

Simulation of potential formation of atmospheric pollution from aboveground storage tank leakage after severe storms

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HIGHLIGHTS

- A model was developed to simulate the fate of evaporated spill materials.
- Different meteorology, materials, and pollution levels were tested.
- Exposure to spilled materials is of significant concern.
- Formation of secondary pollution is enhanced within the downwind plumes.

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ABSTRACT

Damage by severe storms of infrastructure containing chemicals can cause widespread pollution of the atmosphere and nearby bodies of water. Because atmospheric monitoring equipment is inoperable in the periods after these storms, transport and fate modeling approaches are necessary to estimate the regional atmospheric concentrations of evaporated spill material and secondary pollutants from such events. Hypothetical spills from a single storage tank in Houston were used to evaluate the impact of different meteorological scenarios (Hurricanes Harvey in 2017 and Ike in 2008), leaked materials (oils and organic solvents), background chemical conditions, and cloud conditions on simulated air pollution. Due to differences in evaporation rate, downwind oil plumes are predicted to cover a broader region than organic solvent plumes, which remain concentrated along the path of the prevailing wind. Depending on assumptions regarding evaporation, mixing ratios of spilled material of up to 90 parts per million are predicted. Substantial formation of ozone (up to an enhancement of 130 parts per billion) and secondary organic aerosol (up to an enhancement of $30 \mu\text{g m}^{-3}$) could occur in the short-term aftermath of these storms within the downwind solvent plumes, with the magnitude dependent on the solar radiation, type of material, and background pollutant level. This highlights the potential vulnerability of residents and workers in downwind regions to evaporated spill materials and their degradation products.

1. Introduction

The United States (U.S.) is vulnerable to hurricanes and tropical storms. According to data available from the National Oceanic and Atmospheric Administration (NOAA) (NOAA, 2020), approximately 300 hurricanes have made landfall in the U.S. since 1851. In addition to the damage to buildings and other infrastructure caused by the strong winds

and high storm surge, hurricanes in industrially developed regions can potentially cause hazardous chemical spills that contaminate both the atmosphere and nearby bodies of water.

Aboveground storage tanks (ASTs) are typically light relative to other infrastructure and constructed with relatively thin steel shells, making them susceptible to both flotation and buckling in storm events (Romanok et al., 2016). Millions of liters of oils and hazardous chemicals

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were reported to have spilled from damaged industrial storage tanks after recent Hurricanes such as Sandy (2012), Katrina (2005), Rita (2005) and Harvey (2017) (Romanok et al., 2016; Horney et al., 2018; Godoy, 2007). The evaporation of organic spill materials can increase the downwind concentrations of volatile organic compounds (VOCs) and secondary pollutants such as ozone (O_3) and secondary organic aerosol (SOA). For example, Song et al. (2011) reported an 18% increase in O_3 concentrations along the coastline in downwind areas after 12,500 tons of crude oil were spilled near the west coast of Korea. Additionally, substantial increases in downwind VOCs, O_3 , and SOA concentrations after the Deepwater Horizon oil spill in the Gulf of Mexico were reported by Brock et al. (2011) and Neuman et al. (2012). Therefore, it is critical to predict the downwind concentration of evaporated spill materials, as well as of secondary pollutants (O_3 and SOA), after petrochemical spill events. This is especially true after severe storms when air quality monitoring systems likely are not operating, meaning that models provide the only estimate of potential exposure of individuals living and working downwind of the spill.

The Houston Ship Channel (HSC), located in a hurricane-prone region, is home to the second largest petrochemical complex in the world, with ten major refineries and more than 4500 ASTs (Bernier et al., 2017). The impacts of the HSC on the air quality of its surrounding communities and the Houston region under non-hurricane conditions have been reported previously (for example (Yeager et al., 2007; Rivera et al., 2010; Zhang et al., 2017)). Several studies have demonstrated that emissions from the HSC can produce elevated O_3 and particulate matter concentrations over the surrounding area (Daum, 2003; Byun et al., 2007; Bozlaker et al., 2013; Wallace et al., 2018). However, the impact of potential spills in the HSC after hurricanes on Houston air quality has not yet been quantified. Considering the potential environmental threats of the HSC after hurricane events, it is essential to assess the performance of ASTs in the HSC and to consider potential air quality issues in downwind regions after a storm-related petrochemical spill occurs.

The research presented here utilizes surge, AST fragility, and water-phase tracer models to simulate hypothetical spills and develops a mathematical model that couples an atmospheric Lagrangian transport and dispersion model with models focused on chemical transformation. It must be stressed that these results represent a hypothetical scenario and are intended only to provide proof of concept and a first estimate of air quality impacts were a spill to occur. One advantage of this modeling technique is that it is designed to work on a personal computer with low computational cost (typical run time of the model output presented here is 5–8 h, depending on the temporal duration of the simulation and the mass of material released). Also, by including the water-phase tracer simulation results as input, this model explicitly accounts for the effect of the water-phase spill transport on evaporation area. The model developed in this study can be used to track the transport and chemical evolution of downwind atmospheric pollution plumes, including the concentrations of evaporated spill materials, O_3 , and SOA within the plume. The predicted results can provide useful insight for the future development of screening level risk assessment or mitigation strategies after petrochemical spills occur.

2. Methods

2.1. Overview

The modeling framework utilized here begins with a hurricane storm surge model (SWAN + ADCIRC) to forecast the behavior of storm surge of different hurricane scenarios in the HSC (Sebastian et al., 2014). The surge behavior and associated wind speed data are then used as inputs to an AST failure probability simulation. Kameshwar and Padgett (2015) conducted probabilistic performance assessments of the entire regional portfolio of ASTs in the HSC. Using the surge behavior from SWAN + ADCIRC, Kiaghadi et al. (2018) developed a conservative dye tracer model (EFDC-SS, Environmental Fluid Dynamics Code- Storm Surge

model) to predict the trajectory and concentration of chemicals released into floodwaters from industrial facilities located in the HSC during specific hurricane events. The EFDC-SS model is used to evaluate the water quality after a spill event and determine the surface area of the leaked material. While feasible, the EFDC-SS model as used here does not include simulation of residual material left on soil or on changes in spill material concentration or composition within the water body. Details regarding SWAN, ADCIRC, and EFDC-SS are provided in previous publications (Sebastian et al., 2014; Kameshwar and Padgett, 2015; Kiaghadi et al., 2018). In this work, we utilize the results of the tank failure and spill transport modeling as inputs to an atmospheric model to assess the atmospheric downwind concentrations of evaporated material, O_3 , and SOA. It must be stressed that the results presented here are representative of only a limited set of possible scenarios.

