armonk, NY). The goal of this validation was to support the notion that RAWS data collected during the night of 6 January provided an accurate representation of the incident site micro-environment in Graniteville. Although this meteorological validation was performed using HPAC 4.04, the confirmatory results support the use of this same meteorological data with HPAC 5.2. It is important to note that the analysis was recently published (Jani et al, 2015) and will be incorporated into the dissertation project as well.

The final input parameter is the terrain resolution field. Within HPAC 4.04 and 5.2, the models will utilize the resolution field which is best suited for the topography in
the Graniteville area. We anticipate this will be the “native resolution” setting due to the terrain resolution required for the Graniteville area (domain will be kept relatively small). This is generally the standard 1-km resolution terrain and land cover data built into HPAC. This setting was utilized previously while modeling the release in HPAC 4.04.

Sub-Aim 1.2: Using the Industrial Transportation (iTRANS) model in HPAC 4.04 and 5.2, the Graniteville release will be modeled using the source term, meteorological data and terrain settings identified in sub-aim 1.1. The iTRANS model is the de facto HPAC engine used to model the release of a toxic industrial chemical, such as chlorine, from a transportation vehicle. The shape files for both model versions will be plotted using ArcMap on an aerial layer of the Graniteville area for visual purposes.

Using the same source term identified in specific aim 1 to the greatest extent possible, the Graniteville incident will also be modeled in the ALOHA software. The shape file for this model will be plotted utilizing ArcMap on an aerial layer of Graniteville for visual purposes.

Sub-Aim 1.3: The purpose of sub-aim 1.3 is to identify differences between the HPAC 4.04 and 5.2 models. Although the 4.04 model has been our model of choice until now (and was published in Jani et al, 2015), the 5.2 model incorporates several algorithmic improvements which will increase the predictive accuracy of the model itself. Therefore, this sub-aim will compare the 4.04 and 5.2 model assuming that the latter is the de facto and current standard. Various statistical measures such as parametric and nonparametric tests will be utilized to compare concentration outputs at pre-identified and sampled receptor points throughout both plumes. These analyses will attempt to
detect differences in model output between the two versions and that 5.2, based upon known improvements, is the better model to continue with (thereby building and improving upon the currently published research).

*Sub-Aim 1.4:* The purpose of sub-aim 1.3 will be to compare the above produced HPAC models to the ALOHA model. Because the comparison methodology will be slightly different (due to the software abilities of ALOHA), this component of specific aim 1 will be separate from 1.3. The HPAC 4.04, 5.2 and ALOHA model outputs will be compared using pre-identified receptor points based upon the following parameters: downwind, downwind distance to concentration and maximum width to concentration. For downwind distance, these receptor points will be 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0 and 20.0 km from the source location (directly downwind on x-axis). For downwind distance to concentration and maximum width to concentration, the distance and width, respectively, in km will be identified at 2,000 ppm, 400 ppm and 20 ppm. These values have been identified based upon similar comparisons in established literature such as Hanna, et al 2008 and also the comparison of our HPAC 4.04 model to ALOHA in Jani et al, 2015. Receptor points on either side downwind x-axis (crosswind) will also be identified and compared with the same receptor points in HPAC 4.04 and 5.2. These receptor points have not yet been determined. Upwind dispersion due to phenomena such as gravity slumping is not possible to compare here due to the lack of ALOHA’s ability to model this. This sub-aim will also explore the possible reasons between ALOHA and HPAC plume differences, implications for community resiliency and succinctly suggest improvements that could be implemented as the ALOHA code is further developed.
An important component of this project is to show that our HPAC 5.2 model is highly suitable for epidemiologic application, particularly when compared to the mainstream ALOHA (sub-aim 3.2) and other models in frequent use. However, we must also compare the HPAC output to other models of the Graniteville incident which have been published in research. As part of the discussion section, we will identify the published models via literature review (such as Hanna, Buckley and others who have done extensive work in this area) and qualitatively contrast between those and our model. The differences - especially those in source term and/or methodology that lead to profound differences in results - will be discussed. Lastly, a succinct discussion on other available models and capabilities (such as NARAC) will be presented to comprehensively identify any government-derived modeling systems which may have similar outputs and/or improvements to our HPAC model. It is important to note that HPAC is considered as the most accessible advanced model and therefore was the best candidate for this project.

**Specific Aim 2**

In specific aim one, we identified the best available model for evaluation. In the second specific aim, this model will be evaluated against environmental indicator data collected in the aftermath of the Graniteville release. This evaluation is an important first step in the possible validation of this model for epidemiologic application.

**Sub-Aim 2.1:** Although collecting exposure indicator data immediately post-release is nearly impossible due to life-saving priorities, some data was collected in the days and weeks following the Graniteville release. Of note, there exists limited data sets with
animal (dog) health effects (point data), vegetation bleaching (spatial data), air quality sampling (point data) and observations of metallurgical corrosion and similar effects (point data). These data sets will be analyzed to determine the best possible (and feasible) indicator(s) to utilize in evaluation of the model. Because we are trying to validate a model which predicts the acute exposure at the time of release (and few hours after until complete dispersion), data sets which were collected beyond the estimated dispersion time will not be considered. While this limits our available data sets, there are a few which may provide robust evaluation data.

