

Article

Is There a Formaldehyde Deficit in Emissions Inventories for Southeast Michigan?

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Abstract: Formaldehyde is a key Volatile Organic Compound (VOC) and ozone precursor that plays a vital role in the urban atmospheric radical budget on par with water vapor, ozone, and nitrous acid. In addition to modulating radical and ozone production, ambient formaldehyde has both carcinogenic and non-carcinogenic inhalation health effects. This study concludes that ambient formaldehyde in the Southeast Michigan (SEMI) ozone nonattainment area may be underestimated up to a factor of two or more by regional air quality models. The addition of plausible amounts of primary formaldehyde to the U.S. National Emissions Inventory based on estimated formaldehyde-to-CO emission ratios partially alleviates this modeling deficit and indicates the presence of formaldehyde concentrations above 5 ppb at a previously unsuspected location northeast of Detroit. Standard 24-h formaldehyde samples obtained during the Michigan-Ontario Ozone Source Experiment (MOOSE) verified the presence of high ambient formaldehyde concentrations at this location. Moreover, the addition of plausible amounts of primary formaldehyde to VOC emissions inventories may add more than 1 ppb of ozone to ambient air in the SEMI nonattainment area, where ozone design values exceeded the U.S. National Ambient Air Quality Standard (NAAQS) by 1–2 ppb for the 2018–2020 design value period.



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1. Introduction

Formaldehyde (HCHO) is a powerful ozone precursor due to its ability to quickly generate new, unrecycled radicals independently of other Volatile Organic Compounds (VOCs) [1]. The initial radical pool created by the photolysis of HCHO and other primary radical precursors triggers a cascade of secondary radicals from VOCs that lengthens the photochemical reaction chain leading to ozone production. Formaldehyde thus plays a vital role in determining the budget of atmospheric radicals on par with water vapor, ozone, and nitrous acid [2]. It is also an important catalyst in the formation of fine particulate matter (PM_{2.5}) [3]. Besides enhancing atmospheric oxidation capacity, HCHO is a Hazardous Air Pollutant (HAP) with both cancer and non-cancer (e.g., airway irritation and asthma) health effects [4]. The United States (U.S.) Environmental Protection Agency (USEPA, Washington, DC, USA) assigns a unit cancer risk to formaldehyde of 1.25×10^{-5} per $\mu\text{g}/\text{m}^3$ [4,5]. Zhou et al. [6] concluded that HCHO is the most important HAP contributing to cancer risk due to ambient air inhalation in the United States.

Strum and Scheffe [7] analyzed annual average HAP concentrations measured at regulatory monitoring stations in the U.S. in 2011. They found that the 90th percentile of all annual mean HCHO concentrations was $4.0 \mu\text{g}/\text{m}^3$, which is approximately 3.2 parts per billion (ppb) by volume at normal temperature and pressure (NTP), compared to a 10th percentile of around $1.5 \mu\text{g}/\text{m}^3$ (1.2 ppb) and a median value around $2.4 \mu\text{g}/\text{m}^3$ (1.9 ppb).

Atmospheric formaldehyde has two different origins. Primary HCHO is emitted by human activities, mostly incomplete combustion from both stationary and mobile sources, but also leaks and other fugitive sources (e.g., from wastewater treatment) [8–10]. Secondary HCHO is the by-product of the chemical degradation of other VOCs already in the atmosphere, including those of biogenic origin [11]. Lei et al. [10] investigated the role that HCHO emissions play in the urban airshed of Mexico City. They found that primary HCHO enhances total daytime radical production by up to 10% and peak ozone concentrations by up to 8%, with a sustained influence on photochemistry from early morning until early afternoon. The impact of primary HCHO on atmospheric oxidation capacity clearly cannot be ignored even if, as insisted by Parrish et al. [12], the contribution of secondary formation to ambient HCHO concentrations dominates the primary component downwind of emission sources. Moreover, from the perspective of human health risk, primary HCHO may contribute much more than secondary HCHO to toxic exposure very close to large emission sources, particularly in residential neighborhoods immediately bordering industrial facilities in cities such as Detroit, Michigan, USA where environmental justice is a major concern [13].

Several published studies based on field measurements with advanced techniques have shown that direct emissions of formaldehyde may be significantly underestimated in official emission inventories used in regulatory applications [14–16]. Traditional point source emissions reporting in the U.S. does not consider HCHO produced by inefficient combustion of VOCs, as opposed to HCHO that is deliberately burned but incompletely destroyed.

As a product of incomplete combustion, HCHO is closely linked by emission plume chemistry at the source to carbon monoxide (CO). The molar ratio of HCHO to CO in motor vehicle emission plumes is known to vary roughly between 1% and 4% [17]. Data collected by Aerodyne Research, Inc. at the John Zink facility in Oklahoma during the 2010 TCEQ Flare Study [18] suggest that natural gas flares have a HCHO-to-CO molar ratio of around 5%, while flaring of hydrocarbon mixtures broadens this ratio to between 2% and 7% [19]. The State of New Jersey collected data on HCHO emissions from stationary engines based on engine stack tests, from which it can be inferred that natural gas-fired engines have a HCHO-to-CO molar ratio of about 9% (i.e., a mass ratio of 10%) [20]. Stationary engines used in converting landfill gas to energy, on the other hand, can have even larger ratios due to the presence of siloxane residue from landfill gas burned in the engines [21,22]. The application of HCHO-to-CO molar ratios to estimate HCHO emissions from industrial sources in Michigan results in HCHO emissions estimates many orders of magnitude greater than reported values in most cases, especially when very large emissions of CO are known to be present.

Ambient HCHO is known to be systematically underestimated by regional air quality models such as the Community Multi-Scale Air Quality (CMAQ) modeling system [23,24] and the Comprehensive Air Quality Model with Extensions (CAMx) [25]. For example, Leucken et al. [26] used the CMAQ model to attribute HCHO to individual VOCs across the eastern U.S., identifying alkenes—particularly isoprene—as important precursors of secondary HCHO, but had difficulty in reproducing observed HCHO concentrations within a factor of 2. Leucken et al. [27] applied a later version of CMAQ configured for the 2011 U.S. National Air Toxics Assessment (NATA) to compute the sensitivity of HCHO concentrations across the U.S. to major source types and hydrocarbon speciation. Their study generally underestimated HCHO, with an annual mean bias of $-0.9 \mu\text{g}/\text{m}^3$ (-34.2%). They partially attributed this negative bias to difficulties in simulating high-emitting sources.

