

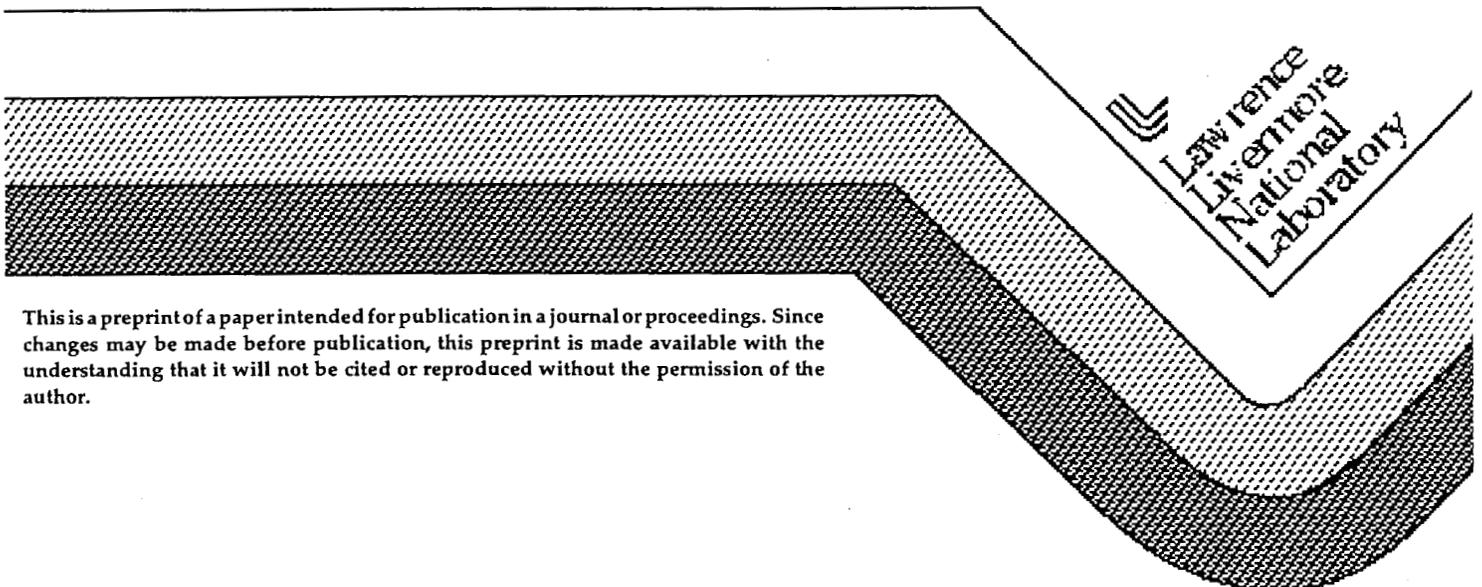
# The Challenge of Emergency Response Dispersion Models on the Meso-Gamma Urban Scale: A Case Study of the July 26, 1993 Oleum Tank Car Spill in Richmond California

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**THE CHALLENGE OF EMERGENCY RESPONSE DISPERSION MODELS  
ON THE MESO-GAMMA URBAN SCALE:  
A CASE STUDY OF THE JULY 26, 1993  
OLEUM TANK CAR SPILL IN RICHMOND, CALIFORNIA**

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## SUMMARY

On July 26, 1993 the Atmospheric Release Advisory Capability (ARAC) at Lawrence Livermore National Laboratory (LLNL)<sup>1</sup> responded to a major rail car spill of oleum in Richmond, Calif. The 3-D MATHEW/ADPIC numerical dispersion model was initialized by real-time meteorological data from Bay Area airports and the Bay Area Air Quality Management District (BAAQMD). This response provides a case study which illustrates the challenge of accurately locating the footprint from a major toxic chemical release in urban areas where models depend on sparse real-time meteorological observations.