One of the most promising sources of data may be the observed effects of chlorine exposure on copper surfaces such as telephone wiring. A research group at the Georgia Tech Research Institute’s Materials Analysis Center, under the direction of Dr. Lisa Detter-Hoskin, has collected data such as the sulfur/chloride concentrations (using x-ray fluorescence [XRF] among other techniques) on common metallurgical surfaces both in the environment (i.e. telephone poles) and the household. Based upon preliminary discussion, these observations can be associated with levels of cumulative exposure derived from benchmarks in existing materials science research. These observations can be utilized in our evaluation of the HPAC 5.2 model in two ways: one, to compare predicted and observed concentrations as known receptor points (i.e. sampling locations), and two, to determine if the model accurately identifies transport direction. It is possible that exposure indicators have been reported at locations which the plume does not identify as exposed; this is one of the biases in assuming that an ensemble is fully representative of the real scenario. We have an established
relationship with Dr. Detter-Hoskin’s group as collaborators on the Graniteville Recovery and Chlorine Epidemiology (GRACE) study, of which this project is a part.

**Sub-Aim 2.2:** Once the suitable indicator data has been identified, the observed data will be compared to the predicted model and this evaluation will be described using statistical performance measures. The established literature encourages first surveying the available through exploratory data analysis, which may include the production of graphical displays such as scatter plots, quantile-quantile plots, box-residual plots and scatter-residual plots (similar to those produced in specific aim 1). As a second step after this exploratory analysis, a more robust statistical analysis will be conducted.

The BOOT software, part of the Model Validation Kit, was developed specifically for the evaluation/validation of plume modeling systems and has been used in previous studies of this type. It is described further in the literature review section. By comparing the observed to predicted values at the same receptor point (i.e. concentration, surface dosage, etc.), the software package outputs statistical performance measures such as the fractional bias (FB), geometric mean bias (MG), normalized mean square error (NMSE), geometric variance (VG), correlation coefficient (R) and fraction of predictions within a factor of two of observations (FAC2). As discussed in the literature review section, the FAC2 is one of the primary benchmarks of predictive accuracy commonly accepted in the research body. A perfect observed to predicted comparison would result in the MG, VG, R and FAC2 equaling 1.0 and FB and NMSE equaling 0.0. The type of observation compared (i.e. concentration, cumulative concentration, surface dosage etc.) will be determined based upon the indicator being utilize for evaluation. For example, while air sampling would be in the form of specific concentrations at a specific
time, the effects of chlorine exposure on metallurgical surfaces would be cumulative
dosage over the 3.5 - 4 hour period before which the plume dispersed completely.

The above approach will be conducted for each suitable exposure indicator in the
form of point data, for which specific receptor points will be identified based upon the
available data. The statistical data will be interpreted and summarized based upon
established standards (see literature review section). These standards will assist us in
determining the usability of our HPAC 5.2 model for eventual epidemiologic application.
Limitations

The predominant limitation here is the biased nature of dispersion models. As described earlier, the dispersion model itself is based upon an ensemble of possible scenarios, whereas the real release would be one natural iteration of an infinite number of scenarios. However, this limitation is one which, based upon the current best available science, is unavoidable. With all of these dynamic parameters, the model must in the end make simplifying assumptions and be an approximation of reality.

Although more advanced models such as HPAC take into account removal rates and other factors which minimize the dispersion of the plume, there are several removal factors which occur in the environment but are not modeled effectively. These removal mechanisms include chemical reactions with ambient chemicals, complete dry deposition and photolytic reactions due to sunlight. The Graniteville release was at night and therefore photolytic reactions would not have been highly influential. Based upon data from the Jack Rabbit I trials, HPAC 5.2 was upgraded to incorporate limited removal caused by deposition into soils. However, it must be noted that these intrinsic limitations with the models do exist.

There are some clarifications that must be made regarding the statistical performance indicators as well. If the distribution is close to lognormal, as it would be for most pollutant concentrations, than the FB and NMSE (as linear measures) would be highly influenced by outliers such as infrequent high concentrations. The logarithmic measures MG and VG would provide a better approach to balance the extreme values. But, even these two values may be influenced by extremely low values, which are common in plume models. Therefore, it is necessary to first identify a low threshold.
(often the limit of detection for a sensor at a receptor site) and omit any readings below this level.

FB and MG measure only systemic errors because they are measures of mean relative bias, but NMSE and VG identify both systemic and unsystemic bias. The correlation coefficient R will not adequately reveal a clear non-linear relation and is sensitive to aberrant data pairs, so some researchers have stated that R is not a good statistical indicator to use. As an alternative, the R-rank, or Spearman correlation coefficient, may be used. This project will determine the best correlation option to use based upon available data. The FAC2 is not influenced by outliers and is therefore well suited for a data set which has extremes. Obviously, it is important to utilize several statistical performance measures to adequately analyze and interpret the data. This project anticipates using all of the measures described in the methodology section, plus more as needed.