Harkey et al. [28] compared HCHO columns from various configurations of CMAQ to satellite HCHO retrievals from the Ozone Monitoring Instrument (OMI). All CMAQ configurations showed low daily correlations with OMI HCHO (Pearson correlation coefficient $r = 0.26\text{--}0.38$). Measurements from ground-based dinitrophenylhydrazine (DNPH) cartridge monitors were also used to evaluate CMAQ estimates of surface layer HCHO. When near-

surface model predictions were compared to local 24-h average ground measurements, HCHO was likewise underpredicted ($r = 0.53\text{--}0.64$).

Marvin et al. [11] used aircraft measurements over southeast U.S. in the summertime and an observationally constrained box model to explore how limitations in second-to-late generation isoprene oxidation in model chemical mechanisms may explain the HCHO deficit in regional air quality models. While the more detailed mechanisms better simulated atmospheric HCHO concentrations, all available chemical mechanisms underestimate ambient HCHO by 15 to 33%. Even if improvements to isoprene oxidation mechanisms may alleviate this deficiency on regional scales, they may not overcome model HCHO deficits in highly industrialized cities where vegetation is scarce relative to rural areas.

The Lake Michigan Air Directors Consortium (LADCO) provides regional air quality modeling and technical support to six states in the U.S. Great Lakes region. LADCO deploys the CAMx model to evaluate control strategies for attaining the U.S. National Ambient Air Quality Standards (NAAQS) in member states. This includes modeling support for the Southeast Michigan (SEMI) ozone nonattainment area encompassing the city of Detroit, where ozone design values (the 3-year average of the annual 4th highest maximum daily 8-h average concentration at each regulatory monitoring site) exceeded the NAAQS by 1–2 ppb for the 2018–2020 period. A CAMx model configuration run by LADCO used 2016 as the emissions inventory base year and is described in a publicly available Technical Support Document [29]. Figure 1 compares the HCHO predictions of alternate configurations of the LADCO CAMx model with 24-h DNPH cartridge measurements at the River Rouge monitoring station in SEMI during 2016. The horizontal resolution of the CAMx configurations is either 4 km (CAMx_LADCO_2016bcc_LADCO4, blue line in Figure 1) or 12 km (CAMx_LADCO_2016bcc_12US2, red line). A third model configuration (CAMx_LADCO_2016v1) employs 12 km resolution and makes use of inputs from a USEPA simulation (green line). Note how all CAMx model configurations underestimate HCHO concentrations by up to a factor of two or more.

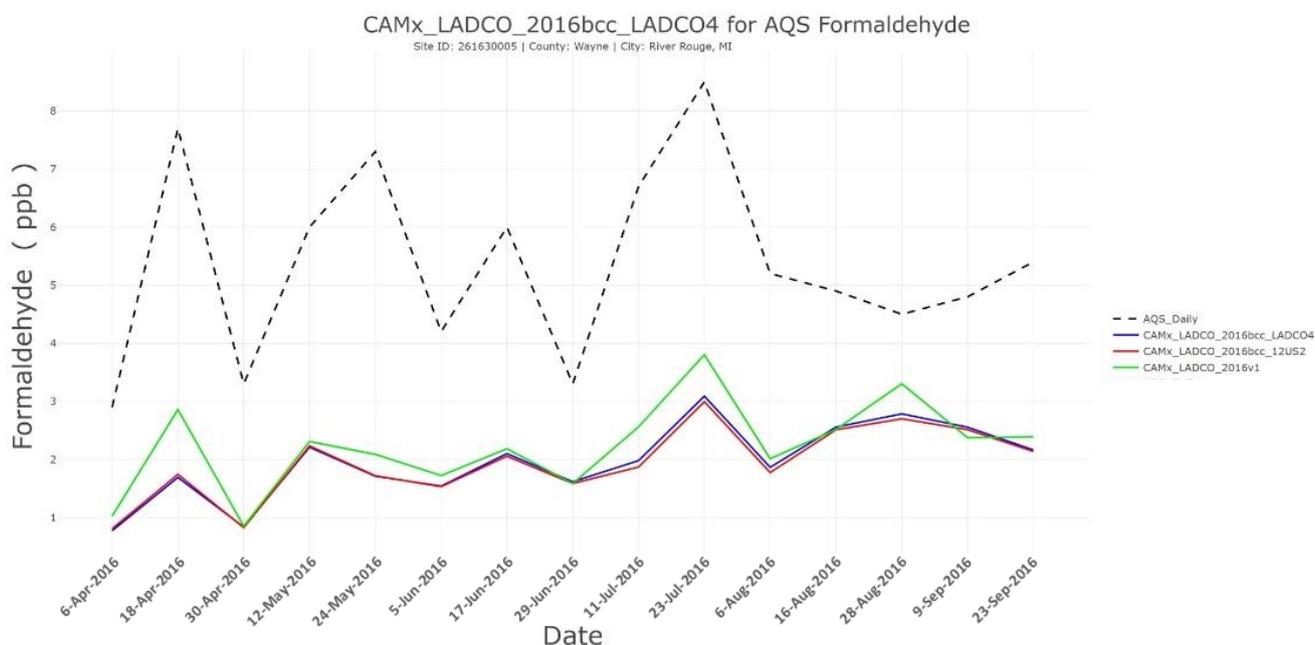


Figure 1. A comparison of 24-h average HCHO concentrations measured at River Rouge, Michigan in 2016 (black dashes) and reported to the USEPA Air Quality System (AQS) versus model predictions with various LADCO configurations of CAMx (solid lines).

This study investigates the possible causes of the HCHO deficit in emissions inventories for the SEMI ozone nonattainment area. Specifically, it shows that plausible additions

of primary HCHO to the 2016 U.S. National Emissions Inventory (NEI) [30] may have significant impacts on both ambient HCHO and ozone simulated by the CAMx model for retrospective ozone episodes in SEMI during the 2016 ozone season. Moreover, the likely existence of uncounted primary HCHO is affirmed by field measurements made by the Michigan Department of Environment, Great Lakes, and Energy (EGLE) during a recent air quality experiment as discussed further below.

2. Methods

Three classes of methods were used in this study, the first being estimates of HCHO emissions based on assumed HCHO-to-CO emission ratios for various source types. The second method involves high resolution regional air quality modeling with CAMx to test the hypothesis that additional primary HCHO in the emissions inventory plausibly accounts for much of the model deficit in ambient HCHO relative to observations. The third method consists of DNPH cartridge sampling of HCHO apart from routine regulatory measurements during the Michigan-Ontario Ozone Source Experiment (MOOSE), a binational air quality field campaign that took place in the late spring and summer of 2021 at the international border region between the U.S. and Canada [31]. This sampling affirmed the plausibility of missing sources of primary HCHO in the emissions inventory by confirming predictions of the CAMx model.

