CHLORINE AND ANHYDROUS AMMONIA CONCENTRATIONS OBSERVED AND SIMULATED IN THE JACK RABBIT FIELD EXPERIMENT, FOR RELEASES OF 1 OR 2 TONS IN A 30 TO 60 SECOND PERIOD

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Abstract: Large amounts of chlorine released in a few minutes from pressurized liquefied storage such as a railcar may form a dense two-phase (gas plus small liquid aerosol drops) cloud at ground level. The time duration of release from the storage tank could be as small as a few seconds for a large hole with diameter exceeding 20 or 30 cm. But even if the release from the tank occurs in a few seconds, a dense two-phase cloud may remain in the area of the tank for many minutes if winds are light enough and/or there is a terrain depression. The 2010 Jack Rabbit (JR) field experiments at Dugway Proving Ground, Utah, demonstrated that a 30 to 60 s release of one or two tons of pressurized liquefied chlorine or anhydrous ammonia gas would result in an initial hold-up of about 30 min of the dense two-phase cloud at winds less than about 2 m/s. In this case, the chlorine gas would be slowly detrained from the surface of the two-phase cloud around the source location, following the 1990 theory of Briggs. The observed cloud hold-up time is proportional to the cube of the wind speed, in agreement with the theory. This detrainment process can be treated as an area source as far as downwind concentrations are concerned.

We have carried out an analysis, considering instrument thresholds, mean biases, and uncertainties, of three types of JR concentration samplers (MiniRae, Jaz, and Canary) operated on arcs at distances from 25 to 500 m from the source. The resulting best estimates of arc-maximum observed 10 min averaged concentrations (important for health effects) at each distance are compared, assuming the two-phase cloud hold-up time as estimated using Briggs' theory.

Key words: *Dense gas dispersion, Detrainment from dense cloud in a valley, Jack Rabbit chlorine and anhydrous ammonia field experiment****.***

INTRODUCTION

Large amounts of chlorine and anhydrous ammonia are transported around many countries in railcars and trucks, and are stored in fixed tanks at industrial facilities and at end-user sites. Most is stored as a pressurized liquefied gas at near-ambient temperatures. In an accident, as much as 50 to 100 tons can be released as a gas-aerosol mixture in a time period of a few minutes or less. Due to combinations of three effects – the high molecular weight (for chlorine), the cold temperature of the release, and the high concentrations of small aerosol drops – the cloud can have an effective initial density as much as 20 times that of ambient air.

Six widely-used dense gas models were applied by Hanna et al. (2008) to three accidents during the past decade involving large (30 to 60 tons) releases of chlorine from railcars (Festus, MO; Macdona, TX; and Graniteville, SC). The six models agreed fairly well with each other for their predictions for the three railcar accidents. Although there were no observations of chlorine concentrations during the initial large release period at the sites of the accidents, there were records of casualties, all within a few hundred meters of the release. If the current accepted relations between concentrations and health effects were assumed to be correct, then the predicted concentrations would imply many more casualties than observed and over a broader area. Several possible reasons for the difference between observed and expected casualties have been suggested. The relation between exposure and health effects is under investigation, and there is removal of chlorine gas and aerosol by chemical reactions, dry and wet deposition, and by collection on vegetation. The uncertainties regarding the source emissions term and the aerosol properties are being assessed (Britter et al., 2011). Another concern, and the subject of the Jack Rabbit field experiment studied here, is the possible "hold-up" of the large dense aerosol cloud formed around the source, especially during light wind stable conditions and with a natural depression in the area (Briggs et al. 1990, Castro et al. 1994, and Strang and Fernando 2004). With a larger "hold-up" time (i.e., release duration), there is expected to be smaller downwind concentrations, at least near the source, since the mass release rate (g/s) is inversely proportional to release duration.

OVERVIEW OF JACK RABBIT FIELD EXPERIMENT

The Jack Rabbit (JR) field experiment took place at a flat desert location in Dugway Proving Ground, Utah, USA, in April and May of 2010 (Fox and Storwold, 2011). A 50 m diameter by 2 m deep bowl-shaped depression was dug in the desert, with the release occurring at the center. The central area of the depression was flat with radius about 12 m. One ton releases of both anhydrous ammonia and chlorine were initially conducted as a test of the release mechanism and measuring systems (Pilot Trials 1-PA and 2-PC). They were followed by the "record tests" consisting of four two ton anhydrous ammonia releases (Trials 3, 4, 9, and 10-RA) and four two ton chlorine releases (Trials 5, 6, 7, and 8-RC). In all cases, the release was directed downwards and took place near dawn, when the boundary layer was likely to be stable.