In this study, a Lagrangian dispersion model was developed using MATLAB (v. R2017a); this model was based on the open-source code of the Flexible Particle (FLEXPART) 9.0 Lagrangian transport and dispersion model (Stohl et al., 2005), the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT) model (Stein et al., 2015), and the HYSPPLIT-Chem model that includes chemical transformations (Stein et al., 2000). The entire pollutant mass released from the AST leakage, once in the atmosphere, is uniformly distributed among a given number of particles (here this refers to tracer particles, not simulated particulate matter). Particles containing the various chemical species experience advection, diffusion, dry deposition, gas-phase chemistry, and aerosol partitioning throughout the simulation domain covering part of south-east Texas (93–98° W; 28–32° N). On the time scale of these simulations, wet deposition is not considered as it is assumed that precipitation associated with the storms has ended; this indicates that the concentrations presented here potentially are upper-bound estimates and that incorporation of a wet deposition scheme into the model is an area for future work. A schematic of the model approach and input data used in this study is shown in Fig. 1. Approaches to the various components of the model are described in the following sections.

To reduce overall computational constraints, two different horizontal grid cell resolutions (750 m and 3 km) are applied in this study, though both are on the same order of size as cells in typical three-dimensional (3-D) air quality modeling efforts. The 750-m grid system is used to calculate particle movement (note again here that particle movement refers to tracing particles for dispersion), while the 3-km grid system is used to simulate gas-phase chemistry, SOA formation, and dry deposition processes. Eight vertical layers are included from the ground surface to 1500 m, with an identical air pressure difference of 25 mbars per layer. The grid cell concentration of chemical species at each time step (2.5 min) is calculated by dividing the sum of the mass of each chemical species by the grid cell volume:

$$C_{i,x,y,z} = \frac{\sum_{j=1}^N m_{j,i}}{\Delta v_{i,x,y,z}} \quad (1)$$

where $\sum_{j=1}^N m_{j,i}$ is the total mass of chemical species i within the grid cell (with the particle number of $j = 1$ to N), and $\Delta v_{i,x,y,z}$ is the volume of the grid cell at the coordinate (x,y,z). Complete mixing is assumed inside each grid cell.

2.2. Evaporation

For organic solvents, the evaporation rate is predicted based on the semi-empirical model developed by Stiver and Mackay (1984):

$$E = k_m A P_l / (RT) \quad (2)$$

where E is the evaporation molar flux (mol s^{-1}), A is the evaporation area (m^2), P_l is the vapor pressure of the bulk liquid (Pa), R is the ideal gas constant ($8.314 \text{ J mole}^{-1} \text{K}^{-1}$), T is the ambient temperature (K),

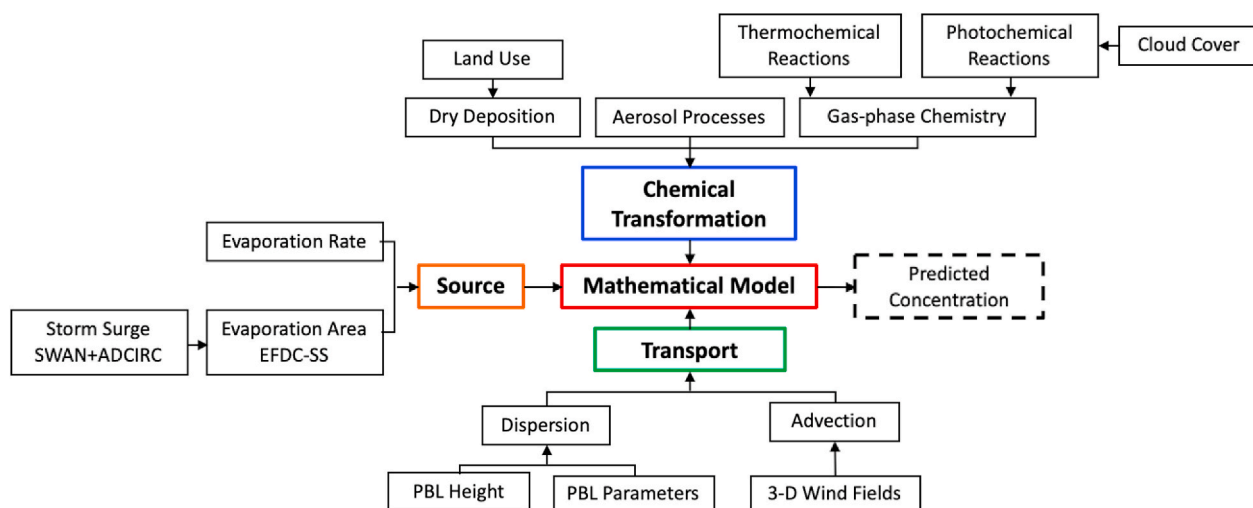


Fig. 1. Schematic of model approach and input data. PBL = planetary boundary layer.

and k_m is the mass transfer coefficient (m s^{-1}). In this study, the mass transfer coefficient is formulated using the ALOHA Puddle Source Strength Model (Jones et al., 2013) solving the conservation of mass and energy equations associated with the bulk liquid; when wind speed is less than 0.5 m s^{-1} , functions developed by Mackay and Van Wesenbeeck (Mackay and Van Wesenbeeck, 2014) are used. Empirical equations proposed by Fingas (2016) are used to predict the evaporation rate of oils. To isolate the impact of the spills, no additional emissions are considered along the plume trajectory.

2.3. Transport and dispersion

For each time step, the advection of a tracer particle is calculated independently based on the 3-D wind velocity vector, $\bar{v}$, from meteorological data. The contribution of the dispersion process is represented by adding a turbulent velocity component to the mean velocity. The particle position integration is calculated using the improved Euler-Cauchy method (Kreyszig and Norminto, 2006), and full reflection is assumed when a particle reaches the surface or the model upper boundary (Wilson and Flesch, 1993). Turbulent velocity components are represented by a Gaussian-Markov sequence using the Langevin equation (Wilson and Flesch, 1993) with corrections for drift to prevent the accumulation of tracer particles in low turbulence regions (Legg and Raupach, 1982) and to account for variation in air density with height (Stohl and Thomson, 1999). The calculations of turbulent velocity variance and time scale follow the scheme proposed by Hanna and Drivas (1996).