2.1. Formaldehyde Emissions Estimates

To estimate plausible HCHO emissions, four categories of emission sources were assumed: (1) stationary engines used in converting landfill gas to energy; (2) stationary engines used at permitted industrial facilities other than landfills; (3) flares; and (4) all other stationary combustion sources. A uniform mass (rather than molar) ratio of HCHO to CO emissions was assigned to each of these source categories. A mass ratio of 15% was assigned to Category 1, a ratio of 10% was assigned to Category 2, a ratio of 5% was assigned to Category 3, and a ratio of 2% was assigned to Category 4. Note that the molecular weight of HCHO exceeds that of CO by only two hydrogen masses, so that there is less than 8% difference between the assigned mass ratios and the equivalent molar ratios. The assigned mass ratios are consistent with available information from stack tests at permitted facilities in Michigan and other states [20], as well as prior field experiments that specifically examined this ratio in combustion emission plumes [19,32].

A database known as the Michigan Air Emissions Reporting System (MAERS) is assembled annually, quality-assured, and maintained by the State of Michigan. It is populated by emissions data reported to EGLE by permitted industrial facilities, as required by Part 55 of the Natural Resources and Environmental Protection Act (Michigan Legislature Act 451 of 1994). Among the data collected is the Source Classification Code (SCC), a system used by the USEPA to classify activities that generate air pollution. For some SCC's, Michigan requires that CO emissions data be collected, making it a valuable tool in estimating HCHO, since HCHO is reported only collectively with other VOCs. The SCC structure was used to apply the four mass ratio categories to specific entries in the MAERS database. An SCC, in the case of stationary or point sources, uses an eight-digit system following a hierarchical, four-level code which gives increasing specificity for different types of processes. The Category 1 mass ratio (15%) was applied to emission unit entries classified with a level one SCC value of 2, denoting internal combustion engines, whenever remaining sublevel values indicated the fuel used was landfill gas. The Category 2 mass ratio (10%) was applied to emission unit entries with the same level one value whenever the remaining three sublevels indicated combustion of fuels other than landfill gas. The Category 3 mass ratio (5%) was applied to a variety of SCC values with at least one of the levels indicating combustion emissions through flaring. The remaining SCCs that appeared to describe combustion sources at any of the four levels were assigned the default mass ratio (2%).

2.2. Modeling Methodology

CAMx v7.10 [25] was used to simulate the air quality changes due to the addition of HCHO emissions in the SEMI region during the 2016 ozone season. The modeling period was from 15 April through 25 September 2016 with a 3-day spin-up starting on 12 April. The modeling grid is shown in Figure 2. It has a 1.33-km horizontal resolution with 35 vertical layers extending from the ground to the top at 50 mb.

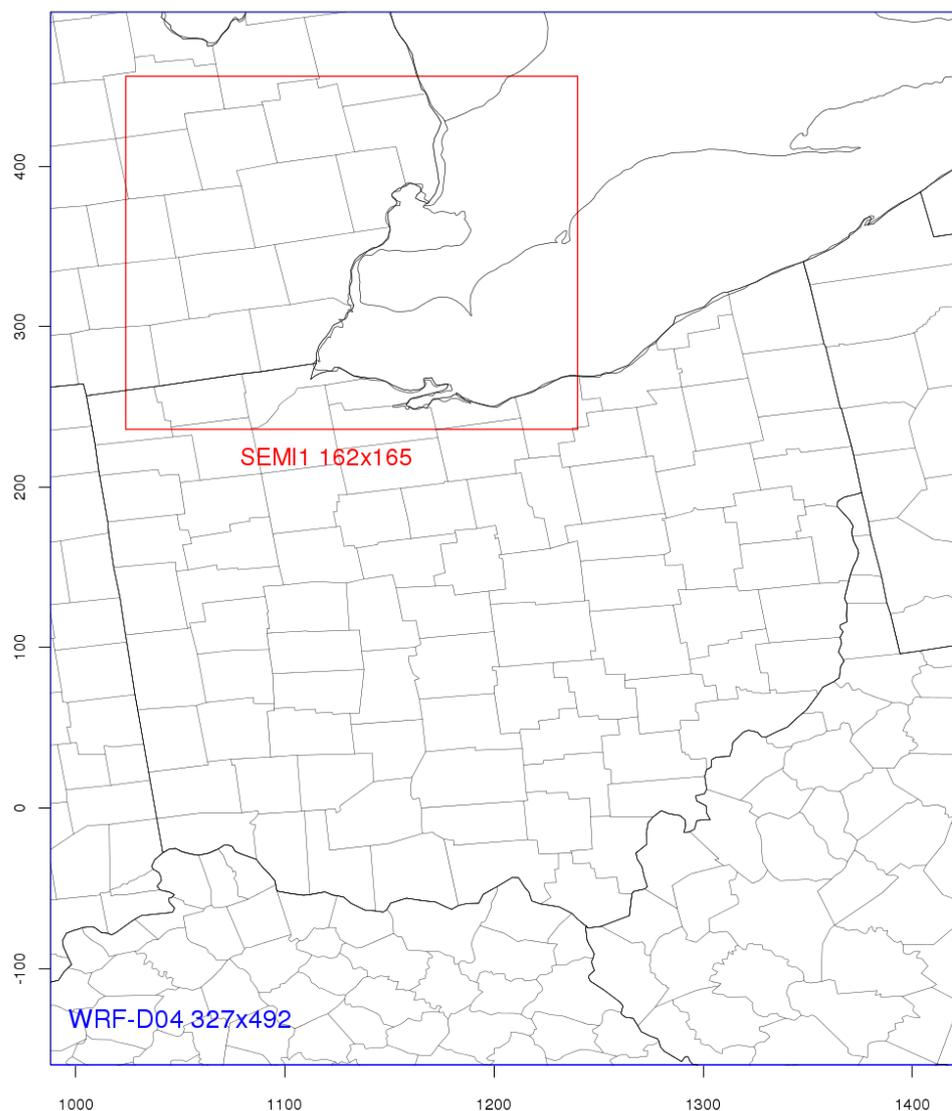


Figure 2. The 1.33-km horizontal resolution CAMx modeling grid (the inner box in red) for the SEMI region, which covers the entire SEMI ozone nonattainment area with 162×165 grid cells. Also shown on the map is the 1.33-km horizontal resolution LADCO D04 Weather Research and Forecasting (WRF) modeling grid (the outer box in blue).

The meteorological data required as inputs to CAMx for the air quality modeling were developed by LADCO [29] using the Weather Research and Forecasting (WRF) model version 3.9.1.1 with North American Mesoscale (NAM) analysis [33]. The WRF outputs cover an area much larger than the SEMI region with the same 1.33-km horizontal resolution (Figure 2) and the same vertical structure. The performance of the LADCO 2016 1.33-km WRF simulations is exceptionally good when benchmarked against all common model performance metrics (see Table 9 in [33]). The initial and boundary conditions (IC/BC) for the air quality fields were also developed by LADCO [29] and were derived from

CAMx simulations (LADCO4) with 4-km horizontal resolution covering the entire Great Lakes region.

