LLNL-TR-401274

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Final Report for LDRD Project 05-ERD-050: "Developing a Reactive Chemistry Capability for the NARAC Operational Model (LODI)"

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February 12, 2008

Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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February 7, 2008

Summary

In support of the National Security efforts of LLNL, this project addressed the existing imbalance between dispersion and chemical capabilities of LODI (Lagrangian Operational Dispersion Integrator - the NARAC operational dispersion model). We have demonstrated potentially large effects of atmospheric chemistry on the impact of chemical releases (*e.g.*, industrial chemicals and nerve agents). Prior to our work, LODI could only handle chains of first-order losses (exponential decays) that were independent of time and space, limiting NARAC's capability to respond when reactive chemistry is important. We significantly upgraded the chemistry and aerosol capability of LODI to handle (1) arbitrary networks of chemical reactions, (2) mixing and reactions with ambient species, (3) evaporation and condensation of aerosols, and (4) heat liberated from chemical reactions and aerosol condensation (which can cause a cold and dense plume hugging the ground to rise into the atmosphere, then descend to the ground again as droplets). When this is made operational, it will significantly improve NARAC's ability to respond to terrorist attacks and industrial accidents that involve reactive chemistry, including many chemical agents and toxic industrial chemicals (TICS). As a dual-use, the resulting model also has the potential to be a state-of-the-art air-quality model.

Chemical releases are the most common type of airborne hazardous release and many operational applications involve such scenarios. The new capability we developed is therefore relevant to the needs of the Department of Energy (DOE), Department of Homeland Security (DHS) and Department of Defense (DoD).

Significance and relevance

This project directly supports the national security efforts of LLNL as one of the premier centers for atmospheric dispersion and effects. LLNL is expanding into an all-threats knowledge system and reachback support role for DHS, and chemical dispersion and fate is a key component within that capability. In addition, chemical fate can have an important role in understanding proliferation signatures, such as release of chemicals associated with the production of special nuclear materials and chemical and biological weapons. Finally, chemical fate can play a key role in pre-strike consequence evaluation of military targets and post-strike evaluation of health effects, such as the Gulf War Syndrome.

Discussion, Background, and Results.

Atmospheric chemistry can have a significant impact on chemical releases. The OH radical, which occurs naturally in the atmosphere, will chemically attack and oxidize most chemicals, including nerve agents. The loss can be dramatic, as illustrated in Figure 1 for a scenario in which an airplane sprays sarin (a nerve agent) near an urban area. Originally, LODI (the NARAC operational dispersion model) could only handle scenarios in which the loss was constant in time and space. However, OH can vary significantly in time and space, so we developed the capability under this project for arbitrary spatio-temporal variability of the first-order loss within the LODI model. We have also developed a parameterization to provide the maximum, minimum, and median OH concentration anywhere in the world for any season and any time of day (derived from the LLNL-IMPACT code, a state-of-the-art global 3D atmospheric chemistry & aerosol model designed to handle the complex global evolution of OH) as shown in figure 2 (left). This capability is fast and designed for use in an operational response mode by NARAC.