## I. INTRODUCTION

Atmospheric modeling of accidental toxic chemical releases requires accurate simulation of wind flows on the 1 to 25 km (meso- $\gamma$ ) scale. Complex meteorological fields have been a challenge to real-time emergency response models for decades especially when wind observations are sparse. The Gaussian model is a reasonable tool for the first few kilometers if the terrain is relatively flat, the wind flow is simple (no vertical structure), and meteorological data are available at the source. Most other situations demand three-dimensional models. Three-dimensional diagnostic wind models depend on available meteorological observations which are subsequently adjusted by mass conservation to create a wind field over the terrain. Even in urban areas with multiple meteorological stations, 3-D diagnostic models may suffer from a lack of sufficient real-time observations. Deterministic models are stressed even more during variable low wind speed or stable atmospheric conditions, especially if the release is denser-than-air. Furthermore, typical wind direction measurement errors of 5 to 10 degrees extrapolated 10 or 20 km cause significant dislocation of downwind concentrations.

## II. REAL-TIME RESPONSE

On the morning of July 26, 1993, oleum was accidentally released from a railroad tank car in

Richmond, California. Midway through the 3-1/2 hour release, state and local agencies requested real-time modeling from ARAC. With approval from the U.S. Department of Energy, ARAC responded to the accident under an Agreement in Principle with the State of California. Air concentration plots describing the location and progress of the toxic cloud to the agencies managing the response. The primary protective action for the public was to shelter in place. Highways, rail lines and public transportation were blocked. The incident was significant enough that over 24,000 people sought medical attention within the week following the release.

### A. Modeling System and Grid

ARAC employs MATHEW (Mass-Adjusted Three-Dimensional Wind field), a diagnostic Eulerian wind field code<sup>2</sup>, and ADPIC (Atmospheric Dispersion by Particle-In-Cell), a hybrid Eulerian-Lagrangian dispersion model<sup>3</sup>, to simulate mesoscale dispersion. Figure 1 shows the model grid and terrain which was built from a worldwide on-line data base for the Richmond response. The domain represents the northeast corner of the San Francisco Bay Area.

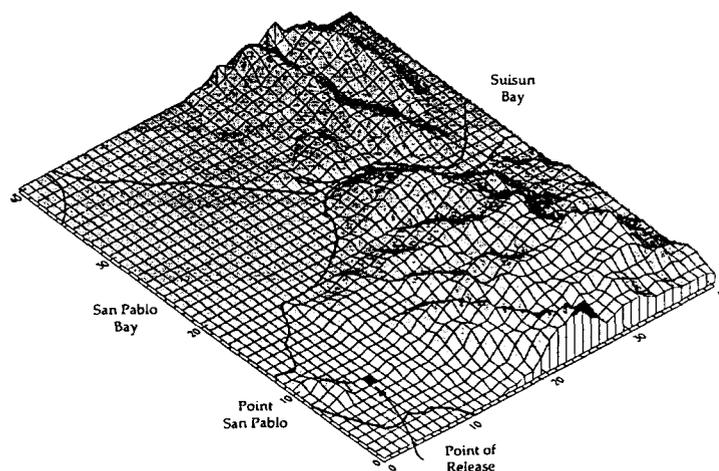


Fig. 1. Perspective view of model grid and terrain

Table 1 lists the grid dimensions that were selected to contain the expected extent of the hazard during the spill.

Table 1. MODEL GRID DIMENSIONS

	North-South × East-West × Vertical
Number of Cells	40 × 40 × 14
Cell Size	1.0 km × 1.0 km × 50 m
Grid Domain	40 km × 40 km × 700 m

### B. Source Term

At about 7:15 a.m. PDT (1415 UTC) on July 26, 1993, while a railroad tank car at the General Chemical Corporation facility in Richmond was being heated during a transfer operation, the pressure relief valve failed to hold. News reports indicated that the  $10^4$ -kg (100-ton) tank car was loaded with  $5 \times 10^4$  liters (13,000 gal) of 35 grade (35%) oleum ( $H_2S_2O_7$ ). Sulfur trioxide ( $SO_3$ ) gas was released to the atmosphere under high pressure and temperature until the tank was capped at about 11:00 a.m. After exiting the 7.5-cm (3-in.) diameter valve opening, the heated oleum rapidly expanded and cooled quickly condensing into a sulfuric acid liquid aerosol in the moist marine environment. For modeling, the sulfuric acid mist was assumed to have a 1- $\mu$ m median diameter and 1 cm/s deposition velocity. Initially the ARAC team was given a worst-case estimate that the full tank contents could be released over 1.5 hr (16,400 g/s). Later the source rate was revised to half the tank car over 3.75 hr (3,276 g/s).