2.4. Gas-phase chemistry

To simulate gas-phase chemistry, the Master Chemical Mechanism (MCM) version 3.3.1 was chosen for this study (Jenkin et al., 2003). The clear day photolysis rate coefficients derived from MCM are corrected based on the cloud cover and solar intensity (Chang et al., 1987; Madronich, 1987). Because the oxidation of aromatic VOCs is known to have a substantial contribution to the formation of secondary air pollutants on the local and regional scale, in the following O_3 and SOA formation study, toluene and benzene are chosen as representative of spilled solvents (Derwent et al., 1996; Calvert, 2002); benzene and toluene also are known to be associated with petrochemical activities and have been shown to influence air quality in the HSC area (Wallace et al., 2018). Due to a lack of air quality data post-storms, evaluation of the gas-phase chemistry model using laboratory data is described in the Supplemental Information (SI).

2.5. SOA formation

The SOA formation modeling for the VOC precursors in this work uses the widely used and well documented volatility basis set (VBS) approach, which includes four SOA-forming oxidation products in separate volatility bins according to their effective saturation concentrations at 298 K: 1, 10, 100, and 1000 $\mu\text{g m}^{-3}$ (Lane et al., 2008). The SOA yields, y_i (defined as the ratio of the mass of SOA produced to the mass of the VOCs oxidized), for the four products can be calculated following partitioning theory (Donahue et al., 2006):

$$y_i = \alpha_i \left(1 + \frac{C_i^*}{M_0} \right)^{-1} \quad (3)$$

where C_i^* is the effective saturation concentration of corresponding volatility bin i ($\mu\text{g m}^{-3}$), α_i is the mass-based stoichiometric coefficient for the species represented by bin i , and M_0 is the mass concentration of SOA ($\mu\text{g m}^{-3}$). Given that the nitrogen oxide (NO_x) emissions are likely minimal during/after hurricanes due to decreased on-road traffic and the probable downtime of industrial facilities, the SOA yields of “low- NO_x ” conditions are used in this study (Table 1) (Lane et al., 2008).

The effect of temperature changes on the saturation concentration is considered using the Clausius-Clapeyron equation (Sheehan and Bowman, 2001; Takekawa et al., 2003):

$$C_i^* = C_{i,0}^* \frac{T_0}{T} \exp \left(\frac{\Delta H_i}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right) \quad (4)$$

where C_i^* is the effective saturation concentration of species i at temperature T (K), $C_{i,0}^*$ is the effective saturation concentration of species i at reference temperature T_0 (K), R is the ideal gas constant, and ΔH_i is the enthalpy of vaporization. It is assumed in this work that all SOA species have the same ΔH_i of 36 kJ mol^{-1} (Volkamer et al., 2006).

The chemical aging approach described by Tsimpidi et al. (2010) is used in this study. Each hydroxyl radical (OH) reaction is assumed to reduce the C_i^* by one order of magnitude with a constant reaction rate constant of $1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (Holzinger et al., 2013).

Table 1
SOA yield scenarios using a four-product VBS with saturation concentrations of 1, 10, 100, and 1000 $\mu\text{g m}^{-3}$ at 298 K (under low- NO_x parameterization, average SOA molecular weight of 150 g mol^{-1} is assumed).

C_i^* ($\mu\text{g m}^{-3}$)	1	10	100	1000
α_i	0.05	0.15	0.25	0.35

Moreover, a small amount of mass (7.5%) is added to the products to account for the mass increase caused by each OH oxidation.

After finding the SOA yield for each volatility bin at each time step, a mass balance is used to calculate the SOA mass concentration:

$$\sum_i \frac{y_i \Delta OCG_i}{M_0} + \frac{POA}{M_0} = 1 \quad (5)$$

where ΔOCG_i is the mass reacted of organic condensable gas (OCG) within corresponding volatility bin i and POA is the initial background organic aerosol concentration (assumed zero post-storm). At a given time step, M_0 is determined by numerically solving equation (5) using the `vpsolve` function in Matlab (2017a). As with the gas-phase chemical model, evaluation of the SOA model is described in the SI.

2.6. Dry deposition

Dry deposition is described by adding a deposition flux vector, F_d , to the surface layer. The detailed calculation method can be found in Seinfeld and Pandis (2006).

2.7. Redistribution of mass

After calculating the physical and chemical interactions, the resulting concentration is used to redistribute proportionally the mass of species contained in each tracer particle following the procedures proposed in the HYSPLIT-CheM model (Stein et al., 2000). This redistribution aims to transfer chemical model output back to the Lagrangian framework to assess further advection and dispersion.

2.8. Simulation cases

In this study, five hypothetical simulation scenarios of different leaked material and meteorological conditions were conducted (Table 2). Because the topography and meteorology are relevant for the HSC and these storms, the results shown here represent specific scenarios. However, the methodology developed can be translated to other areas impacted by significant petrochemical spills.

Detailed descriptions of meteorology for Hurricane Ike and Hurricane Harvey are found in Sebastian et al. (2014) and Van Oldenborgh et al. (Van Oldenborgh et al., 2017), respectively. The 3-D wind fields (and those of other meteorological parameters such as temperature) are prepared using the North American Mesoscale Forecast Model (Rogers, 2009). NASA Terra and Aqua satellite sensor measurements are used to determine cloud properties in this study (Platnick, 2017). Spatial and temporal variations of PBL heights in Houston measured by Hama et al. (2012) are applied over the model domain to determine the tracer mixing layer thickness.

In the benzene and toluene (termed 'solvents') scenarios, the 'background' NO_x concentration is set to be 6 ppb with a nitric oxide (NO) to nitrogen dioxide (NO_2) ratio of 1:9 over the model domain (Suciu et al., 2017); this simplification is made because emission inventories and

monitoring data of NO_x post-storms are not available. In the diesel oil scenarios, the complex chemical mixture of diesel oil vapor presents challenges in predicting the chemical behavior of species within the plume. Because of the lack of information available regarding the exact chemical components of diesel oils in ASTs along the HSC, simulations were conducted as maximum-concentration scenarios for primary material, as they do not account for any chemical reactions or transformation among the species within the diesel plume.

