NUMERICAL SIMULATION OF HAZARDOUS MATERIAL ATMOSPHERIC DISPERSION FOLLOWING AN ACCIDENTAL RELEASE IN AN INDUSTRIAL SITE: THE EFFECTS OF ATMOSPHERIC CHEMISTRY DURING DISPERSION

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Abstract: The results for the atmospheric dispersion simulations following an accidental release in an industrial site at Bourges area (France) are presented. The emission scenario is represented by an ethanol pool fire. Primary emissions are determined by the combustion chemical kinetics. Subsequent decays in the composition of the emissions are determined by appropriate atmospheric chemistry models. Dispersion simulations are performed for representative diurnal / nocturnal and seasonal atmospheric conditions. The mesoscale solver WRF (Weather Research and Forecasting Model) is used to obtain atmospheric conditions. QUIC dispersion modelling system is used for determining the flow field over the considered area and the simulations of the atmospheric dispersion. The results obtained concern the hazardous material atmospheric concentrations over the considered area.

Key words: *Atmospheric dispersion, accidental release, hazardous material, emissions, atmospheric chemistry*.

INTRODUCTION

This paper concerns prompt estimation of the atmospheric dispersion characteristics of hazardous materials following a release over an industrial site. That is of crucial importance for the emergency responders. Quick, yet accurate predictions of the contaminated area are required. For this purpose, it is necessary to assess the influence of different parameters such as the real time wind field, building topography and composition-decay characteristics of the initially emitted species. Dispersion models consider these parameters at different accuracy levels taking the into account computational time.

Conventional Computational Fluid Dynamics (CFD) models are used for capturing the physics of dispersion. Large eddy simulation methods are promising tools for flows over urban canopy when computational rapidity is not a requirement. Cai et al. (2008) used LES to study the dispersion and transport characteristics of flows over street canyons and compared results with experimental data. Schatzmann et al. (2011) presented LES based dispersion results for Hamburg inner city area. The simulations are based on a high resolution LES contaminant transport model (FAST3D-CT) (Boris 2002). Xie and Castro (2009) presented LES computations of wind tunnel tests for a site at the central London area. The authors show that "the near field" flow is sensitive to the source location and initial source turbulence parameters. Pielke et al. (1992) used mesoscale atmospheric wind field results coupled with 2D CFD simulations of dispersion.

Use of CFD models offer high accuracy but this comes at the cost of long computational time and lack of "user friendliness". Alternatively, the simulations can be performed in two parts: At first, the average flow solution is computed considering the obstacles (buildings, vegetation etc.); Then, dispersion is simulated using the Lagrangian particle methods (Hanna et. al 20011, Singh et al. 2011). LPDM models like Micro-Swift SPRAY (Tinarelli et al. 2007) and QUIC (Pardyjak and Brown 2001; Williams et al. 2002) produce results faster and with acceptable accuracy (both based on the theory by Röckle, 1990). Nibart et al. (2011), performed dispersion simulations using the Reynolds averaged Navier Stokes equations based CFD solver for the average flow field coupled with Micro-SPRAY for the dispersion of release. Toxic release dispersion in New York City is simulated by Duchenne and Armand (2010) using MM5 for the atmospheric flow simulations, NSWIFT for adding the effects of the obstacles and Micro-SPRAY for Lagrangian dispersion. Williams et al. (2005), presents the dense gas dispersion results, obtained by QUIC-PLUME model for an open air release on a flat terrain and a wind tunnel experiment, including obstacles. Gant and Atkinson (2011) used QUIC-PLUME model for the simulation of the flammable, cold and dense vapour cloud, which evaporates out of an overfilled large tank. As for the CFD models it is indicated that the near field wind plays a key role in the dispersion simulations.

The decay mechanisms of released species are mostly affected by the temperature, sun light irradiation induced photolysis and by the reactions with the main atmospheric oxidants such as hydroxyls, nitrate radicals and ozone. Since these parameters are time dependent, the diurnal variations should be considered for decay rates (Burns et al. 2012).

In this work we investigate the atmospheric dispersion characteristics of an accidental release in an industrial site. The release can be due to explosions or fires of flammable stored compounds or after a leakage and subsequent evaporation. The global aim is to provide emergency responders with sufficiently accurate and rapid data in order to allow them to decide the emergency measures to be taken (such as the evacuation of the surrounding population). We are focusing on an industrial site near the city of Bourges in France. Details of the considered site will be given in the numerical simulations section below. The release scenario considered in this paper is a pool fire of ethanol of 100 m^2 area. The duration of release is taken equal to 1 hour. In the first part of the paper, we present the model for ethanol pool fire and the production and decay rates of major released compounds. The temperature and wind data are obtained using the mesoscale solver WRF. The chemistry and atmospheric data are then used to feed the dispersion modelling system QUIC to obtain concentration contours of some selected toxic compounds.