### C. Meteorological Conditions

Figure 2 shows the 1200 UTC (5:00 a.m. PDT or one hour before sunrise) rawinsonde sounding taken at Oakland Airport about 23 km south of the accident. The sounding provided the only data to initialize the vertical

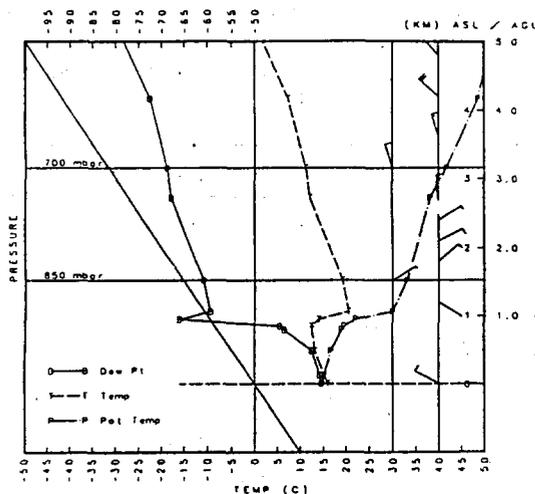


Fig. 2. Oakland upper air sounding at 5:00 a.m. PDT on July 26, 1993

profile in the wind field. It indicated a 750-m deep mixed layer capped by a strong subsidence inversion. It also showed easterly flows 1-3 km above sea level due to higher pressure over northwestern Nevada. The sulfuric acid mist was not observed to penetrate the inversion into this layer of elevated off-shore flow.

Figure 3 indicates a weak (3-5 m/s) westerly surface flow into the Bay Area existed at 7:00 a.m. PDT (1400 UTC). This was driven by a weak on-shore pressure gradient. Shallow patchy stratus covered most of the northern Bay Area that morning. The marine layer was cool and moist with surface temperatures ranging from 16 °C (60°F) at 7:15 a.m. to 20 °C (68°F) by 11:00 a.m. and relative humidities decreasing from 92 to 78% over the same period.

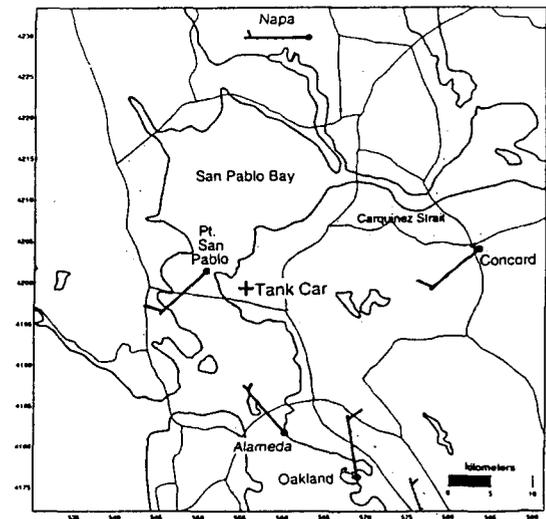


Fig. 3. Surface wind barbs from northern Bay Area at 7:15 a.m. PDT on July 26, 1993

By the end of the release, the stratus had evaporated and moderate heating of the interior Central Valley generated a 6 m/s sea breeze flow throughout the Bay Area. Consequently, the winds persisted from the southwest in the Richmond area during the spill.

### D. Wind Field Modeling

The proximity of meteorological stations to the release and cloud location plays a major role in how accurate a diagnostic model can determine the plume position. MATHEW surface layer cells are initialized by weighting the input station's wind vector by the inverse of the square of the distance from the station to the cell ( $1/r^2$ ). Figure 3 shows that the accident was situated between three airports--Napa 32 km to the north, Concord 26 km to the east, and Alameda Naval Air Station 17 km to the south. Interpolating between these three stations produced a wind direction from 280° at 7:00 a.m. when it was known the wind was actually from the southwest. Wind data from the airports alone were insufficient to reasonably determine the wind direction at the accident.

Fortunately ARAC was able to acquire in real time 15-minute average wind data from a Bay Area Air Quality Management District (BAAQMD) tower at Pt. San Pablo, about 5 km west of the accident. Figure 3 shows a 3 m/s wind from 221° at the start of the release at Pt. San Pablo. By 8:00 a.m., the wind shifted to and remaining between 200 and 211° for the rest of the release period. Without this tower data the diagnostic wind model would have been off by 60°. Beyond the source location, the plume position was determined by interpolating between hourly observations from Napa and Concord.