Previous work assembled an inventory of all AST located in the HSC and further assessed their hurricane performance using an AST fragility model (which provides the probability of failure under given hazard conditions), in which a dual-layer metamodel-based approach is proposed to develop parameterized fragility functions for ASTs subjected to hurricane-induced storm surge (Bernier et al., 2017; Kameshwar and Padgett, 2015). Although the framework posed is flexible in order to accommodate a range of spill locations and spill volumes, two locations that are at high risk of spill during storm events were isolated. According to the ASTs inventory, fragility models, and simulations of historic (Ike) and synthetic storms, Galena Park located in the west HSC and Baytown located at the mouth of the HSC are predicted to be the two most vulnerable areas (Bernier et al., 2017). In all simulations of the current study, a specific tank located in the middle of the HSC between these two locations with a 30-m diameter and a 9-m height is chosen as representative of the potential leaking tanks along the HSC. The discharge flow rate of the spilling material from the tank was simulated following the method in Kiaghadi et al. (2018).

Different simulation start times are considered in this study. To provide enough solar radiation to activate the photolysis reactions in the O_3 and SOA formation mechanisms, the spill release time of toluene and benzene scenarios is set to start in the morning after the storm surge peak. The spilled toluene and benzene in this study is simulated to evaporate into air within 15 min, which is a relatively short timespan compared to the total simulation duration of 10 h. Thus, in toluene and benzene solvent scenarios, we assume all the chemicals instantaneously spill and evaporate into the air during the first time step. In the Diesel scenarios, the spill is assumed to begin after the storm surge reaches its peak at the HSC.

It should be noted that the diesel and organic solvent scenarios performed in this study are representative of two conditions: continuous evaporation without chemical transformations (diesel oil) and instantaneous evaporation with gas-phase chemistry and SOA formation (solvents represented by toluene and benzene). However, a range of possibilities between these two scenarios is possible.

3. Results and discussion

3.1. Downwind diesel plume under different scenarios

The evolution of the spill water plume along the HSC from EFDC-SS is shown in Figs. S2 (Ike) and S3 (Harvey); these plumes provide critical input to the evaporation model. Corresponding diesel atmospheric plumes are shown in Fig. 2 (Ike) and S4 (Harvey). For both diesel storm scenarios, the water plume movement to the east along the HSC causes an eastward expansion of the downstream plume near the release, which further affects the shape of the downwind air plumes (Fig. 2 and S4). Incorporation of the transport of spills in the water likely improves the accuracy of the downwind air plume prediction, especially over short distances from the leak.

The averaged concentration below the top of the PBL is used to represent the downwind plume concentration because well-mixed conditions are predicted to be achieved within 15 min for all five scenarios. As shown in Fig. 2, a plume originating from the oil surface and developing along the wind direction is predicted under the Diesel_Ike scenario. The plume concentration is predicted to vary from 0 to 50 ppb, with relatively high concentrations near the release location. The high concentration region expands slowly from 8.4 km² at 13:00 CST to 42.2

Table 2

Summary of the five simulation scenarios in this work.

Simulation Scenarios	Spilled Mass (tons)	Released Number of Tracer Particles	Simulated Time (CST)
Diesel_Ike	4320	2,000,000	09/14/2008 12:00–22:00
Diesel_Harvey	4320	2,000,000	08/30/2017 00:00–10:00
Toluene_Ike_cloud	867	1,000,000	09/14/2008 08:00–18:00
Toluene_Ike_clear	867	1,000,000	09/14/2008 08:00–18:00
Benzene_Ike_cloud	867	1,000,000	09/14/2008 08:00–18:00

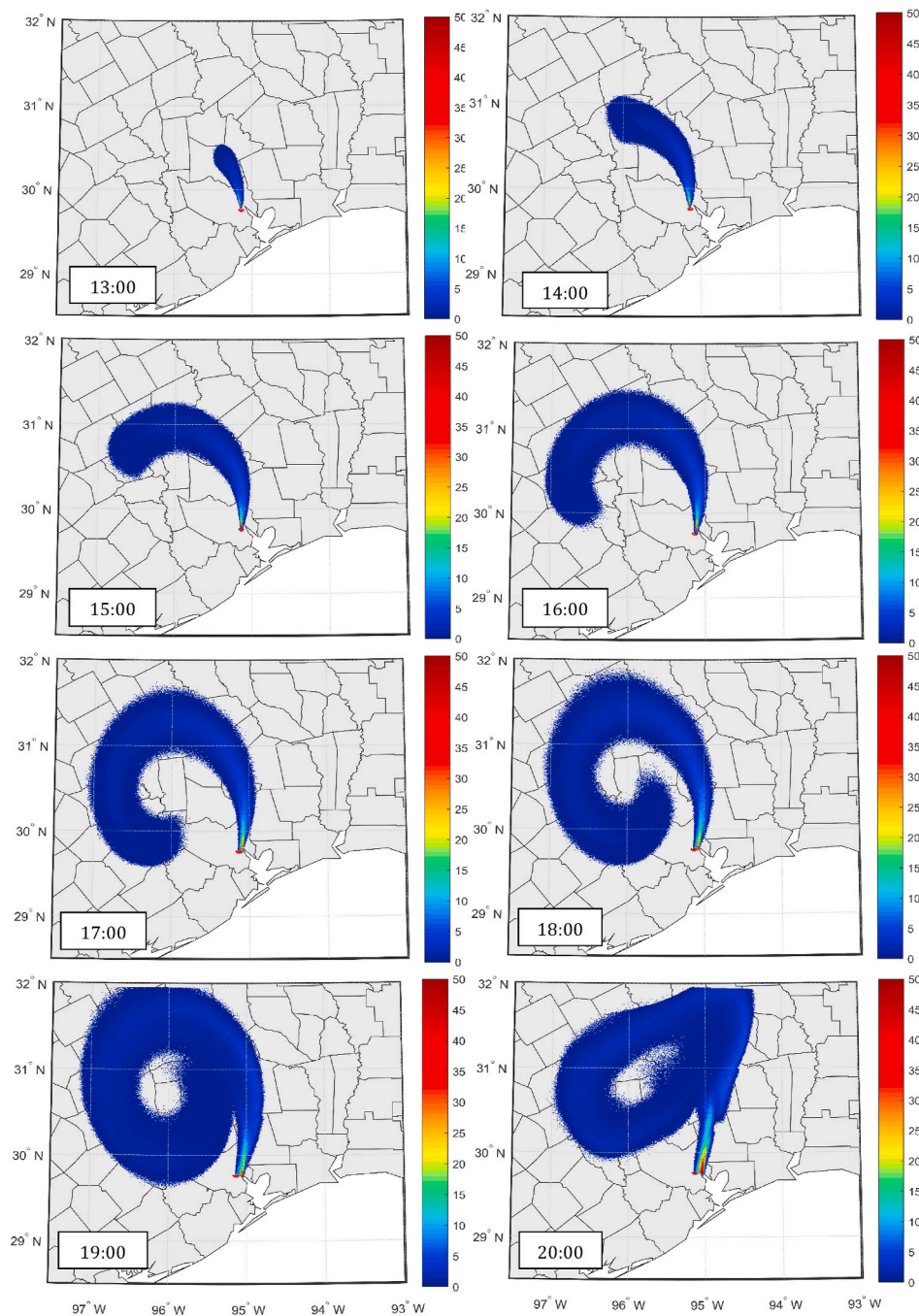


Fig. 2. Atmospheric concentration distribution (in ppb, as shown in the color scale) of the downwind diesel plume for the first 8 h of the Diesel_Ike simulation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

