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Research Highlights

- An approach to account for the effect of concentration fluctuations on toxic load is investigated in the context of land-use planning for major hazard sites.
- For momentum-dominated free-jets of CO_2 gas, the approach is shown to be conservative.
- For low-momentum dense CO_2 plumes, the validity of the approach is uncertain
- Recommendations are provided for additional analysis of experimental data and numerical simulations in order to address this uncertainty.
- Measurements of concentration fluctuations in large-scale CO_2 release experiments would be beneficial

Abstract

In Great Britain, advice on land-use planning decisions in the vicinity of major hazard sites and pipelines is provided to Local Planning Authorities by the Health and Safety Executive (HSE), based on quantified risk assessments of the risks to the public in the event of an accidental release. For potential exposures to toxic substances, the hazard and risk is estimated by HSE on the basis of a "toxic load". For carbon dioxide (CO_2), this is calculated from the time-integral of the gas concentration to the power eight. As a consequence of this highly non-linear dependence of the toxic load on the concentration, turbulent concentration fluctuations that occur naturally in jets or plumes of CO_2 may have a significant effect on the calculated hazard ranges. Most dispersion models used for QRA only provide estimates of the time- or ensemble-averaged concentrations. If only mean concentrations are used to calculate the toxic load, and the effects of concentration fluctuations are ignored, there is a danger that toxic loads and hence hazard ranges will be significantly under-estimated.

This paper explores a simple and pragmatic modification to the calculation procedure for CO_2 toxic load calculations. It involves the assumption that the concentration fluctuates by a factor of two with a prescribed square-wave variation over time. To assess the validity of this methodology, two simple characteristic flows are analysed: the free jet and the dense plume (or gravity current). In the former case, an empirical model is used to show that the factor-of-two approach provides conservative estimates of the hazard range. In the latter case, a survey of the literature indicates that there is at present insufficient information to come to any definite conclusions.

Recommendations are provided for future work to investigate the concentration fluctuation behaviour in dense CO_2 plumes. This includes further analysis of existing dense gas dispersion data, measurements of concentration fluctuations in ongoing large-scale CO_2 release experiments, and numerical simulations.

Keywords

Concentration fluctuations, carbon dioxide, toxic load, free jet, dense plume, land-use planning

1. Introduction

In Great Britain, advice on land-use planning decisions in the vicinity of major hazard sites and pipelines is provided to Local Planning Authorities by the Health and Safety Executive (HSE), based on Quantified Risk Assessments (QRA) for the risks to the public in the event of an accidental release. For potential exposures to toxic substances, QRA is based on estimates of individual or societal risk for exposures to amounts of substances that would result in certain levels of toxicity. The toxicological hazard is determined by HSE, based on the duration of exposure as specified according to the Toxic Load (TL) (HSE, 2008). Risk estimates are based on the likelihood of a hypothetical individual receiving an exposure equal to or greater than a threshold level of TL known as the Specified Level of Toxicity (SLOT). The TL relating to the mortality of 50% of an exposed population is also specified by a threshold level known as the Significant Likelihood of Death (SLOD). Further information on the SLOT and SLOD concepts is provided by Fairhurst and Turner (1993) and Franks et al. (1996).

To calculate the TL, HSE uses the well-known formula of ten Berge (ten Berge and van Heemst, 1983; ten Berge et al., 1986):

$$TL = \int_0^T \tilde{c}^n \, dt \qquad (1)$$

where $\tilde{c}$ is the instantaneous gas concentration at a point in space, T is the duration of exposure and n is the ten Berge toxic load exponent, which is specific to the particular substance released. Values of n together with SLOT and SLOD levels are provided for chemicals of major hazard interest by HSE (2008). For a review of alternative toxic load models, see for example Sommerville et al. (2006).

The index n is unity for some substances, in which case the ten Berge formula reverts to the simple linear model of Haber (1924). The toxic load can be calculated using predicted mean concentrations in this case, since Equation (1) simplifies to the product of mean concentration and duration of exposure.

However, for substances where n is greater than unity, fluctuations in concentration over time can have a significant effect on the toxic load. In the study of chlorine releases by Mylne (1988), in which it was assumed that $n = 2.75$, it was estimated that typical fluctuations could increase the toxicity by between a factor of 10 and 20 above that due to exposure to a constant concentration with the same mean value. More recently, Bogen and Gouveia (2008) used data from the Joint Urban 2003 Oklahoma City field trials (Allwine et al., 2004) to show that lethal or severe effects resulting from a hydrogen cyanide release could occur over an 18 or 25 times larger area if concentration fluctuations were taken into account.

For carbon dioxide, the ten Berge exponent n is eight (HSE, 2008), reflecting the highly non-linear response to exposure. A factor of two increase in CO_2 concentration therefore produces a factor of 256 increase in the toxic load. Any fluctuations in concentration above the mean level will very quickly tend to increase the toxic load. Basing TL calculations for CO_2 solely on the mean concentration could therefore lead to a significant under-estimate of the hazard range.

In practically all foreseeable releases of CO_2, the dispersion of the gas will involve some fluctuations in concentration over time due to turbulence. Turbulence is produced from the strong shear layers induced by high-momentum jets, from frictional effects from a dense current rolling along the ground, or from turbulence already present in the atmosphere. Even if gas is produced at the source at a constant rate, an observer at some distance downstream will in nearly all circumstances be subjected to a time-varying concentration.

This phenomenon is very well known and has been the subject of extensive study, e.g. Ride (1984), Griffiths and Harper (1985), Yee (1999). However, most risk assessments for toxic gas releases are currently based on exposure to a predicted time-averaged concentration or, in the case of a time-varying release (from vessel blowdown, for example) from a predicted ensemble-averaged concentration, where the ensemble represents multiple realizations of the release (e.g. Kazantzis and Kazantzi, 2010).

