Neutralization of Airborne Contaminants

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1   Introduction

This paper addresses the following question: Can an airborne cloud of a chemical or other unwanted agent be neutralized effectively in an urban geometry by injecting a suitable reacting "remediant" into the cloud in sufficient amounts and at appropriate locations? The transport and dispersion of potentially dangerous, contaminants is controlled principally by the wind in an outdoor environment, its turbulent gusts, and how this complex airflow interacts with the geometry of the buildings and terrain. The possible effectiveness of reactive agent neutralization, or mitigation, is a complex matter involving chemical reaction of the agent and the remediant, progressive dilution of the two reactants, and fluid dynamic mixing of the reactants over time. Anyone contemplating in *situ* remediation needs to know where and when to deliver a remediant and what amounts are necessary.

We are considering an unconfined outdoor release of a chemical agent in a region of complex geometry where the wind varies significantly in both space and time. Once we understand the physical and chemical aspects of neutralization, we need to know how effective neutralization of an expanding windborne cloud could be under reasonable time and cost constraints and what are the limits of the possible effectiveness. Remediation with high efficiency seems unlikely. This paper lays the foundations for such a study and presents a simple nonlinear solution for downwind agent neutralization that can be applied to a range of possible scenarios.

Some previous efforts have considered the possibility of mitigating a confined release. A number of patents have been filed for various corona discharge devices and chemicals that can be applied to limited regions (e.g., [1]). The literature generally considers buildings, tunnels, or underground bunkers where the remediant and the agent may be confined and co-resident for some time and where the temperatures and possibly even pressures may be elevated enough to accelerate the neutralizing reaction [2, 3]. Even in these cases the analysis presented here may apply once the agent and co-located remediant break free from confinement. This paper considers problems from two classes of unconfined (outdoor) localized sources, a single "acute" (instantaneous) release and a "steady" (continuous) source. For even these idealized cases one can imagine numerous strategies for delivering a

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neutralizing remediant. To study these possibilities, we must first treat the neutralizing reaction of the remediant with the airborne agent, a highly nonlinear process. We do this here using an idealized, two-species chemical reaction model that can also be a surrogate for neutralization of bio-agents. This equation can be solved analytically, yielding a simple formula to apply. We then add a simple qualitative but calibrated model for dilution of the two reactants with uncontaminated air. This model also allows for delayed reaction when the remediant mixes with the agent sometime after the agent has been released. In the conclusions, possible detailed numerical simulations in the future are considered to answer detailed questions about the dilution and delayed mixing.

First consider some obvious constraints on the problem. These are independent of the particular agent and remediant. For a given amount of any agent there is a corresponding minimum amount of the remediant, if properly deployed, which is sufficient, at least in principle, to neutralize the agent that has already been released. We can measure the delivered amount of the remediant in units of the released agent without loss of generality. Thus one unit of remediant is that amount that can exactly neutralize the agent under ideal conditions. However, even when the timing and location of the remediant release coincide with those of the agent and there is more than enough remediant, some of the agent may remain un-neutralized. If the neutralizing release begins somewhat after the agent release, even if the remediant is released exactly at the source location, a portion of the contaminant cloud moving downwind will be un-neutralized because the remediant cannot catch up. If the remediant is injected into the advancing cloud somewhat downwind of the source location, the highest density regions of the cloud near the source will have been entirely un-neutralized. Clearly the scenarios become even more complicated when there are multiple remediant release locations and possibly even distinct agent sources.

2   A Simple Neutralization Equation for Airborne Agents

To analyze contaminant neutralization, we track a small volume of air containing both the contaminating agent and the remediant as it moves downwind. The residual agent fraction in this volume will be a function of time and is denoted by $A(t)$. The residual remediant fraction is $R(t)$. The word *residual* is being used to remind us that the important quantities we are solving for is the amount of agent and remediant remaining after some time. These fractions are defined relative to the agent concentration that would exist if no neutralizing reactions had taken place. This focuses specifically on tracking the progress and effectiveness of the neutralizing reaction. The initial agent fraction is $A(0) \equiv A_0 = 1$ by definition.

Thus $R(t = 0) \equiv R_0 = A_0 + \delta R$ deviates from $A_0 = 1$ by δR, a signed remediant 'excess' which does not change in time and signals either initial excess or shortage ($\delta R < 0$) of remediant respectively. These fractions $A(t)$ and $R(t)$ only change (decrease) when a neutralizing reaction is taking place. The actual densities of the reacting species decrease due to progressive dilution in the flow, as controlled by Eq. (3) below, even when there is no neutralizing reaction. Not all of the agent can be neutralized when δR is negative. Clearly R_0 itself must be greater than zero for any neutralizing reaction to take place. For example, $A(t) = 0.1$ at some time t after reaction begins means that 90% of the agent molecules/particles have been neutralized. If $R_0 = 1.3$ initially, specifying excess remediant, $R(t)$ would be 0.4 at the time t when $A(t) = 0.1$.

