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# Observed chlorine concentrations during Jack Rabbit I and Lyme Bay field experiments



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# HIGHLIGHTS

• Chlorine concentrations observed during two field experiments with releases of several tons are analyzed.

• The 1927 Lyme Bay and the 2010 Jack Rabbit I field experiments are studied.

• Normalized concentrations Cu/Q decrease with distance as  $x^{-1.5}$  to 200 m and as  $x^{-2}$  from 200 m to 3 km.

• Results can be used to evaluate models and plan future field experiments.

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# ABSTRACT

As part of planning for a series of field experiments where large quantities (up to 20 tons) of pressurized liquefied chlorine will be released, observations from previous chlorine field experiments are analyzed to estimate the ranges of chlorine concentrations expected at various downwind distances. In five field experiment days during the summer 2010 Jack Rabbit I (JR I) field trials, up to two tons of chlorine were released and concentrations were observed at distances, x, from 25 to 500 m. In the 1927 Lyme Bay (LB) experiments, there were four days of trials, where 3-10 tons of chlorine were released in about 15 min from the back of a ship. Concentrations were sampled at LB from four ships sailing across the cloud path at downwind distances in the range from about 350 to 3000 m. Thus, the distances from which JR I concentrations were available slightly overlapped the LB distances. One-minute arc-maximum chlorine concentrations, C (g/m<sup>3</sup>), were analyzed from four JR I trials and two LB trials. Normalized concentrations (Cu/Q) were plotted versus x (m), where u (m/s) is measured wind speed at heights of 2–10 m and Q (g/ s) is continuous mass release rate. It is found that the IR I and LB Cu/Q observations smoothly merge with each other and fall along a line with approximate slope of -2 at distances beyond about 200 m (i.e., Cu/Q is proportional to  $x^{-2}$ ). At x < 200 m, where dense gas effects are more important, the slope is less (about -1.5). Most of the data points are within a factor of two of the "best-fit" line.

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# 1. Introduction

When large amounts (on the order of 10 tons) of chlorine are released to the atmosphere as a result of railcar accidents or other causes, there is a need to inform emergency responders of the expected magnitude and extent of the hazardous chlorine cloud. Dense gas dispersion models and/or results of field experiments can be used to guide this decision process. Because of the obvious

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http://dx.doi.org/10.1016/j.atmosenv.2015.11.029 1352-2310/© 2015 Elsevier Ltd. All rights reserved. hazards, there have been very few field experiments carried out where the mass of chlorine released was more than about one ton. Model simulations are uncertain because of several physical and chemical complications such as accounting for the time-dependent two phase chlorine releases with significant rainout of aerosol drops, the dense gas slumping, the evaporation effects, and the chemical reactions and deposition. Hanna et al. (2008) showed that the predictions of six widely-used dense gas models agreed fairly well with each other (all within a factor of plus and minus three at any given downwind distance out to 20 km) for three major chlorine railcar accidents (Festus, Macdona and Graniteville). However, no chlorine concentration data were available at these sites, and a



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discrepancy existed because, although the predicted concentrations indicated significant health effects at distances out to 10 km, there were casualties only in the near field. As mentioned above, there are several possible causes for the discrepancies, and they are the subject of current research.

Thus the Jack Rabbit I (JR I) field experiment was conducted in 2010, with one and two ton releases of pressurized liquefied chlorine, and concentration measurements out to distances of 500 m (Fox and Storwold, 2011). Hanna et al. (2012) and Bauer (2013) analyzed the JR I concentration observations and Hearn et al. (2013) analyzed the deposition observations. The Jack Rabbit II (JR II) field experiment is planned for 2015-2016 with larger releases of chlorine (as much as 10 tons). To aid in planning the siting of JR II concentration monitors, a search was initiated for additional chlorine field observations for very large mass releases. The major additional chlorine field experiment resource in the literature is the Lyme Bay (LB), England, data archive (Wheatley et al., 1988). The current paper focuses on the combined analysis of the two field data sets. There are two major objectives: 1) Determine whether normalized observed chlorine concentrations at JR I and LB agree; and 2) Determine whether the observed normalized concentrations (e.g., Cu/Q) follow expected power laws with distance, x, where u is wind speed and Q is mass release rate (e.g., see Britter and McQuaid, 1988).