Many dispersion models used for risk assessment purposes are unable to provide reliable estimates of the concentration fluctuations over time. A notable exception is the FROST software developed by GL Noble Denton (P. Cleaver, Personal Communication, January 2011) which assumes profiles for both peak and mean concentrations, and hence allows the effects of concentration fluctuations to be included in a simple manner. Although some models, such as DRIFT (Webber et al., 1992; Jones et al., 1993), incorporate statistical correlations that take into account fluctuations in concentration, these are for the variation in mean concentration over multiple realizations of a release, not for the time-varying concentration fluctuations due to turbulence. More sophisticated models have been developed to account for concentration fluctuations in determining the toxic load, and these are reviewed briefly later in this paper, for application to dense CO_2 clouds.

To provide a practical and simple means of moving forward, the present paper examines a simple and pragmatic modification to the calculation procedure for CO_2 toxic load. It involves the assumption that the concentration fluctuates by a factor of two with a prescribed square-wave variation over time, i.e. it is assumed that the concentration is twice the mean for half of the time, and zero for the remaining time. This rudimentary approach is not intended to provide a realistic reflection of actual turbulent fluctuations, but is merely aimed at incorporating the effects of fluctuations on the toxic load to a very basic degree. The utility of such an approach is that it can be readily implemented in simple dispersion models and therefore provides a practical solution methodology at the present time. In the future, more robust scientifically-based models will no doubt be proposed for use in risk assessment.

The notion of a factor of two variation about the mean to account for turbulent concentration fluctuations is not a new concept. It is commonly used in the context of flammable vapour clouds, where hazard ranges are often defined as the location where the predicted average gas concentration reaches half of the Lower Flammability Limit (50% LFL), e.g. Kaiser (1978). An analysis of the justification for this approach is provided by Webber (2003).

To analyse whether the methodology involving a factor-of-two variation about the mean is valid for CO_2 toxic load calculations, two idealised scenarios are examined in the present work: the free jet and the dense plume (or gravity current).

2. Free Jets

The empirically-based toxic load model for free jets examined here is derived from the flammability factor model of Gant et al. (2011a, 2011b). This model estimates the likelihood of flammable gas igniting locally at a given position within a jet, based on the proportion of time that gas concentrations at any position are within the flammable range. Gant et al. (2011b) demonstrated that the model produces reliable predictions of the ignition probability, by comparing its predictions to the measurements of Birch et al. (1981) and Smith et al. (1986).

To calculate the toxic load requires two simple modifications of the flammability factor model. Firstly, the concentration Probability Distribution Function (PDF) is integrated between concentration volume fraction limits of zero and one (rather than just between the flammable limits) and, secondly, the concentration is raised to the ten Berge toxic load exponent, as follows:

$$TL = \int_0^1 \tilde{c}^{\,n} p(\tilde{c}) d\tilde{c} \qquad (2)$$

where $p(\tilde{c})$ is the concentration PDF, and the time-varying concentration, $\tilde{c}$, is expressed as a volume fraction. In the model of Gant et al. (2011a, 2011b), the shape of the PDF is assumed, and is fully specified by the mean and variance of concentration, and the turbulence intermittency. Profiles of these quantities are taken from empirical correlations, as follows:

- The mean concentration along the jet centreline is determined from empirical profiles from Chen and Rodi (1980), with some minor changes (see Appendix);
- In the radial direction, Gaussian profiles are assumed for the mean concentration, using spreading rates given by Birch et al. (1978);
- The RMS concentration fluctuation is determined using the α-β model of Chatwin and Sullivan (1990);
- The turbulent intermittency in the jet is determined using the empirical model of Kent and Bilger (1976);
- The shape of the PDF is assumed to comprise the sum of a delta function and a truncated Gaussian, using conditionally sampled mean and Root-Mean-Square (RMS) values, based on the model of Birch et al. (1981);

The notion of modifying flammability models to examine toxic load was suggested previously by, for example, Griffiths and Harper (1985).

The present model was implemented in MatLab and the integration of Equation (2) was performed numerically using one of its in-built mathematical functions. To ensure that the model was coded correctly a verification test was performed, where results were compared to an analytical solution of Equation (2) for a chlorine release (see Appendix). This demonstrated that the model had been coded correctly.

The predicted mean concentration field produced by a hypothetical gaseous CO_2 release is shown in Figure 1. Three pairs of solid bold lines are shown in the figure, indicating the position of the SLOT and SLOD from three different toxic load predictions:

1. Assuming no fluctuations, i.e. calculating *TL* from Equation 1 using the mean concentration;
2. Assuming a factor-of-two square wave concentration fluctuation about the mean level;
3. Using the empirically-based PDF model (Equation 2).

In each case, it was assumed that the exposure duration was 30 minutes. The SLOT and SLOD for CO_2 are 1.5×10^{40} ppm^8.min and 1.5×10^{41} ppm^8.min, respectively (HSE, 2008).

The results show, as expected, that the smallest hazard range is produced if concentration fluctuations are ignored and only the mean concentration is used to determine the toxic load. Assuming a factor-of-two variation about the mean produces the largest hazard range. The distance from the jet source to the SLOT or SLOD is approximately 50% higher when the factor-of-two model is adopted, compared to the approach where concentration fluctuations are ignored.

Results from the PDF model suggest that the factor-of-two approach is conservative in terms of the distance to the SLOT and SLOD on the centreline of the jet. Since the intensity of the fluctuations increases towards the periphery of the jet, the PDF model predicts the toxic effect to extend over a wider area near the base of the jet than the other two model results, which are based solely on the mean concentration contours.

