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## **The Role of Deposition in Limiting the Hazard Extent of Dense-Gas Plumes**

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**Abstract** - Accidents that involve large (multi-ton) releases of toxic industrial chemicals and form dense-gas clouds often yield far fewer fatalities, casualties and environmental effects than standard assessment and emergency response models predict. This modeling study, which considers both dense-gas turbulence suppression and deposition to environmental objects (e.g. buildings), demonstrates that dry deposition to environmental objects may play a significant role in reducing the distance at which adverse impacts occur – particularly under low-wind, stable atmospheric conditions which are often considered to be the worst-case scenario for these types of releases. The degree to which the released chemical sticks to (or reacts with) environmental surfaces is likely a key parameter controlling hazard extents. In all modeled cases, the deposition to vertical surfaces of environmental objects (e.g. building walls) was more efficient in reducing atmospheric chemical concentrations than deposition to the earth's surface. This study suggests that 1) hazard extents may vary widely by release environment (e.g. grasslands vs. suburbia) and release conditions (e.g. sunlight or humidity may change the rate at which chemicals react with a surface) and 2) greenbelts (or similar structures) may dramatically reduce the impacts of large-scale releases. While these results are demonstrated to be qualitatively consistent with the downwind extent of vegetation damage in two chlorine releases, critical

knowledge gaps exist and this study provides recommendations for additional experimental studies.

**Key Words:** dense gas, dry deposition, chlorine, urban

## 1. Introduction

Releases of large (multi-ton) quantities of toxic industrial chemicals (TICs) at industrial manufacturing sites and along major transit corridors where large quantities of TICs (multiple railcars) are transported have long been considered to be a threat to surrounding populations. Once released, many TICs form concentrated, low-lying clouds (termed *dense-gas clouds*) that are denser than the ambient atmosphere either by virtue of being colder or physically heavier (i.e. a concentrated aerosol or a gas with a high molecular weight) than the ambient atmosphere, or often a combination of both. These dense-gas clouds can convey high concentrations of toxic chemicals to downwind populations. For example, the formation of a dense-gas cloud directly contributed to the large number of fatalities observed during the Bhopal, India incident [1] and, on a smaller scale, to fatalities associated with the accidental breaching of chemical storage containers (e.g. *Buckley et al.* [2]).

Such threats have spurred the development of numerous dense-gas models which are routinely used for research, hazard assessment, and emergency response purposes, including (but not limited to) ALOHA [3], SLAB [4], DEGADIS [5], and HGSYSTEMS [6]. However, despite several decades of development, model predictions often yield population and environmental impacts that are significantly greater than actually observed [7]. In addition, recent work has suggested that models should also more accurately incorporate the protection

provided by buildings [8, 9], more refined methods of calculating health effects [10], and more detailed consideration of the initial material release [7, 11].

The topic of dense-gas deposition to environmental surfaces has received limited attention and some have considered it likely to be of limited importance [7]. We are aware of only three analyses that have directly considered dense-gas deposition effects: *Jonsson et al.* [12]; the deposition module within the HGSYSTEM dense-gas model [6]; and the greenbelt design guidance provided by *Kahn and Abbasi* [13] (and references therein). None of these cases include the well-known suppression of vertical turbulence<sup>1</sup> within dense-gases [14, 15], which would significantly reduce the actual deposition rate relative that assumed in these studies.<sup>2</sup> The *Jonsson et al.* analysis demonstrates that deposition to the earth's surface can significantly reduce the downwind extent of a hazard zone (e.g. 50% of the released material may be lost in <500 m) and is most important under stable (clear-sky, nighttime, low wind) conditions in which the released material is confined close to the ground. Similar conclusions are available from the output of the HGSYSTEM model. In contrast, *Kahn and Abbasi* neglect loss to the earth's surface and only consider deposition to tight vegetation canopies. However, their conclusions are similar to *Jonsson et al.* and significant losses are predicted under stable atmospheric conditions. For the cases studied, depositional

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<sup>1</sup> Vertical turbulence is the process by which chemicals are transported vertically within the chemical cloud.

<sup>2</sup> The HGSYSTEM documentation explicitly notes this fact and states that the deposition module provides an upper-bound on the loss of material from the dense-gas cloud. The *Kahn and Abbasi* analyses account for dense-gases effects on cloud path and width, but do not include the effects of vertical turbulence suppression.

losses increased with increasing greenbelt width, tree height, vegetation density, and release proximity.

This paper re-examines the impact of deposition on dense-gas concentrations. In contrast to prior work, it considers both the effects of dense-gas turbulence suppression and the effects of deposition to both environmental objects (e.g. buildings) and the earth's surface. This analysis will suggest that standard EPA Risk Management Program hazard assessments, which assume highly stable, low-wind conditions [16], but do not include deposition, may significantly overestimate the impacts (including hazard extents and casualties) in urban, suburban, or forested regions.

Due limited knowledge concerning key parameter values and the dearth of experimental datasets available to validate the study hypothesis,<sup>3</sup> this analysis is limited to demonstrating that deposition to environmental objects may be prove to be a significant loss pathway. In demonstrating this point, this study uses two complementary methods to qualitatively illustrate some key features of this effect and demonstrate that it is likely to be present in a variety of scenarios (and not limited to a single illustrative case).

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<sup>3</sup> In this context, we refer to experimental datasets that have examined reactive dense-gases released within congested environments. Numerous high-quality dense-gas datasets have been developed over the last several decades, but those involving reactive materials (e.g. Desert Tortoise and Goldfish [14]) took place over flat terrain and those involving complex terrain (e.g. PERF 93-16 [17]) used inert materials. In neither case, did the experimenters report the significant depletion of the dense-gas cloud due to deposition (consistent with the results of this study).

First, critical parameter values (and parameterizations) that were poorly constrained by prior work were either a) bounded by extreme ranges; b) chosen to be equal to a best-estimate value and the importance of accurately characterizing this parameter value (within the context of the study's stated goals) was assessed with a limited, local sensitivity analysis using bounds derived by information available in the literature; or c) chosen to be equal to a bounding value, known to be biased, but sufficient for the study goals. The particular method used was chosen based on the best evidence currently available in the literature and the context of the parameter in the overall analysis.

Second, a small set of illustrative cases were examined. While it is not expected that these illustrative cases will span all reasonable combinations of variables; however, they do represent an important sample of possible conditions that are likely to actually occur in the environment. As such, they support both the conceptual validity of the model in these specific instances. Also, the examples provided support the likelihood that the model offered may, in the future, be developed further and see practical application.

In addition, this study provides both a qualitative comparison between the modeling results and environmental damage data from known accidents and recommendations for experimental studies to clarify key analysis parameters that are poorly characterized.

## 2. Estimating Dense Gas Deposition

### 2.1. The Resistance Theory of Deposition

Deposition of gases from a pollutant cloud to an outdoor surface is controlled by its atmospheric concentration, the rate at which material travels to the surface, and the degree to which the surface reacts with, or retains, the depositing gas. The rate at which material deposits is defined as [18]:

$$F = C(z_{ref}) v_d(z_{ref}) \quad (\text{eq. 1})$$

where

$F$  is the flux of depositing material to the surface ( $\text{mg m}^{-2} \text{s}^{-1}$ );

$C(z_{ref})$  is the air concentration of the depositing material at height  $z_{ref}$ , ( $\text{mg m}^{-3}$ );

$v_d$  is the deposition velocity at height  $z_{ref}$  ( $\text{m s}^{-1}$ ); and

$z_{ref}$  is the height at which the other parameters are defined (m).