# 2. Description of two field experiments involving chlorine releases

The 1927 Lyme Bay (LB) and 2010 Jack Rabbit I (JR I) chlorine field tests are described. The emphasis of this paper is on the maximum concentration observations at any distance arc and their variation with downwind distance, because that information is a primary need of decision-makers and emergency first responders. Details of the geographic position of the cloud and its lateral spread are also needed but those parameters could not be precisely measured during the field experiments.

### 2.1. Lyme Bay

The LB chlorine field experiments were carried out in May, 1927, by the UK Chemical Defense Establishment (CDE, 1927), at Lyme Bay (off the southern coast of England). At the time the concern was driven by the possible use of chlorine as a chemical weapon (see Marshall, 1989, for analysis of gas attacks in World War I). The CDE (1927) report, which focusses on describing the gas sampling, had very limited distribution. That report was reviewed by the UK Health and Safety Executive (HSE) scientists in the mid-1980s and used by Wheatley et al. (1988) to test several dense gas models.

There were four daytime field trials where about 3-10 tons of chlorine were released in 15 min from cylinders on a ship deck, over water (Lyme Bay) several km from shore. Sampling was done from four moving submarines steaming roughly perpendicular to the expected plume at distances from about 350 m to 5 km from the source ship. The releases were doped with chlorosulphonic smoke to make them visible. Details of the source methodology are not available (e.g., tank pressure and temperature; hole size, shape, and location on tank). Weather observations were available from the source ship, the four submarines, a "weather ship", and coastal land sites. Reported wind speeds are from a height of about 10 m. Each moving submarine had five sampling stations at z = 3-9 m above sea level. There was a lack of significant variation of observed concentration (C) with height in this shallow layer at the downwind distances (ranging from a few hundred m to a few km) where samples were measured.

Concentration measurements were based on bubbling sampled

gas through a chemical mixture and subsequent analysis of that mixture. Accuracy of the observed concentrations was estimated by HSE to be 20%. Listed observations are a) averages over the five samplers and the sampling time (about 15 min while in the plume) and b) peak one-min average C. The latter was used in the comparisons with JR I. Distance x is the average for a moving ship and trial. The peak (max) one min C observed along the farthest arcs during each trial are:

Trial III (u = 3.1 m/s), C = 8 ppm at x = 1032 m

Trial IV (u = 2.5 m/s), C = 8 ppm at x = 1320 m  $\,$ 

Trial V (u = 4.1 m/s), C = 12 ppm at x = 2896 m

Trial VI (u = 3.6 m/s), C = 111 ppm at x = 1416 m

Thus the max one-min C is observed to be between 8 and 111 ppm at downwind distances from about 1 to 3 km. This is for total chlorine mass released ranging from 3.2 to 10.4 tons.

The observations from the last two Lyme Bay field experiments (Trials V and VI) are said by Wheatley et al. (1988) to be much better than the first two because the procedures improved over the course of the experiment. Therefore, Trials V and VI are used in Section 3 for comparisons with JR I observations and for development of scaling relations.