The USEPA Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system applied to the 2016v1 platform [30] was used to prepare the 2016 default emissions input files for the SEMI 1.33-km CAMx modeling grid (referred to as “basecase” hereafter). The Biogenic Emission Inventory System (BEIS) was used to simulate biogenic emissions. Updated HCHO emissions were then estimated based on the assumed emission mass ratios of HCHO to CO for the chosen source categories, as discussed in Section 2.1. The updated emissions were incorporated into the 2016v1 platform as a replacement for the default HCHO emissions. A second CAMx simulation was run using the enhanced HCHO emissions (referred to as “semihcho” case hereafter).

The CAMx model was configured with the CB6r5 mechanism, the CF2E Particulate Matter treatment, the Piecewise Parabolic Method (PPM) advection solver, the Eulerian Backward Iterative (EBI) chemistry solver, and the ZHANG03 algorithm for dry deposition. The post-processed CAMx outputs included the local time 24-h average HCHO concentrations and daily maximum 8-h average ozone concentrations (MDA8 O₃).

2.3. Field Measurements

Field measurements were conducted at the New Haven, Michigan, USA air monitoring station, located at the New Haven High School on 24–28 June 2021. The monitoring station routinely measures ozone, PM_{2.5}, and meteorological parameters. Sampling of carbonyl compounds was conducted with DNPH cartridges based on USEPA Method TO-11A for aldehydes and ketones. The ATEC 8000 multi-channel programmable sampler was installed in the climate-controlled air monitoring shelter. In accordance with the method, the sample line was Teflon material and met the USEPA monitoring siting criteria as described in 40 CFR (U.S. Code of Federal Regulations) Part 58 Appendix E for ambient air measurements. The flowrate for sampling was 750 cc/min. Sampling was performed for 24 h for five days and included a field blank. After sampling, the cartridges were properly packaged, kept cold to 4 °C, and shipped cold to Atmospheric Analysis and Consulting (AAC) in Ventura, California, USA. The laboratory analyzed the cartridges using high performance liquid chromatography (HPLC) consistent with USEPA TO-11A.

3. Results

3.1. CAMx Modeling

Figure 3 shows the distribution within the CAMx model domain of the ratio of the updated HCHO emissions to the default emissions in the NEI for 12 July 2016. Table 1, on the other hand, compares the total updated emissions to the total default emissions for the two states (Michigan and Ohio) with areas within the model domain. Note how the updated emissions are up to an order of magnitude larger than the NEI values, both locally and in the state totals.

Table 1. Total default (2016 NEI) versus updated emissions of HCHO in short tons per year (tpy) in Michigan and Ohio grid cells within the CAMx model domain.

State Area	Default Emissions (tpy)	Updated Emissions (tpy)	Ratio
Michigan	121.5	1203	9.9
Ohio	58.6	152	2.6

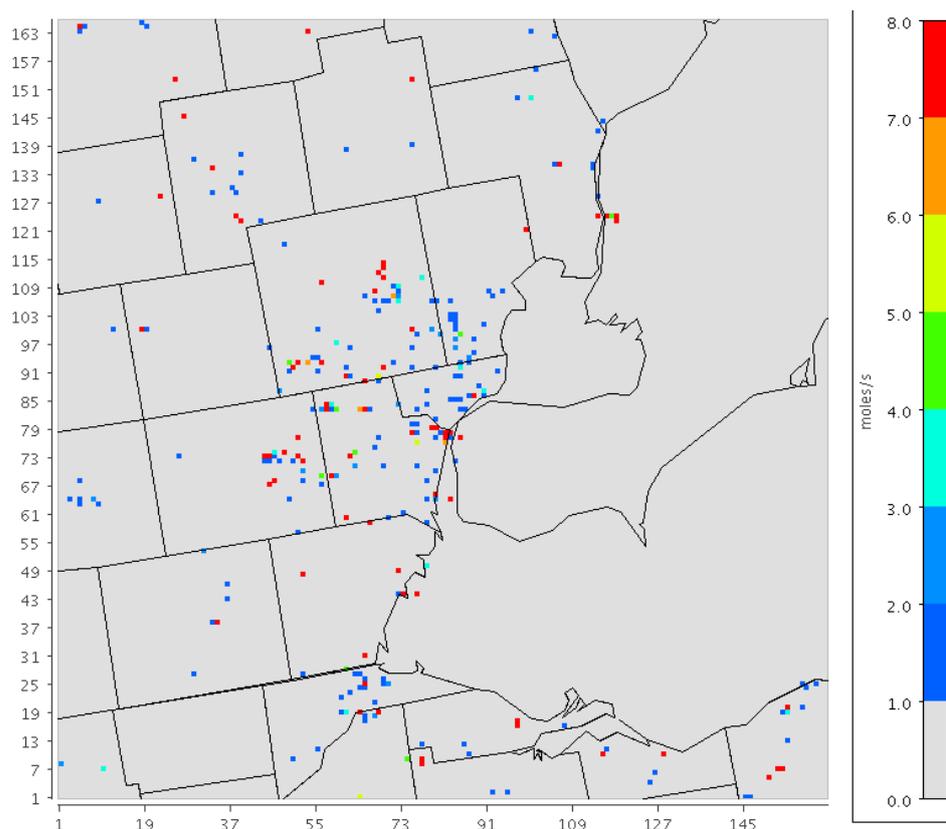


Figure 3. Ratio of updated HCHO emissions to the default emissions for 12 July 2016 within the CAMx model domain.

The CAMx model performance for ozone was evaluated against observations at 10 regulatory monitoring sites in the SEMI nonattainment area focusing on mean normalized bias and error for MDA8 O₃:

$$\text{Normalized mean bias (NMB): } \text{NMB} = \frac{\sum_{i=1}^N (P_i - O_i)}{\sum_{i=1}^N O_i} \times 100 \quad (1)$$

$$\text{Normalized mean error (NME): } \text{NME} = \frac{\sum_{i=1}^N |P_i - O_i|}{\sum_{i=1}^N O_i} \times 100 \quad (2)$$

where N is the number of observation (O) and simulation (P) pairs of MDA8 O₃. The evaluation results show that the additional HCHO emissions did not change the NMB of MDA8 O₃ with 60 ppb cutoff from “basecase” to “semihcho” (−8.8% in both cases), though they slightly decreased the NME (from 12.4% to 12.3%).