In turn, the *deposition velocity* is typically represented in terms of three resistances taken in series [18, 19]:

$$v_d = \frac{1}{r_a + r_b + r_c} \quad (\text{eq. 2})$$

where

$r_a$  is the *aerodynamic resistance*, which characterizes how fast turbulent air motion moves material through the atmosphere to a layer of air just above the surface ( $\text{s m}^{-1}$ );

$r_b$  is the *boundary layer resistance*, which characterizes how fast material diffuses across a very thin layer of air just above a surface (commonly called the quasi-laminar boundary layer) ( $\text{s m}^{-1}$ ); and

$r_c$  is the *surface resistance*, which characterizes how readily depositing material is retained on the surface ( $\text{s m}^{-1}$ ).

Equations (1) and (2) are convenient for estimating the deposition of gases onto ideal, flat surfaces, but mask some of the complexities in estimating deposition to many realistic surfaces. For example, when considering deposition to plant canopies (such as trees), the surface resistance is often written to incorporate not only the ability of the surface to retain the material, but also the canopy surface area (often parameterized in terms of leaf area) and the transport of the material within the canopy (effectively reducing the surface resistance relative to a similar flat surface). Furthermore, it can include the explicit consideration of gas uptake onto different types of surfaces including actively transpiring and non-transpiring vegetation (e.g. leaves vs. twigs, respectively) (e.g. *Wesley* [19]). Likewise, the boundary layer resistance used for plant canopies, which as defined above strictly applies only very locally to the depositing surface (i.e. the air above a leaf surface), may have significantly different dimensional characteristics and

governing turbulence characteristics when expanded to characterize complex environmental objects, e.g. trees.

In this paper, we use realistic ranges of boundary layer and surface resistances identified in previous studies to highlight the significant effect that dry deposition can have on hazard assessment predictions and the importance in appropriately characterizing these processes under a range of environmental conditions. As such, we implicitly assume quasi-ideal surfaces and do not delve into details of the specification of boundary layer and surface resistances for all reasonable environmental surfaces.

In addition, we assume that the boundary layer and surface resistance terms, as derived below, are not significantly affected by a) relatively small changes in atmospheric density, b) reasonable variations in wind orientation, or c) deposition onto vertical surfaces. These assumptions are likely reasonable for gases.<sup>4</sup> We also neglect thermophoretic effects – implicitly assuming the cloud and ground are at the same temperature.

*Boundary Layer Resistance ( $r_b$ ):* Molecular diffusion controls the rate at which gases travel across the thin layer of air above the surface. For this study, we use the following first order estimate of the boundary layer resistance [20 and references therein]:

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<sup>4</sup> Particle deposition is known to vary with surface orientation, particularly for larger particles ( $> 5 \mu\text{m}$ ).

$$r_b = \frac{5(v/D)^{2/3}}{u_*} \quad (\text{eq. 3})$$

where

$v$  is the kinematic viscosity of air ( $\sim 1.4 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  [21]);

$D$  is the molecular diffusivity of the gas in air ( $\text{m}^2 \text{ s}^{-1}$ ); and

$u_*$  is the friction velocity of the ambient atmosphere ( $\text{m s}^{-1}$ ).

For context,  $r_b$  is approximately  $50 \text{ s m}^{-1}$  if we use molecular chlorine as our illustrative gas<sup>5</sup> and we assume a friction velocity of  $0.276 \text{ m s}^{-1}$  to be consistent with the illustrative plume described in section 4.1 below. Usually, this term is an order of magnitude lower than the either surface or aerodynamic resistance term so that large uncertainties in  $r_b$  do not translate to large uncertainties in deposition estimates. However, this term can become more important when the aerodynamic resistance and surface resistance are both small ( $r_a + r_c < r_b$ ). This would likely be the case for a very reactive gas released in unstable conditions. However even in this case, uncertainty in the boundary layer resistance does not markedly affect the conclusions of this study.

*Surface Resistance ( $r_c$ ):* For common toxic industrial chemicals, there is extremely limited data concerning the likelihood of materials to be retained on

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<sup>5</sup> We estimated the chlorine molecular diffusivity,  $D$ , to be approximately  $4 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$  (at  $0^\circ\text{C}$ , 1 atm) based on theoretical considerations of the mean-free path and average molecule speed via equations and data available in *Aktins and de Paula* [21].

surfaces (see below). Therefore we consider two bounding cases: highly reactive and moderately reactive gases. These two cases allow us to 1) determine the importance of surface resistance to the study conclusions and 2) bound the impact of deposition on the *hazard extent* (the maximum distance from the release at which hazards are expected) without the study conclusions being subject to uncertainties in the choice of a specific surface resistance. Actual hazard extents are expected to lie somewhere within the results of these two bounding cases.

Highly reactive gases (e.g. nitric acid) are lost from the atmosphere as soon as they contact a surface (therefore  $r_c$  is assumed to be zero). Implicitly, we assume that the surface is not saturated and desorption is not important. For the high deposition rates implied by this analysis these assumptions may not be accurate, but are consistent with our upper bound assumptions.

Moderately reactive gases are more selective in which surface they will readily deposit and so often deposit slower than highly reactive gases. For example, the deposition rate for ozone and sulfur dioxide (both moderately reactive gases) is significantly higher when plant stomata are open and higher reactivity surfaces are exposed. To provide an estimate of moderately reactive gas deposition rates, we consider the case in which the surface resistance,  $r_c$ , is  $700 \text{ s m}^{-1}$ . The value was chosen to be consistent with the slowest surface resistance (corresponding to winter conditions) expected for moderately reactive gases ozone and sulfur dioxide in urban environments [18, 19]. This value is similar to the  $500 \text{ s m}^{-1}$  used

by *Brandt et al.* [23] in DREAM (the Danish Rimpuff and Eulerian Accidental Release Model) for the deposition of radioactive gaseous iodine (another moderately reactive gas) which was validated against data collected after the Chernobyl accident.

For context, two literature reports on chlorine deposition (indoor environments [24] and onto alfalfa plants [25]) demonstrate that chlorine is deposited at a rate similar to other moderately reactive gases (e.g. ozone and sulfur dioxide).

The *aerodynamic resistance* ( $r_a$ ) term used in this analysis is from *Seinfeld and Pandis* [18]. For deposition to horizontal surfaces (such as the earth's surface), the aerodynamic resistance is defined as:

$$r_a = \int_{z1}^{z2} K_z^{-1} dz \quad (\text{eq. 4})$$

where

$K_z$  is the vertical eddy-diffusivity coefficient which describes how fast material diffuses vertically ( $\text{m}^2 \text{s}^{-1}$ ); and

$z_1$  and  $z_2$  are two elevations between which the deposition rate is measured (m).