km² at 19:00 CST, then expands rapidly to 500 km² at 22:00 CST (Fig. 3). The initially slow expansion indicates that the evaporated mass input slightly overrides the effect of dilution near the release location. After 7 h, the decreasing PBL height, which reduces the mixing volume of the plume, becomes the dominant control on the expansion of the high concentration region. Although a large downwind area of diesel plume is predicted under Diesel_Ike, the downwind concentration decreases substantially as the distance from the release location increases due to the high wind speeds and well-mixed conditions during the daytime.

The shape and the concentration distribution of the downwind plume during the Diesel_Harvey scenario (Fig. S4) are predicted to be different than the Ike scenario due to the differences in PBL conditions and wind fields. In Diesel_Harvey, the lower PBL height associated with

the stable PBL condition during the nighttime (Fig. S5b) leads to a more narrow and concentrated downwind plume. The predicted downwind plume concentration of Diesel_Harvey ranges from 0 to 200 ppb, about four times higher than that of Diesel_Ike. A significant dilution of the downwind plume occurs from 06:00 CST to 10:00 CST due to the enhanced dispersion and the increasing PBL height after sunrise.

The effects of different wind fields on plume movement are clear when comparing Fig. 2, S4, and S5. The predicted plume pathways for both simulation scenarios are in general agreement with the forward wind trajectory predictions from NOAA's HYSPLIT model (Fig. S5 (Stein et al., 2015)), which provides confidence in the dispersion model developed here.

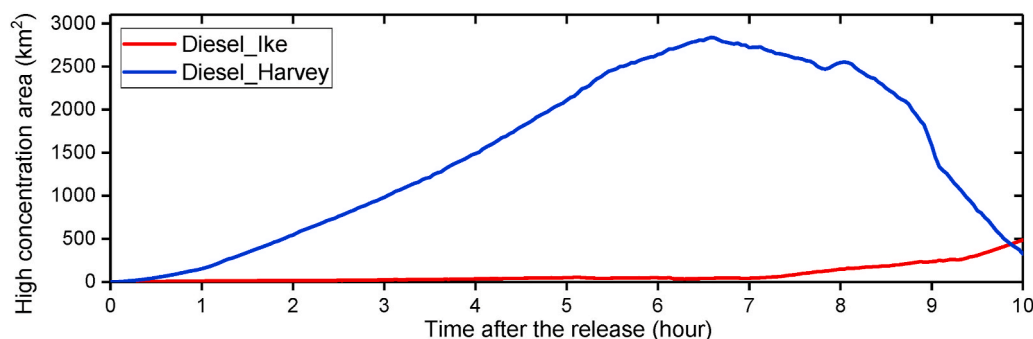


Fig. 3. Area of high concentration region (according to (NIOSH, 2019)), defined as the region with diesel concentration larger than 20 ppb) of Diesel_Ike and Diesel_Harvey.

3.2. Downwind toluene/benzene plume under different scenarios

The concentration distribution of the downwind plume from an instantaneous evaporation input of 1,000,000 L of toluene under the Toluene_Ike_cloud scenario is shown in Fig. 4. Compared to Fig. 2, the effects of assuming instantaneous evaporation are easily observed in Fig. 4.

At the beginning of the simulation, the large amount of initial toluene input leads to high concentrations near the release location. After 1 h (at 09:00 CST), the averaged concentration of the toluene plume is predicted to be 5290 ppb, with the highest concentration approximately up to 95 ppm at center of the plume. Although the predicted toluene concentration is much higher than the typical background level in the range of 2–20 ppb in an urban area (Kerchich and Kerbach, 2012), it is still below the toluene short-term (15 min) exposure limit of 150 ppm recommended by National Institute for Occupational Safety and Health (NIOSH) (NIOSH, 2019). However, the predicted surface level concentrations within the first 5 min are approximately up to 1000 ppm, higher than the NIOSH Immediately Dangerous to Life or Health Concentration of 500 ppm, suggesting that the failure of organic solvent ASTs potentially could cause severe health impacts on nearby workers and communities at the very beginning of a release, assuming the scenario of instantaneous evaporation. Due to the high wind speed, reaction, and efficient mixing, the concentrated toluene plume mixing ratio decreases rapidly by two orders of magnitude. The plume moves along the direction of the prevailing wind toward the northeast, with area increasing approximately from 55 km² at 09:00 CST to 3812 km² at 16:00. The plume pathway is again consistent with the HYSPLIT forward wind trajectory initiated at 08:00 CST, as shown in Fig. S6.

Under the same meteorological conditions and initial released mass, the shape and pathway of the downwind plume under Benzene_Ike_cloud is similar to that under Toluene_Ike_cloud. The averaged benzene concentration is predicted to be 12.3 ppm at 09:00 CST, then decreases to 48 ppb at 16:00 CST. The higher concentration of benzene relative to toluene is due to the lower reactivity of benzene with OH. Due to the higher toxicity of benzene, a more stringent short-term (15 min) exposure limit of 5 ppm is recommended by NIOSH (NIOSH, 2019), which leads to a significant downwind risk area (defined as the area with pollutant concentrations above the exposure limit) under the Benzene_Ike_cloud scenario. As shown in Fig. 5, a broad downwind region is vulnerable to the high airborne benzene exposure in the first 2 h, suggesting that mitigation strategies should be implemented to minimize the health risks to people residing in the HSC and downwind communities under these scenarios.

