

## PAPER

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## Anthropogenic secondary organic aerosol and ozone production from asphalt-related emissions†‡

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Liquid asphalt is a petroleum-derived substance commonly used in construction activities. Recent work has identified lower volatility, reactive organic carbon from asphalt as an overlooked source of secondary organic aerosol (SOA) precursor emissions. Here, we leverage potential emission estimates and usage data to construct a bottom-up inventory of asphalt-related emissions in the United States. In 2018, we estimate that hot-mix, warm-mix, emulsified, cutback, and roofing asphalt generated ~380 Gg (317 Gg–447 Gg) of organic compound emissions. The impacts of these emissions on anthropogenic SOA and ozone throughout the contiguous United States are estimated using photochemical modeling. In several major cities, asphalt-related emissions can increase modeled summertime SOA, on average, by 0.1–0.2  $\mu\text{g m}^{-3}$  (2–4% of SOA) and may reach up to 0.5  $\mu\text{g m}^{-3}$  at noontime on select days. The influence of asphalt-related emissions on modeled ozone are generally small (~0.1 ppb). We estimate that asphalt paving-related emissions are half of what they were nearly 50 years ago, largely due to the concerted efforts to reduce emissions from cutback asphalts. If on-road mobile emissions continue their multidecadal decline, contributions of urban SOA from evaporative and non-road mobile sources will continue to grow in relative importance.

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### Environmental significance

Liquid asphalt is a petroleum-derived material commonly used as a binder or sealant in construction. Historically, emissions from asphalt paving processes occurring near-ambient temperatures have been included in the U.S. EPA's National Emissions Inventory. Recent research has chemically-speciated a range of volatile organic vapors emitted from asphalt, including intermediate-volatility and semivolatile organic compounds, at temperatures associated with heated paving processes. Here, we develop a nationwide inventory of asphalt-related emissions, including emissions from both heated and near-ambient temperature processes, and subsequently use the inventory as inputs to a photochemical air quality model to quantify potential impacts on criteria pollutants. Our results suggest that asphalt paving contributes significantly to nationwide volatile organic compound emissions and that these emissions can enhance local, predominantly urban, fine particulate matter concentrations.

## Introduction

Liquid asphalt is a petroleum-derived material commonly used as a binder or sealant in construction. In 2018, ~20 Tg of liquid asphalt was consumed in the United States for paving

processes, including the construction or re-surfacing of roads and parking lots, as well as non-paving uses, such as the application of asphalt roofing coatings and manufacturing of roofing shingles.<sup>1–3</sup> To produce liquid asphalt, petroleum feedstocks are vacuum distilled to an equivalent of +500 °C to

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remove the majority of more volatile components for other downstream products.<sup>4</sup>

In paving processes, liquid asphalt is mixed with an aggregate and can be applied at near-ambient or heated temperatures. If applied at near-ambient conditions, additional components must be added to lower the viscosity of the mixture.<sup>5</sup> Following application, these added components largely evaporate. Cutback asphalt is applied at ambient temperatures and involves mixing asphalt binder and aggregate with petroleum solvents (*e.g.*, naphtha, kerosene, diesel), which vary depending on the desired cure rate. Emulsified asphalt is also applied in ambient conditions and utilizes water-based solvents with an emulsifying agent. In contrast to cutback asphalts, emulsified asphalts have become more common in recent years due to lower emissions of traditional volatile organic compounds (VOCs) and energy savings.<sup>5</sup>

Hot-mix asphalt is the most common application method for asphalt paving and involves combining liquid asphalt, which is stored hot on-site, with aggregate at a mixture temperature of approximately 150 °C. The mixture is then hauled to the usage site, where it is moved, placed, compacted, and ambiently cooled without the need for added solvents. Warm-mix asphalt is a more recent approach that enables paving to occur using cooler temperature mixtures and constitutes ~20% of heated asphalt paving.<sup>6</sup> Lower paving temperatures require additives (water, organic-based, or a hybrid) to reduce the viscosity of the mixture, but also promote energy savings through reductions in fuel use and are designed to generate fewer organic emissions during application.<sup>7</sup>