Figure 4 zooms in on the heavily industrialized area near the neck of the Detroit River, where three EGLE monitoring stations (Dearborn, Southwest Detroit, and River Rouge) are located, and where 24-h average concentrations of HCHO are routinely measured. These measurements compared well against corresponding 24-h average concentrations measured by Aerodyne Research, Inc. using a Tunable Infrared Laser Direct Absorption Spectrometer (TILDAS) during the 2021 MOOSE campaign. The additional HCHO emissions improved the agreement between the CAMx-simulated 24-h average HCHO concentrations and the DNPH cartridge measurements at these three stations, with NMB decreasing from −52.7% (“basecase”) to −41.7% (“semihcho”) and NME decreasing from 53.3% to 44.6%. In contrast, the model CO performance (as indicated by a comparison of the simulated 1-h average CO concentrations against measurements at all eight CO stations in SEMI) remained unchanged from the “basecase” to “semihcho” simulations, with NMB at −47.2% and NME at 50.2%.

Note that the HCHO performance was worse than the CO performance in the “basecase” but became better with additional HCHO emissions scaled from the CO emissions.

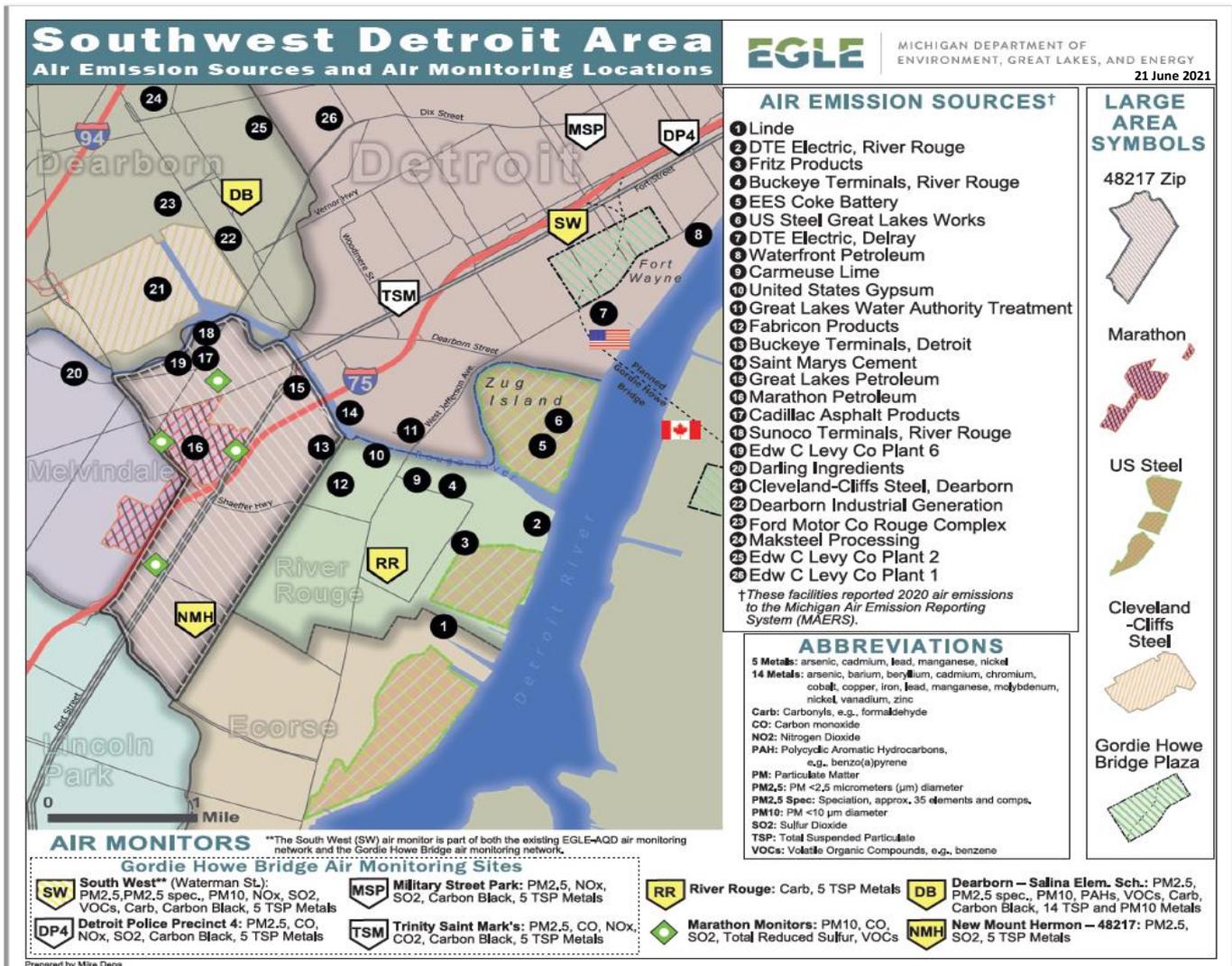


Figure 4. Map of the Detroit River area showing the locations of various industrial facilities, as well as regulatory monitoring stations run by EGLE. Note that 24-h DNPB cartridge measurements of HCHO are routinely made at the Dearborn (DB), SW Detroit (SW), and River Rouge (RR) sites.

Figures 5–7 compare the predictions of ambient HCHO by the CAMx model for the primary HCHO-enhanced and base case scenarios at the three HCHO stations in Figure 4. Also shown are corresponding 24-h average concentrations measured with DNPB cartridges during 2016. While the additional primary HCHO substantially alleviates the model HCHO deficit at Southwest Detroit and less so at Dearborn, there is hardly any improvement at the River Rouge station. It is possible that the CAMx model resolution is still too coarse to simulate the impact on the River Rouge monitor of elevated plumes of primary HCHO from tall stacks beside the Detroit River. Nevertheless, there is a clear indication that additional HCHO emissions are necessary to explain the routine observations at regulatory monitoring sites in SEMI.

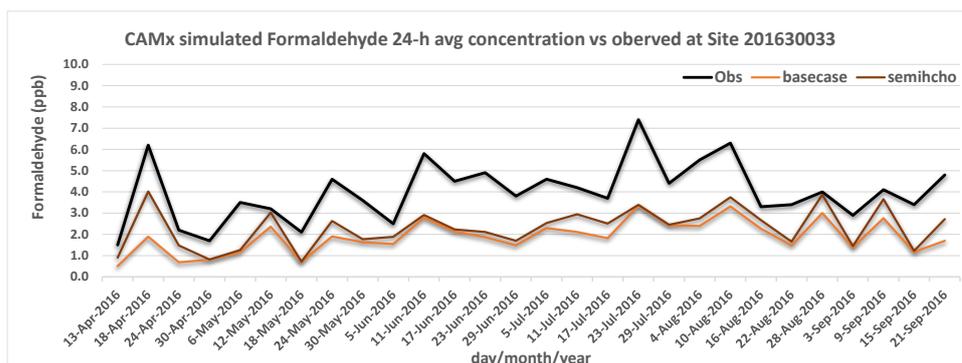


Figure 5. Comparison of high-resolution CAMx model predictions for the base case and primary HCHO-enhanced simulations versus 24-h DNPB cartridge measurements of HCHO in 2016 at the EGLE Dearborn monitoring station.