The results shown in Figure 1 are based on a source diameter of 0.5 m and a release velocity of 50 m/s. The sensitivity of the maximum hazard range to the exit velocity and the source diameter is shown in Figures 2 and 3. The distances shown in these figures are measured from the source to the SLOT and SLOD location on the centreline of the jet. The results show that the factor-of-two square wave approach provides consistently conservative (i.e. larger) predictions of the hazard range than the PDF model.

The PDF on which the present model is based was derived from experimental measurements of gas concentration in free jets by Birch et al. (1978), who used a high frequency response laser Raman system. The model has been demonstrated to capture the correct behaviour of short duration fluctuations that produce, momentarily, concentrations within the flammable range. However, Birch et al. (1981) acknowledged that the shape of the PDF did not fully account for the broadening of the delta function away from the jet centreline that was observed in the measurements. Adopting the same PDF to calculate toxic load is expected to be conservative, since breathing has the effect of averaging the gas concentration over a period of a few seconds, which would give rise to a lower toxic load.

The results shown here are for free jets in a quiescent environment. Commonly, risk assessments consider releases in non-zero wind-speeds. The present model is not valid under these conditions. Gas jets in a cross flow were studied experimentally by Birch et al. (1989) who showed that it was possible to ignite the flow at positions where the mean concentration was well below the LEL on the periphery of the jet, but that full light-up of the jet did not occur downwind of the point where the mean concentration fell below the LEL. Further work is necessary to establish that the factor-of-two toxic load model is conservative for this case.

3. Low-Momentum Dense Plumes

Although CO_2 is likely to be stored and transported at high pressure, perhaps in the supercritical or dense-phase state (DNV, 2008), there are conditions that could give rise to a low-momentum gas release. For example, a release from small hole in a buried pipeline could lead to gas escaping through pores in the ground to produce a low speed vapour cloud on the surface. Alternatively, a release within an enclosure such as a compressor room could contain much of the initial momentum of the release, with the gas escaping subsequently at low speed through ventilation openings. Under these conditions, near the source the vapour cloud will behave as a dense gas due to both the high molecular weight of CO_2 and its temperature. In some release scenarios, the temperature will be much lower than ambient, due to the rapid expansion of CO_2 from the pressurized vessel or pipeline, or production of gaseous CO_2 from sublimation of a bank of solid CO_2. In the case of a subterranean release, as the gas percolates through the ground to the surface it is likely to initially tend towards equilibrium with the ground temperature, and so buoyancy effects are likely to be predominantly due solely to the high molecular weight of CO_2.

As the dense CO_2 vapour cloud spreads along the ground away from the source it will entrain fresh air and dilute. However, unlike many toxic gases such as chlorine, which remains toxic down to very low concentrations, the short-term exposure levels for CO_2 are relatively high. Its Immediately Dangerous to Life and Health (IDLH) concentration is 4% vol/vol (40,000 ppm) compared to just 0.001% vol/vol (10 ppm) for chlorine (NIOSH, 1995). If it is assumed that the source of CO_2 gas is at its sublimation temperature at atmospheric pressure (-78.5 ˚C), and the ambient temperature is 0˚C, then by the time that the CO_2 has diluted to 4% vol/vol, the CO_2-air mixture will have a density 5% greater than ambient. At a higher CO_2 concentration of 10% vol/vol, which causes unconsciousness after 30 minutes exposure (NORSOK, 2001), the gas mixture will be 11% denser than ambient. Therefore, over the range of concentrations of practical interest, it is likely that a large, low-momentum CO_2 release will exhibit gravity effects. The CO_2 cloud will not behave as a passive or neutral tracer gas.

Dense gas clouds exhibit different dispersion behaviour to those of neutrally-buoyant gases. Gravitational forces act to accelerate the cloud, whilst the vertical density gradient tends to suppress turbulence and reduce dilution. Concentrations inside the spreading dense plume tend to be more uniform than those in the equivalent passive plume. Therefore, as the dense plume meanders it produces lower intensity fluctuations in the core and higher intensity fluctuations on the periphery as compared to equivalent passive plumes (see Britter, 1988, and Wilson, 1995).

The bulk of research efforts to analyse concentration fluctuations in gas dispersion have been undertaken for passive, neutrally-buoyant plumes. Early work in this area includes that of Ride (1983) who proposed a modified binomial PDF for the gas concentration, based on the idealised concept of fluctuations arising from a sea of zero concentration in which passes discrete spherical clouds of gas. Ride (1983) calibrated the model constants to obtain good agreement with the methane jet experiments of Birch et al. (1978) and the passive instantaneous plumes of Jones (1982). Subsequently, Ride (1984) and Griffiths and Harper (1985) examined the increase in toxic load due to turbulence intermittency, where they noted that in the limit of very high frequency fluctuations, the breathing duration provided essentially an averaging time.

Further work on concentration fluctuations has been undertaken by Wilson and co-workers at the University of Alberta (Wilson et al., 1982a, 1982b, 1985; Wilson, 1991, 1995; Hilderman et al., 1999; Hilderman and Wilson, 1999). The extent of the hazardous cloud following a hydrogen sulphide (H_2S) release was determined by Wilson (1991) according to the toxic load, either with or without concentration fluctuations. The results showed that using only mean concentrations led to a significant underestimate of the hazard range. Wilson used the EXPOSURE-1 model, in which H_2S was treated as a passive tracer, and a two-part PDF for the concentration fluctuations, which comprised a blend of a log-normal distribution and a delta function. Hilderman and Wilson (1999) later developed a model to generate fluctuating concentrations in dispersing passive vapour clouds, which took as input parameters the intermittency and fluctuation intensity. They showed that a log-normal PDF provided good agreement with measurements of plume dispersion in a water channel and noted that the model could be used to generate sample realizations of concentration time series in order to determine the toxic load. Since each time series would represent an individual realization, the model could also be used to examine the potential variability between multiple realizations of the same flow.