The starting point for the analysis is the model nonlinear chemical neutralization equation for the residual agent fraction $A(t)$:

$$A_0 \frac{dA(t)}{dt} = -\gamma(t)A(t)\,(A(t) + \delta R).$$ Eq. (1)

The initial value $A_0 = 1$, displayed on the left in Eq. (1), reminds us of the binary nature of this neutralization reaction. $\gamma(t)$ is the rate of the reaction between the remediant and the agent (units of sec^{-1}). As written, the agent fraction $A(t)$ decreases with time from its initial value 1 to some smaller fraction, or possibly even to zero when there is enough remediant $R(t)$ and when the reaction rate is large enough. $\gamma(t)$ is made explicitly time dependent here, to include the important fluid dynamic effect of dilution:

$$\gamma(t) = \frac{\gamma_0\, t_d^\alpha}{(t + t_d)^\alpha}\ .$$ Eq. (2)

Here γ_0, the reaction rate (sec^{-1}) at t = 0, is essentially a free parameter in the analysis. In Eq. (2) the power law of the reaction rate is specified as α not 2α. Although both reactant and agent densities decrease with time as $(t + t_d)^{-\alpha}$ in Eq. (1), the agent density on the left hand side also decreases with dilution. When plotting the time-dependent agent fraction, it is convenient to use the characteristic initial reaction time $\tau_0 = 1/\gamma_0$ rather than the reaction rate directly.

Equation (2), folding in turbulent dilution, was clearly chosen to make the nonlinear Eq. (1) easy to integrate in closed form. However, the corresponding power-law formula for the agent (and remediant) density in the cloud,

$$\rho(t) = \frac{\rho_0\, t_d^\alpha}{(t + t_d)^\alpha},$$ Eq. (3)

has been fit by least squares, using a variable dilution time **t$_d$**, dilution power **α**, and an agent density at the source of **ρ$_0$**, to a contaminant transport (CT) simulation of an urban release performed using the CT-Analyst® [4-7] system. This fit of the diluting density as a function of time downwind from the source, for a practical case that will be presented, uses the parameters $\rho_0 = 206$ mg/m^3, $t_d = 46.5$ seconds, and $\alpha = 1.54$ in Eq. (1). The average RMS error of this fit is only about 0.2 mg/m^3.

The formula for the 'residual agent fraction,' from integrating Eqs. (1) and (2), is:

$$A(t) = \frac{\delta R}{\left(R_0 \exp\left[\delta R \dfrac{\gamma_0\, t_d}{(\alpha - 1)}\left\{1 - \dfrac{1}{(t/t_d + 1)^{\alpha-1}}\right\}\right] - 1\right)}.$$ Eq. (4)

In the limit of large dilution time t_d, much larger than times t of interest, Eq. (4) simplifies, describing agent neutralization in a parcel of contaminated air with slow dilution. Linearizing the second term in the curly bracket of Eq. (4) for small t/t_d gives

$$A(t) = \frac{\delta R}{(R_0 \exp[\delta R\,\gamma_0 t] - 1)}$$ Eq. (5)

basically an exponential decay. When $\delta R > 0$, $A(t)$ goes to zero as t increases. When $\delta R < 0$, $A(t)$ goes to δR, the deficit in the amount of remediant provided.

3   Results

Figure 1, derived from Eq. (4), shows where in parameter space agent neutralization using an airborne remediant might be effective and exposes an important 'freeze out' phenomenon when dilution is rapid. Using the parameters $t_d = 50$ seconds and $\alpha = 1.5$ limits discussion to one realistic physical case. The free parameters $\tau_0 \equiv 1/\gamma_0$ and R_0, as well as the independent variable time t, still leave a complex parameter space to study. Figure 1 shows the residual agent fraction as a function of both time (seconds, X-axis) and initial reaction timescale τ_0 (seconds, Y-axis) in a two-dimensional log-log representation where the remaining free parameter, R_0 was fixed at 2.0, corresponding to twice as much remediant as agent initially present and to a dilution timescale and power law consistent with a typical urban plume.