### 2.2. Jack Rabbit I

One or two tons of pressurized liquefied chlorine were released at about 7 am on each of five JR I trial days in summer 2010 at Dugway Proving Ground, Utah, USA. The experiment is described by Fox and Storwold (2011), and three journal articles have been published on the JR I data analysis (Hanna et al., 2012; Hearn et al., 2013; and Bauer, 2013). The Hanna et al. (2012) article focusses on the concentration observations used in the current paper. IR I was intended to address worst case conditions related to pressurized liquefied chlorine releases from railcars and trucks. Thus the hole in the tank was at the bottom and the release system was designed so that no flashing occurred before the chlorine exited the hole. The initial jet pointed downwards and a terrain depression (2 m deep with radius 25 m) surrounded the release, so as to minimize initial transport and dispersion away from the source. The field experiments took place at dawn, when the ambient atmosphere was still stable, again minimizing ambient dispersion. Once the chlorine cloud was transported or dispersed out of the initial depression, though, its subsequent transport and dispersion was over a flat desert surface. Real-time fast response chlorine concentration samplers were located on arcs at distances 25, 50, 100, 300, and 500 m from the source. The 25 m arc was at the top of the edge of the depression. Because limited numbers of samplers were available, the samplers were sparse at the farther arcs (100 and beyond).

For the current analysis, the four chlorine trials (numbers 5, 6, 7, and 8) with 2 ton releases are used. Trial 2, with one ton released, was called a "pilot trial" and is not used in the current analysis. It was intended primarily to test the samplers and other instrumentation and improve the methodology for later trials. The peak (max) one-min averaged concentrations on several JR I downwind arcs (25, 50, 100, 300, 500 m) are used for comparison with Lyme Bay. The wind speed used in our analysis was measured at a height of 2 m. The chlorine release occurred at a hole in the bottom of the tank, about 1 m above ground (e.g., see Fig. 1, where the release took place during a low wind (0.6 m/s) speed period and hence the dense momentum jet spreads out nearly uniformly in all directions). The two-phase jet lasted for about 30–60 s (until most of



Fig. 1. JR I Trial 2 at 22 s. One ton chlorine release with u = 0.6 m/s.

the pressurized liquefied chlorine was released).

Because there was a 50 m diameter, 2 m deep depression dug around the source location (see Fig. 1), the dense chlorine cloud tended to persist in the depression during trials with wind speeds less than about 2 m/s. Chlorine gas was detrained from the surface of the cloud in the depression, and Hanna et al. (2012) showed how the time to detrain most of the chlorine was a function of the excess density in the cloud and the cube of the wind speed. This time was as much as 10 min for these four JR I field trials. Thus in our analysis in the next section, where the rate of mass release, Q, is used, that rate equals the total mass (2 tons) divided by the total duration of the release, t<sub>d</sub>, which equals the sum of the time duration of the high-momentum two-phase release, plus the time duration of the subsequent release due to detrainment from the cloud in the depression.

#### 3. Analysis of observations

As stated earlier, the current analysis focusses on the observations at LB and JR I. There have been several dense gas dispersion models previously applied to the two databases (e.g., see Wheatley et al., 1988 and Ziomas et al., 1989 for LB, and Hanna et al., 2012 and Bauer, 2013 for JR I) but no models will be evaluated here. Our primary objective is to use the field experiment observations to estimate the downwind chlorine concentrations expected during the JR II field experiment, where the release masses will be 5–10 tons and the sampler arcs will extend from 25 m to 11 km. Another objective is to provide a table of LB and JR I data that is sufficient to be used by others to develop and evaluate models.