A significant body of research on concentration fluctuations has been undertaken over the last 30 years by Chatwin, Mole, Nielsen and co-workers at Sheffield University and Risø National Laboratory (Chatwin, 1982; Carn and Chatwin, 1984; Chatwin and Sullivan, 1990, 1993; Lewis and Chatwin, 1997; Lewis, 1999; Chatwin, 2002; Nielsen et al., 2002; Mole and Ku, 2007; Mole, 2010). Their work includes the EU-sponsored “Concentration Fluctuations in gas releases by industrial accidents” (COFIN) project, which involved analysis of measurement data, and development and validation of concentration fluctuation models (Nielsen et al., 2002). In this work, although they acknowledged that dense gas dispersion was of key interest to industrial risk assessment, their analysis considered only passive dispersion. They justified this choice on the basis that there was insufficient dense gas dispersion measurement data available. The models developed as part of COFIN are significantly more complex than those commonly used in risk assessment, although they were coded into the freely-available COFINBOX software. A more pragmatic approach was developed and validated for passive dispersion by Lewis (1999). In recent years, research by this group has focussed more on sophisticated theoretical developments (Chatwin, 2002; Mole, 2010).

Research into concentration fluctuations with more focus on practical models for risk assessment has been undertaken by Yee (Yee et al., 1994, 2009; Yee and Chan, 1997; Yee, 1999, 2008; Yee and Biltoft, 2004). In the most recent study, Yee et al. (2009) developed a concentration fluctuation model for passive plume dispersion, based on a standard k-ε Reynolds-averaged Navier-Stokes (RANS) model. To avoid the complexities associated with modelling a transported PDF, they used a clipped-gamma PDF which had been shown previously to provide a good fit to concentration data in plumes dispersing in open terrain (Yee and Chan, 1997) and through idealized obstacle arrays (Yee, 2008). The work aimed to provide a practical tool for application to probabilistic risk assessments of toxic releases in urban environments.

Other related work in this field includes the statistical analysis of concentration in dense gas clouds by Davies (1990, 1992a, 1994). In these studies, Davies showed that many of the parameters of interest in dispersing dense gas plumes, such as the maximum concentration and dose, exhibit a log-normal probability distribution in repeat experiments. Similar findings were reported by Sweatman and Chatwin (1996). This led to development of the DRIFT dense gas dispersion model to produce confidence intervals on the mean concentration (Jones et al., 1994). Although this work considered concentration fluctuations, the PDF model that was developed accounted for the uncertainty associated with repeated instances of a release, rather than the fluctuations in concentration over time due to turbulence. It is therefore not relevant to the present work, although it provides a useful indication of the likely maximum degree of accuracy that could potentially be achieved with dense gas dispersion models (see also Davies, 1992b).

None of the work examined as part of this literature review was found to provide a model for concentration fluctuations in dispersing dense gas clouds that could be used to calculate the toxic load. However, some previously reported studies provide anecdotal evidence of the potential magnitude of certain relevant parameters. Griffiths and Megson (1984) reported that in the Burro field-scale Liquefied Natural Gas (LNG) trials, where concentrations were measured at a rate of 3-5 Hz and mean concentrations were generated over 10 s, the ratio of the peak-to-mean concentration was as much as 16. They noted that this was significantly greater than the usual factor of two variation used in risk assessment for flammable releases, i.e. the 50% LEL criteria. Peak to mean concentration ratios were also investigated by Hanna et al. (1993), who compared predictions of fifteen gas dispersion models to measurement data.

Statistical analysis by Carn (1987) of the instantaneous dense gas releases in the Thorney Island trials showed that the intensity of the concentration fluctuations (i.e. the ratio of RMS to mean concentration) was typically around 0.5. Carn (1987) also reported that a similar scale of fluctuations was observed in other dense gas trials. Although this fluctuation intensity is half of the level implied in the factor-of-two square wave model assessed in the present work, without knowing the shape of the concentration distribution over time it is not possible to assess whether or not the factor-of-two model is more or less conservative in terms of the toxic load than indicated by these measurements.

4. Future Directions

The literature survey has not revealed any further useful insight into concentration fluctuations in dense gas releases, to validate the proposed factor-of-two model. Three potential avenues for future work are as follows:

Firstly, a thorough assessment of previous field-scale dense gas dispersion experiments involving time-resolving gas concentration measurements could be undertaken. The measurements need to have been taken at a rate equal to, or faster, than the human breathing rate (approx. 0.3 Hz). In some cases, it may be possible to infer concentration values from thermocouple measurements of fluctuating temperature, using an approach similar to that adopted by Witcofksi and Chirivella (1984). It has already been established that dense gas experiments exhibit a degree of scatter due to the stochastic nature of the flow (Davies, 1990, 1992a; Sweatman and Chatwin, 1996) and so any analysis would need to consider a sufficiently large sample of data, preferably spanning a range of Richardson numbers. Potentially useful studies include the Warren Spring tests reported by Hall et al. (1991), which involved measurements at three different Richardson numbers, and the work of Stretch (1986) who examined concentration fluctuations in both neutral and passive plumes, although both of these were reduced-scale wind tunnel tests.