The JR gases were stored as a pressurized liquefied gases at ambient temperature, with high enough pressure that the two-phase release (a mixture of about 20 % gas and 80 % liquid, by mass) generated small aerosol drops (about 10 μm) which did not settle out (i.e., rain-out) appreciably. A photograph of the Trial 2-PC cloud is shown in Figure 1. The downwards pointing two-phase jet is seen as well as the doughnut-shaped chlorine cloud, which is nearly filling the depression at this time.

Figure 1. Trial 2-PC chlorine cloud, at 22 s after the release began.

The dense cloud was observed to be held-up for a relatively long time (about 30 min) in the depression due to the very light winds (0.6 ms^{-1}) during Trial 2-PC. For JR Trial 6-RC, with the largest (6.2 ms^{-1}) wind speed, there was no significant chlorine cloud persistence beyond the 30 s release duration period. The Trial 6-RC cloud did not extend across the entire depression but was seen to be swept downwind with minimal hold-up.

Concentrations were measured by three types of samplers (Jaz, Canary, and MiniRAE), with data averaged over a few seconds. The samplers were installed on circles at distances of 25, 50, 100, 200, 300, and 500 m. Many photos and videos also are in the JR data archive. Extensive meteorological measurements were taken; e.g., winds were observed by a network of standard anemometers as well as by several sonic anemometers.

Because the JR sampler observations required extensive analysis to determine thresholds, maximum concentration limits, corrections after calibrations, and the magnitudes of possible errors, the authors have only recently completed the comprehensive concentration data archive. This exercise required communications with the several groups who collected the data. Our previous papers (Hanna et al., 2012, and Hanna and Chang, 2012) contained preliminary analyses of JR Trials 2-PC and 6-RC, and the current paper extends this analysis to all trials and to a number of averaging times, T_A, ranging from 1 sec to 30 min. The wind speed, u, used in all of these analyses is the average of the 16 PWIDS observations at 2 m height on the sampling network.

BRIGGS ET AL. (1990) THEORY OF CLOUD HOLD-UP IN VALLEY

As discussed in the Introduction, it was hypothesized that a two-phase dense cloud might be "held-up" in a depression or valley in the area of the source. Hanna et al. (2012) noted that Briggs et al. (1990) provided a theoretical explanation (calibrated with wind tunnel observations) for how long a dense cloud might be held up in a valley subject to a cross-wind, and postulated some formulas for the detrainment rate from the top surface of the dense cloud. Castro et al. (1994) extended this theory to less-dense initial clouds. Strang and Fernando (2004) further extended the analysis with emphasis on rectangular cavities such as urban street canyons. A key aspect of the Briggs theory is that the time scale, t_f, for the cloud hold-up is inversely proportional to the cube of the wind speed, u, measured "above the cloud":

$$t_f = A g_i' u^{-3} \tag{1}$$

where A is the cross-sectional (x-z) area of the dense cloud in the depression (proportional to along-wind depression width times its depth), and $g_i' = g(\rho_c - \rho_a)/\rho_a$, where ρ_c is the initial density of the cloud and ρ_a is the ambient air density. Hanna et al. (2012) showed that this u^{-3} relation provided a good approximation for the difference in hold-up times for JR trials 2-PC (with u = 0.6 ms^{-1}) and 6-RC (with u = 6.2 ms^{-1}).

Briggs also suggested that the two-dimensional volume flux, ν, of cloud material passing through a vertical plane on the downwind edge of the 2-D valley was proportional to u^3/g_i'. Using dimensionless variables, $V' = \nu g_i'/u^3$ and $T = t/t_f$, he proposed the following general dimensionless relation:

$$V' = 0.06\exp(-0.05T) \quad (2)$$

where the "constants" 0.06 and 0.05 were determined using the results of Briggs' EPA FMF wind tunnel experiments. However, we recognize that the JR scenario is different in many aspects from the Briggs theoretical or wind tunnel scenarios. For example, Briggs studied a 2-D valley while JR is a 3-D depression. Therefore, in the current paper we describe our use of the JR observations to "tune" the constants in the Briggs' formulas, so that the theory can be applied to circular depressions.