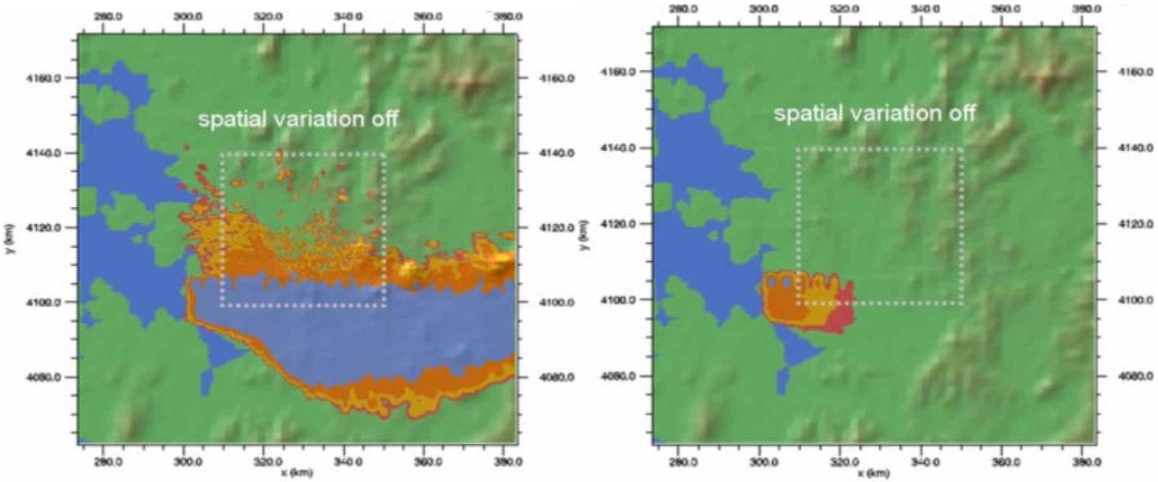

Figure 1: The panels show two scenarios involving an airplane spraying a tonne of Sarin along a 10km line at 300m altitude in a north-south line to the left of the bottom left hand corner of the marked square. Each panel shows colored contours of integrated sarin exposure at the surface (mg.min/m^3) superimposed on a map of the terrain, which includes lakes and mountains. The colored contours are where integrated exposures exceed values (in mg.min/m^3) of 10^{-1} (blue), 10^{-2} (orange), 10^{-3} (yellow), and 10^{-4} (red). The CDC "safe" level for the general public is $ECt_{50} = 1.4x10^{-3}$ mg.min/m^3 (approx. the yellow contour). The wind is primarily blowing from left to right. The simulations are for 10 hours. The domain is 100 km in each direction. The square is 40km across and represents a hypothetical city. The difference between the two panels shows the integrated sarin exposure resulting from the destruction of sarin caused by the naturally occurring OH radical. **Left:** Sarin exposure with no loss due to OH. **Right:** Sarin exposure with constant loss due to OH. In this scenario OH causes first-order loss of sarin with a half-life of 20 minutes, corresponding to a typical sunny summer day in an urban area.

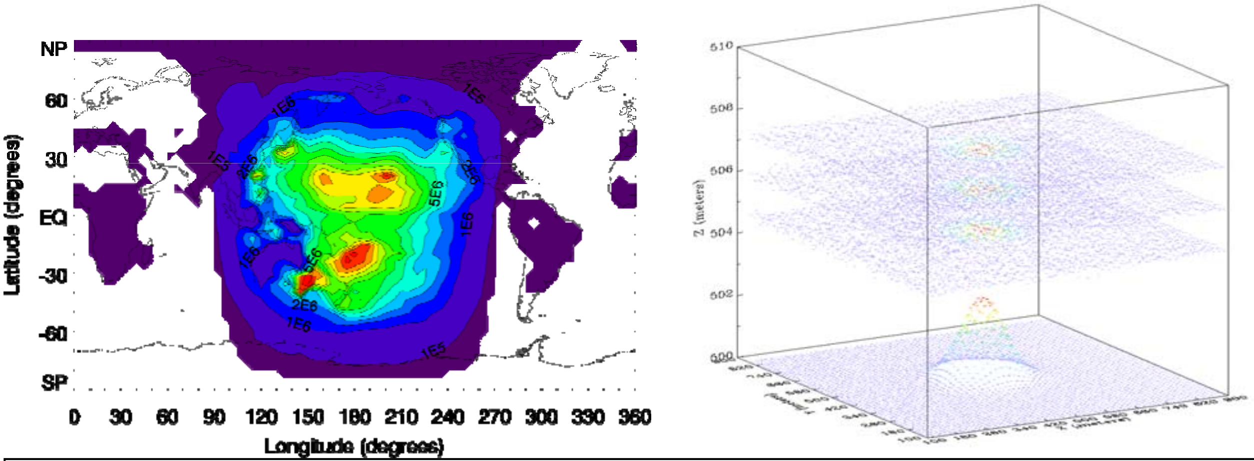

Figure 2. **Left:** The spatial distribution of maximum OH from our global parameterization for midnight GMT, March 15. **Right:** Representation of a chemical tracer with an initial Gaussian distribution using our semi-Lagrangian advection scheme after 1 second of integration. The upper 3 surfaces show the actual parcel distribution, and are color coded with concentration (red is high). The bottom surface shows the projection of the particles on to the ground, with the same color code, but with vertical displacement also representing concentration.