When  $K_z$ , the eddy-diffusivity coefficient is defined for stable atmospheric conditions as:

$$K_z = \frac{ku_*z}{\Phi(\xi)}; \quad (\text{eq. 5})$$

the aerodynamic resistance is:

$$r_a = \left( \frac{1}{ku_*} \right) \left[ \ln \left( \frac{z}{z_o} \right) + 5(\xi - \xi_o) \right] \quad (\text{eq. 6})$$

where

$k$  is von Karman's constant ( $k = 0.4$ );

$u_*$  is the ambient friction velocity ( $\text{m s}^{-1}$ );

$z$  is the height above ground (m);

$z_o$  is the roughness layer height (m);

$\Phi(\xi)$  is the atmospheric stability correction factor =  $1 + 5\xi$  for stable atmospheres;

$\xi = z/L$ ;

$\xi_o = z_o/L$ ; and

$L$  is the Monin-Obukhov length (a measure of atmospheric stability) (m).

## 2.2. Dense Gas Effects

For dense gas clouds in thermal equilibrium with the surroundings, cloud stability can be predicted by a modified Monin-Obukhov length,  $L$ , [15, 26, 27]:

$$L^{-1} = L_a^{-1} + 2gk^2(\rho - \rho_a)/(\rho_a u_*^2) \quad (\text{eq. 7})$$

where

$L_a$  is the ambient atmosphere Monin-Obukhov length (m);

$\rho$  is the cloud density ( $\text{g m}^{-3}$ );

$\rho_a$  is the ambient air density ( $\text{g m}^{-3}$ ); and

$g$  is the gravitational constant ( $\text{m s}^{-2}$ ).

The aerodynamic resistance is expected to decrease as the cloud evolves (i.e. cloud density/stability decreases with time). For context, this formula predicts that for moderately and weakly stable dense-gas conditions ( $L = 1$  and  $10$  m, respectively;  $u_* = 0.276 \text{ m s}^{-1}$ ),  $r_a$  is  $500 \text{ s m}^{-1}$  and  $60 \text{ s m}^{-1}$ , respectively.

We recognize that Monin-Obukhov theory (upon which this parameterization is based) is not theoretically valid for the strongly stable atmospheric conditions present in a dense-gas cloud. Empirically however, this formulation is used by the FEM3 dense-gas model (K-theory local equilibrium version [26]) and has been validated against a series of dense-gas experiments performed over relatively smooth surfaces (e.g. desert environments) [14, 15, 27].

We also recognize that for passive gases, the eddy-diffusivity theory described above is most accurate for locations well above the surface object (e.g. building)

height. While eddy-diffusivity theory can be extended to provide predictive capability for passive gases at heights below the object height (e.g. *Hanna and Britter* [28]), it is not clear to what degree this limitation applies to dense-gas clouds, whose micrometeorological conditions are strongly controlled by cloud density rather than the ambient atmosphere. Therefore we use this parameterization for our analysis because 1) there is a lack of validated dense-gas turbulence parameterizations for use in congested environments and 2) our study conclusions depend upon the approximate magnitude of the vertical and, as described below, horizontal turbulent flux, not the specific  $K_z$  value or details of the  $K_z$  vertical structure. This approach is qualitatively supported by the results of the Petroleum Environmental Research Forum (PERF) 93-16 project which demonstrated that: 1) dense-gas dispersion phenomenology in congested environments (including turbulence suppression and ambient air entrainment) is similar to that previously observed in flat terrains and 2) that methods of estimating the vertical entrainment of ambient air into the dense-gas cloud in common use are reasonable to use in congested environments (see *Hanna and Steinberg* [17] and references therein). The latter is particularly relevant as vertical entrainment depends sensitively upon vertical turbulence – implying that the parameterization used in this study is reasonable in magnitude.<sup>6</sup>

To provide a sensitivity analysis of our particular choice of turbulence parameters to model results, we performed two analyses in which we 1) multiplied and 2)

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<sup>6</sup> The vertical turbulence parameterization used in this study was not validated in [17], but other parameterizations, previously demonstrated to yield similar results, were.

divided the vertical (and horizontal) eddy diffusivity coefficient by a factor of 5 and examined the impact on the study conclusions. The factor of 5 was chosen as it is presumed that an order of magnitude error in the dense-gas turbulence parameterization would have been identified in the PERF study described above as the vertical entrainment rate, which is proportional to the vertical eddy diffusivity, was validated to within 30%. Our study conclusions regarding the likely overall importance of deposition, the relative importance of deposition to the earth's surface vs. environmental objects, and the importance of accurately estimating the surface resistance term were not changed.

### *2.3. Deposition to Vertical Surfaces*

The deposition parameterization previously described only applies to material depositing onto horizontal surfaces. Here we extend this theory to deposition onto the vertical surfaces of environmental obstacles such as building walls.

#### *Horizontal Turbulence*

For consistency, we use the FEM3 dense-gas parameterizations for our estimates of horizontal turbulence. In FEM3, the horizontal ( $K_h$ ) and vertical ( $K_z$ ) eddy-diffusivity coefficients are related as:

$$K_h = \beta K_z \quad (\text{eq. 8})$$

where

$\beta$  is a constant equal to 6.5.<sup>7</sup>

We consider this parameterization to be very approximate (see below) and consider it likely to *underestimate* the horizontal turbulence (although the degree of underestimate is not well characterized). Due to the importance of deposition to environmental objects through horizontal transport, we recommend revisiting this parameterization in future work.

We have three reasons for believing this parameterization is likely to underestimate the horizontal turbulence. First, the value of  $\beta$  chosen was derived from studies of passive gas dispersion and that other studies have suggested higher ratios (10 to 25) may be appropriate for stable conditions, e.g. *Havens* [29].

Second, we note that few experiments have validated horizontal turbulence parameterizations. In contrast to vertical turbulence, validation against concentration data provides limited guidance on the accuracy of dense-gas horizontal turbulence parameterizations. Gravity flow contributes significantly to the overall horizontal spreading of the dense-gas cloud and so the horizontal evolution of the dense-gas cloud is less sensitive to horizontal diffusion relative to the corresponding vertical case. In addition, there are few laboratory or field experiments that have directly measured dense-gas turbulence, particularly

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<sup>7</sup> The number of significant figures is that provided in the FEM3 model documentation and is repeated here for consistency.

horizontal, within a congested environment. However, some information relevant to this study is available. In a series of wind-tunnel experiments, *Zhu et al.* [30] studied dense-gas releases within congested environments to demonstrate that: 1) vertical and horizontal turbulence intensities decrease within and above dense-gas clouds (relative to the ambient atmosphere); 2) the reduction in turbulence varies with height above the surface, distance downwind from the source, and ambient wind speed; and 3) the dense-gas reduction in horizontal turbulence, while present, is smaller than the corresponding reduction in vertical turbulence. Thus *Zhu et al.*'s data suggest that  $\beta$ , which is proportional to the ratio of horizontal to vertical turbulence, will increase within the dense-gas cloud relative to the passive gas ratio given above.

Third, theoretical considerations suggest that, for a given environment, the ratio of horizontal to vertical turbulence increases with increasing stability. *Andronopoulos et al.* [31] and *Statharas et al.* [32] demonstrate accurate dense-gas model predictions in congested environments can be based on a turbulence parameterization which assumes that turbulence length scales near the ground depend primarily upon the nearness of solid boundary surfaces and local stability. The vertical turbulence length scale decreases with increasing stability due to buoyancy considerations. In contrast, the horizontal turbulence length scale is not affected (the horizontal turbulence intensity will still decrease due to the overall turbulence suppression). Thus at any given location  $\beta$ , which is proportional to the

ratio of horizontal to vertical turbulence length scales, increases with increasing stability.