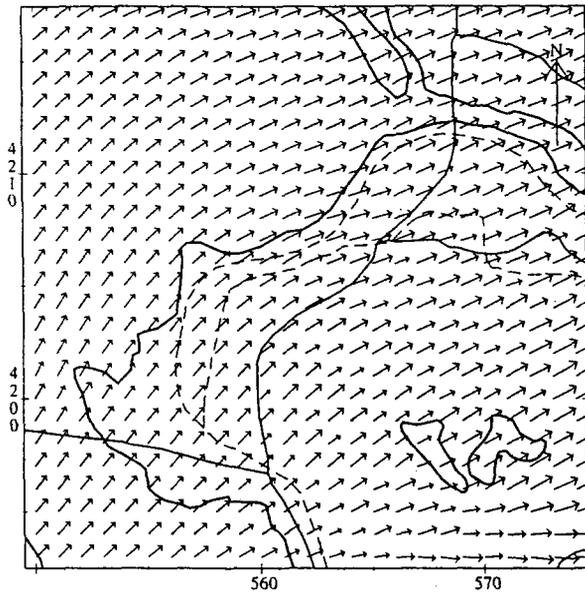


Fig. 4. Mass-adjusted wind field for 7:15 a.m. on July 26

### E. Dispersion Modeling

Diffusivities in ADPIC were derived from the standard deviation of wind direction (sigma theta) at the Pt. San Pablo tower. Neutral conditions existed for the first few hours with sigma thetas between 7.5 and 12.5°. After 10:00 a.m. the sigma theta was between 12.5 and 17.5° indicating a slightly unstable boundary layer.

ARAC produced the first set of plots for the worst-case full-tank-car release just as the release was ending. These were used by the California Office of Emergency Services and the California Department of Health Services to initially scope the magnitude of the potential health effects. Later in the afternoon ARAC used the half-tank-car source rate to refine the calculation. Figure 5 shows the hour-average air concentration for the second hour after the release began for the half-tank-car source rate. The highest two contours represent Emergency Response Planning Guidelines (ERPGs). The potentially life-threatening 30 mg/m<sup>3</sup> ERPG-3 contour extends 2 km from the source and ERPG-2 (potential for serious health effects) extends 3 km. The lowest two contours, 1.0 and 0.2 mg/m<sup>3</sup>, represent levels of significant and brief irritation especially by asthmatics.

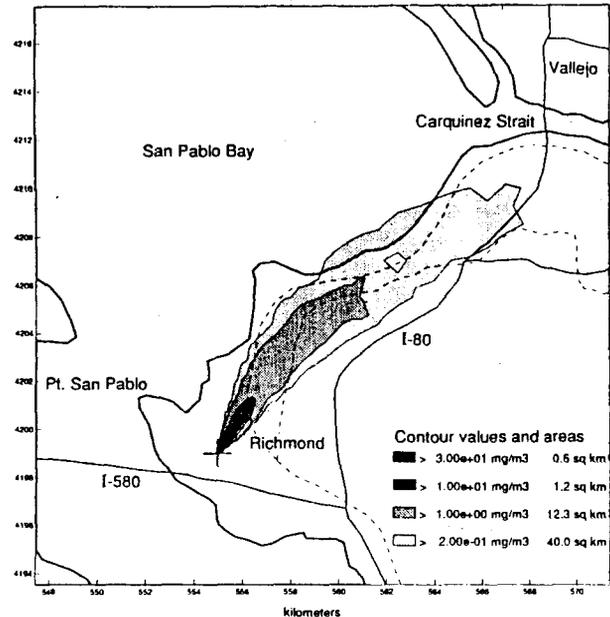


Fig. 5. Second-hour average H<sub>2</sub>SO<sub>4</sub> air concentration for half-tank car release rate

## III. POST-ACCIDENT ANALYSIS

For detailed health-effects studies, state and local agencies requested that ARAC remodel the accident after better source and meteorological data were collected.<sup>4</sup>

### A. Revised Source Term

Dip rod readings taken after the accident revealed that only a fraction of the potential SO<sub>3</sub> contained in the tank car was actually released to the atmosphere. Contra Costa County Health Services Department recommended using a total SO<sub>3</sub> release of 7258 kg (8 tons) for the final assessment. Instead of the steady source rate as was used in the response, time-varying release rate curves were manually generated assuming initial values of either 1500 g/s (6 tons/hr) for 45 min or 1000 g/s (4 ton/hr) and decreasing for the remainder of the 3.75-hr release.