Unfortunately, the chemistry for many chemicals of concern is often more complicated than the first-order loss considered above. For example, chlorine (Cl_2) is a toxic industrial chemical (TIC) of current concern to the US Congress that is toxic, corrosive, abundant, and stored in large quantities. In the atmosphere, chlorine photolyzes and attacks ambient hydrocarbons to produce hydrochloric acid, which is also toxic but with very different properties (such as its solubility and acidity) that would be highly relevant to emergency responders. The exact chemistry is non-linear and complex, so using a first-order loss in this case would be totally inadequate. A full chemistry capability is also required for simulating local and regional air-quality, and simulating the breakdown sequence of chemicals in the atmosphere, which is of interest for detecting clandestine chemical factories.

The ability to solve the chemical reactions for these situations is already available in IMPACT, using a sophisticated GEAR solver (SMVGEAR II), which we will implement into LODI. However, solving the chemistry requires an Eulerian framework. Therefore, in order to facilitate a general chemistry capability within LODI, we have designed a semi-Lagrangian advection scheme that takes advantage of the existing Lagrangian advection capability of LODI, and naturally provides an Eulerian framework for chemistry, as well as providing an easy platform to handle *in situ* aerosol generation and re-evaporation/re-suspension of material deposited on the ground, and a more natural framework for inclusion of a dense gas simulation in the future.