Table 1 contains the LB and JR I field experiment observations that have been analyzed here. We have followed Britter and McQuaid's (1988) suggested approach of first defining appropriate ways to scale the observations (i.e., use basic physics insights to generate dimensionless groups from the major parameters). For analyzing cloud transport and dispersion, the dimensionless groups depend on whether the cloud can be considered continuous or instantaneous (puff). The major difference between the two is that the puff is affected by along wind dispersion in the upwind and downwind directions. If the release is continuous, then the mass release rate (Q in mass per unit time) and the downwind distance x are used as fundamental parameters. If instantaneous (puff), then the total mass released ( $Q_t$  in mass) and the travel time,  $t_t = x/u$ , are used. In both cases, the maximum one minute (max one min) average concentration C (mass per unit volume) and the wind speed u are used as fundamental parameters. As Britter and McQuaid (1988) show, the choice of continuous or instantaneous depends on the ratio of the travel time, t<sub>t</sub>, to the release duration time, t<sub>d</sub>. For the LB and JR I field data being analyzed, t<sub>t</sub> is always less than t<sub>d</sub>, implying that the cloud can be considered to be continuous. Thus plotting of the dimensionless variable,  $Cux^2/Q$ , versus x should produce a universal curve. When logarithms of the variables are plotted, power law relations are revealed as straight lines. In Fig. 2. In Cu/O is plotted versus In x. We also examined the normalized formulas assuming an instantaneous release. In that case, C/Qt is plotted versus tt, but the data points are more scattered and do not fall along a universal curve as well as they do for the continuous assumption. Note that the observed chlorine concentrations, C, are in units of ppm in Table 1. To produce the values of Cu/Q for plotting versus x in Fig. 2, C (ppm) must be converted to C  $(g/m^3)$ . This conversion could be done precisely for each field experiment trial knowing the pressure and temperature, but these details were not known for LB. We therefore assumed a simple constant for the conversion,  $C(g/m^3) = 2640 C (ppm)$ , as used in Hanna et al. (2012).

The release duration time,  $t_d$ , was listed as 15 min (900 s) for LB (Wheatley et al., 1988). Because no information is provided regarding time variability, we assume that the emission rate was constant over the 900 s. Thus, for LB, Q = (release mass)/(900 s), yielding Q = 11,500 g/s for LB V and 7020 g/s for LB VI. For the four JR I trials, calculation of  $t_d$  and Q are based on Hanna et al. (2012) and are briefly described in the last sentence of Section 2 above. Thus the JR I Q values range from 3030 to 35,088 g/s (see Table 1).

Prior to starting the analysis of Fig. 2, we recall (see Hanna et al., 1996) that the formula  $Cu/Q = A/x^2$  (where A is a "constant") has been shown to be a good approximation for non-dense plumes released near the surface during the daytime at x < about 10 km. This is an indication that both plume width and plume depth increase in proportion to x. However, at small distances from the source, where the dense gas slumping is significant and the cloud's vertical dispersion is suppressed, Britter and McQuaid (1988) find that the vertical rate of dispersion decreases and the power on x is less (about 1–1.5). For the LB and JR I data in Fig. 2, the 1.5 power provides a better fit at x < about 300 m.

The following formulas provide good fits for the Cu/Q versus x observations in Fig 2 for the combined LB and JR I chlorine field experiments.

For the near-field (25 < x < 280 m),

$$Cu/Q = 6/x^{1.5}$$
 (1)

where C is in g/m<sup>3</sup>, u is in m/s, Q is in g/s, and x is in m. The "constant", 6, has units m<sup>-0.5</sup> in eq. (1). It is not dimensionless because our simplified analysis has not yet accounted for a dimensionless group describing the density effects, such as the initial cloud Richardson number,  $Ri_0 = (g(\rho_c - \rho_a)/\rho_a)h/u^{*2}$ , where g is the acceleration of gravity, h is the initial cloud depth, u\* is the ambient friction velocity, and  $\rho_c$  and  $\rho_a$  are the initial cloud and ambient densities respectively (see Briggs et al., 2001).

For 280 < x < 2900 m,

$$Cu/Q = 100/x^2$$
 (2)

with variables in the same units as above. In this case the constant 100 is dimensionless, because the effects of increased cloud density have become insignificant at distances beyond about 280 m.