Historically, emissions from cutback and emulsified asphalt have been estimated for the U.S. EPA's National Emissions Inventory (NEI).<sup>8</sup> Due to the enhanced organic emissions from their solvent additions, these processes were viewed as the dominant source of reactive organic carbon (ROC) emissions from asphalt paving. Here, ROC is defined as all non-methane organic gases and organic aerosol.<sup>9,10</sup> While heat-driven application processes represent most paving activity, it had been assumed that emissions were minimal due to the removal of more volatile compounds during vacuum distillation. Recent research has chemically-specified a range of volatile organic vapors emitted from asphalt, including intermediate-volatility and semivolatile organic compounds (IVOCs, SVOCs), at temperatures associated with hot-mix, warm-mix, and post-application temperatures.<sup>7</sup> The photochemical oxidation of VOCs, IVOCs, and SVOCs, from a mix of anthropogenic and biogenic sources, can lead to the formation of secondary organic aerosol (SOA), which is often the dominant component of organic aerosol (OA) in urban environments.<sup>11–13</sup> Since fine particulate matter (PM<sub>2.5</sub>) is associated with impacts on human health and wellbeing,<sup>14,15</sup> quantifying these emissions is important for building useful platforms for air quality policy analysis.

In this study, we develop a nationwide inventory of asphalt-related emissions, including emissions from both paving and non-paving processes, test the sensitivity of emissions to uncertain parameters using a Monte Carlo analysis, and subsequently use the inventory as inputs to the Community

Multiscale Air Quality (CMAQ) model. Within CMAQ, this study models the aging and transformation of lower volatility organics using the Community Regional Atmospheric Chemistry Multiphase Mechanism<sup>16</sup> (CRACMM). We simulate air quality throughout the continental United States and quantify the potential impacts of asphalt emissions on criteria pollutants (*i.e.*, PM<sub>2.5</sub>, O<sub>3</sub>). In addition, we explore trends in historical asphalt usage and estimated emissions by process type to provide context on how air pollutants have evolved from asphalt-related emissions in recent years.

## Materials & methods

### Asphalt emissions and speciation

Asphalt usage varies by process and year. Here, we apply process-specific, 2018 usage statistics from an industry survey<sup>1</sup> that reports annual usage of asphalt cement, cutback asphalt, emulsified asphalt, and roofing asphalt. The U.S. Energy Information Administration (EIA)<sup>3</sup> also reports the supply of total asphalt and the difference in 2018 total asphalt usage between the two datasets is ~4%, which provides confidence in the overall usage patterns used here. Asphalt cement usage is further split between hot-mix and warm-mix processes using state-specific statistics from a separate industry report.<sup>6</sup>

The Asphalt Institute survey<sup>1</sup> specifies usage at various state-level aggregations (ranging from 1–3 states). We disaggregate these values to each state using state-specific usage statistics of hot-mix and warm-mix asphalt.<sup>6</sup> For roofing asphalt, we allocate usage to the state-level using construction expenditure statistics from the U.S. Census Bureau.<sup>17</sup> To further allocate emissions to the county-level, we use estimates of paved vehicular miles traveled for paving and population for non-paving asphalt applications. Temporally, emissions are translated from annual-to-monthly using product supply statistics from the U.S. EIA<sup>3</sup> for asphalt processes applied heated and flat for asphalt processes applied under ambient conditions. Further, diurnal profiles are applied to emissions, with a peak at midday and nadir at night.

Emissions from all asphalt processes are estimated during both application and “in-use” periods, with “in-use” representing the emissions occurring at environmental temperatures following the application process. Both application and in-use emission factors for hot- and warm-mix paving asphalts, and roofing asphalt, as well as the in-use emission factors for cutback and emulsified asphalt, are based on measurements from Khare *et al.*<sup>7</sup> Emission factors associated with the application of cutback and emulsified asphalt paving follow the methods used in the U.S. EPA's NEI,<sup>8</sup> which are based on compositional information reported in Material Safety Data Sheets.