Secondly, if sufficient concentration fluctuation data does not yet exist, it could be generated by new field-scale experiments. There are difficulties in interpreting data from reduced scale wind tunnel tests due to the need to scale dimensionless parameters for both buoyancy and turbulence simultaneously. Often, wind tunnel tests are performed at lower Reynolds numbers, which do not feature the full range of turbulence scales, or the slow changes in conditions which are present in the atmosphere. At the present time, a number of field-scale CO_2 releases are planned in order to support the risk assessment of planned carbon capture, transport and storage infrastructure. This includes the medium-scale and field-scale tests to be undertaken as part of the EU-funded CO_2PipeHaz project[1], and the large-scale tests to be undertaken as part of the National Grid COOLTRANS project. In view of this, it would be advantageous to maximise the potential benefits from these large and costly experiments by recording time-varying CO_2 concentrations (or at least temperatures), which could subsequently be used to develop concentration PDFs.

Thirdly, the matter could be investigated by numerical simulations, using methods in which time-varying concentrations are resolved. The most promising avenue is to use Large-Eddy Simulation (LES). This approach has previously been used to assess concentration fluctuations in passive and buoyant plumes by Sykes and Henn (1992), Zhou et al. (2001) and Xie et al. (2004). Such simulations would require careful consideration of the spatial and temporal resolution, atmospheric turbulence levels, source conditions and the effects of surface roughness or obstructions. A reliable study would probably involve many tens of simulations to adequately consider the sensitivity of the predictions to the model parameters and physical conditions, and would also need to be validated against a reliable experimental dataset, although this could be at reduced scale. Given the current state-of-the-art in computing power and CFD software, this should be achievable in practice.

Once these analyses have been performed, it would be beneficial to revisit the factor-of-two square-wave model proposed here. If it was shown to be significantly under- or over-conservative, other alternatives could be investigated, such as the use of prescribed triangular or sinusoidal variations in concentration over time.

5. Discussion and Conclusions

The present work has examined the validity of a simple approach to account for the effect of concentration fluctuations in calculating the toxic load for atmospheric CO_2 releases. It is based on the assumption that the concentration at any point in space fluctuates by a factor of two with a prescribed square-wave variation over time.

Analysis of free jets of CO_2 using a PDF-based model originally derived to predict the ignition probability of flammable gas jets has shown that this factor-of-two approach produces conservative predictions of the hazard range, in terms of the maximum distance to the SLOT and SLOD.

For low-momentum plumes of dense CO_2 gas, a review of the literature has shown that, at present, it is not possible to establish the validity of the factor-of-two model. Suggestions have been provided for future work to address this matter, involving analysis of existing data, new field-scale measurements and numerical simulations using LES.

It is clear from the literature review and analysis presented in the current work that if only mean concentrations are used to calculate the toxic load, hazard ranges for CO_2 releases are likely to be significantly under-predicted. Given the current state of knowledge, it is unclear whether in all circumstances the proposed factor-of-two model will always give rise to conservative predictions. However, at the very least this approach provides a step in the right direction, and incorporates the effect of fluctuations on the toxic load in a way that can be easily adopted using the current generation of quantified risk assessment models. Impact analysis will show whether or not the approach leads to untenable (over-conservative) hazard ranges in scenarios of practical interest. As scientific understanding develops, and more

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[1] http://www.co2pipehaz.eu

sophisticated, practical models are developed, it will be necessary to reassess this methodology.

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Glossary

a_C	model constant
$\tilde{c}$	instantaneous (time-varying) concentration
c	concentration fluctuation about the mean
$\sqrt{\overline{c^2}}$	Root Mean Square (RMS) concentration
$\overline{c_c^2}$	conditional concentration variance
C	mean concentration
C_c	conditional mean concentration
C_{cl}	mean concentration on the jet centreline
C_0	mean concentration at the orifice
D	jet orifice diameter
erf	error function
Fr	Froude number
g	gravitational acceleration
I	turbulent intermittency
K	model constant
K_C	model constant
n	ten Berge toxic load exponent
$P()$	probability
r	radius
TL	toxic load
U_0	gas velocity at the orifice
x'	axial distance from virtual origin of the jet
x^*	dimensionless axial distance
α	model constant
β	model constant
$\delta()$	Dirac delta function
ρ_a	ambient density
ρ_0	gas density at the orifice

Appendix: Toxic Load Model Details

The toxic load model for free jets is based on a number of empirical profiles for the mean and RMS concentration, and turbulence intermittency. The mean concentration profiles along the centreline of the jet are taken from Chen and Rodi (1980), and consist of two equations which are valid in separate regions of the flow: the momentum-dominated region near the jet orifice and an intermediate region further downstream where inertial forces are weaker and buoyancy forces start to become important. The boundary between these two regions is defined using a dimensionless axial distance, x^*:

$$x^* = Fr^{-1/2}\left(\frac{\rho_0}{\rho_a}\right)^{-1/4}\left(\frac{x'}{D}\right) \qquad \text{(A.1)}$$

where x' is the axial distance from the virtual origin of the jet (see Chen and Rodi, 1980), D is the orifice diameter, ρ the density and subscripts "*a*" and "0" refer to ambient and jet orifice values respectively. The Froude number, Fr, is given by:

$$Fr = \frac{U_0^2}{gD(\rho_a - \rho_0)/\rho_0} \qquad \text{(A.2)}$$

where U_0 is the velocity at the jet orifice and g is the acceleration due to gravity. In the momentum-dominated region near the jet, where $x^* < 0.5$, the mean centreline centreline concentration, C_{cl}, is given by:

$$C_{cl} = 5C_0\left(\frac{\rho_0}{\rho_a}\right)^{-1/2}\left(\frac{x'}{D}\right)^{-1} \qquad \text{(A.3)}$$

whilst in the intermediate region, where x^* is between 0.5 and 5.0, it is given by:

$$C_{cl} = a_C C_0 Fr^{1/8}\left(\frac{\rho_0}{\rho_a}\right)^{-7/16}\left(\frac{x'}{D}\right)^{-5/4} \qquad \text{(A.4)}$$

Beyond this intermediate region, where x^* is greater than 5.0, buoyancy forces become dominant and the flow exhibits plume-like behaviour. However, since the SLOT and SLOD for CO_2 jet releases lie in the momentum-dominated and intermediate regions, it is not necessary to consider the buoyancy-dominated region.