### *Aerodynamic Resistance*

If  $\Delta x$  is the closest horizontal distance that gas molecules must travel to deposit, then equations 3, 4, and 7 combine to yield the aerodynamic resistance for a gas to travel to a vertical surface,  $r_{a,h}$ :

$$r_{a,h} \approx \left( \frac{1 + 5\left(\frac{z}{L}\right)}{\beta k u_* z} \right) \Delta x \quad (\text{eq. 9})$$

For context, under moderately stable dense-gas conditions ( $L = 1$  m;  $u_* = 0.276$  m s<sup>-1</sup>)  $r_{a,h}$  equals  $7.2\Delta x$  s m<sup>-1</sup> at  $z = 5$  m or  $36$  s m<sup>-1</sup> for a  $\Delta x = 5$  m.

### *2.4. Dense-Gas Deposition Velocities*

Using equation 2, we estimate the dense-gas deposition velocity by combining the aerodynamic, boundary layer, and surface resistance terms derived in the previous section. In this section, we assume  $z_0 = 1$  m (effectively a 10m obstacle height) and  $u_* = 0.276$  (chosen to be consistent with the illustrative plume discussed below). Similar figures are obtained when  $u_*$  is varied from 0.1 to 0.5 m s<sup>-1</sup>. We note that equations 6 and 9 were derived for stable atmospheres and similar equations were derived for use in neutral and unstable atmospheres using  $\Phi(\zeta) = 1$  and  $(1-15(z/L))^{-1/4}$ , respectively [18]. The deposition velocity to the earth's surface and to vertical surfaces is referenced ( $z_{\text{ref}}$ ) to 5 m agl - roughly half the 10

m obstacle height. **Figure 1** shows the resulting deposition velocity as a function of cloud stability for a) highly and b) moderately reactive gases. In this figure, the deposition velocity to the earth is depicted as a blue line and the deposition velocity to vertical surfaces (e.g. building walls) is depicted as red dotted and green dashed lines for short ( $\Delta x = 1$  m) and long ( $\Delta x = 5$  m) travel distances, respectively. We note that this figure does not indicate the relative losses of the cloud with respect to deposition as the effects of cloud height and obstacle geometry has not been accounted for (this is addressed in the next section).

As shown in Figure 1, the relative magnitude of deposition velocities to environmental obstacle walls and the earth's surface depends strongly upon the stability within the cloud. For neutral and unstable (passive-gas) clouds ( $L^{-1} \leq 0$ ), there is little difference between the deposition velocities to the earth's surface and environmental obstacle walls. However under stable conditions ( $L > 0$ ), the deposition to the earth's surface rapidly decreases with increasing stability and deposition estimates using passive-gas parameterizations are likely to significantly overestimate the deposition to the earth's surface. In contrast, deposition to environmental obstacle walls is predicted to decrease less rapidly with increasing  $L$  and (as shown below) can contribute to significant deposition loss rates.

### **3. Dense Gas Depositional Losses**

The degree to which deposition will affect the evolution of a dense-gas cloud is event specific. Thus we illustrate the importance of deposition on predicted hazard extents in two stages. In the first stage, we develop an illustrative scenario loosely based on a catastrophic breach of a chlorine railcar. Using this scenario, we examine the degree to which the gas is lost to deposition and determine the distance downwind at which deposition losses significantly affect the predicted cloud concentrations. In the second stage, we expand the initial analysis to more broadly characterize the conditions under which deposition is expected to significantly affect cloud concentrations.

In both stages, we make several simplifying assumptions that should be revisited if a quantitative model is developed. First, we assume that the dense-gas cloud properties are unaffected by the loss of material due to deposition. While this assumption is valid only in regions where deposition has not significantly altered the cloud concentration, it is a reasonable assumption for our analysis as we are interested in obtaining a qualitative estimate of the downwind distance at which deposition significantly affects the cloud concentration. We recommend caution in interpreting the results of this analysis beyond the distance at which the deposition significantly affected the cloud concentration.

Second, our dense-gas dispersion modeling does not *explicitly* account for environmental objects, but rather assumes a large surface roughness value ( $z_0 =$

1m, which roughly corresponds to 10 m high objects). This approach; while not providing detailed descriptions of dense-gas flow around buildings, trees, and other objects; does account for the effect of obstacles on bulk cloud properties (such as cloud width, height, and turbulence intensities) used in this analysis (see *Hanna and Steinberg* [17] and references therein). However, we note that our analysis does not consider the effects of local perturbations to the bulk cloud properties nor the physical exclusion of the dense-gas cloud by buildings and other large objects.

Third, we assume all deposition surfaces are quasi-ideal flat planes (i.e. equations (6) and (9) are valid) that are aligned along the ambient wind direction.

Fourth, we assume fixed reference distances for deposition to both vertical and horizontal surfaces. For deposition to the earth's surface, we use a deposition reference height,  $z$  in equation (6), that is the lower of the cloud height or 5m above the ground (for most cases, the cloud height was above 5 m). For deposition to vertical surfaces, we reference the deposition velocity calculations to the shortest horizontal travel distance,  $\Delta x$  in equation (9), to either 1 or 5 m (termed loosely and tightly packed environments, respectively). To account for the variation in deposition velocity with height, we use a dense-gas cloud deposition velocity that is the average of individual horizontal deposition velocities calculated at 5 evenly spaced heights within the lower of 1) the cloud height or 2) 10 m (the assumed object height).

Fifth, we neglect deposition to horizontal environmental object surfaces (e.g. building roofs).

These assumptions allow us to qualitatively model those losses expected from a dense-gas cloud as it flows down a series of streets 2 or 10 m wide, respectively, oriented parallel to the ambient wind direction. We expect that this approach will overestimate the amount of material deposited to the earth's surface to a greater extent than that deposited to environmental obstacles.

### 3.1. *Deposition of an Illustrative Plume*

For the purposes of this illustration, we assume the entire contents of a 90-ton railcar filled with a highly reactive gas with chemical properties assumed to be identical to chlorine are instantaneously released into a congested environment with a stable atmosphere and a slow ambient wind speed (E class stability,  $z_0 = 1$  m, ambient wind speed =  $2 \text{ m s}^{-1}$  at 10 m agl, and  $\Delta x = 5 \text{ m}$ ). We use the SLAB dense-gas model [4] to provide an initial estimate of cloud properties as a function of time and distance from release. It has been well documented that other models would produce similar results [7, 33, 34]. For this illustration, we define:

$$\tau_{d,Earth} \equiv \frac{H_c}{v_{d,Earth}} \quad (\text{eq. 10})$$

$$\tau_{d,Obstacles} \equiv \left[ \frac{\Delta x}{2v_{d,Obstacles}} \right] \left[ \frac{H_c}{\min(H_c, H_o)} \right] \quad (\text{eq. 11})$$

$$\tau_{d,All}^{-1} \equiv \tau_{d,Earth}^{-1} + \tau_{d,Obstacles}^{-1} \quad (\text{eq. 12})$$

where

$\tau_{d, \text{Earth}}$  is the cloud lifetime with respect to deposition to the Earth's surface (s),

$\tau_{d, \text{Obstacles}}$  is the cloud lifetime with respect to deposition to environmental obstacles (s),

$\tau_{d, \text{All}}$  is the cloud lifetime with respect to deposition to both the Earth's surface and environmental obstacles (s),

$H_c$  is the cloud height (m)

$H_o$  is the obstacle height (m)

$v_{d, \text{Earth}}$  is the deposition velocity with respect to the Earth's surface ( $\text{m s}^{-1}$ ),

and

$v_{d, \text{Obstacles}}$  is the deposition velocity with respect to environmental obstacles ( $\text{m s}^{-1}$ ).