During the hot-mix application process, the asphalt mixture is applied at elevated temperatures (~150 °C). Measurements indicate that emissions are highest when heated and decline over time following an exponential decay curve. Like Khare *et al.*,<sup>7</sup> we estimate the application-related emissions over a 5 hours period with, which yields an average emission factor of ~4 g kg<sup>-1</sup> of asphalt binder (Table 1). Warm-mix asphalt



**Table 1** Nationwide usage and application, in-use, and total emission factors for the asphalt-related processes and products considered here. Note that the activity factor used here is in tons of liquid asphalt binder (*i.e.*, excludes mass of aggregate)

| Type/process | Usage [Gg asphalt] | Application-related emissions [g kg <sup>-1</sup> asphalt] | In-use emissions [g kg <sup>-1</sup> asphalt] | Total emissions [g kg <sup>-1</sup> asphalt] |
|--------------|--------------------|------------------------------------------------------------|-----------------------------------------------|----------------------------------------------|
| Hot-mix      | 12 231             | 4.0                                                        | 1.0                                           | 5.0                                          |
| Warm-mix     | 3182               | 2.2                                                        | 1.0                                           | 3.2                                          |
| Cutback      | 153                | 407                                                        | 1.0                                           | 408                                          |
| Emulsified   | 1960               | 98                                                         | 1.0                                           | 99                                           |
| Roofing      | 2910               | 0.2                                                        | 17.8                                          | 18                                           |

application generally occurs at 20–40 °C cooler temperatures. Reducing the asphalt temperature from 140 °C to 120 °C reduces the initial magnitude of emissions by ~46% (Fig. S5† of Khare *et al.*<sup>7</sup>). As such, we adopt an average warm-mix application emission factor of ~2 g kg<sup>-1</sup> asphalt. Cutback and emulsified application emission factors includes a volatilization fraction of 95% for all added solvent components and yields an emission factor of ~407 g kg<sup>-1</sup> asphalt for cutback asphalt and ~98 g kg<sup>-1</sup> asphalt for emulsified asphalt.<sup>8</sup> For roofing-related asphalt application, we apply the hot-mix asphalt application emission factor for the limited use of hot roofing application at present day (~5%) since most roofing asphalt is applied with limited heating.<sup>18</sup>

In-use emissions continue after application, occur at ambient temperatures, and are influenced by local climate. They are enhanced with elevated surface temperatures and a total of ~1 g kg<sup>-1</sup> were observed over sustained, 82 hours heating at 60 °C, with decaying but continued emissions beyond the timescale of the experiment.<sup>7</sup> Asphalt surface temperatures will vary with location, season, and time of day, with some locations more frequently experiencing asphalt surface temperatures ≥60 °C. While these emissions will expectedly vary spatiotemporally, total in-use emission potential for all asphalt paving processes of ~1 g kg<sup>-1</sup> (ref. 7) (Table 1) is applied across the contiguous U.S. In-use roofing asphalt emissions also occur with elevated roof temperatures and a total potential in-use emission factor of 17.8 g kg<sup>-1</sup> is used here from prior work.<sup>7</sup>

Like many sources, emission factors can be expected to vary across asphalt products and processes, with variations due to factors such as production and application methods, duration of application processes, chemical composition, and environmental conditions. As such, emissions measurements from experiments have expectedly yielded a range of values, both larger and smaller than those adopted here, and the inclusion of solar exposure (with or without the presence of a water layer) can greatly enhance emissions.<sup>7,19–21</sup> The range of influencing factors all indicate that both application and in-use asphalt-related emissions factors could greatly vary across source category types, though prior work indicates a sizable reservoir of IVOCs and SVOCs in common asphalt binders.<sup>22</sup> To incorporate the sensitivity of known and unknown parameters, we employ a Monte Carlo analysis and perform 10 000 simulations on emission factor estimates (Fig. 1a–c). Our simulations take random samples within prescribed uncertainty bounds for process-specific asphalt usage, the percent of asphalt binder applied at reduced temperatures (*i.e.*, warm-mix

asphalt), and both application and in-use emission factors for all paving activities (Table S1†).