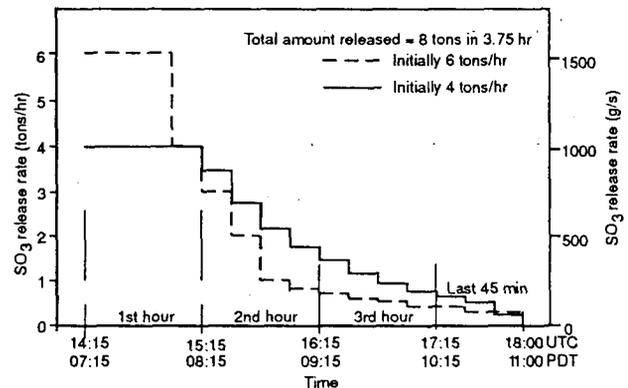


Fig 6. Revised source rates for post-accident analysis

### B. Revised Meteorological Data

Figure 7 shows the tower locations in the vicinity of the accident. The BAAQMD Pt. San Pablo tower which directed the initial plume trajectory during the response had an upwind fetch over the open cool Bay water. However, the air upwind of the accident traveled over the 100-m high ridge of Pt. San Pablo in an urban and industrialized area much more rugged than the open water. For the post-accident analysis, data was provided by Chevron 1.5 km north of the accident. Consequently, the post-accident analysis showed the air flow was initially slightly unstable instead of neutral and the 15-min average wind directions were up to 40° more clockwise than indicated at Pt. San Pablo. Figure 8 compares the wind directions and sigma thetas for the two tower nearest the tank car. The wind speeds were generally within 1 m/s of each other during the release period. They were 3-4 m/s at the beginning and about 6 m/s at the end of the release.

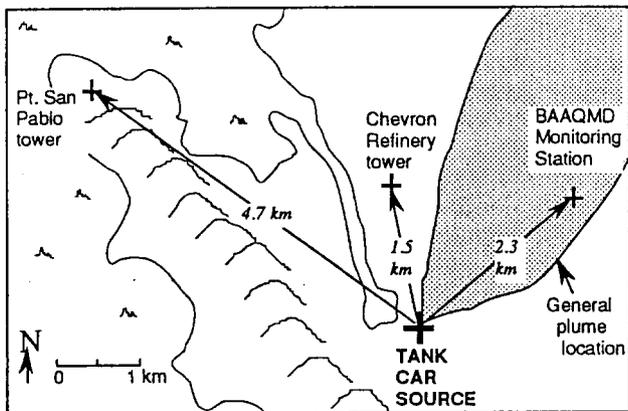


Fig. 7. Proximity of towers and monitoring station to source

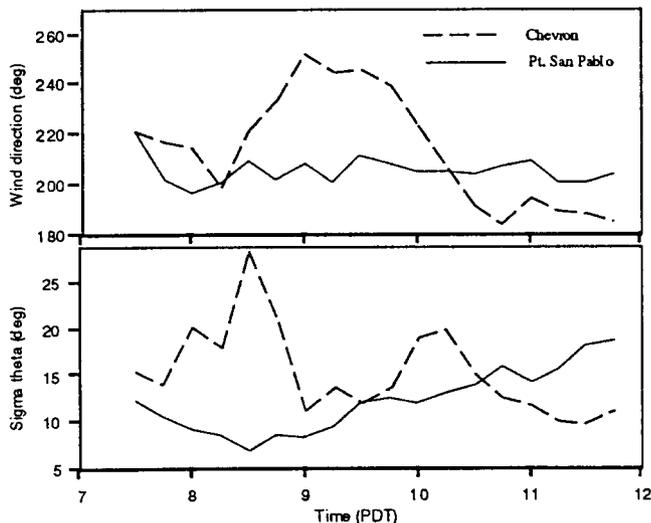


Fig. 8. Comparison of wind data from Chevron and Pt. San Pablo towers

### C. Final Modeling Results

Figure 9 shows the second hour (8:15-9:15 am PDT) average air concentration for the revised 8-ton release with the initial 6 ton/hr source rate. The contours near the source are rotated clockwise about 15 degrees when compared to the real-time response due to the influence from the nearby Chevron tower. Greater diffusion and the reduced source rate substantially reduced the areas of the 30, 10 and 1 mg/m<sup>3</sup> contours.