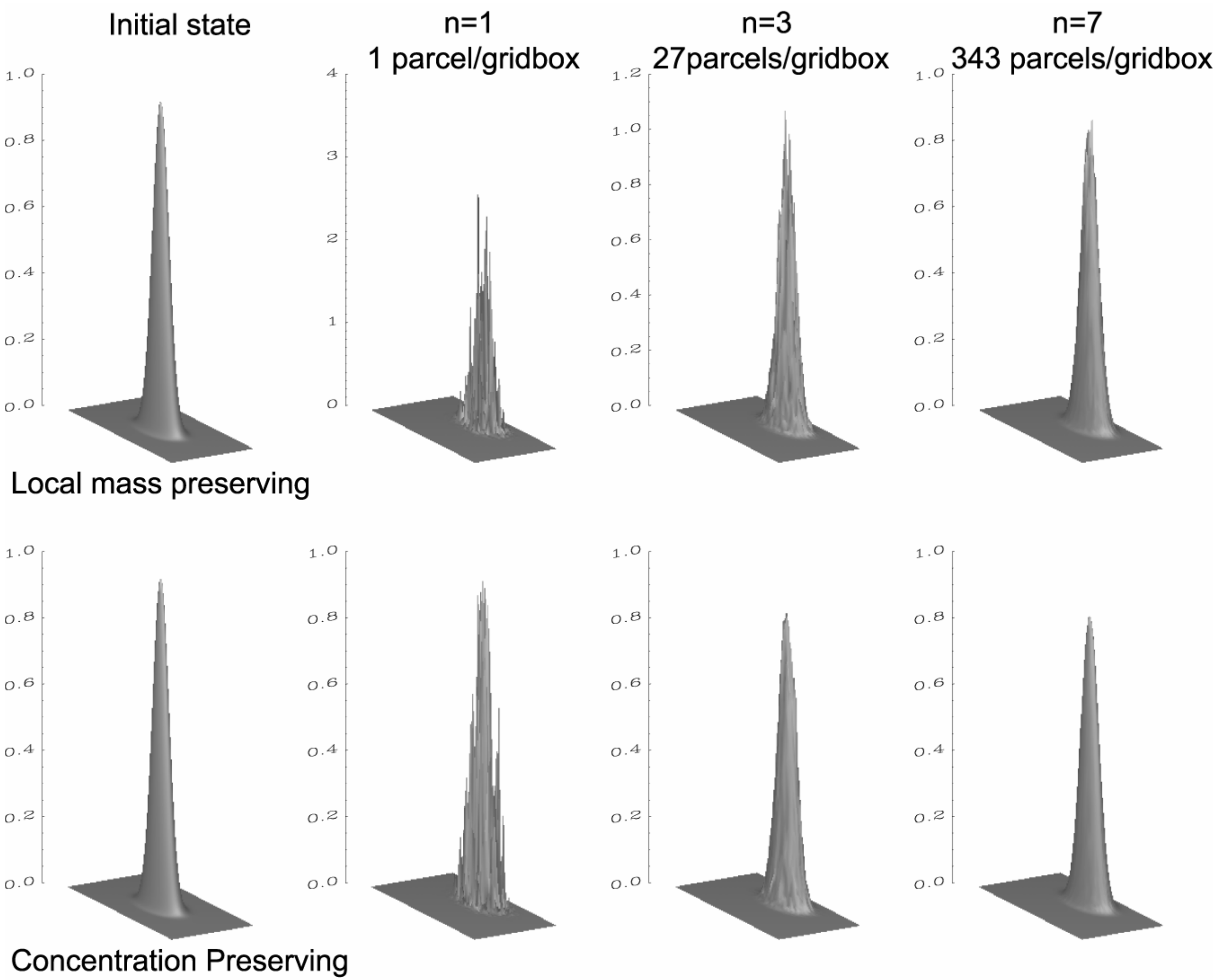

Figure 3. Advection of a horizontal Gaussian concentration distribution in a 3 minute simulation using our semi-Lagrangian advection scheme in LODI. The panels on the top show the resulting concentrations when using the local mass preserving option (total tracer mass in each gridbox divide by grid-box mass). The panels below show the resulting concentrations when using the concentration preserving option (total tracer mass in each gridbox divided by the airmass associated with the air parcels). The column on the left shows the initial distribution, while the other panels show the concentration state after 3 minutes when using n=1,3,7 (ie 1, 27, and 343 Lagrangian parcels per grid box). Note that the distribution for n=3 with the concentration preserving mode is as good as the distribution for n=7 with the local mass preserving mode, yet is an order of magnitude faster. The Eulerian grid is 80x80x80 gridcells.

The initial implementation of our semi-Lagrangian advection scheme is illustrated in figures 2 (right), 3, and 4. Figure 2 (right) shows the distribution of Lagrangian parcels representing a Gaussian tracer distribution. Note that the Lagrangian parcels are uniformly distributed, but the tracer mass they carry is varying. We specify the number of Lagrangian parcels along one dimension of each Eulerian box by ‘n’, so that the number of parcels per box in a simulation is given by n^3. The effect of ‘n’ on the quality of the simulation is shown in figures 3 & 4. We used a real wind field, so the initial distribution should not be preserved exactly, but for this time scale it should not have evolved much. Clearly, as ‘n’ increases, the Gaussian distribution is better preserved during advection. However, it is also clear that using the concentration preserving formulation dramatically improves the result for a given ‘n’, which offers the opportunity for an order of magnitude saving of computational resources.