For product usage, we assume there is ±25% uncertainty (95% CI) at the state-level aggregations from the Asphalt Institute survey<sup>1</sup> for all asphalt processes (*i.e.*, both paving and non-paving). This is likely conservative as multiple national-level datasets report similar 2018 total asphalt usage. Annual statistics on the amount of asphalt binder applied at warm-mix asphalt temperatures features considerable state-to-state variability, so we apply ±25% uncertainty (95%) to the calculated split between hot- and warm-mix asphalt paving at the state-level. Mean emission factors associated with application follow the methods of Khare *et al.*,<sup>7</sup> which estimates the application-related emissions over a 5 hours period, though these emissions could occur over different timescales depending on conditions and project specifics. However, application timescales may vary based on the distance between the asphalt plant and construction site, environmental conditions, and other variables. To incorporate this uncertainty, we assume application-related emissions from hot-mix asphalt, warm-mix asphalt, and roofing asphalt feature non-negative, skewed lower distributions with a threshold max value equivalent to a 6 h timescale of emission and approximate mean of a 5 h timescale of emission (Fig. S1a and c†). For cutback and emulsified asphalt, we assume the application emission factor uncertainty is ±25% (Fig. S1b†). Measurements associated with in-use emissions featured continued emissions beyond the timescale of the experiment but were capped at a mean of ~1 g kg<sup>-1</sup> for the main analysis. In the Monte Carlo analysis, we assume these emissions are lognormally distributed across the mean value of ~1 g kg<sup>-1</sup> for all paving applications (Fig. S1d and e†) and lognormally distributed with a mean value of ~17.8 g kg<sup>-1</sup> for roofing asphalt (Fig. S1f†).

The speciation of hot-mix, warm-mix, and roofing asphalt emissions used here were reported by Khare *et al.*<sup>7</sup> (Fig. 1), which was focused on C10 and larger compounds and thus does not include C9 and smaller single-ring aromatics that are also SOA precursors. For hot- and warm-mix asphalt, speciation from a test at 140 °C were used for both processes (Fig. 1d). These emissions are dominated by IVOC compounds ( $3 \times 10^2 \mu\text{g m}^{-3} < \text{C}^* < 3 \times 10^6 \mu\text{g m}^{-3}$ ) that span multiple functionalities, including significant quantities of oxygenates, aromatics, polycyclic aromatic hydrocarbons, cyclic alkanes, and straight-chained alkanes. The speciation of roofing asphalt-related emissions utilize the results from a 75 °C experiment to simulate peak daytime roofing temperatures.<sup>7</sup> These non-pavement