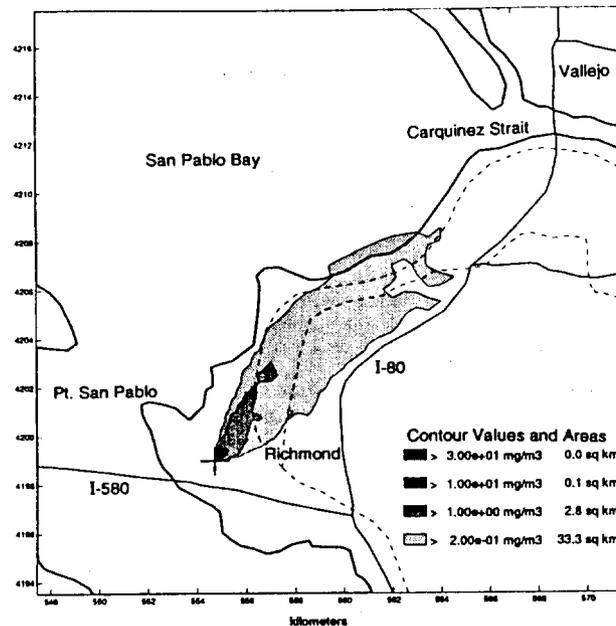


Fig. 9. Second-hour average H<sub>2</sub>SO<sub>4</sub> air concentration for final 8-ton source with 6-ton/hr initial release rate

### IV. MODEL COMPARISONS WITH MEASUREMENT

The BAAQMD took a single 3-hr average measurement of sulfuric acid on a high-volume sampler 2.3 km downwind on the east side of the plume (see Figure 7). Table 2 shows that each of the model results were within a factor of 2 of this value. Obviously a single measurement can only suggest which model run was the best. The initial real-time calculation which had neutral stability and a 1.5 hr long release did not have the correct source rate or time period. The refined real-time run had 20% of the initial release rate over 3.75 hr and overestimated the measurement by 77%. With the revised metadata the cloud experienced greater diffusion, more wind direction variability, and was rotated clockwise more toward the monitoring station from 8:15 to 10:15 a.m. The two reduced final source rates produced concentrations which closely bracketed the measurement.

Table 2. COMPARISON OF MODELED H<sub>2</sub>SO<sub>4</sub> AIR CONCENTRATIONS (mg/m<sup>3</sup>) WITH THE BAAQMD MEASUREMENT

MODEL RUN	7:15 to 8:15 PDT	8:15 to 9:15 PDT	9:15 to 10:15 PDT	10:15 to 11:15 PDT	8:15 to 11:15 PDT
Initial real-time	8.06	1.30	0.001	0.0	0.433 (124%)*
Refined real-time	0.647	0.317	0.907	0.003	0.619 (177%)*
Final 6-ton/hr initial rate	0.056	0.569	0.217	0.0	0.262 (74%)*
Final 4-ton/hr initial rate	0.037	0.740	0.453	0.0	0.398 (114%)*

\*Percent of the 0.350 mg/m<sup>3</sup> measured value

## V. CONCLUSIONS

The Richmond, California oleum tank car spill illustrates how the accuracy of urban-scale diagnostic modeling depends on the number, the accuracy, and the representativeness of meteorological observations. Determining wind fields in the San Francisco Bay Area requires a detailed consideration of sea breeze flows as modified by terrain. Improvement in model accuracy on the meso- $\gamma$  (1-25 km) scale may require including spatially-varying effects of mixing height, land use and surface roughness as well as local features, such as small hills, lakes and shorelines. Recognizing this need ARAC has embarked on a model development effort to simulate detailed flows with better diagnostic,<sup>5</sup> as well as prognostic models.<sup>6</sup> To quantify the improvement of future model developments, ARAC will also test each significant change against a set of benchmark model evaluation cases.

There will always be a place for computationally fast diagnostic models in emergency response. Real-time 3-D modeling of major toxic spills in urban areas can readily benefit from access to automated meso-networks of tower and upper air (sodar and profiler) meteorological systems, such as from air quality management districts and industry.

## ACKNOWLEDGEMENTS

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