3.3. O₃ and SOA formation within the toluene/benzene plumes

Fig. 6 shows the concentration distribution of O₃ produced within the Toluene_Ike_cloud plume from 11:00 CST to 16:00 CST. Within the

downwind plume, organic peroxy radicals formed from toluene oxidation react with available NO_x, leading to O₃ formation. The plume-averaged O₃ concentration increases approximately by 41.5 ppb from 09:00 CST to 17:00 CST, which is in general agreement with simulations and measurements of the ambient O₃ concentration post petrochemical spill events by Song et al. (2011) and Neuman et al. (2012), respectively. It should be noted that the O₃ concentrations here are on top of any background O₃ present, which would presumably lead to even higher O₃ concentrations.

Fig. S7 (a) indicates that O₃ concentrations grow slowly in the morning because of the low concentration of OH. As solar radiation intensifies, OH concentrations increase, leading to growth of O₃ concentrations in the early afternoon. The O₃ concentration then decreases again, suggesting that dilution becomes dominant as the concentration gradient increases with time. For 6 h, the O₃ concentration stays relatively stable due to the balance between O₃ production and loss. The center concentration at 16:00 CST is predicted to be more than 130 ppb. In contrast to the predicted toluene concentration distribution shown in Fig. 4, in which the toluene concentration continually decreases from the plume center to the edges, O₃ concentrations are only slightly elevated in the plume center relative to the edges, likely because the O₃ production mechanism switches from a “VOC-limited” regime at the plume edge to a “NO_x-limited” regime at the plume center. In that case, O₃ formation is roughly proportional to NO concentration and independent of toluene concentration at the plume center.

The SOA spatial distribution from 12:00 CST to 17:00 CST under the Toluene_Ike_cloud scenario is shown in Fig. 7. The SOA concentration distribution pattern is similar to the toluene concentration distribution shown in Fig. 4 because the SOA formation is proportional to the concentration of its precursors (toluene, in this case). As shown in Fig. S7 (a) there is no significant SOA formation observed in the first 3 h because of the very small OH concentrations in the cloudy morning; SOA increases later in the day with increased photochemistry. The plume-averaged SOA concentration (in addition to any background SOA) then increases from approximately 0.05 μg m⁻³ at 12:00 CST to 6.5 μg m⁻³ at 17:00 CST.

As discussed above, both O₃ and SOA formation are sensitive to OH concentration, which largely depends on the solar radiation intensity. Given that cloud cover may be expected in the downwind pathway of the plume following hurricanes, the solar radiation intensity would be reduced by the cloud absorption and attenuation of sunlight, which will further affect the O₃ and SOA formation within the plume. According to Fig. S7 (a) and (b), the higher predicted OH concentration under the clear-day scenario leads to both higher O₃ and SOA formation (2.3 times higher for O₃, and 4.6 times higher for SOA).

In-plume formation of O₃ and SOA under the Benzene_Ike_cloud scenario was also simulated and is shown in Fig. S7 (c). According to MCM v3.3.1 (Jenkin et al., 2003), the reaction rate coefficient between OH radicals and benzene is ~20% of that between OH radicals and toluene. Therefore, less SOA formation is predicted within the

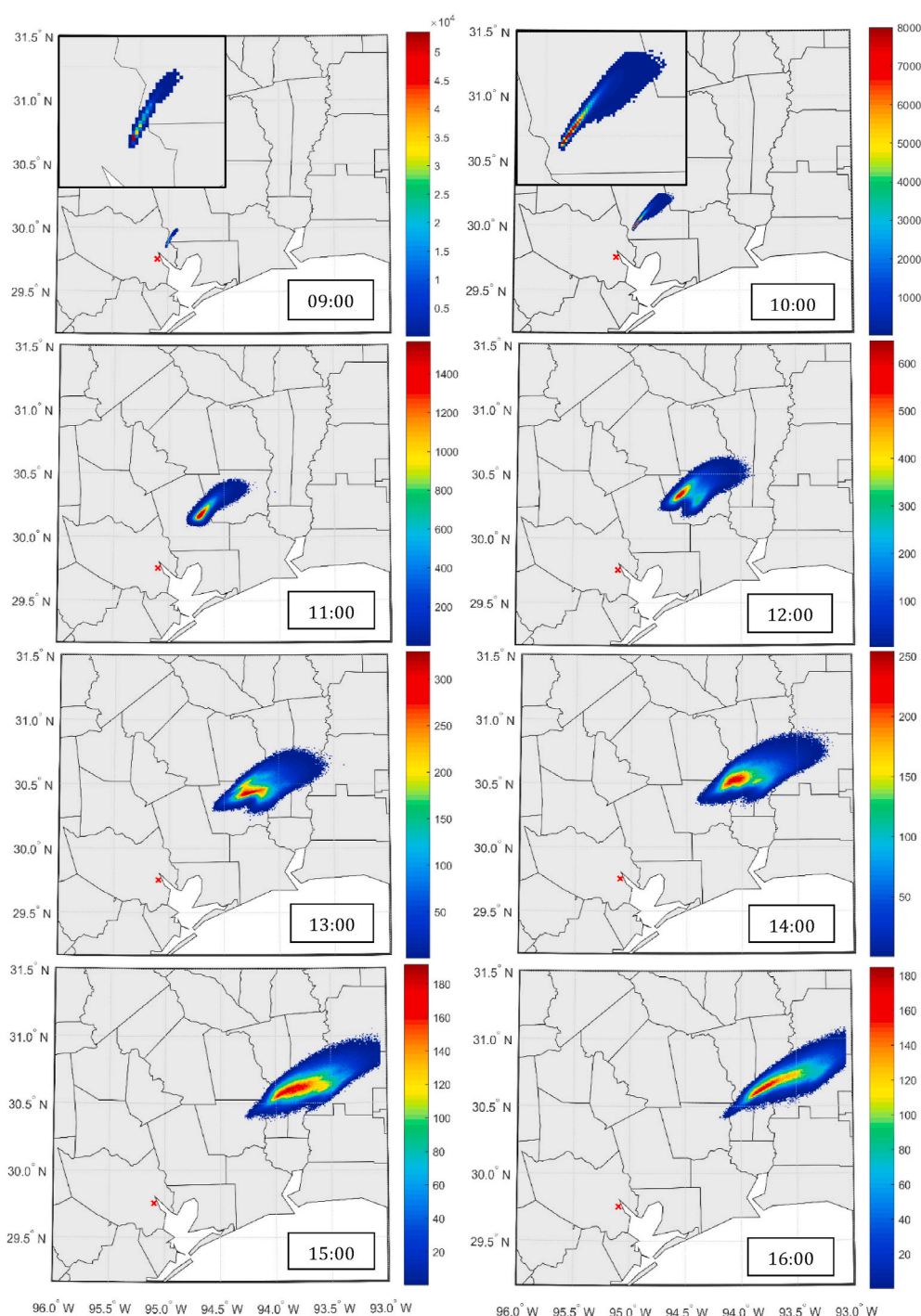


Fig. 4. Atmospheric concentration distribution (in ppb, as shown in the changing color scale) of the downwind toluene plume for the first 8 h of the Toluene_Ike_cloud simulation. Note that the color scales in the panels differ to better illustrate the concentration distribution within the downwind plume. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

downwind benzene plume.

