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Incorporation of Chemical Reactions into Building-scale Flow

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INCORPORATION OF CHEMICAL REACTIONS INTO BUILDING-SCALE FLOW

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6.3 INCORPORATION OF CHEMICAL REACTIONS INTO BUILDING-SCALE FLOW

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1. INTRODUCTION

Many hazardous atmospheric releases involve chemical reactions that occur within a few kilometers of the source. Reactions with commonly occurring atmospheric compounds such as the OH radical, can transform and potentially neutralize original release compounds. Especially in these cases, accurately resolving flow around nearby structures and over surrounding topography can be critical to correctly predicting material dispersion, and thus, the extent of any hazard.

2. PROGRAM COMPONENTS

The finite element computational fluid dynamics (CFD) code FEM3MP (Chan and Stevens, 2000) runs with a horizontal domain size on the order of kilometers, a maximum grid resolution on the order of one meter, and a time step on the order of one second. Individual buildings within the domain are resolved with no-slip boundary conditions. Winds with around 0.5 – 5 m/sec at building level have transit times across the computational domain around an hour or two. The code solves for a steady or time-dependent velocity field, depending on the use of a RANS or LES turbulence model. These velocity fields advect passive tracers as continuous scalars. (Humphreys, *et al.*, 2003)

To track chemical reactions among these passive tracers, we incorporated into the code the chemical reaction solver SMV Gear II (Jacobson, 1999). This solver is called at every time step in alternation with the velocity solver, evolving the chemical composition at each grid point with no reference to neighboring points.

3. PHYSICAL CONSIDERATIONS

Chemical reactions relevant to flows within this computational system must thus occur on timescales between one second and a couple hours. Reactions occurring faster than one second are combined with slower reactions, while reactions taking longer than a couple hours are omitted. Reactions with only minor product pathways are also omitted. While photolytic decay is easily included in the simulation, rates are highly dependent on temporal variations, e.g., cloud cover, and may need to be modified for each situation.

No changes have been made at present to link the reactions and the energy equation, i.e., reactions neither absorb heat from nor inject heat into the flow. This is a reasonable assumption for the diffuse, non-energetic reactions typical of the atmosphere.

4. ASSEMBLY AND TESTING

A set of reactions and reaction constants in a text file is automatically processed to produce Fortran program files encoding the chemical mechanism. This processing is done by scripts written by Peter Connell at LLNL (Dickinson, 1976). (By “mechanism”, I refer to a set of interconnected reactions and reaction rates for them.) These are included in the code during compilation. This fixes the mechanism within the executable program, but means that new mechanisms can be implemented with no changes to the rest of the code. Mechanisms generated so far model the decay of compounds relevant to the production or release of chemical weapons, but applications to industrial compounds or air quality issues are also being investigated.

Using a trial mechanism for the decay of dimethyl ether (based on Good, 2000), the SMV Gear II interface subroutine produced the same results as a separate “box” (one-dimensional) reaction model. These results were again duplicated within the joint FEM3MP / SMV Gear II code in a domain in which all cells were identical and there was no velocity of diffusion. Given the constraints on the mechanism and the validation of the CFD and chemistry solvers separately, we conclude that the joint code is accurate and valid. Any references to data of the chemical and spatial evolution of an atmospheric release would be most welcome.

5. DEMONSTRATIONS

Simulations of reacting plumes with different chemical mechanisms reveal features relevant to hazard assessment in an urban environment. The ground of the image in Figure 1 is colored by the (log of the) concentration of the initial release material. Note the entrainment of the plume in

the wake of the tower in front of the source. The 3D gray isoconcentration represents one of the reaction products. The extent of its maximum concentration area is much less than that of the main plume due to a moderate reaction rate and the spread of the main plume due to obstacles in the flow. Faster reactions could significantly limit the spread of the main plume.