CHEMICAL KINETICS OF AN ETHANOL POOL FIRE

The pool fire numerical simulations are performed with fixed an equivalence ratio of 4. The pressure is 1 atm and the temperature of the flame is set at 1400K as recommended by Weckman and Strong (1986). They investigated a pool fire with methanol as fuel and gave experimental results for the fire flame characteristics. The residence time - the mean time a molecule stays in the reaction zone- can be estimated with the height of the reaction zone and the induced axial velocity of the flow in the flame, due to inflow and buoyancy effects. Thomas empirical correlation (Rew et. al. 1997) gives the size of the reaction zone as in equation 1.

$$\frac{L}{D} = 42 \cdot \left(\frac{m'}{\rho_a \cdot (g \cdot D)^{1/2}} \right)^{0.61} \tag{1}$$

where L is the flame height (m), ρ_a is the density of air at ambient conditions (kg.m^{-3}), g is the gravitational acceleration (m s^{-2}), D is the pool diameter (m), and m' the mass burning rate of fuel (kg.m-2.s^{-1}). Rew et al. (1997) gave for the mass burning rate of ethanol the value of 0.020 kg.m^{-2}s^{-1}. The flame length for a 0.073 m^2 pool is around 8 cm in Weckman and Strong (1996) conditions for a methanol pool fire. Assuming the same mass burning rate for ethanol and methanol flames we found a residence time in the reaction zone of the order of magnitude of 0.1 seconds. After fixing these parameters we performed chemical kinetic simulations using Dagaut (1992) mechanism for the oxidation of vaporized ethanol. The compositions of the species produced out of the ethanol flame are computed with CHEMKIN-PSR (Glarborg et al. 2011). 12 major species having the highest mole fractions are tabulated (inert N_2 is dismissed). The sum of the mole fractions of the 12 species represents more than 0.9975. The toxicity properties of molecules are also included in Table 1.

Table 1. Mole fractions and toxicity of the combustion products from an ethanol pool fire

Products	Mole fractions	Safety
Carbon monoxide (CO)	0.16508	Flammable, toxic gas
Hydrogen (H_2)	0.16321	Extremely explosive and flammable gas
Water (H_2O)	1.54 E-01	No toxicity
Methane (CH_4)	3.94 E-02	Highly flammable gas, simple asphyxiant
Carbon dioxide (CO_2)	2.27 E-02	Asphyxiant, not toxic gas
Acetylene (C_2H_2)	1.70 E-02	Flammable gas
Ethylene (C_2H_4)	1.19 E-02	Flammable gas
Oxygen (O_2)	2.77 E-03	May cause or intensify fire
Benzene (C_6H_6)	6.59 E-04	Flammable, toxic gas
Ethane (C_2H_6)	4.14 E-04	Highly flammable gas, simple asphyxiant
Ethanol (C_2H_6O)	3.38 E-04	Highly flammable
Toluene (C_7H_8)	3.16 E-04	Flammable, toxic gas
1-butene (C_4H_8)	1.67 E-04	Flammable gas, simple asphyxiant, toxic.

ATMOSPHERIC DATA

The mesoscale atmospheric flow model WRF is used for atmospheric conditions at 15th of each month for the year 2012 (Skamarock et al. 2008) for the Bourges area using the Research Data Archive at the National Center for Atmospheric Research[1]. The following figures show diurnal and nocturnal variations of the temperature and wind velocity. Information on the average orientation of the dominant wind is also available from these data bases.
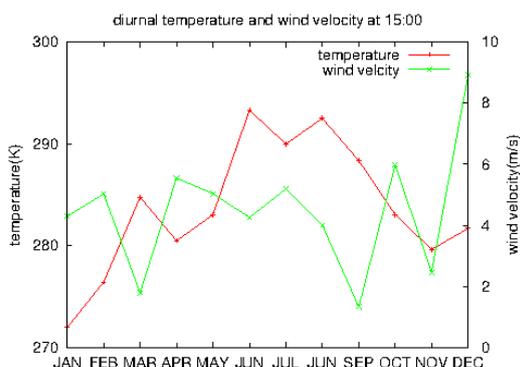

Figure 1. Diurnal temperature and wind velocity (10 m height) at 15th of each month for 2012

Figure 2. Nocturnal temperature and wind velocity (10 m height) at 15th of each month for 2012

DECAY RATES:

The products of ethanol combustion have been determined and their concentration computed. Their atmospheric degradation rates are necessary for modelling their atmospheric dispersion. The major atmospheric removal or degradation mechanism is the photochemical oxidation by hydroxyl (OH) radicals (NO_3 radicals and ozone reactions should also be considered for 1-butene). In order to estimate the atmospheric lifetime of a compound, the rate coefficient for the reaction with OH radicals and the atmospheric OH concentration is needed. The Arrhenius expressions for the rate coefficients of major combustion products of ethanol are well known. IUPAC (Derwent) has produced a chemical kinetic database where rates coefficients for a large number of reactions are proposed with their temperature range and data sources. From these expressions the rate coefficients for day and night temperatures have been calculated for emission products. Degradation rates of fast decaying species are shown on Figures 3-4 (Atkinson et al., 2006 and iupac-kinetic.ch.cam.ac.uk).
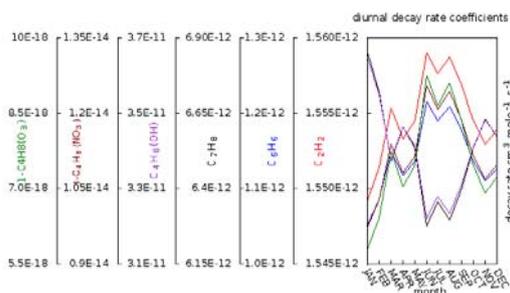