RESULTS OF ANALYSIS OF TIME SCALE FOR CLOUD HOLD-UP AT JR

The JR videos, taken from about six viewpoints, were viewed in order to estimate the times at which certain phenomena occurred, such as the end time of the jet release from the tank, the time when the flat top of the cloud decreased to a 1 m height, the time when the visible cloud could first be "seen through", and the time when the last visible wisps of cloud vanished. We decided that the single most robust estimate of the time scale in equations (1) and (2) was the time when the visible cloud could first be seen through. Table 1 contains the characteristics of the JR trials and lists several of the time scales. Note that, for Trial 7-RC, the cloud was never opaque. Figure 2 tests the relation $t_f \approx u^{-3}$ for the nine trials with valid observations. The line $Dt = 350u^{-3}$ (for Dt in s and u in ms^{-1}) provides a fair fit. There is no significant difference between the chlorine or anhydrous ammonia points, implying that the density is primarily due to the imbedded aerosols. The points at either extreme are somewhat uncertain because the small Dt value (a few s or less) is difficult to measure during higher winds in Trial 6-RC, and the small u values (0.6 ms^{-1} or less) have uncertainties at that extreme.

Assuming a JR visible cloud width, W, of 20 m and depth, h, of 1 m in the depression, and assuming that g_i' in the mist cloud ranges from about 22 ms^{-2} (for pure chlorine gas) to 100 ms^{-2} (for a two-phase mixture with small aerosol drops), then equation (1) can be used to calculate that t_f is in the range from about (400 to 2000 m^3s^{-2})u^{-3}. Next it is assumed that the observed Dt is where the detrainment rate drops to 0.1 of its maximum value. Therefore Briggs' "constant" of 0.05 in the exponential term in equation (2) is determined from the JR data to be in the range from 0.07 to 0.4 (slightly larger). This estimate itself is affected by uncertainties in $g_i' = g(\rho_c - \rho_a)/\rho_a$, W and h in the initial cloud. The initial cloud density, ρ_c, was not observed during JR due to the large aerosol density (not measured) and the corrosiveness and health danger in the cloud.

Table 1. JR trial summary and key times related to visible cloud behavior (from the videos). Grey-shaded is the suggested estimate, Dt, for cloud hold-up for use in the Briggs et al. (1990) formula.

Trial	Release date (2010) and time UTC	Time when visible jet ends (s)	Dt for cloud seen through[1] (s)	End of visible cloud[2] (minutes)	Wind Speed u $m\ s^{-1}$	u^3 m^3s^{-3}
1-PA	4/7 1400	65	**235**	14	0.3	0.027
2-PC	4/8 1345	65	**655**	34	0.6	0.216
3-RA	4/27 1315	118	**162**	32	1.3	2.20
4-RA	5/1 1420	110	**70**	11	1.4	2.74
5-RC	5/3 1320	64	**176**	19	1.6	4.10
6-RC	5/4 1340	56	**1**	17	6.2	238.3
7-RC	5/5 1405	60	**always[3]**	49	1.4	2.74
8-RC	5/7 1250	69	**351**	59	1.2	1.73
9-RA	5/20 1245	40	**100**	14	1.5	3.38
10-RA	5/21 1250	40	**30**	10	3.5	42.88

[1]Dt = (time when mist can be seen through) – (time when visible jet ends)
[2]Minutes after the release ends when the cloud is no longer visible; sometimes extended due to delayed emissions from the ground surface.
[3]Trial 7-RC was unique in that the cloud never was opaque and so the "time that cloud can be seen through" has no meaning.