Constant a_C in Equation (A.4) is given a value 4.2, which differs from the values given by Chen and Rodi (1980) and Smith et al. (1986), who used, respectively, $a_C = 0.44$, and $a_C = 4.4$. Its value has been chosen to produce a smooth transition in concentration between the momentum-dominated and intermediate regions (see Gant et al., 2010, for further details). In the radial direction, the mean concentration is approximated using a Gaussian profile:

$$\frac{C}{C_{cl}} = \exp\left[-K_C\left(\frac{r}{x'}\right)^2\right] \qquad \text{(A.5)}$$

where constant K_C is given a value of 73.6, based on that determined by Birch et al. (1978). The RMS concentration is determined using the α-β model of Chatwin and Sullivan (1990):

$$\overline{c^2} = \beta C\left(\alpha C_{cl} - C\right) \tag{A.6}$$

where constants α and β are given values of 1.27 and 0.14, respectively, based on Chatwin and Sullivan's (1990) analysis of the methane jet experiments of Birch et al. (1978). The turbulent intermittency, I, is calculated using the empirical formula of Kent and Bilger (1976):

$$I = \frac{K+1}{\left[\left(\dfrac{\overline{c^2}}{C^2}\right)+1\right]} \tag{A.7}$$

where K is a constant given a value of 0.25 by Kent and Bilger (1976).

To account for the change in shape of the concentration PDF with radius, the model adopts the two-part PDF proposed by Birch et al. (1981) which smoothly varies between a truncated Gaussian distribution and a delta-function, based on the intermittency:

$$p(\tilde{c}) = \underbrace{(1-I)\delta(\tilde{c})} + I\frac{A}{\sqrt{2\pi\sigma^2}}\exp\left[-\frac{(\tilde{c}-\mu)^2}{2\sigma^2}\right] \tag{A.8}$$

where values of σ and μ are determined using a maximum likelihood estimation method to obtain the following mean and variance for the truncated Gaussian:

$$C_c = \frac{C}{I} \tag{A.9}$$

$$\overline{c_c^2} = \frac{\overline{c^2}}{I} - \frac{C^2(1-I)}{I^2} \tag{A.10}$$

The subscript 'c' is used here to denote conditionally sampled values, i.e. values pertaining only to the turbulent jet, not the non-turbulent ambient flow. The scaling factor, A, in Equation (A.8), is given by:

$$A = \frac{2}{erf\left(\dfrac{1-\mu}{\sqrt{2\sigma^2}}\right) - erf\left(\dfrac{-\mu}{\sqrt{2\sigma^2}}\right)} \tag{A.11}$$

where *erf*() is the error function, and μ and σ are the mean and standard deviation of concentration, respectively.

To calculate the toxic load requires the integration of the product of the PDF and the concentration to the power of the ten Berge toxic load exponent (Equation 2). In the present work, this integration was performed numerically, using the adaptive Simpson quadrature method that is available in MatLab (the "quadgk" function). The underbraced delta-function term in Equation (A.8) is effectively ignored in this integration, since it only has finite amplitude when the concentration is zero. In calling the quadrature function in MatLab, it was found necessary to use a low tolerance of 10^{-6} in order to account fully for the long tail of the Gaussian PDF. Using a higher tolerance resulted in anomalies in the predicted toxic load on the periphery of the jet.

To demonstrate that the MatLab implementation and numerical integration was correct, results were compared to an analytical solution that was obtained for a jet of chlorine gas, for which the ten Berge exponent is 2 (HSE, 2008). Chlorine was chosen for this comparison, since for substances with higher values of the ten Berge exponent, the derivation of the analytical solution becomes protracted. The analytical integration of Equation (2) using the PDF given in Equation (A.8) with $n = 2$, results in the following expression:

$$TL = \frac{\left(\mu^2 + \sigma^2\right)}{2}\left[erf\left(\frac{1-\mu}{\sqrt{2\sigma^2}}\right) - erf\left(\frac{-\mu}{\sqrt{2\sigma^2}}\right)\right] - \\ \frac{1}{\sqrt{2\pi}}\left\{\sqrt{\sigma^2}(1+\mu)\exp\left[-\frac{(1-\mu)^2}{2\sigma^2}\right] - \mu\sigma\exp\left(-\frac{\mu^2}{2\sigma^2}\right)\right\} \tag{A.12}$$

This was implemented independently in MatLab. Predictions of the toxic load using the numerical and analytical methods are compared in Figure A.1 for a chlorine gas jet with a release velocity of 50 m/s and source diameter of 2 inches, based on a 30 minute exposure duration. The two methods produce identical solutions, providing verification that the numerical model used for the toxic load calculations was implemented correctly.