## Asphalt-Related Emission Factors

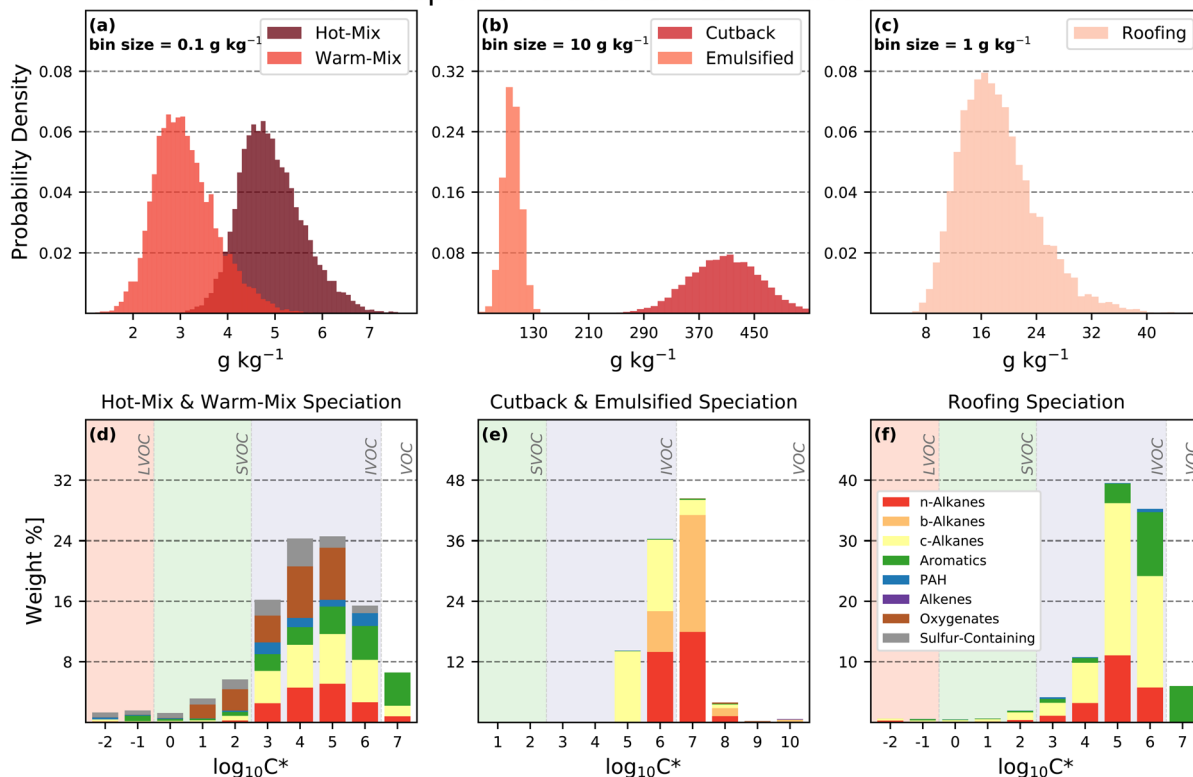


Fig. 1 Total emission factors (*i.e.*, application-related + in-use emissions), in  $\text{g kg}^{-1}$  of liquid asphalt, from the Monte Carlo analysis, for (a) hot- and warm-mix paving asphalt, (b) cutback and emulsified paving asphalt, and (c) roofing asphalt. Emissions speciation of (d) hot- and warm-mix paving asphalt, (e) cutback and emulsified paving asphalt, and (f) roofing asphalt.

emissions are relatively more volatile on average than the hot- and warm-mix asphalt emissions and are predominantly aromatics, cyclic alkanes, and straight-chained alkanes (Fig. 1f). Cutback asphalts always, and emulsified asphalts sometimes, contain organic solvents that vary based on the desired cure rate.<sup>5</sup> These solvents may include gasoline, naphtha, kerosene, and diesel. Here, we assume the organic solvent used in both processes is kerosene (*i.e.*, a medium cure rate solvent), though we acknowledge that the use of diesel or gasoline as solvents would increase the solvent's SOA and/or  $\text{O}_3$  formation potential. Kerosene is a petroleum-based hydrocarbon blend, largely consisting of C6–C16 branched and straight-chained alkanes, as well as polycyclic aromatic hydrocarbons.<sup>23</sup> As such, we utilize a composite profile for lighter fluid from the U.S. EPA's SPECIATE database<sup>24</sup> (profile 95820) that fits this chemical description (Fig. 1e) for both cutback and emulsified asphalt speciation. Using the SOA structure activity relationship (SAR) screening tool from Pye *et al.*,<sup>16</sup> the estimated SOA yields from the heated (Fig. 1d), emulsified/cutback (Fig. 1e), and roofing asphalt (Fig. 1f) speciation profiles are 35%, 15%, and 38%, respectively, with variations influenced by the chemical structures of the complex gas-phase precursor mixtures.

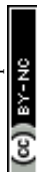
### Photochemical modeling and evaluation

Air quality for 2018 is modelled using CMAQv5.4 at 12 km resolution over the contiguous United States (CONUS).