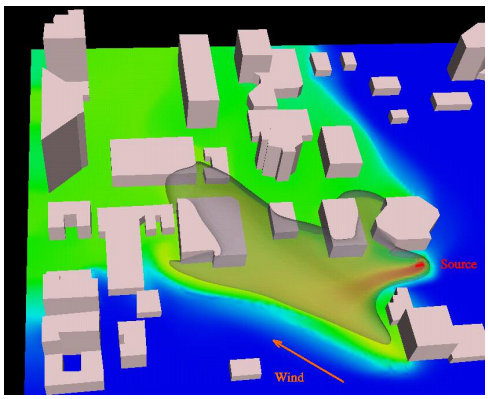

Fig. 1 In this reacting plume, the ground is colored by the concentration of the initial release material. The gray isosurface is that of a reaction product.

Plumes of reaction products have features not shared by the main plume. As seen in Figure 2, the maximum of the product plume can be separated from the source.

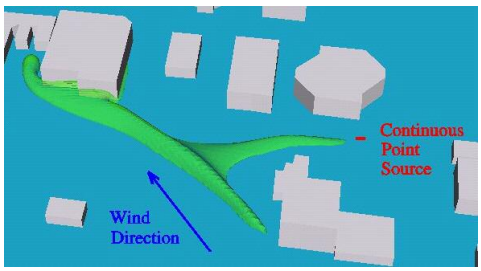

Fig. 2 This isosurface of a breakdown product is displaced from the main plume source.

In addition, product maximums can be noncontiguous, tending to form in regions of slower-moving air. At the center of Figure 3, we see a product maximum in the wake to the side of a building.

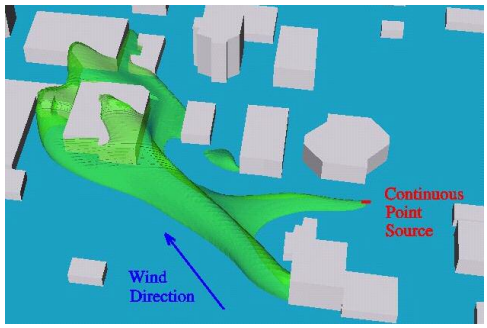

Fig. 3 An isolated local maximum of reaction product concentration forms in the recirculation region on the side of a building.

Solving a mechanism with thirteen species and ten reactions increased the computational costs of a time step by about one third over advection and diffusion of thirteen species without reactions. We estimate that solving for a velocity field and chemically reacting species dispersed within it would take about twice as much time as solving for the velocity field alone.

6. CONCLUSIONS

Accurate prediction of material dispersion around complex geometries near the source of an atmospheric release requires high-resolution computation. Further complications arise if the compounds released undergo chemical reactions which could alter the extent of the main plume. The reaction products form dispersion patterns separate from, and often more complicated than, the original plume.

Directions for future work include expanding the library of chemical reaction mechanisms, adding capabilities for aqueous and heterogeneous reactions, and integrating this model within larger-scale models. We plan that the larger-scale models will provide meteorological and chemical boundary conditions, and that this model could provide a source term in larger-scale models, both for momentum and for dispersed compounds.

7. REFERENCES

Chan, S, and D. Stevens, 2000: Validation of two CFD Urban Dispersion Models Using High-Resolution Wind Tunnel Data. Third Int. Sym. on Environ. Hydraulics, Arizona State University, Tempe, AZ, Dec 5-8, 2001, 107.

Dickinson, R. P., R. J. Gelinas, and R. L. Tarp, 1976: A General Kinetics Preprocessor Program. Lawrence Livermore National Laboratory Preprint, UCRL 78809.

Good, D. A., and J. S. Francisco, 2000: Tropospheric Oxidation Mechanism of Dimethyl Ether and Methyl Formate. J. Phys. Chem. A, 104 (6), 1171-1185.

Humphreys, T., S. Chan, and R. Lee, 2003: Validation of CFD Near-building Dispersion with Urban 2000 Data for Steady and Time-dependent Boundary Conditions. Seventh Annual GMU Transport and Dispersion Modeling Workshop, Fairfax, VA, June 17-19, 2003.

Jacobson, M. Z., 1999: Improvement of SMVGear II on Vector and Scalar Machines Through Absolute Error Tolerance Control. *Atmos. Environ.*, 32, 791-796.

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