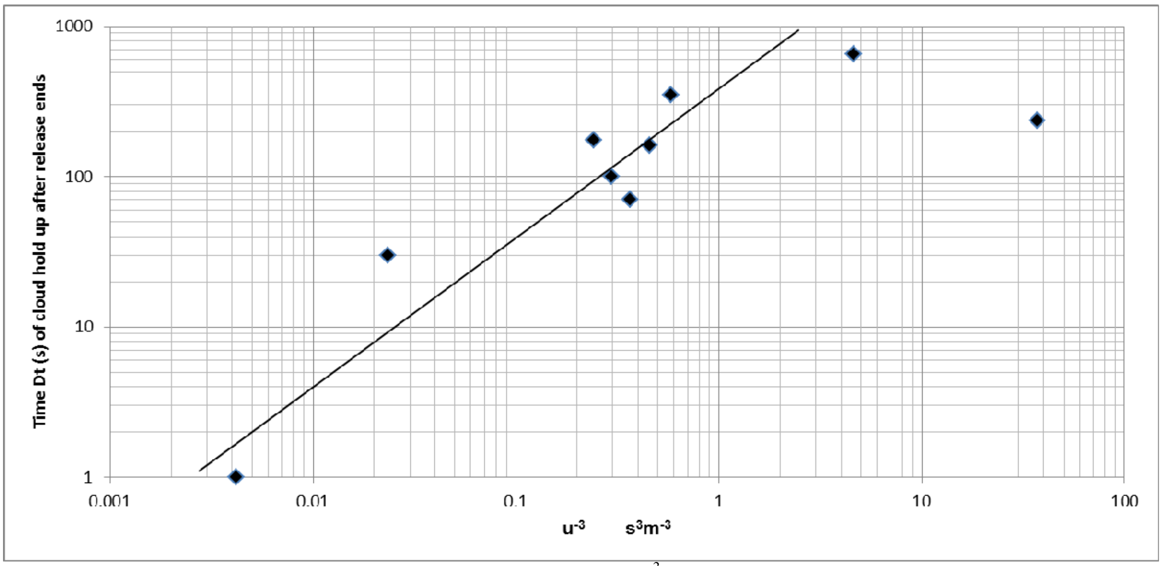

Figure 2. Scatter plot of observed cloud hold-up time Dt versus $1/u^3$ for nine JR trials (from Table 1). A straight line, Dt = 350 u^{-3} provides a good fit to these points and is consistent with the power law suggested by Briggs et al. (1990).

RESULTS OF ANALYSIS OF CONCENTRATIONS AT JR

As mentioned above, we produced a revised set of QA/QC'd JR concentration observations, removing some of the uncertainties and mean biases in the previously-available preliminary data. The Hanna et al. (2012) paper made use of arc maximum 20-s averaged concentration observations during two chlorine trials (2-PC and 6-RC) and focussed on differences between the low-wind trial 2-PC and the high-wind trial 6-RC, verifying the potential use of the Briggs theory. In our revised concentration data archive, tables are available of concentrations from all ten trials using averaging times of 10, 20, and 30 s; and 1, 2, 5, 10, 20, and 30 min. These nine different averaging times are used because different investigators are using several different health effects criteria, and because some of the concentration time series exhibit only brief (< 1 min) periods of significant values, while other time series exhibit significant concentrations lasting an hour or more. A floating "background" is often seen and varies by trial and sampler.

We are still trying to resolve difficulties associated with some samplers that could not record above certain "maximum values" (such as 10,000 ppm for the MiniRAEs), either due to the basic characteristics of the instruments or due to settings by the experimentalists. From a health effects point of view, any concentrations above about 1000 ppm are extremely hazardous for both chlorine and anhydrous ammonia. From a basic physics point of view, though, such as attempting to verify the Briggs theory, the entire range of concentrations is of interest.

Figure 3 contains plots of maximum 10-min averaged concentrations observed by each sampler during each of the nine JR trials with data. This is an example of the type of analysis possible with the data archive. Different symbols are used for the three different types of samplers (MiniRAE, Canary, and Jaz). In the aerosol clouds, some ambiguity exists between conversions from ppm to mass per unit volume concentrations, such as gm^{-3}, since the aerosol drop sizes and concentrations are not determined during JR. This will affect any comparisons with model predictions of concentrations, which are in units of mass per unit volume, based on emissions estimates of mass per unit time. Figure 3 shows that the 10-min average concentrations marking the upper envelope of the points decrease approximately with x^{-2}, as found in other dense gas field studies. In fact the simple relation $C = Ax^{-2}$, with $A = 10^8$ ppm-m^2, is a fair representation of the nine JR trials plotted in Figure 3. Much more analyses of the comprehensive JR data archive will take place over the next year.