Meteorological and non-asphalt emission inputs, including wildland fires, are retrieved from the U.S. EPA's Air Quality Time Series (EQUATES) project<sup>25</sup> and all simulations feature a 10 days spin-up beginning in December 2017 to minimize the influence of initial conditions. Additional modeling options used here include: (1) an updated parameterization of aerosol deposition in the M3DRY model,<sup>26</sup> including bidirectional ammonia exchange,<sup>27</sup> (2) biogenic emissions generated inline using the Biogenic Emission Inventory System (BEIS) v4,<sup>28</sup> (3) runtime emissions processing using the Detailed Emissions Scaling, Isolation, and Diagnostic (DESID) module,<sup>29</sup> (4) and gas- and aerosol-phase chemistry simulated using the Community Regional Atmospheric Chemistry Multiphase Mechanism (CRACMM) version 1.0 chemical mechanism.<sup>16</sup>

The impact of asphalt-related emissions on SOA and ozone is quantified by taking the difference between two photochemical modeling simulations. The first simulation incorporates the newly developed inventory and the second contains no asphalt-related emissions but maintains all other anthropogenic and biogenic emissions. To generate gridded emissions, we allocate county-level emissions using total road miles and low/medium/high development intensity from the National Land Cover Database (NLCD) as proxies for paving and non-paving asphalt applications, respectively.

To evaluate modeling performance, predictions of organic carbon (OC),  $\text{PM}_{2.5}$ , and the maximum daily 8 hours (MDA8)  $\text{O}_3$  concentrations from the simulation including the newly





developed asphalt-related inventory are compared with observations from the U.S. Environmental Protection Agency's Air Quality System (AQS). The model evaluation is facilitated using the Atmospheric Model Evaluation Tool<sup>30</sup> and performance metrics utilize aggregated statistics from Emery *et al.*<sup>31</sup> The performance metrics consider the absolute magnitude of modelled normalized mean bias (NMB) and compare results to top 33rd percentile ("goal") and top 67th percentile ("criteria") of past evaluation applications for OC, PM<sub>2.5</sub>, and MDA8 O<sub>3</sub>. The top 33rd percentile of OC, PM<sub>2.5</sub>, and MDA8 O<sub>3</sub>, NMB are less than ±15%, ±10%, and ±5%, respectively, and the top 67th percentile of NMB for OC, PM<sub>2.5</sub>, and MDA8 O<sub>3</sub> are less than ±50%, ±30%, and ±15%, respectively.

## Results

### Asphalt-related emissions

Emissions from heated asphalt paving are predominantly from hot-mix asphalt processes (Fig. 2a). In 2018, we estimate that hot-mix asphalt (~12.2 Tg of usage) generated ~60 Gg of organic emissions (95% CI: 45 Gg – 79 Gg), with most emissions occurring during application (Fig. S1a†). By comparison, emissions from warm-mix asphalt paving were substantially smaller (~10 Gg, 95% CI: 6 Gg – 15 Gg) due to both lower application-related emission factors (Fig. S1a†) and less usage (~3.2 Tg of usage; ~21% of total heated asphalt paving nationally). However, since application emissions from warm-mix asphalt are lower than application-related emissions from hot-mix asphalt (Fig. S1a†), the proportion of emissions occurring in the in-use period are notably higher (~32% for warm-mix asphalt vs. ~20% for hot-mix asphalt).

Emulsified asphalt paving is estimated to generate the most asphalt-related emissions of any process (Fig. 2b) despite occurring at ambient temperatures. This is due to both its abundant usage (~1.9 Tg of liquid asphalt usage) and high application-related emission factor (Fig. S1b†). In 2018, we estimate that emulsified asphalt paving generated ~193 Gg of organic emissions (95% CI: 143 Gg – 245 Gg). Cutback asphalt paving, which features an extremely large emissions potential per mass usage (Fig. 1b), was estimated to generate ~62 Gg of

organic emissions (95% CI: 46 Gg – 80 Gg). This mass is nearly equivalent to the emissions from hot-mix asphalt paving, despite being only a fraction (~1%) of the usage (~153 Gg).