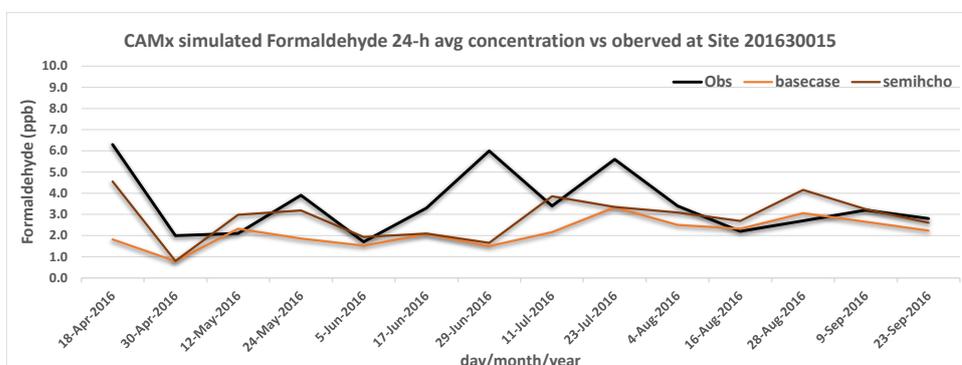


Figure 6. Same as in Figure 4, but for the Southwest Detroit monitoring station.

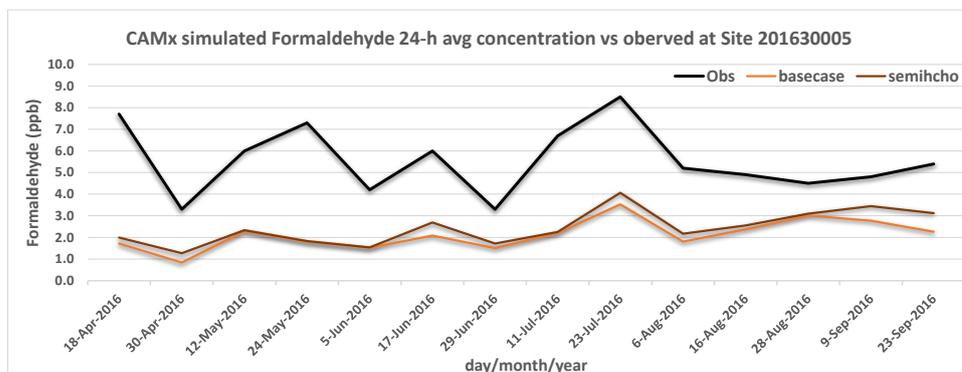


Figure 7. Same as in Figure 4, but for the River Rouge monitoring station.

Figure 8 shows the difference in near-surface ambient HCHO between the CAMx model run including additional primary HCHO based on the assumed HCHO-to-CO mass ratios and the base case run with the default NEI values for an episode on 18 April 2016. There exist two major maxima within Michigan in the additional HCHO concentrations over the base case scenario. The first maximum is, as expected, at the neck of the Detroit River in the vicinity of Zug Island. This is the location of multiple heavy industries and power plants that frequently combust natural gas or other fuels likely to produce primary formaldehyde emission plumes (see Figure 4).

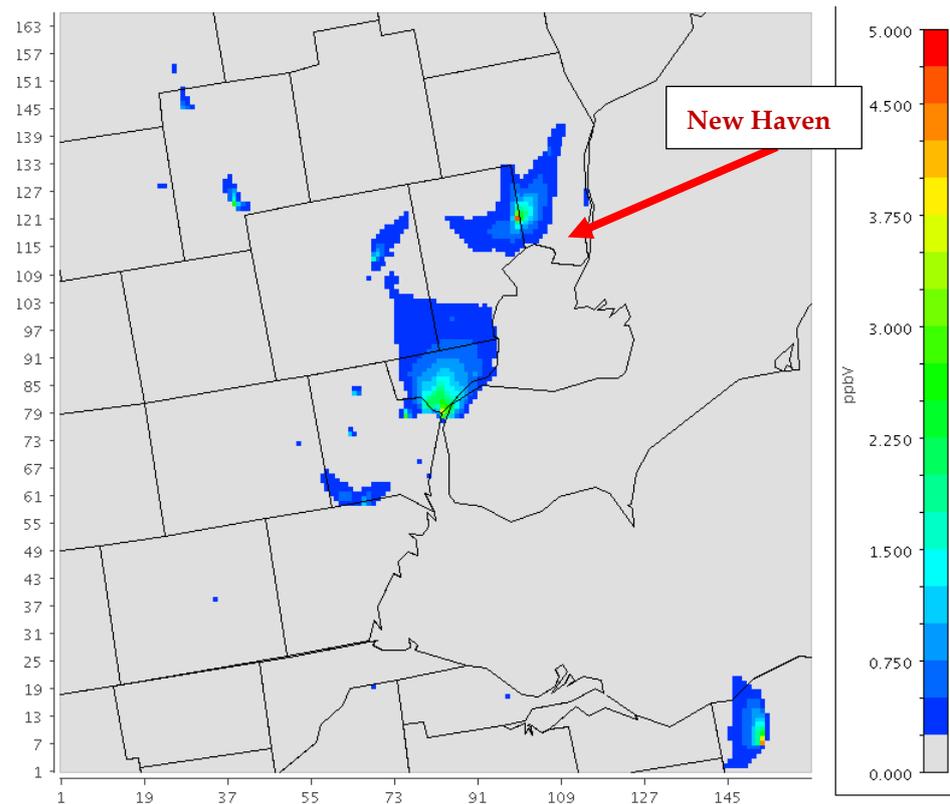


Figure 8. Additions to near-surface ambient 24-h average (LST) HCHO concentrations due to plausible primary HCHO in excess of default emissions in the base case episode for 18 April 2016 as predicted by the CAMx model. Note the maximum in the vicinity of New Haven, Michigan.