In Fig. 2, 76% of the 26 points are within a factor of two of the best fit line. At distances where there is some overlap of observed concentrations from LB and JR I (at 300 m < x < 700 m), the observed values of Cu/Q from the two field experiments also overlap. In our analysis, we did not attempt to fit a single formula to the data (i.e., possibly adding Ri<sub>o</sub>). That type of analysis will take

 Table 1

 Lyme Bay and lack Rabbit I chlorine release trails that were analyzed.

| LB V 10,350 900 11,500 4.1 725 238<br>1444 56<br>2173 28<br>2896 12<br>LB VI 6318 900 7020 3.6 354 476<br>709 159<br>1062 109<br>1416 111 | ppm |
|---|-----|
| LB VI 6318 900 7020 3.6 1444 56<br>2173 28<br>2896 12<br>2896 12<br>709 159<br>1062 109<br>1416 111                                       |     |
| LB VI 6318 900 7020 3.6 2173 28<br>7020 3.6 354 476<br>709 159<br>1062 109<br>1416 111  |     |
| LB VI 6318 900 7020 3.6 354 476<br>709 159<br>1062 109<br>1416 111  |     |
| LB VI 6318 900 7020 3.6 354 476<br>709 159<br>1062 109<br>1416 111  |     |
| 709         159           1062         109           1416         111   |     |
| 1062 109<br>1416 111  |     |
| 1416 111  |     |
|   |     |
| JR 1 5 2000 240 8333 1.6 25 58,600  |     |
| 50 27,800   |     |
| 100 13,500  |     |
| 300 3410  |     |
| 500 2030  |     |
| JR 1 6 2000 57 35,088 6.2 25 55,600   |     |
| 100 9780  |     |
| 300 1100  |     |
| 500 330   |     |
| JR 1 7 2000 660 3030 1.4 25 67,120  |     |
| 50 25,700   |     |
| 100 6080  |     |
| 300 301   |     |
| 500 75  |     |
| JR 1 8 2000 410 4878 1.2 25 58,200  |     |
| 50 24,100   |     |
| 100 8000  |     |
| 300 1060  |     |



place once we add the data from the August–September 2015 JR II field experiment to the LB and JR I data set.

As seen in Table 1, for the LB and JR I field data sets, the maximum concentrations observed at the farthest distances downwind were 12 ppm at 2896 m in LB trial V and 111 ppm at x = 1416 m in trial VI. In Fig. 2, the 12 ppm point is very close to the line defined by Eq. (2), while the 111 ppm point is a factor of about three above the line. This is also approximately the maximum difference between the observed points and the line in the figure and could represent the uncertainty range (about plus and minus a factor of three). Applying the factor of three uncertainty to the 12 ppm point, we can say that observation could be as high as 36 ppm. Thus, for planning future experiments with this magnitude release of chlorine, as a first estimate, the one min max

concentrations might be expected to be about 100 ppm at x = 1400 m and about 30–40 ppm at x = 2900 m. This is based entirely on available field observations of large releases of chlorine.

## 4. Further comments

We have shown that the observed concentrations from the LB and JR I chlorine field experiments follow expected basic dispersion relations and the normalized concentrations from both field experiments form a smooth and consistent curve. Thus the observations that we report should be useful in others' dispersion model development and evaluation efforts.

The LB experiments are the only previous chlorine field experiments that we have discovered where the releases were the same magnitude as planned for JR II (5–20 tons). Although the 1927 LB observations lack information regarding the release conditions and other details, at this time there is no one to ask about the missing information. Moving ships are not the best platforms to measure concentration distributions, and deposition of chlorine to the sea surface is not measured or accounted for. Nonetheless, there is striking agreement between the LB and JR I chlorine field experiments at far different locations and separated by 83 years in time.

The JR I field experiments were carried out with downward pointing flashing jets and an artificially built depression. Thus the near-field cloud transport and dispersion are influenced by this unique scenario. The effects of the initial scenario are likely less important after the cloud passes the 50 m sampling arc in JR I. For larger distances, the main effect of the depression is to increase the time duration of the release (and thus reduce the effective continuous release rate Q).