Roofing asphalt, by contrast, are dominated by emissions that occur during the in-use period (~99%). We estimate that ~54 Gg of organic emissions (95% CI: 28 Gg – 93 Gg) occurred in 2018 from this process (Fig. 2c). While usage of roofing asphalt (~2.9 Tg) was ~4× less than hot-mix asphalt and ~20× greater than cutback asphalt, emissions from these three processes was roughly equivalent. Nationally, the span of emissions estimates from paving and non-paving processes were predominantly driven by uncertainty associated with application and in-use emission factors, respectively.

Spatially, total potential asphalt-related emissions were highest in Texas (34 Gg) and California (31 Gg). A secondary state-level peak occurred in the upper midwest, where emissions eclipsed 15 Gg in Ohio, Michigan, Illinois, Wisconsin, and Indiana (Fig. S2†). Several less populated states with more sparse highway infrastructure (*e.g.*, Montana, Wyoming, North Dakota), as well as smaller states in the upper Northeast (*e.g.*, New Hampshire, Vermont, Maine), featured total state-level emissions <5 Gg. Due to the allocation methods employed in this analysis (*i.e.*, mostly paved vehicular miles traveled), county-level emissions tend to congregate in the urban centers of each state.

### Model performance

The normalized mean bias for 24 seasonal and regional (4 seasons and 6 regions) aggregations using the simulation with updated asphalt-related emissions were included in the model evaluation of predicted OC, PM<sub>2.5</sub>, and MDA8 O<sub>3</sub> (Fig. S3, Table S3†). OC model performance featured significant seasonal variation, with positive bias (+66% NMB throughout the CONUS) in the winter and low bias in the summer (−34% NMB). In the summertime, low OC bias is largest in the western half of the United States and coincides with even lower relative PM<sub>2.5</sub> bias, suggesting wildland fire emissions may be a driver for this performance. Of the 24 seasonal and regional aggregations evaluated here for OC, 4 reached the NMB "goal" defined by

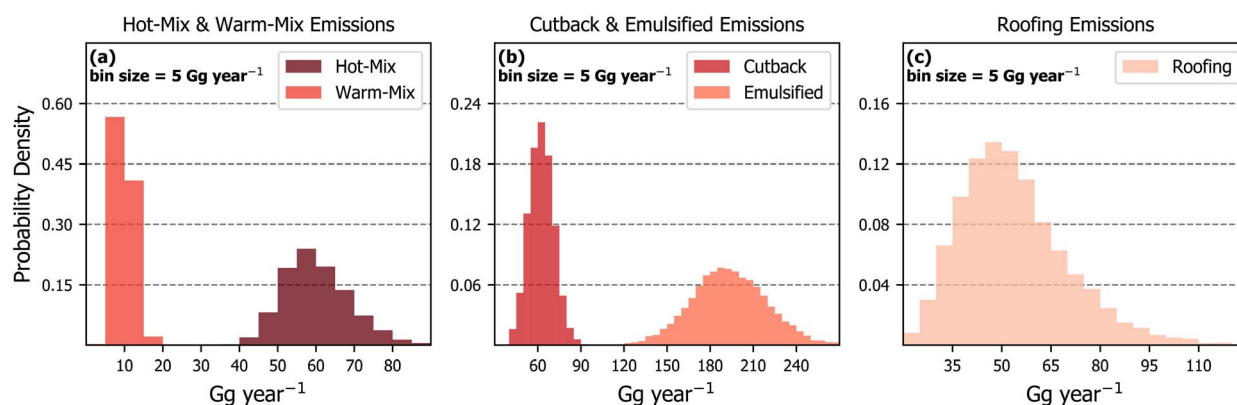


Fig. 2 Distributions of national-level annual emissions estimates from (a) hot- and warm-mix paving asphalt, (b) cutback and emulsified paving asphalt, and (c) roofing asphalt.