A logarithmic color scale displays the residual agent fraction in Fig. 1. With excess remediant (i.e., $R_0 > 1$) agent fractions substantially less than one are possible when the reaction time τ_0 is at least a factor of 2 smaller than the dilution time t_d. Saturated red, the upper and left areas of the figure, indicates that the agent has not been appreciably neutralized by the elapsed time shown on the X-axis. Red shades to red-orange when the agent has been 90% neutralized. This factor of 10 is marked by the upper black contour in the figure (labeled 0.1). The lavender contours in the 'agent slightly neutralized' region indicate 10% levels of fractional neutralization between 90% and 10% in the first decade where the logarithmic color scale is greatly stretched and thus color differentiation is not very helpful.
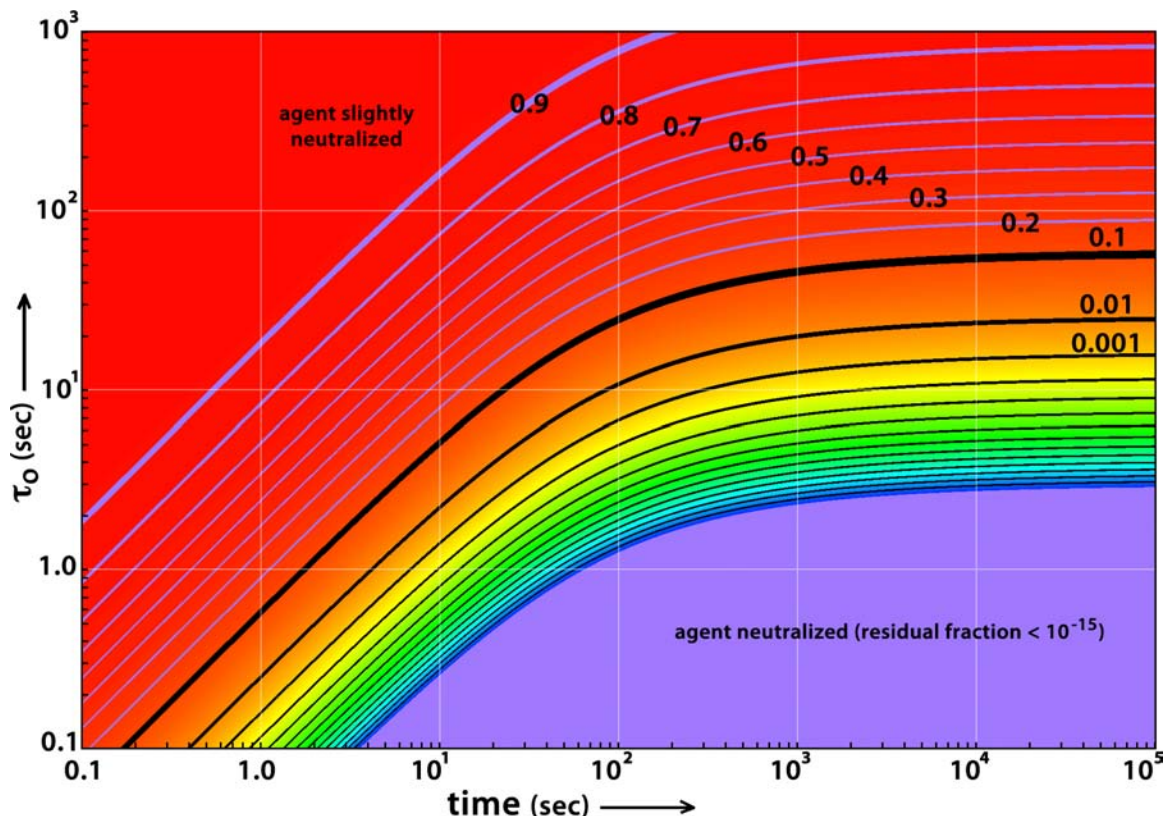

Figure 2. Residual agent fraction as a function of elapsed time (X-axis) and the neutralizing reaction time $\boldsymbol{\tau_0 = 1/\gamma_0}$ (Y-axis). The downwind characteristic dilution time $\mathbf{t_d}$ was set to 50 seconds, $\alpha = 1.5$, and $\mathbf{R_0}$ was set to 2.0, twice as much remediant as agent. 10^5 sec is more than a day.

Perhaps the most striking aspect of these results is the flattening of the contours of constant agent fraction with time on the right of Fig. 1. The remediant appears to stop neutralizing the agent in time even though there appears to be appreciable remediant, as a fraction, remaining. This 'freeze out' phenomenon, caused by the progressive dilution of both reactants, begins as the time exceeds t_d. Freeze out occurs because the effective reaction rate decreases quadraticly in time from Eq. 1 as each reactant separately dilutes steadily after t_d while the overall time for reaction to occur increases only linearly. In the scenario of Fig. 1 there would be enough remediant to consume the agent entirely were the reaction fast enough (i.e. the lavender lower right region labeled 'agent neutralized'). Freeze out sets in in this case when the reaction time exceeds about half the dilution time even though there is plenty of excess remediant.

In the limit as t approaches infinity Eq. (2) can be transformed to show the limiting value $A(\infty)$ where the reaction completely 'freezes out':

$$A(\infty) = \frac{\delta R}{\left(R_0 \exp\left[\delta R \frac{\gamma_0\, t_d}{\alpha - 1} \right] - 1 \right)} \qquad \text{Eq. (5)}$$

For $\alpha > 1$ and $R_0 > 1$ freeze out will occur at smaller and smaller values of $A(\infty)$ as the dilution gets slower.

A number of cases will be presented and a generalization discussed that includes a simple model for delayed mixing due to turbulent interpenetration of agent and remediant streams. Accurate inclusion of non-premixed neutralization will depend on detailed, high-resolution CFD simulations.

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