The second and more intense maximum in Figure 8 occurs near New Haven, Michigan. The model-predicted enhancement of ambient HCHO due to primary emissions was originally not expected at this suburban location and suggested that actual ambient concentrations near New Haven might be over 5 ppb. Transport of secondary HCHO is unlikely to explain this level of ambient HCHO, since the maximum is very locally confined and does not appear to be associated with a broad regional plume. The surface winds on this day (18 April) were frequently calm and under 2 m/s during most of the daytime. Moreover, the wind was generally southerly/southeasterly during the episode, rather than southwesterly as is more typical of high ozone events in SEMI, so that plumes from Detroit were likely not involved in producing the simulated HCHO maximum. In addition, the time of year (April) limits local biogenic emissions to well below their peak in summer.

Figure 9 illustrates the additional near-surface ozone associated with the primary HCHO-enhanced model simulation compared to the base case scenario for an ozone episode on 18 June 2016. The wind direction during this episode was generally ESE. The surface winds during daytime were mostly 3–4 m/s but went as high as 4–5 m/s during the afternoon. Note how a maximum 8-h ozone concentration enhancement above 1 ppb is evident downwind of the Detroit industrial core.

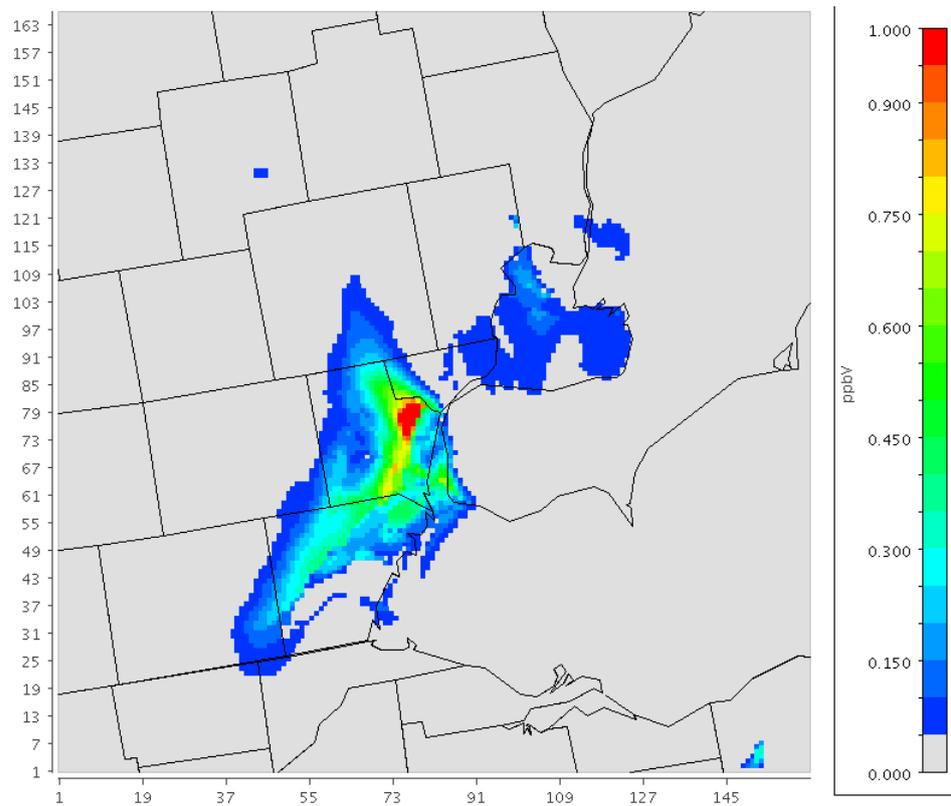


Figure 9. Additions to near-surface ambient MDA8 ozone concentrations due to plausible primary HCHO in excess of default emissions in the base case episode for 18 June 2016 as predicted by the CAMx model. Note the maximum ozone enhancements greater than 1 ppb downwind of the Detroit industrial core.

Table 2 displays the increase in simulated MDA8 O₃ from “basecase” to “semihcho” case corresponding to the larger-than-60-ppb MDA8 O₃ concentrations observed at the 10 ozone monitoring sites in SEMI during the 2016 ozone season. While the average increases of the simulated MDA8 O₃ at the 10 sites are all under 0.1 ppb, the maximum increase in simulated MDA8 O₃ due to the addition of HCHO emissions on an individual day at a specific site can be as large as 0.75 ppb, which is significant. Note that the monitoring sites in Table 2 with ID 261470005 (Port Huron) and 261630019 (Detroit-East 7 Mile) have simulated maximum increases in MDA8 O₃ of approximately 0.5 ppb or higher. Both these sites are currently in nonattainment by only 1 ppb.

Table 2. Increase in simulated MDA8 O₃ from “basecase” to “semihcho” case corresponding to the larger-than-60-ppb MDA8 O₃ concentrations observed at the 10 ozone monitoring sites in SEMI during the 2016 ozone season.

Ozone Monitoring Site ID	Average Increase in Simulated MDA8 O ₃ (ppb)	Maximum Increase in Simulated MDA8 O ₃ (ppb)	Number of Observations of >60 ppb MDA8 O ₃
260990009	0.037	0.22	24
260991003	0.035	0.18	23
261250001	0.037	0.21	23
261470005	0.070	0.64	16
261610008	0.017	0.07	18
261619991	0.024	0.1	17
261630001	0.011	0.06	19
261630019	0.065	0.49	30
261630093	0.006	0.01	2
261630094	0.084	0.75	18

3.2. HCHO Measurements

The results of the HCHO sampling with DNPH cartridges are summarized in Table 3, whereas Figure 10 displays a wind rose describing the range of wind speeds and directions that prevailed during the sampling period. In this case, the winds were mostly southerly, although there was also a weaker southwesterly component and an even weaker southeasterly flow regime. The measured ambient HCHO concentrations at the New Haven station were all above 5 ppb, confirming the predictions of the CAMx model.

Table 3. Results of 24-h DNPH cartridge monitoring at New Haven, Michigan during MOOSE. Note that the laboratory reporting limit for the analyzed samples was 0.029 ppb.