3.4. NO_x sensitivity analysis for O_3 and SOA formation

In the discussion above, a constant background NO_x concentration of 6 ppb was assumed. However, ambient NO_x concentrations after hurricanes could be much lower due to the decreased amounts of traffic and industrial activities. To investigate the effect of background NO_x concentrations, O_3 and SOA formation modeled in the Toluene_Ike_cloud scenario under varying NO_x concentrations are shown in Fig. S8.

Predicted O_3 decreases with decreasing background NO_x level, further indicating that O_3 formation in the VOC-rich downwind pollution plume is in the “ NO_x -limited” regime. While the model uses constant NO_x concentrations, in reality, ambient concentrations will likely depend on the speed and direction of the prevailing wind. If the plume is rapidly transported out of the urban core, NO_x concentrations likely will drop rapidly with time, potentially leading to a scenario in which O_3 and SOA formation occur primarily during the first few hours of plume transport. Predicted SOA also decreases with decreasing NO_x level, reflecting the greater importance of oxidation capacity relative to increased SOA

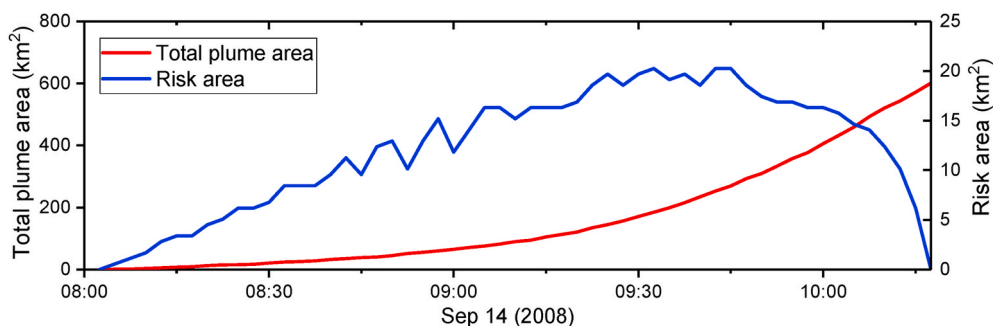


Fig. 5. Time series of risk area and benzene plume area under the Benzene_Ike_cloud scenario.

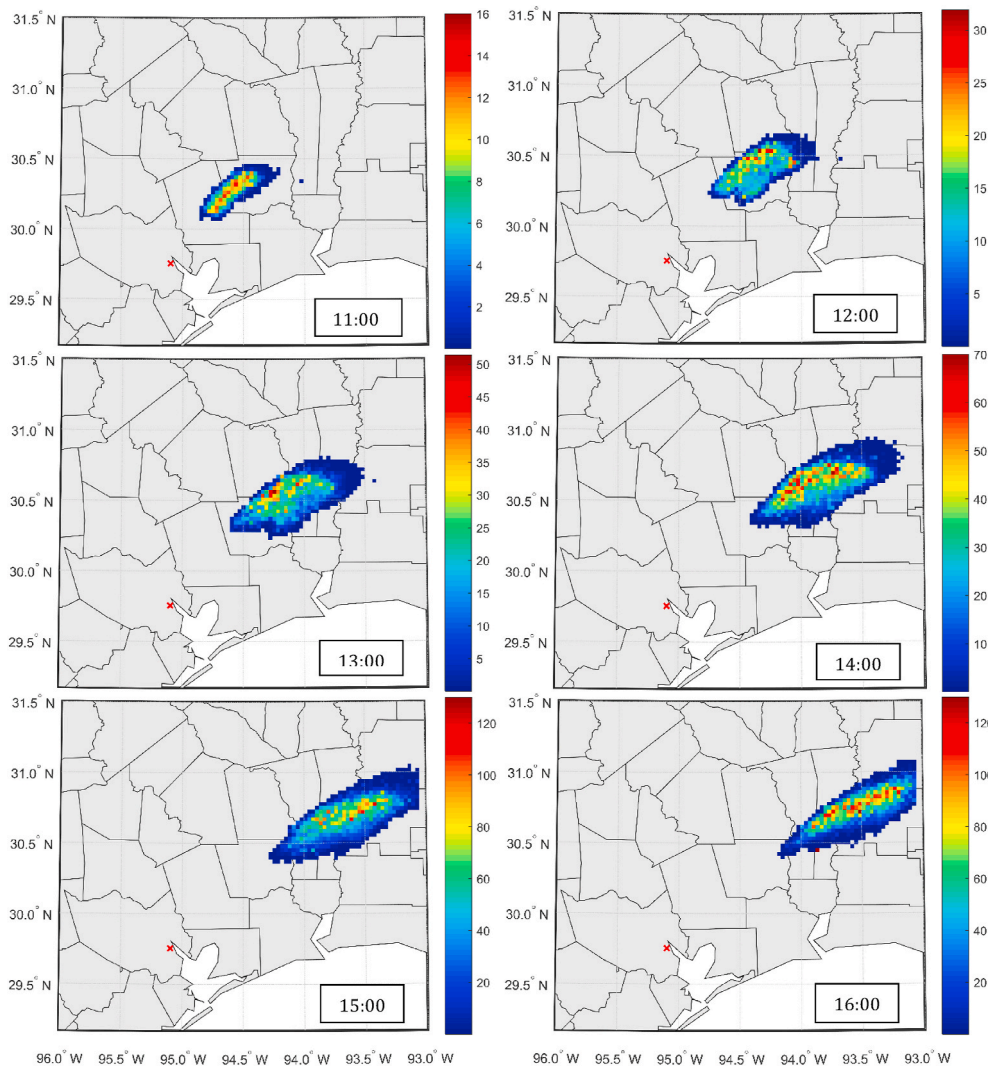


Fig. 6. Atmospheric concentration distribution (in ppb, as shown in the changing color scale) of O_3 produced in the downwind plume for the first 6 h of the Toluene_Ike_cloud simulation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

yields at low NO_x (Griffin et al., 2018).