**Figure 2** shows several parameters (as a function of downwind distance) describing the evolution of our illustrative plume. The top panel shows the cloud height (H) and stability ( $L^{-1}$ ). The second panel shows the deposition velocity with respect to the earth (blue open circles) and environmental objects (green squares). The third panel shows the cloud lifetime when only deposition to the earth (blue open circles) or environmental object surface (green squares) are considered and when all (red line) surfaces are considered. Finally, the fourth panel shows the fraction of cloud remaining after accounting for: deposition only

to the earth (open blue circles), only to environmental objects (green squares), and all (red line) surfaces.

As Figure 2 illustrates, the cloud concentrations are predicted to be significantly impacted by deposition after the cloud has moved just over a hundred meters downwind due to the combination of low cloud height and deposition to environmental objects. We define  $X_{50}$  as the distance at which the cloud centerline concentration at ground level is predicted to be reduced by 50% by deposition. For this illustrative case,  $X_{50}$  is 150 m (Figure 2, bottom panel).

We note that for this case (and presumably other cases in which environmental objects are present), deposition to the earth contributes a negligibly small fraction to the overall depositional loss due to the suppression of vertical turbulence within the dense gas cloud.

### 3.2. *Additional Illustrative Cases*

In this section, we expand the illustrative example discussed above to explore additional cases in which depositional losses may be important. These cases were selected to qualitatively highlight a few key features of this loss pathway and demonstrate that the significance of this loss pathway is not likely to be restricted to the single illustrative case examined above. It is recognized that this set of cases does not span all reasonable combinations of input parameter values or interesting scenarios. For simplicity, we restrict our analysis to isothermal dense

gases (such as chlorine). We note that some widely-transported TICs, such as ammonia and hydrogen fluoride, rapidly form aerosols and also undergo significant thermal changes in the atmosphere and so will require an expansion of the deposition parameterizations described in this study. Unless explicitly noted, each scenario parameter is identical to the illustrative plume described above. Here we examine the variation of  $X_{50}$  with ambient atmospheric stability (ranging from unstable, or B class atmospheric stability; neutral, or D class stability; and stable, or E class stability), gas reactivity (high and moderate), and obstacle spacing (loosely (10 m) and tightly (2 m) packed objects). **Figure 3** shows the results of this parameter study for highly (top panel) and moderately (bottom panel) reactive gases. The x-axis denotes the distance at which 50% of the plume is predicted to be lost to deposition ( $X_{50}$ ). The blue and red bars indicate the 10 m and 2 m obstacle separation ( $\Delta x = 5$  and 1), respectively.  $X_{50}$  values of greater than 500 m indicate that deposition has a negligible effect on plume concentrations.  $X_{50}$  values less than 100 m should be interpreted as  $X_{50} < 100$  m.

This analysis predicts that, for the cases considered, there will be a dramatic difference between the highly and moderately reactive gases – with most of the depositional losses due to deposition to environmental obstacles. This result suggests that the surface resistance of the depositing species is a critical parameter. This conclusion is underscored by the fact that we have likely *underestimated* the rate at which material is deposited to environmental objects.

These results also illustrate another key feature of this system. Since deposition to environmental obstacles is the critical loss mechanism, depositional losses only matter if most of the released material remains sufficiently close to the ground to deposit to the obstacles (limited in this study to 10 m above the ground). Under unstable (shown) or high wind (not shown) conditions, the rate at which the dense-gas cloud breaks up (and diffuses above 10 m) may be sufficiently high relative to deposition rates that deposition is a negligible loss term. Therefore we expect the depositional losses will be maximized for stable atmospheric conditions with tightly-packed objects. We also note that if we have, as is likely, underestimated the rate of deposition to environmental objects, then the distance at which deposition losses become important will more closely resemble the tightly-packed object case (shown in red). This is particularly true for the moderately reactive species in which the surface resistance is the dominant factor controlling depositional losses.

### *3.3. Qualitative Comparison to Vegetative Damage Extents*

Patterns of vegetation damage observed during the recent Graniteville, SC accident and an earlier accident in Alberton, MO are qualitatively consistent with our hypothesis that dense-gas deposition is an important factor.

During the Graniteville accident, ~40 tons of chlorine were catastrophically released into a suburban/forested area on a lightly stable night with low wind

speeds (roughly corresponding to the illustrative plume case discussed above<sup>8</sup>) [2]. The local terrain significantly affected the evolution of the chlorine plumes by limiting the horizontal dispersion, turning the plume direction from the ambient wind direction, and likely extending the plume extent greater than the flat earth case modeled here. *Hunter* [35] and *Buckley et al.* [2] noted that 1 month after the release, vegetation damage (primarily pine and juniper trees) extended approximately 2 km downwind of the release location. A similar (55 ton) nighttime release of chlorine in a forested river valley near Alberton, MO produced measurable damage to Ponderosa Pine and Douglas Fir trees at distances greater than 0.8 km, but less than 1.5 km downwind [36].

Plant species vary in their sensitivity to chlorine concentrations [37, 38] and the extent of injury is correlated non-linearly with concentration and exposure time (see *Griffiths and Smith* [38] and references therein). However, a detailed study of chlorine exposure to three pine species demonstrated that these three species: 1) responded similarly to chlorine exposure at a variety of concentrations and exposure times and 2) vegetative damage occurred at concentrations between 1 and 10 ppm for short (15 min) exposures [39]. While we do not know if the species tested were among those observed in the Graniteville accident (they were not the same as those examined in the Alberton accident), the species tested were resistant to ozone damage (another moderately reactive gas) relative to other pine

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<sup>8</sup> Only half of the 90 ton chlorine tank was catastrophically released. While additional material was released over an extended time period at a much slower rate, this secondary release does not affect the discussion and conclusions presented in this study. We note that the graphs in Figure 3 and 4 show the impacts of a complete (90 ton) tank release.

species. Additionally other, more sensitive plants are known to be damaged by concentrations 10x lower than those affecting the three pine species tested [37, 39]. Thus for the purposes of this qualitative comparison, we consider a 10 minute average air concentration of 10 ppm likely to produce noticeable damage to vegetation within the plume.

In a recent post-event simulation of the Graniteville chlorine plume, *Hanna* [7] demonstrated that 6 commonly used dense-gas models (including SLAB) predict peak 10-minute chlorine concentrations 10 km from the release site to be well above (<5x) the 10 ppm concentration expected to produce noticeable vegetation damage. Indeed at the extent of vegetation damage in the Alberton and Graniteville releases, (~1 and ~2 km, respectively), all models predicted ground level concentrations greater than 1,000 and 300 ppm, respectively.

While our limited understanding of the chlorine surface losses (see section 2 above) and accident details prevent a quantitative comparison, we note that the observed vegetation damage extents are: 1) clearly shorter than predicted by traditional models, 2) between the bounds predicted by the highly reactive and moderately reactive gas cases described above and 3) shorter for the more tightly packed environment (e.g. the Alberton release).