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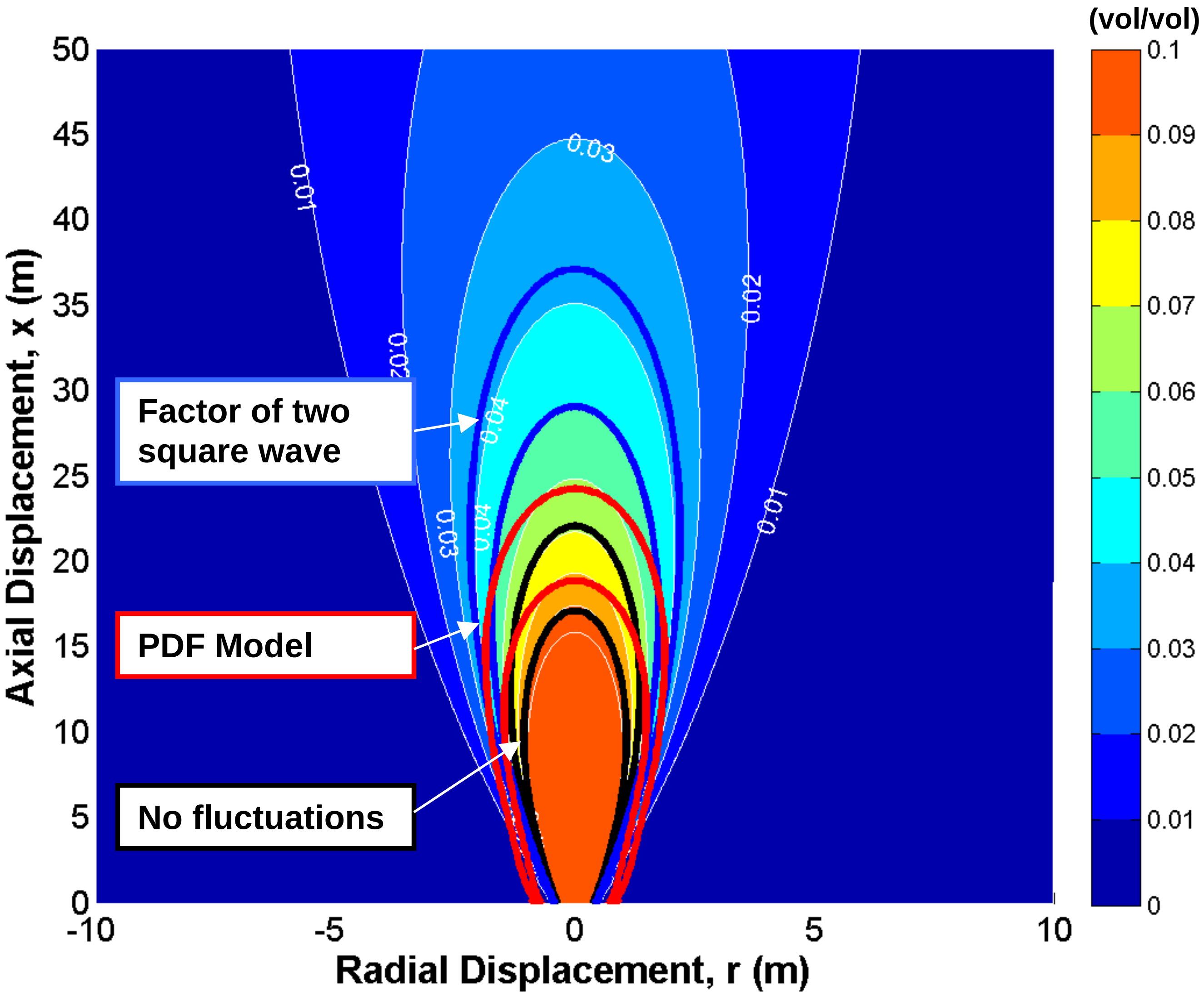

Figure 1 Predictions of mean concentration in a CO_2 jet from a source with diameter of 0.5 m and exit velocity of 50 m/s. Coloured contours show the CO_2 gas concentration and the three pairs of bold curves show the locations of the SLOT and SLOD calculated using different toxic load models.

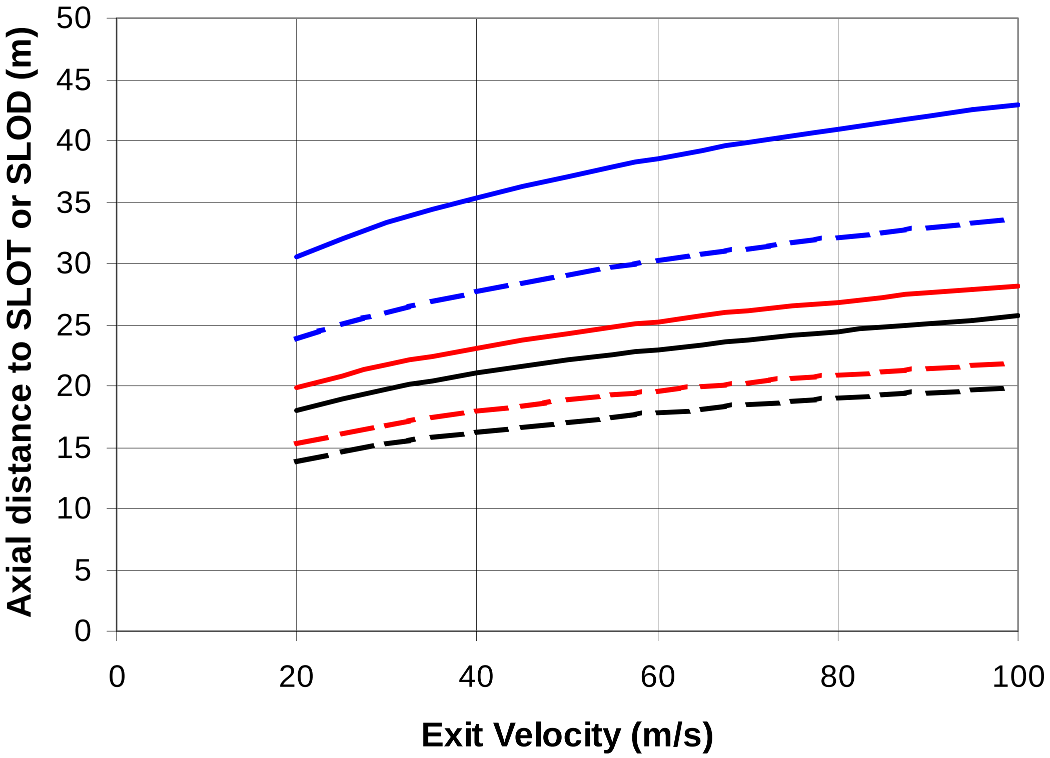

Figure 2 Predicted SLOT and SLOD distances for different jet exit velocities, using three different toxic load models: — factor-of-two square wave model; — PDF model; — no fluctuations. Solid lines indicate SLOT and broken lines SLOD.