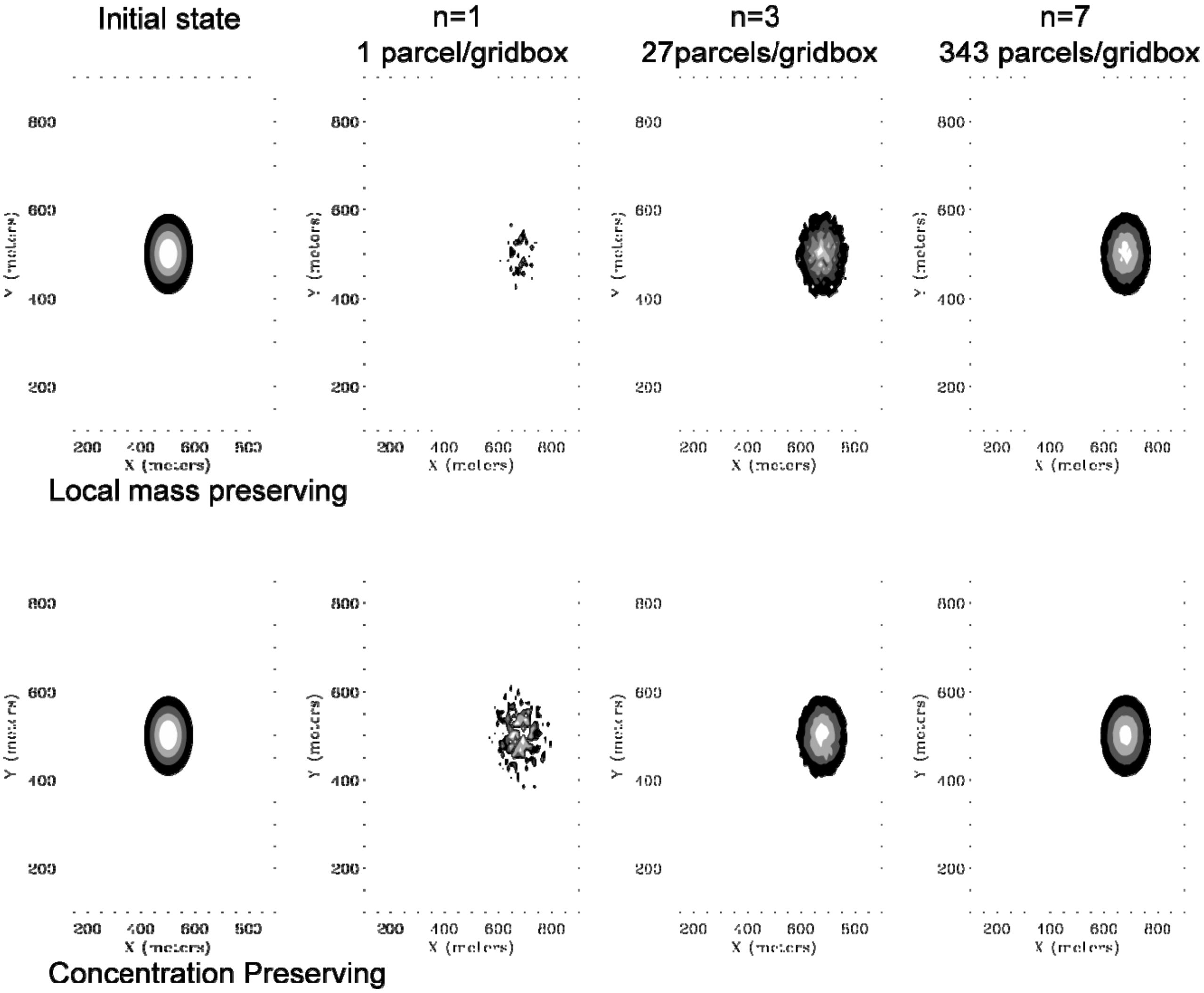

Figure 4. This is the identical to the result displayed in figure 3, but using contour plots instead of surface plots.

On top of this semi-Lagrangian capability we added a full reactive chemistry ODE solver (SMVGEAR II [2]), which we have used very successfully in our global atmospheric chemistry model (IMPACT [1]). The atmospheric chemistry is performed at every time-step, when the concentration has been transformed from the Lagrangian frame to the Eulerian frame. After the chemistry, the modified concentrations are mapped back to the Lagrangian particles.

As an example, we started with an initial Gaussian distribution of dimethyl-ether (DME, a chemical weapon surrogate) and ran it on an actual 3D LODI grid and windfield. We had 11 chemical species reacting and transporting in an 80x80x80 set of grid cells, with 4 million Lagrangian parcels.