#### **4. Discussion and Conclusions**

##### *4.1. Implications for Modeling Hazard Extents*

To put our results into the context of risk to human populations, we provide a zero-order estimate on the effect that depositional losses may have on hazard extents. For this illustration, we define a measure of the hazard posed by a release as the maximum distance at which sensitive individuals are expected to be lethally affected following a catastrophic release of 90 tons (1 railcar) of chlorine. We adopt the commonly used U.S. emergency response methodology and follow the National Research Council Acute Exposure Guideline Level 3 (AEGL3) guidance to estimate atmospheric concentrations at which individuals may die (a 10 min exposure to at least 50 ppm) [40]. This level is designed to protect the most sensitive individuals and is known to overestimate the hazards posed to the average individual.

As before, we have assumed that the dense-gas cloud properties (except concentration) are not affected by the removal of material. As such, the hazard extents presented in this section should be considered to be rough estimates of the true hazard extent and should not be used for emergency response or planning purposes.

**Figure 4** shows hazard extents corresponding to the atmospheric conditions shown in Figure 3 (note that the Figure 3 and 4 x-axes are not identical). Consistent with the above analysis, the reduction in hazard extent is predominately controlled by how readily material is retained on the surface (i.e. surface resistance) with a smaller dependence on atmospheric conditions.

#### 4.2. Comparison to prior work

This analysis demonstrates that the suppression of vertical turbulence significantly reduces the amount of material lost to the earth's surface. Indeed in the absence of environmental objects (such as buildings and trees), the loss of material due to deposition is modest (for example, see Figure 2). This conclusion suggests that the prior analyses of *Jonsson et al.* [12] and the HGSYSTEM deposition module (both of which neglect the reduction in dense-gas turbulence) may significantly overestimate the losses to the earth's surface. However due to the importance of deposition to environmental objects (which was not included in the prior analyses), the current analysis supports the prior conclusions that deposition is most important for stable, low-wind conditions in which the plume is confined to be relatively low to the ground.

While the current analysis did not directly analyze deposition within vegetation canopies, it is consistent with the general conclusions of *Khan and Abbasi* [13] that greenbelts (strips of vegetation surrounding a potential release site) offer the potential to significantly reduce the impacts of the large-scale releases of toxic industrial materials – with the greatest reductions associated with stable atmospheric conditions (commonly considered to be the “worst-case” for these types of releases). However, in contrast with the *Kahn and Abbasi* conclusions, this analysis suggests that relatively wide object spacing (2 to 10 m distance between objects) may be sufficient to achieve rapid reductions in atmospheric

concentrations – particularly if the released material is readily retained on environmental surfaces.

#### *4.3. Impact of Neglected Factors*

This analysis did not consider several key factors that have the potential to alter dense-gas dispersion and deposition rates. In this section, we qualitatively discuss the potential implications of including these effects in this analysis. We note that while some of these effects may reduce the overall importance of depositional losses, these effects are unlikely to eliminate significant deposition losses in all scenarios of interest.

First, this study did not consider how dense-gas cloud properties (except concentration) were changed by the removal of material by deposition. As the cloud concentration decreases, the cloud becomes less stable and behaves more like a passive (neutrally buoyant) gas. This implies that the cloud turbulence increases, increasing the deposition velocity to both environmental objects as well as the earth's surface (in Figure 1, this corresponds to moving to the right along the x-axis). In addition, the cloud mixes more rapidly with the ambient atmosphere, further reducing the cloud concentration, increasing the cloud height, and decreasing the cloud width (relative to that assumed in this study).

Paradoxically, in some cases the net impact of these processes may extend the range at which low concentration hazards will exist relative to those shown in

Figure 4. The higher loss rates near the surface are offset by the lofting of hazardous material above the deposition zone (which can then mix back down to the surface further downwind). For example, deposition reduced a passive-gas cloud concentration by 50% at 6 km downwind from the release for a case similar to the illustrative plume discussed above [12].<sup>9</sup> For context, the cloud concentration in the illustrative dense-gas plume was reduced by 50% less than 100 m from the release. This stark contrast between the passive and dense-gas losses suggests that the overall importance of deposition is related the relative rate of deposition loss versus vertical mixing.

Second, this study also did not consider thermophoretic effects – implicitly assuming that the cloud and depositing surfaces are at the same temperature. This assumption is incorrect for some hazardous materials of interest (e.g. ammonia). For dense-gases that are colder than the surrounding environment, thermophoretic effects may reduce the deposition losses through two mechanisms. First, the addition of heat from the surrounding environment will reduce the dense-gas stability (see above). Second, the rate at which gas is transported to the wall to deposit will likely decrease (decreasing the overall deposition rate).

Third, this study considered a single, idealized object geometry and did not consider the spatial or temporal details of air-flow around objects. In studies of dense-gas flow around individual objects (e.g. [31, 32, 41] and references therein), the presence of objects resulted in significant perturbations to the dense-

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<sup>9</sup> Deposition to environmental objects was not considered in [12].

gas cloud concentrations and flow properties (including flow direction, concentration, and turbulence). This is particularly evident on the downwind side (i.e. the building wake) in which the dense-gas cloud often rises well above the unperturbed cloud height and locally enhanced mixing noticeably decreases cloud concentrations. Laboratory and field experiments with environmental object arrays have demonstrated that while the above effects are evident as the dense-gas cloud first encounters the object array, once the dense-gas cloud equilibrates to the presence of the objects array, the effects of subsequent perturbations depend strongly on flow conditions and range from minimal to significant (with the latter occurring at high Reynolds number flows corresponding to very low wind speeds) (e.g. [17, 30, 42]).

This study implicitly assumes that the dense-gas flow is such that environmental obstacles cause limited local perturbations and so the average cloud properties calculated by the SLAB model are generally representative of the overall cloud (see section 3). While the above studies suggest that this is a reasonable assumption for many scenarios of interest, investigations into other flow conditions and the role that local perturbations may play in enhancing (due to locally enhanced turbulence) or decreasing (due to locally decreased concentration) the importance of deposition to environmental obstacles should be addressed in future work.

#### *4.4. Suggestions for Future Work*

This analysis qualitatively demonstrates that dry deposition may play a significant role in controlling atmospheric concentrations of large-releases of toxic industrial chemicals. However, significant knowledge gaps prevent the current work from being directly applied to develop reliable predictive models for assessment and emergency response purposes. In this section, we provide suggestions for future work to address the critical knowledge gaps identified by this work. If future investigation confirms the results of this initial study, the author recommends the inclusion of this effect in hazard assessment models, both simplified and complex, as well as the consideration of using this effect to reduce the hazards associated with this type of accident (e.g. greenbelts).

First, this analysis examined the deposition of isothermal dense-gases to quasi-ideal surfaces. Many important toxic industrial chemicals (e.g. ammonia, hydrogen fluoride, and oleum ( $\text{SO}_2/\text{SO}_3$ )) are known to readily form aerosols and undergo significant chemical and thermal changes when released into the atmosphere. All three of these factors have the potential to alter deposition rates; therefore we recommend extending this analysis to include these effects. In addition, we recommend *quantitatively* examining the relative efficiency of different environmental objects (e.g. trees vs. buildings) and geometries (e.g. suburban streets vs. forests) on the reduction of atmospheric concentrations due to deposition.

