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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INTRODUCTION

Prompt estimation of the atmospheric dispersion characteristics of hazardous materials following a release over an industrial site is of crucial importance for the emergency responders. Quick, yet accurate predictions of the contaminated area are required.

parameters:

- the real time wind field
- building topography
- composition-decay characteristics of the initially emitted species.

The 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

The location is an industrial site near the city of Bourges in France.

The release scenario is a pool fire of ethanol of 100 m^2 area.

The duration of release is taken equal to 1 hour.

QUIC (Pardyjak and Brown 2001) atmospheric dispersion modeling system is used.

CHEMICAL KINETICS OF AN ETHANOL POOL FIRE

parameters:

- equivalence ratio of 4
- pressure is 1 atm.
- the temperature of the flame is 1400K (Weckman and Strong)

Thomas empirical correlation (Rew et. al. 1997) gives the size of the reaction zone as:

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

- L is the flame height, is computed to be 0.08 m for a 0.073 m^2 pool
- 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)
- m' the mass burning rate of fuel is taken to be 0.020 kg.m^{-2}.s^{-1} for ethanol.

CHEMKIN-PSR (Glarborg et al. 2011) model with Dagaut (1992) mechanism used for kinetic simulations (Table).

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 (Figure 1).

DECAY RATES

The atmospheric degradation rates of the products of ethanol fire are necessary for modelling their atmospheric dispersion.

The photochemical oxidation rate coefficients for the reaction with OH radicals (and NO_3 radicals and ozone reactions for 1-butene) are taken from IUPAC database.

The atmospheric lifetimes of the released compounds are given by

$$\tau_{OH} = 1/(k_{OH} \cdot c_{OH}) \quad (2)$$

- k_{OH} are the bimolecular rate constants for the reaction of OH radicals with the compounds
- c_{OH} is the OH concentration that is taken as 2x10^6 and 0.5x10^6 (molecules/cm^3) during daytime and night time, respectively (Lu & Khalil, 1992).

In the case of 1-butene:

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

where c_{NO3} = 0-5x10^8 (molecules/cm^3) and c_{O3} = 1x10^{12}-2x10^{11} (molecules/cm^3) during daytime and night time, respectively (Geyer 2000; Pudasainee et al., 2006).

1-butene has the shortest lifetime: 210 minutes (daytime).

Toluene is more stable with its shortest lifetime equal to 1200 min.

Products	Mole fractions	Safety
Carbon monoxide (CO)	0.16508	Flammable, toxic gas
Hydrogen (H2)	0.16321	Extremely explosive and flammable gas
Water (H2O)	1.54 E-01	No toxicity
Methane (CH4)	3.94 E-02	Highly flammable gas, simple asphyxiant
Carbon dioxide (CO2)	2.27 E-02	Asphyxiant, not toxic gas
Acetylene (C2H2)	1.70 E-02	Flammable gas
Ethylene (C2H4)	1.19 E-02	Flammable gas
Oxygen (O2)	2.77 E-03	May cause or intensify fire
Benzene (C6H6)	6.59 E-04	Flammable, toxic gas
Ethane (C2H6)	4.14 E-04	Highly flammable gas, simple asphyxiant
Ethanol (C2H6O)	3.38 E-04	Highly flammable
Toluene (C7H8)	3.16 E-04	Flammable, toxic gas
1-butene (C4H8)	1.67 E-04	Flammable gas, simple asphyxiant, toxic.

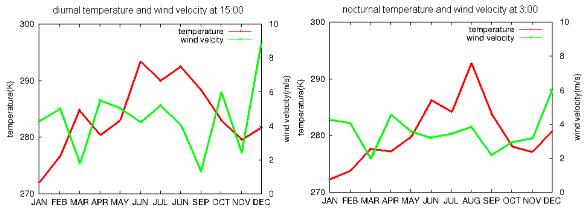

Figure 1. Diurnal and Nocturnal temperature and wind velocity (10 m height) at 15th of each month for 2012.

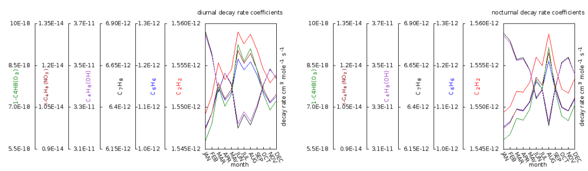

Figure 2. Diurnal and Nocturnal decay rates (cm3 molecule-1 s-1) for 15th of each month in 2012.

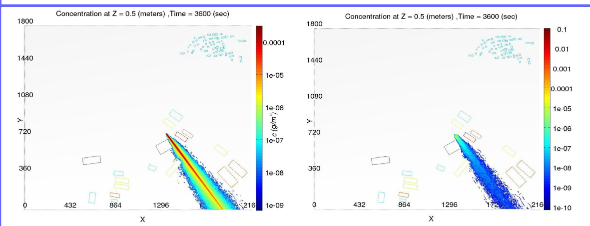

Figure 3. QUIC dispersion model results of 1-butene (left) and toluene (right) dispersion (September 15th 2012 night).

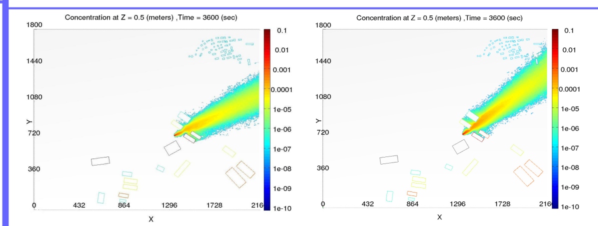

Figure 4. QUIC dispersion model results of 1toluene dispersion (June 15th 2012 day (left) and night (right).

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
- 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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