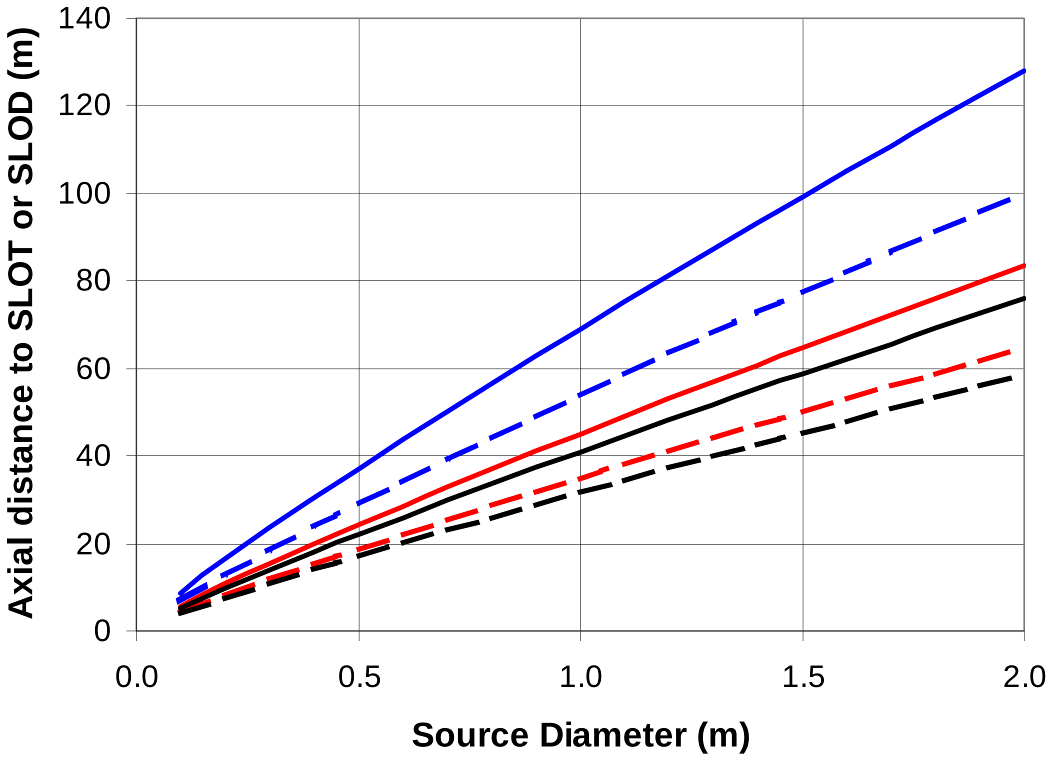

Figure 3 Predicted SLOT and SLOD distances for different source diameters, using three different toxic load models: — factor-of-two square wave model; — PDF model; — no fluctuations. Solid lines indicate SLOT and broken lines SLOD.

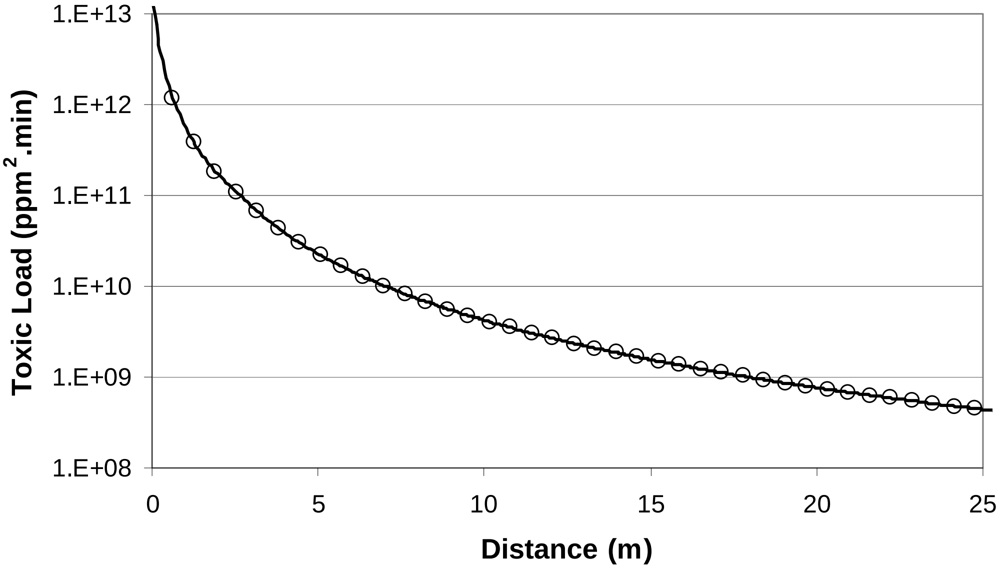

Figure A.1 Toxic load predictions for a chlorine release using the numerical method (solid line) and analytical method (symbols).