4. Conclusions

Case studies were performed to predict the downwind transport and transformation of evaporated spill materials, as well as the related O_3 and SOA concentrations, under hypothetical post-storm scenarios. Results show that downwind plume behavior for oils and organic solvents are different based on assumed evaporation characteristics. For oils

(assumed to be diesel in this study), plumes originating from the oil surface and developing along the wind direction were predicted to cover broad downwind areas. For evaporated organic solvents (toluene and benzene), isolated and concentrated plumes were predicted to travel along the wind direction due to the assumption of instantaneous evaporation. All scenarios modeled in this work illustrate that the PBL height and mixing conditions are the dominant factors affecting the concentration distribution of downwind plumes.

Substantial plume-averaged O_3 mixing ratio enhancements of 30–40

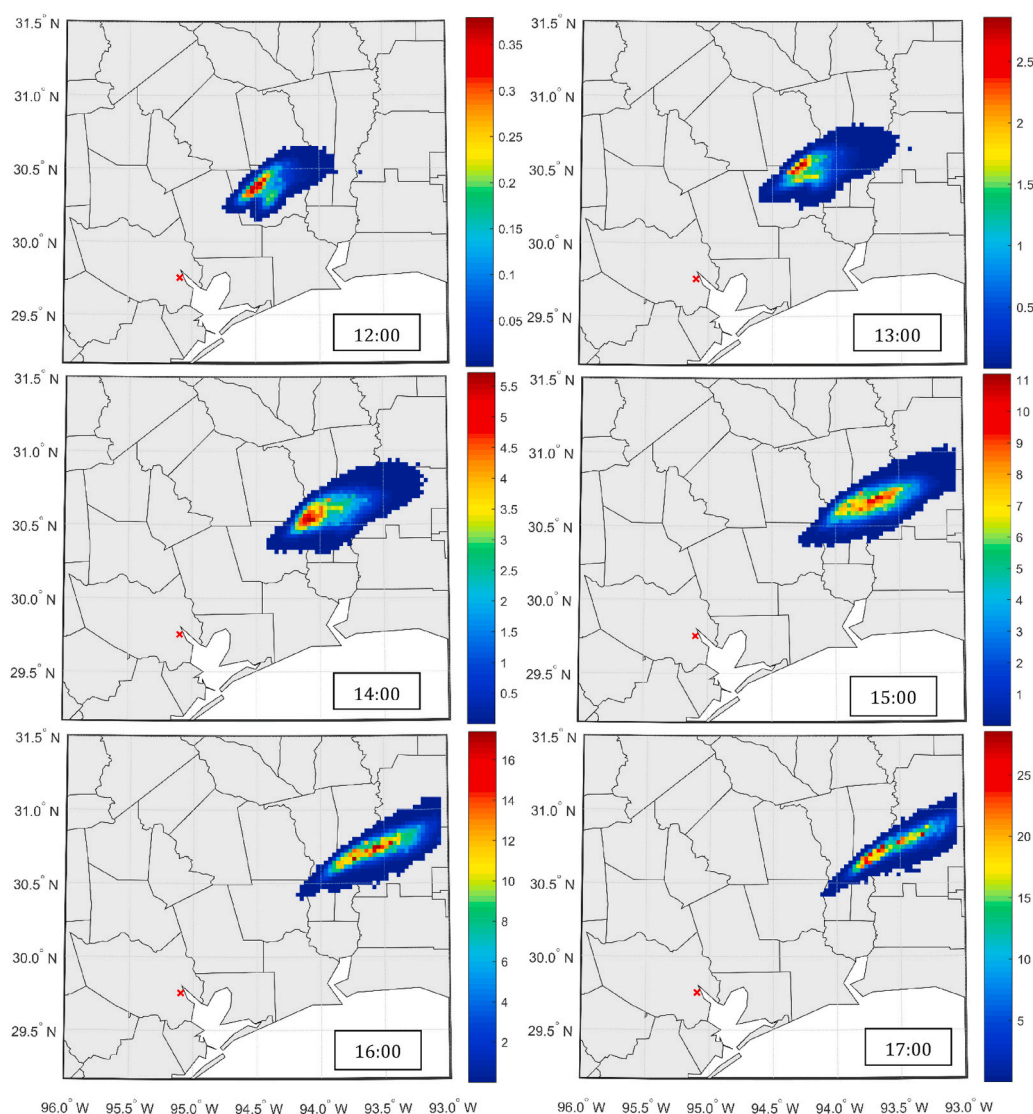


Fig. 7. Atmospheric concentration distribution (in $\mu\text{g}/\text{m}^3$, as shown in the changing color scale) of SOA produced in the downwind plume for the first 6 h of the Toluene_Ike_cloud simulation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

ppb were predicted under both the toluene and benzene scenarios, illustrating the capability of evaporated spill materials to impact O_3 formation. In contrast to O_3 formation, downwind SOA formation largely depends on the nature of the evaporated materials. Higher plume-averaged downwind SOA concentration enhancements of $65 \mu\text{g m}^{-3}$ were predicted in the toluene scenarios compared with the benzene scenarios, confirming that the capacity of toluene to generate SOA is much larger than that of benzene due to its increased reactivity.

Ultimately, the novel, integrated modeling framework developed in this study is able to demonstrate potential air quality impacts due to AST failure after severe storms. This is critical due to the lack of operation of many air quality monitoring networks following natural disasters such as severe storms. The results indicated here demonstrate that, while secondary chemistry appears important, the greatest danger likely is to come from exposure to evaporated spilled material.

CRediT authorship contribution statement

Shiyang Bi: Methodology, Formal analysis, Writing - original draft. **Amin Kiaghadi:** Methodology, Writing - review & editing. **Benjamin C. Schulze:** Methodology, Writing - review & editing. **Carl Bernier:** Methodology, Writing - review & editing. **Philip B. Bedient:**

Methodology, Writing - review & editing. **Jamie E. Padgett:** Methodology, Supervision, Writing - review & editing. **Hanadi Rifai:** Methodology, Supervision, Writing - review & editing. **Robert J. Griffin:** Conceptualization, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2021.118225>.

Data availability

Model output and code are available from the authors upon request.

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