The LB observations extend out to 2900 m. Thus the  $x^{-2}$  power law in eq. (2) is a good fit between distances of about 200–3000 m. We note that, in field experiments with neutral gases, the vertical dispersion eventually becomes constrained by the mixing depth,  $z_i$ , in the daytime, and a power less than 2 is found at distances past about 10 km (Hanna et al., 1996). Typically  $z_i$  averages about 1000 m.

All of the LB and JR I experiments took place in the daytime

(either early morning or the middle of the day). At night, due to the ambient vertical turbulence suppression, the vertical dispersion would be further constrained. But due to the very hazardous conditions associated with chlorine releases, the experiment planners avoid nighttime releases.

Also, at larger distances, the time of travel,  $t_t$ , of any cloud will obviously be larger, and the cloud from a finite duration release is eventually (as  $t_t > t_d$ ) going to behave like a puff rather than a continuous plume, as suggested by Britter and McQuaid (1988) and Hanna et al. (1996). With the addition of the along-wind component of dispersion, the rate of decrease of concentration in a puff is greater than that in a plume.

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## References

Bauer, T.J., 2013. Comparison of chlorine and ammonia concentration field trial data with calculated results from a Gaussian atmospheric transport and dispersion model. J. Hazard. Mater. 254–255, 325–335.

- Briggs, G.A., Britter, R.E., Hanna, S.R., Havens, J.A., Robins, A.G., Snyder, W.H., 2001. Dense gas vertical diffusion over rough surfaces: results of wind-tunnel studies. Atmos. Environ. 35, 2265–2284.
- Britter, R.E., McQuaid, J., 1988. Workbook on the Dispersion of Dense Gases. HSE Contract Research Report No. 17/1988. Health and Safety Executive, Sheffield, UK, 158 pp.
- Chemical Defense Establishment (CDE), 1927. Report on Naval Anti-gas Trials Carried Out May 19th 1927 off Lyme Bay. Porton Report No. 503, Serial No. 17, 49 pp.
- Fox, S.B., Storwold, D., 2011. Project Jack Rabbit: Field Tests. Chem. Security and Analysis Center, Science and Tech. Directorate, US Dept. of Homeland Security, CSAC 11-006, 162 pp.
- Hanna, S.R., Britter, R.E., Chang, J., Argenta, E., 2012. The Jack Rabbit chlorine release experiments: implications of dense gas removal from a depression and downwind concentrations. J. Hazard. Mater. 213–214, 406–412.
- Hanna, S.R., Dharmavaram, S., Zhang, J., Sykes, I., Witlox, H., Khajehnajafi, S., Koslan, K., 2008. Comparison of six widely-used dense gas dispersion models for three recent chlorine railcar accidents. Proc. Saf. Prog. 27, 248–259.
- Hanna, S.R., Drivas, P.J., Chang, J.C., 1996. Guidelines for Use of Vapor Cloud Dispersion Models. AIChE/CCPS, 345 East 47th St., New York, NY, 285 pp + CD.
- Hearn, J.D., Weber, R., Nichols, R., Henley, M., Fox, S., 2013. Deposition of Cl<sub>2</sub> on soils during outdoor releases. J. Hazard. Mater. 252–253, 107–114.
- Marshall, V.C., 1989. The predictions of human mortality from chemical accidents with especial reference to the lethal toxicity of chlorine. J. Hazard. Mater. 22, 13–56.
- Wheatley, C.J., Crabol, B., Carpenter, R.J., Jagger, S.F., Nussey, C., Cleaver, R.P., Fitzpatrick, R.D., Byrne, A.J., 1988. Comparison and Tests of Models for Atmospheric Dispersion of Continuous Releases of Chlorine. UK Atomic Energy Authority Safety and Reliability Directorate, Report No SRD R438, ISBN 0-853563047, 95 pp.
- Ziomas, I.C., Zerefos, C.S., Bais, A.F., 1989. Design of a system for real-time modelling of the dispersion of hazardous gas releases in industrial plants. J. Loss Prev. Process Ind. 2, 194–199.