Sample Number	Sample Date	24-h HCHO (ppb)
211143	24 June 2021	5.46
211141	25 June 2021	5.22
211142	26 June 2021	5.05
211138	27 June 2021	5.65
211139	28 June 2021	5.62

New Haven 24/06/2021 to 28/06/2021

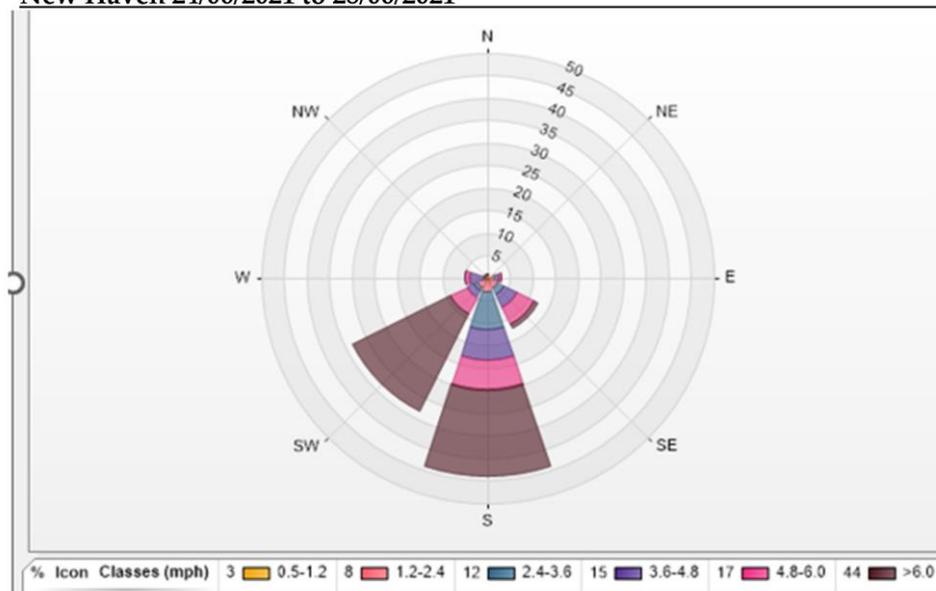


Figure 10. Wind rose illustrating the variation of wind speed and direction during the HCHO sampling conducted by EGLE at New Haven, Michigan during MOOSE. Wind speeds are in miles per hour (mph), as denoted by the color scale.

There are several facilities located within and around the New Haven area that may have emissions contributing to elevated ambient concentrations of HCHO. Among them are a landfill and landfill gas-to-energy conversion facilities located roughly 6 km northeast of the New Haven monitoring station and immediately west of the county line, roughly in the location indicated by the concentration maximum of Figure 8. These contributors contain emission units that use both Category 1 (15% mass ratio) and Category 3 (5% mass ratio) classifications for formaldehyde emissions estimates. The estimated total HCHO emissions from these contributors are roughly 100 short tons per year.

Several additional facilities that may have contributed to elevated ambient HCHO levels are located south and southwest of the New Haven area, and include natural gas pipeline transmission, asphalt paving mixture and block manufacturing, air transportation, paint and coating manufacturing, and motor vehicle parts manufacturing. The total of these additional sources likely makes up less than two percent of the combined emissions from

landfill and landfill gas-fired electrical generation facilities on an annual basis. It is possible, however, that short-term excursions from the annual mean emissions from these sources to the south and southwest of New Haven may have resulted in larger contributions to ambient HCHO concentrations measured during MOOSE.

Note that the DNPH cartridge measurements at New Haven in conjunction with the CAMx model predictions provide local evidence that there are likely direct emissions of HCHO that significantly impact ambient HCHO concentrations. However, this conclusion can also be extended to urban areas that have not only large inefficient combustion sources but also considerably less biogenic emissions than the suburban New Haven area, as is the case in Detroit.

4. Discussion

Our study has shown that a HCHO deficit exists in air quality model simulations for the SEMI ozone nonattainment area that is more likely to be explained by the lack of primary HCHO in current emissions inventories than by missing reactions in available chemical mechanisms. Confirmation of the missing primary HCHO hypothesis is supplied by the discovery of unsuspected high concentrations of ambient HCHO in New Haven, Michigan during MOOSE, which can likely be attributed to nearby industrial emissions rather than to regional-scale transport of secondary HCHO or to local biogenic emissions of isoprene. Plausible enhancements of primary HCHO can significantly alleviate the HCHO deficit in regional air quality model simulations for the SEMI ozone nonattainment area and add over 1 ppb to peak ozone in the airshed. This is a significant ozone enhancement, considering that the SEMI region exceeds the U.S. ozone NAAQS by only 1–2 ppb. Moreover, the ozone response to entire control strategy packages is often only a few tenths of a ppb [34].

The existence of significant unreported emissions of HCHO in SEMI and presumably elsewhere in the U.S. has important regulatory and policy implications. First, there must be a coordinated effort to correct the U.S. NEI so that ozone attainment demonstrations are based on more reliable modeling assumptions. The additional ambient HCHO implied by this correction to emissions inventories will enhance radical concentrations and ozone production in models as well as the simulated efficacy of control strategies. Further modeling associated with this study indicates that, not only are VOC controls more effective than NO_x controls in reducing ozone design values at the most problematic monitoring sites in SEMI, but control strategies targeting primary formaldehyde as opposed to generic VOCs may also be five times more effective on a pound-for-pound basis than control of nitrogen oxides (NO_x) in bringing marginal or moderate nonattainment areas in the U.S. into attainment of the O₃ NAAQS [34]. These strategies potentially include flare minimization at steel mills and coking facilities, as successfully implemented by the petrochemical industry in recent years, and the use of oxidation catalysts in stationary engines at oil and gas pipeline compressor stations, landfills, and power plant peaker units. Control of fugitive emissions of HCHO at wastewater treatment plants, chemical manufacturing facilities, and coating operations at automotive assembly sites may also be necessary.

Corrections to the HCHO emissions inventory can be brought about by using more contemporary measurement techniques, such as Imaging and Multi-Axis Differential Optical Absorption Spectroscopy (DOAS) [35,36] in addition to Fourier Transform Infrared Spectroscopy (FTIR) that is already used in engine stack tests. Moreover, inverse modeling of emissions based on 3D fine-scale models and mobile real-time measurements with laser-based techniques is now possible, as demonstrated by Olaguer et al. [32] for HCHO emissions from a refinery in Texas City, Texas, USA. In effect, modeling and measurement technologies have sufficiently evolved to enable the problem of HCHO deficits in air quality model simulations to be solved. Solving this problem will not only reduce ozone in nonattainment areas but also alleviate toxics exposure, given that HCHO is likely the most important HAP contributing to human health risk in the United States.

5. Summary and Conclusions

While this study focuses on the SEMI ozone nonattainment area, the main conclusions are broadly applicable throughout the United States and other regions of the world where out-of-date HCHO emission factors are used as a basis for emission inventories and ozone modeling. These conclusions are as follows:

- Primary HCHO is significantly underestimated in current emissions inventories due to the under-deployment of contemporary emission measurement techniques.
- Ambient HCHO concentrations near the surface in heavily industrialized urban areas are likely under-predicted by air quality models due to a deficit in primary HCHO, and not merely because existing model chemical mechanisms under-predict secondary HCHO due to biogenic isoprene emissions.
- The MDA8 O₃ attributable to missing HCHO emissions can approach or exceed 1 ppb in areas downwind of HCHO emission sources.
- Controlling emissions of HCHO may yield significant human health benefits beyond mitigating human exposure to ambient ozone by reducing toxics exposure, especially in industrial fence line communities.

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