Second, this analysis points to an urgent need for new experimental investigations to further understand and validate dense-gas deposition in congested environments. Unfortunately, there is a dearth of relevant experimental datasets and so we recommend the following experiments and analysis. 1) We recommend further study of reactive gas deposition rates (including surface resistances) – with particular attention to chlorine in different sunlight and humidity conditions. Chlorine is readily photolabile by sunlight and the resulting chlorine radicals (and other potential chemical products) may be more readily deposited during daylight hours than the two nighttime accidents discussed in this study. 2) We recommend investigating the magnitude and stability dependence of dense-gas turbulence within a variety of congested environments (obstacle geometries), particularly with respect to horizontal turbulence. Further analysis of currently available experimental datasets (e.g. [17, 30, 41]) may serve as a useful first step in this investigation. 3) We recommend a release of reactive materials within congested environments to directly measure the effects of vertical and horizontal deposition on plume extent.

While a detailed description of how the above uncertainties may be investigated is beyond the scope of this study, we offer the following suggestions. First due to the number of knowledge gaps and variables to be examined, we recommend performing laboratory studies using representative objects in deposition chambers (analogous to *Hill* [25]) and wind tunnels in which key parameters (e.g. wind speed, turbulence, dense-gas concentration, temperature, and the obstacle type

and geometry) would be systematically varied. Second, these experiments could be followed by larger-scale wind-tunnel studies (analogous to the Hawk test series which examined the removal efficiency of hydrogen fluoride with respect to water sprays [43]). Finally, large-scale outdoor releases in a remote environment (e.g. the Nevada Test Site – the location of the previous large-scale ammonia and hydrogen fluoride releases, respectively) would be used to test if the knowledge gained from the laboratory and large-scale wind tunnels tests were sufficient to describe full-scale releases.

We note that many key industrial chemicals are highly toxic and/or corrosive. Therefore the judicious use of surrogate compounds will likely be critical, particularly to leverage existing wind-tunnels and deposition chambers during the laboratory phase. We note that the key parameter in such an investigation is the *relative* affinity between the depositing gas (or aerosol) and the surface – not the absolute reactivity of the depositing material. As such, the careful selection of the depositing gas and surface (e.g. a weak acid/base pair, an inert aerosol/tacky surface, a mildly reactive gas/high surface area object) may offer the possibility to reduce the hazard and environmental impact posed by conducting such an experiment – reducing the cost and increasing the number of potential experimental sites.

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**Figure 1 (Deposition Velocities).** Deposition velocity as a function of cloud stability for highly (top) and moderately (bottom) reactive gases.

**Figure 2 (The Illustrative Plume).** Top Panel: the dense-gas cloud stability and height; Second Panel: deposition velocity with respect to the earth and environmental objects; Third Panel: cloud lifetimes with respect to deposition to the earth, environmental objects, and all surfaces; and Bottom Panel: fraction of the cloud remaining airborne with respect to deposition to the earth, environmental objects, and all surfaces.  $X_{50}$  is the distance at which the cloud centerline concentration at ground level is predicted to be reduced by 50%.

**Figure 3 (Parameter Study).** The downwind distance at which deposition is predicted to reduce plume concentrations by 50%,  $X_{50}$ , for highly (top panel) and moderately (bottom panel) reactive gases. Both cases include deposition to the earth and environmental objects. When deposition negligibly affects the plume concentrations,  $X_{50}$  is greater than 500 m.  $X_{50}$  values less than 100 m should be interpreted as  $X_{50} < 100$  m.

**Figure 4 (Hazard Extents).** The Hazard Extent (as determined by the furthest distance that the centerline 10 min average ground level concentration exceeds 50 ppm) for highly (top panel) and moderately (bottom panel) reactive gases under the atmospheric conditions shown in Figure 3 (note that the Figure 3 and 4 x-axes are not identical). For context, we have included the hazard extent assuming no

deposition (green bar) which corresponds to standard EPA hazard assessment modeling.