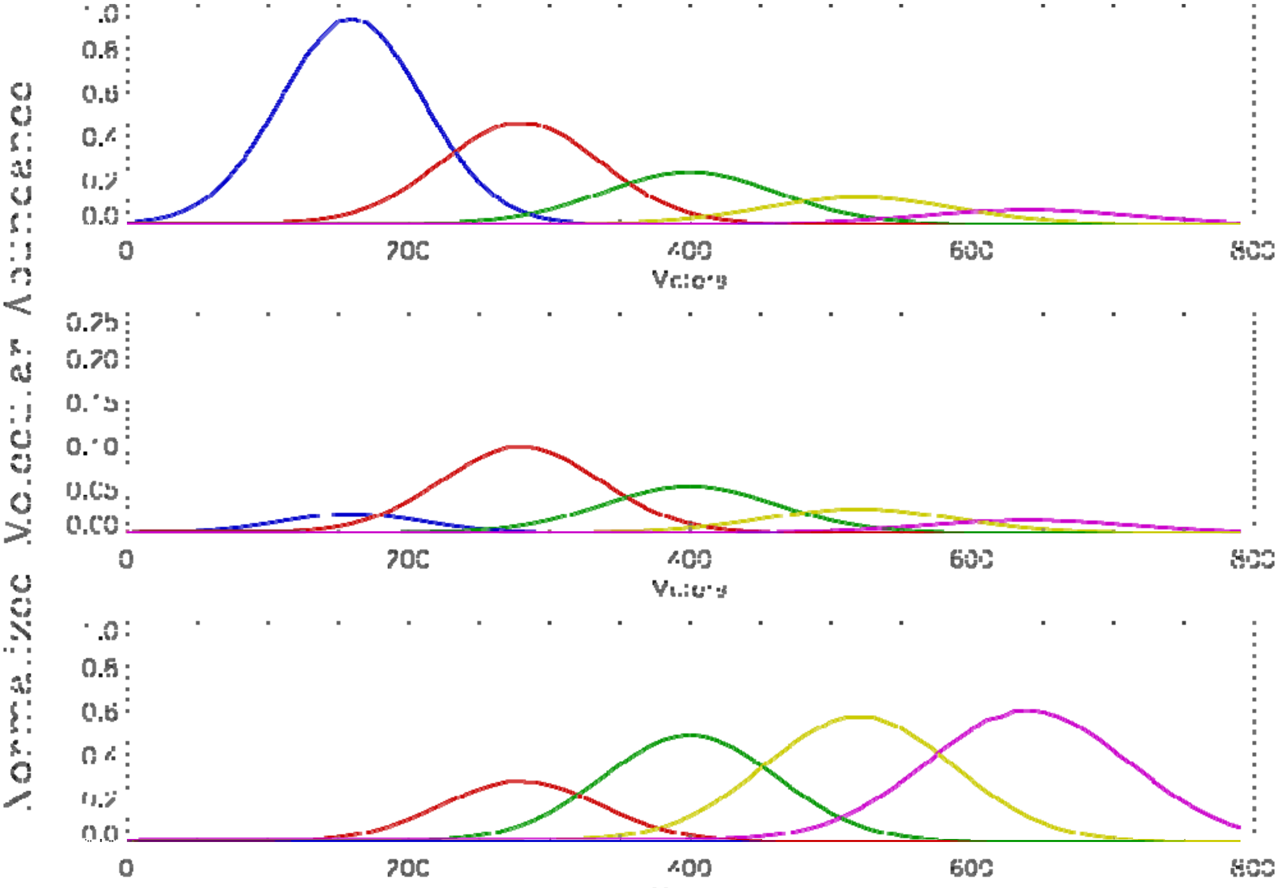

Figure 5. The effect of full chemistry on simulation of dimethyl ether (DME). The plots show abundance of DME (top), an intermediate decay product (middle), and carbon monoxide (a final product). The different colors are the distributions at different times. The wind is blowing from left to right, so the succession of peaks moving to the right shows the time progression. We calculated the full 3-D distribution, but this plot shows the abundance integrated over two dimensions (vertical and cross-wind) to make it easy to visualize.