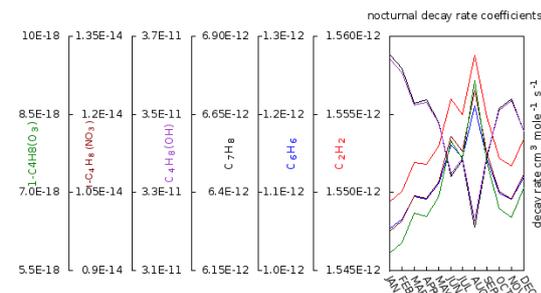Figure 3. Diurnal decay rates (cm^3 molecule^{-1} s^{-1}) for 15th of each month in 2012.

Figure 4. Nocturnal decay rates (cm^3 molecule^{-1} s^{-1}) for 15th of each month in 2012.

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[1] National Centers for Environmental Prediction, National Weather Service, NOAA, U.S. Department of Commerce. NCEP FNL Operational Model Global Tropospheric Analyses. http://rda.ucar.edu/datasets/ds083.2. Accessed§ 10 March 2013.

The atmospheric lifetimes of these compounds are estimated using the following expression:

$$\tau_{OH} = \frac{1}{\left(k_{OH} \cdot c_{OH}\right)}$$ (2)

where k_{OH} is the bimolecular rate constants for the reaction of OH radicals with the compounds and c_{OH} is the OH concentration that is taken as 2×10^6 and 0.5×10^6 (molecules/cm^3) during daytime and night time, respectively (Lu & Khalil, 1992). In the case of 1-butene, it is necessary to use the following expression:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{OH}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O3}}$$ (3)

where $c_{NO3} = 0\text{-}5\times10^8$ (molecules/cm^3) and $c_{O3} = 1\times10^{12}\text{-}2\times10^{11}$ (molecules/cm^3) during daytime and night time, respectively (Geyer, 2000 and Pudasainee et al., 2006). We have chosen 1-butene which has the shortest lifetime equal to 210 minutes during daytime and 687 minutes at night for preliminary simulations. We have also performed some computations with toluene which is a toxic compound and released in higher molar fractions but more stable with its shortest lifetime equal to 1200 min.

NUMERICAL SIMULATIONS AND PRELIMINARY DISPERSION RESULTS

Representative simulation results are shown in Figures 5 to 7 for computed dispersion contours for 1-butene and toluene over an area of 2160 m x 1800 m located at 47.08 N, 2.31E coordinates. The accident scenario considered is an ethanol pool fire of 100 m^2 area active for 1 hour. Additional results will be presented at the conference in order to discuss the detailed effects of atmospheric chemistry on dispersion models.
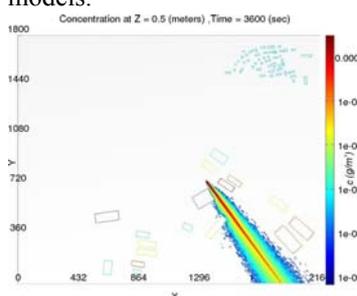

Figure 5. QUIC dispersion model result of 1-butenne dispersion for September 15th 2012 night.
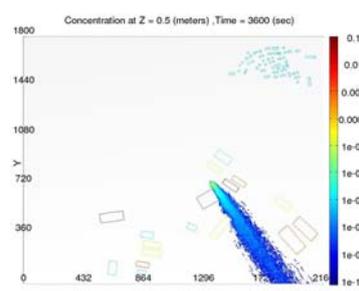
Figure 6. QUIC dispersion model result of toluene dispersion for September 15th 2012 night.
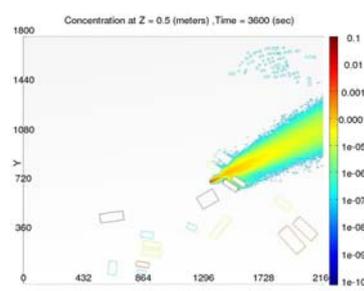
Figure 7. QUIC dispersion model result of toluene dispersion for June 15th 2012 day.

CONCLUSIONS

QUIC atmospheric dispersion modeling system has been successfully used to estimate the dispersion characteristics of an ethanol pool fire over an urban area with the inclusion of atmospheric chemistry models. It is observed that the knowledge of the wind field is of crucial importance for the correct evaluation of the dispersion parameters. The importance of the chemical species atmospheric degradation rates depends on the size of the considered area and the degradation lifetimes. This preliminary study will be extended to real case accidents where several release scenarios will be considered for the specific compounds stored in the investigated industrial sites.

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