The data for 20-s averages for Trials 2-PC and 6-RC were previously used by Hanna et al. (2012) and Hanna and Chang (2012) for verification of the Briggs et al. (1990) theory and for evaluations of the SLAB dense gas model. The Hanna and Chang (2012) study showed how the cloud near the source dispersed like a continuous plume, but after a time of travel roughly equal to the cloud hold-up time in the depression, the cloud dispersed like a puff. Thus the rate of decrease of concentrations with distance would change.

We are continuing analysis of the complete set of concentration data, including comparisons with simplified theory and with dense gas models such as SLAB.

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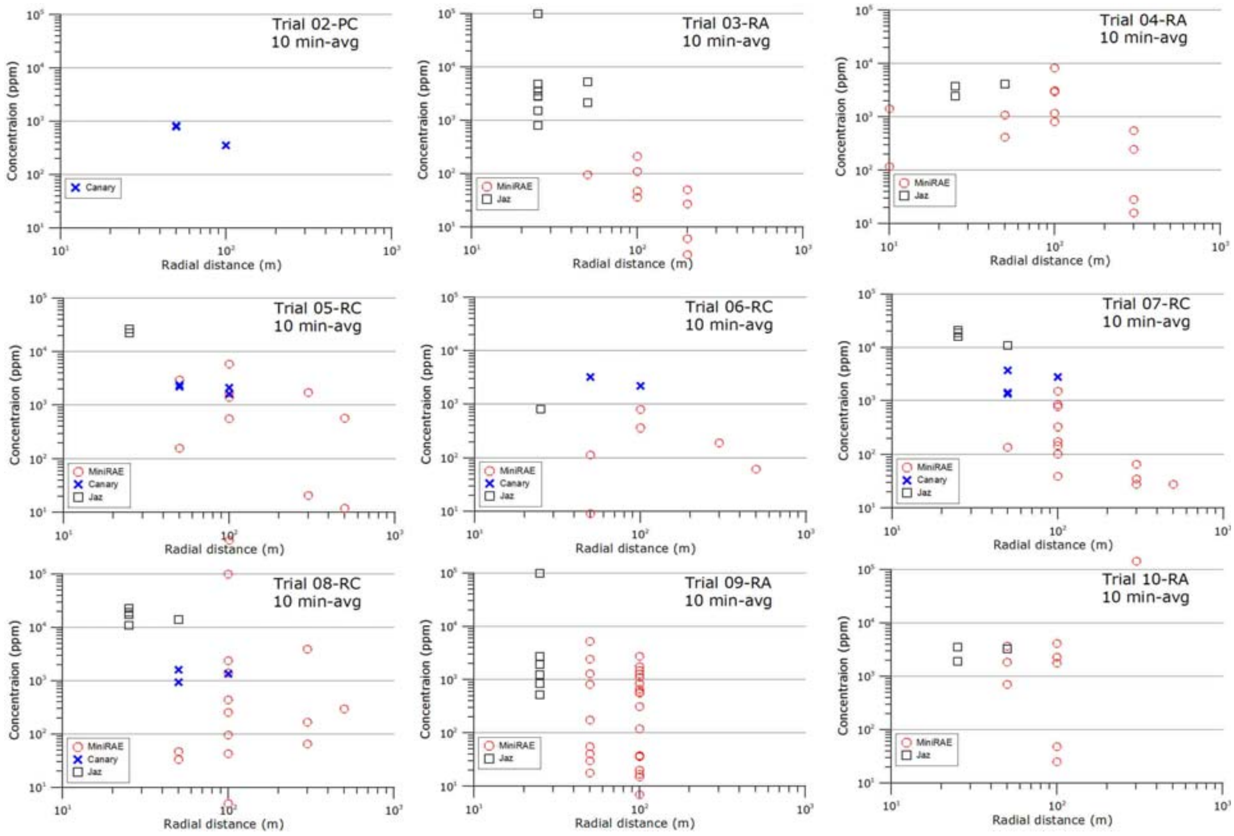

Figure 3. Observed 10-min averaged maximum concentration for each JR trial for each sampler with acceptable data.

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