In figure 5, the top plot is for DME, the middle plot is for one of the intermediate breakdown products, and the lower plot is for carbon monoxide (one of the final products). The full 3D distribution was simulated, but we integrated over two dimensions (vertical and cross-wind) to make it easy to visualize. The different colors are the distributions at different times. The wind is blowing from left to right, so the succession of peaks moving to the right shows the time progression. The story told is thus: the initial chemical gets destroyed, creating intermediate breakdown products that are then further destroyed to give the final species.

Note that there is some broadening of the plume spreading as it gets advected downwind, but that the main cause of changes in this scenario comes from the chemical destruction.

This simulation took about 10 minutes to run on 32 CPUs, and scales well with the number of CPUs.

In addition to DME, we have developed detailed chemical mechanisms for chlorine (Cl_2) and ozone (O_3). We also went further than our original plans and developed a detailed chemistry-aerosol mechanism for sulfur trioxide (which is given off by oleum) which has the added complication that the rate of condensation of aerosol is a function of itself (because the heat liberated from condensation affects the rate of condensation). The heat we calculate from the chemical reactions and aerosol formation for sulfur trioxide, can be sufficient to cause a cold and dense plume hugging the ground to rise into the atmosphere, then descend to the ground again as droplets.

A detailed description of that capability is provided in "*An Aerosol Condensation Model for Sulfur Trioxide*" [3].

In order to ensure that the capabilities we developed would truly benefit NARAC and its mission, we spent a lot of time interacting with the NARAC development team to educate them on the principles and capabilities we developed, and facilitate migration of our improvements into the main LODI code base, which started during the final year of the project and is ongoing.

Summary of Results

1. Implemented the capability for spatially and temporally varying first-order chemical losses in LODI (to handle the far field effects for species such as nerve-agents).
2. Developed a parameterization and look-up table to instantly provide the climatological maximum, minimum, and median OH concentration for any location on Earth, for any season and time-of-day (for operational response use).
3. Developed a semi-Lagrangian advection scheme that will integrate smoothly with, and complement, the existing Lagrangian advection capability of LODI, and will provide the platform for several new capabilities:
    a. A full atmospheric chemistry capability,
    b. *In situ* production of aerosols,
    c. Re-evaporation/re-suspension of material deposited on the ground.
4. Implemented a Gear general chemistry ODE solver (SMVGEAR II) which has a long history of use for solving atmospheric chemistry equations [1,2].
5. Developed detailed chemical mechanisms for dimethyl-ether (DME), chlorine (Cl_2), and ozone (O_3),
6. Developed a detailed chemical and aerosol mechanism for sulfur-trioxide (SO_3, released by oleum), which includes the relevant hydration reactions, aerosol growth, and heat liberation processes (details in the companion report [3]).
7. We improved the multi-processor scaling and memory usage of LODI in order to expedite reactive chemistry simulations for emergency response use.
8. We interacted with the NARAC development team to educate them on the principles and capabilities we developed, and migration of our improvements into the main LODI code base has already started to occur.

Conclusion

We developed and implemented the capability to simulate arbitrary networks of chemical reactions within the LLNL/NARAC emergency response atmospheric dispersion model (LODI), so that it can handle the reactions relevant to nerve agents, chlorine, ozone, and the *in situ* creation of aerosols from species such as oleum (SO_3) and UF_6. We also went further than our original plans and developed the capability to calculate the heat generated from chemical reactions and aerosol formation, which can significantly affect plume behavior.

Auspices

This work was performed under the auspices of the U. S. Department of Energy (DOE) by the University of California, Lawrence Livermore National Laboratory (LLNL) under Contract No. W-7405-Eng-48. The project (05-ERD-050) was funded by the Laboratory Directed Research and Development Program at LLNL.

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