**Figure 1**

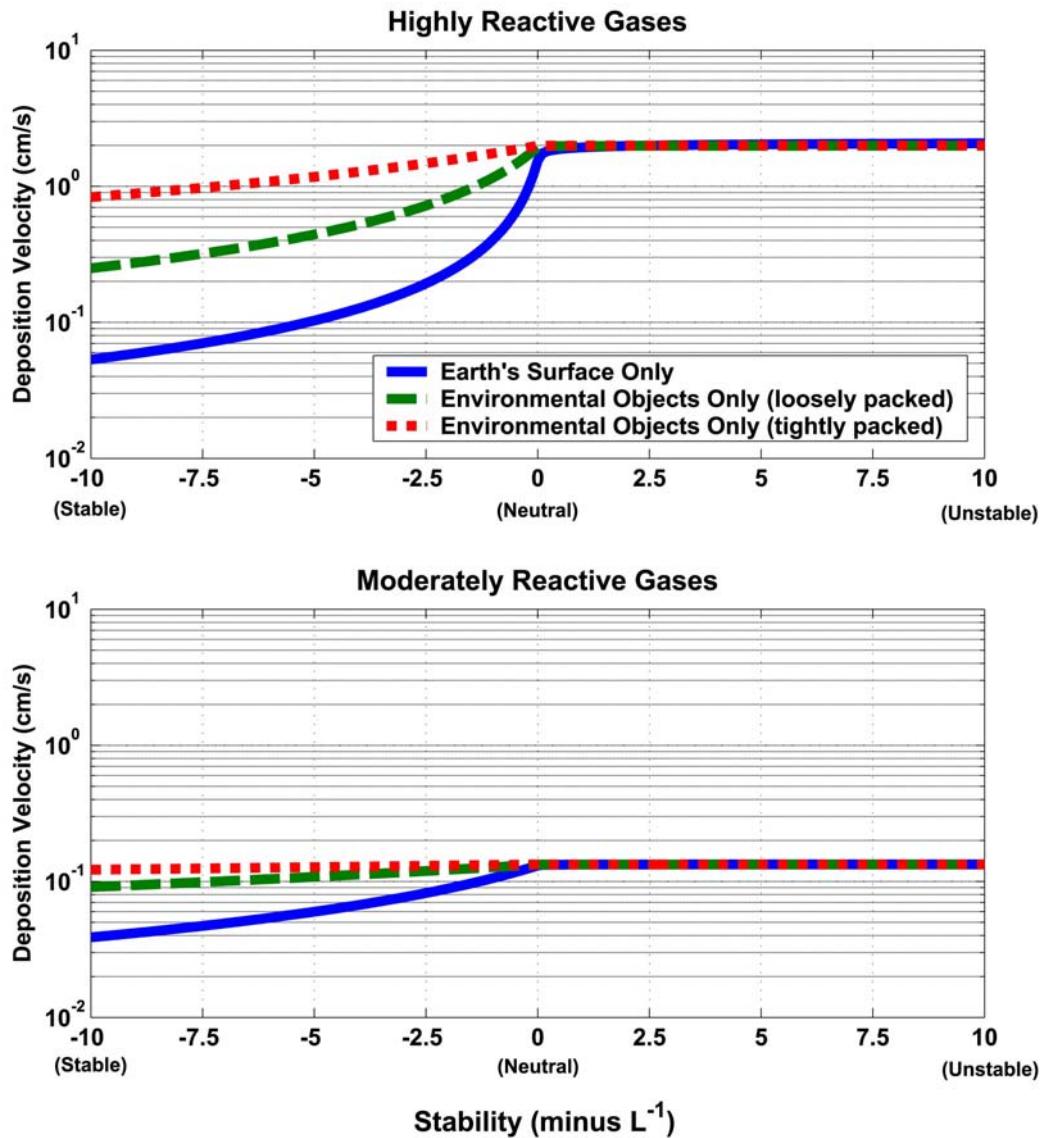
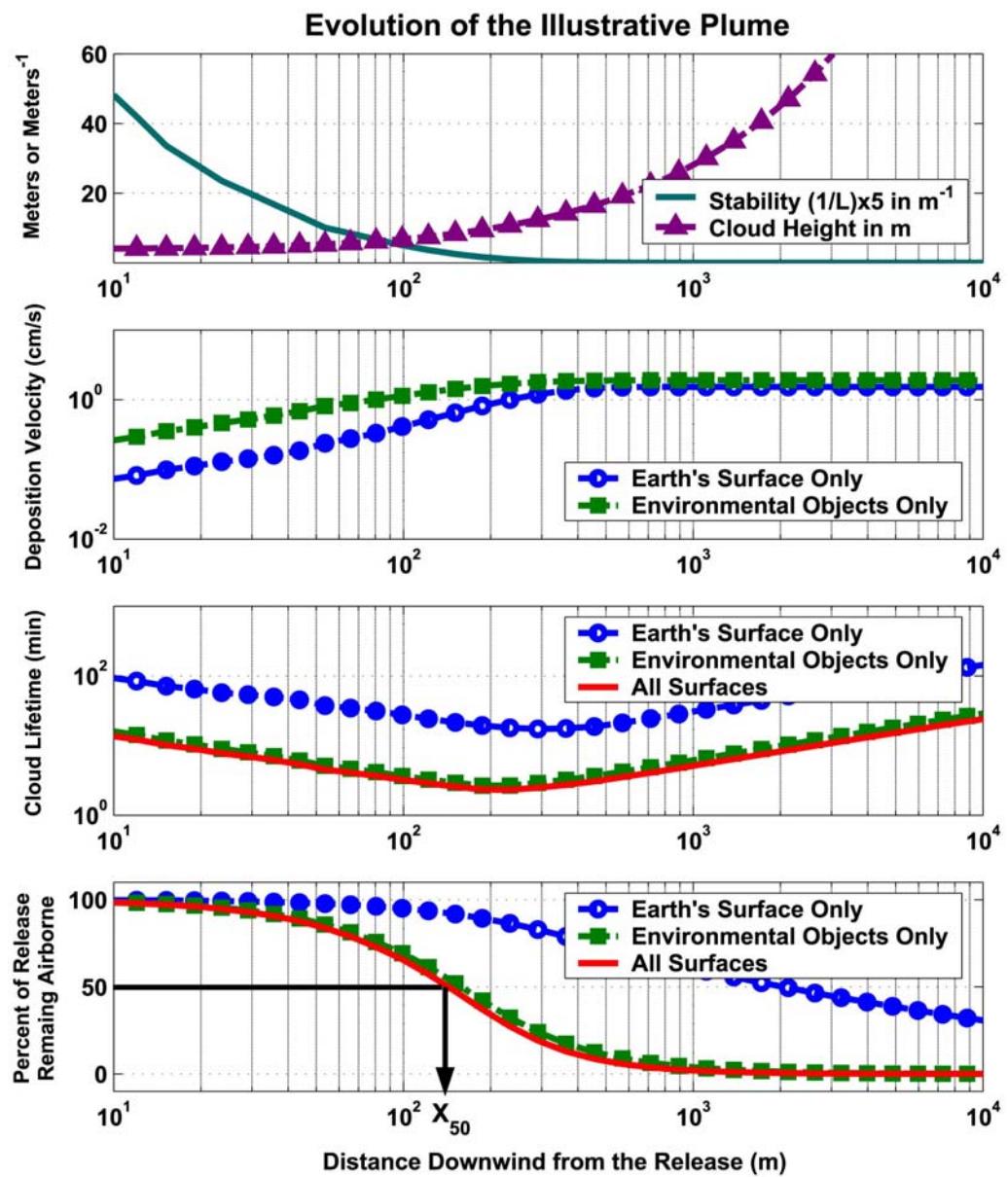
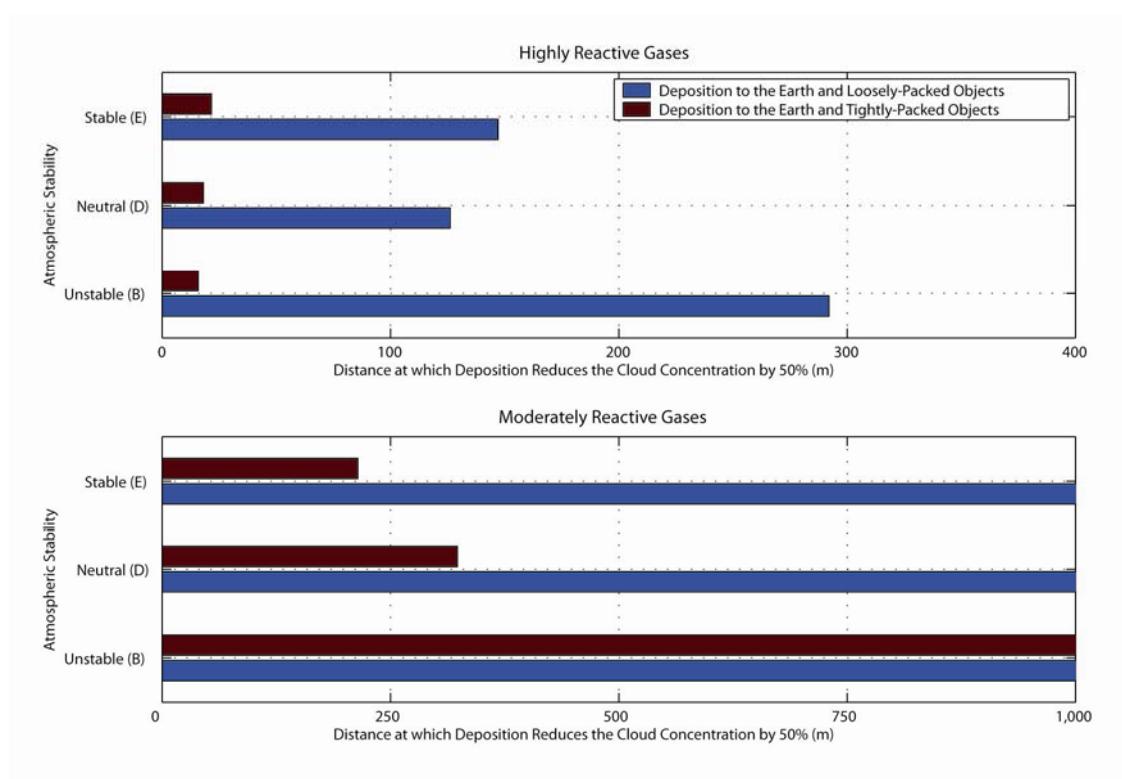


Figure 2



**Figure 3**



**Figure 4**