Emery *et al.*,<sup>31</sup> 15 met the “criteria,” and 5 met neither. PM<sub>2.5</sub> performance was seasonally consistent with the OC model performance (*i.e.*, generally high bias in the cooler months and low bias in the warmer months). In contrast to OC and PM<sub>2.5</sub>, modelled O<sub>3</sub> performance was consistent with prior CMAQ work.<sup>32</sup> This includes a low bias throughout the CONUS for springtime months, a low bias in the southwest spanning all seasons, and high bias in the midwest for non-springtime months. In addition, the model was 11–17% high biased in the eastern half of the United States in the fall. These modelled biases have been previously attributed to underestimated lateral boundary O<sub>3</sub> in the winter and spring, and uncertainty in dry deposition and emissions.<sup>33</sup> For MDA8 O<sub>3</sub>, 6 of the evaluation aggregations met the modeling performance NMB “goal,” 14 met the “criteria,” and 4 met neither.

### Air quality impacts from asphalt-related emissions

Anthropogenic SOA enhancements from asphalt-related emissions were highest in the summertime (Fig. 3), with population-weighted peaks of 0.1–0.2  $\mu\text{g m}^{-3}$  in Southern California, New York City, and several counties in the upper Midwest. These seasonal average concentrations account for 2–4% of the modelled, county-level SOA. Wintertime enhancements were roughly half as large due to the slower photochemistry and less emissions during the cooler months. Diurnally, SOA enhancements were typically largest in the middle of the day and featured significant day-to-day variation. In Queens County, NY, average noontime SOA enhancements from asphalt-related emissions were 0.2  $\mu\text{g m}^{-3}$ , but several modelled days featured enhancements eclipsing 0.5  $\mu\text{g m}^{-3}$ . Similar day-to-day variability was also observed in other highly populated cities, such as Los Angeles, Denver, and Chicago (Fig. 3), and in all seasons.

Notably, results for both Texas and Florida indicate very little enhancements of asphalt-related SOA despite considerable emissions (34 Gg and 9 Gg, respectively). The proportion of

asphalt-related emissions from heated applications (hot-mix, warm-mix, and roofing), which result in relatively lower volatility components than paving asphalt applied under ambient conditions (Fig. 1), are similar in California, the upper Midwest, and Texas (23–31%). Since emissions from asphalt-related sources are dominated by IVOCs, OA formation pathways predominantly rely upon oxidation of the primary, evaporative vapors. This process can be modulated by the abundance of local oxidants<sup>34</sup> and this appears to be the driver of the low asphalt-related SOA in both Texas and Florida (Fig. S4†). For example, the average noontime O<sub>3</sub> concentration in both Houston, TX and Orlando, FL was  $\sim 10$  ppb less than the concentrations in Los Angeles and New York City.

The influence of asphalt-related emissions on MDA8 O<sub>3</sub> also peaked in the summertime but was generally small (Fig. S5†). Outside of Southern California and the urban cores of other major cities, asphalt-related emissions increased summertime MDA8 O<sub>3</sub> by  $<0.1$  ppb, and mostly only by  $<0.01$  ppb. According to ground- and satellite-based observations, most of the CONUS outside major urban areas is NO<sub>x</sub>-limited for O<sub>3</sub> formation,<sup>35</sup> which is consistent with the small impact of asphalt emissions on O<sub>3</sub> seen here. In Los Angeles, the population-weighted, summertime average MDA8 O<sub>3</sub> enhancement from asphalt-related emissions is 0.2 ppb. However, like modelled SOA, there is significant day-to-day variation in impacts and enhancements could nearly double ( $\sim 0.4$  ppb) on select days. Similar enhancements were modelled in the New York City region, though were generally half as large ( $\sim 0.1$  ppb) in other major cities (*e.g.*, Chicago, Denver) and below 0.01 ppb in most other areas. These concentrations translate to 0.1–0.4% of the modelled, county-level MDA8 O<sub>3</sub> in the summertime.

### Historical trends of asphalt emissions

Process-level usage of liquid asphalt exhibits long-term trends that are reflected in emission estimates (Fig. 4). Over the period

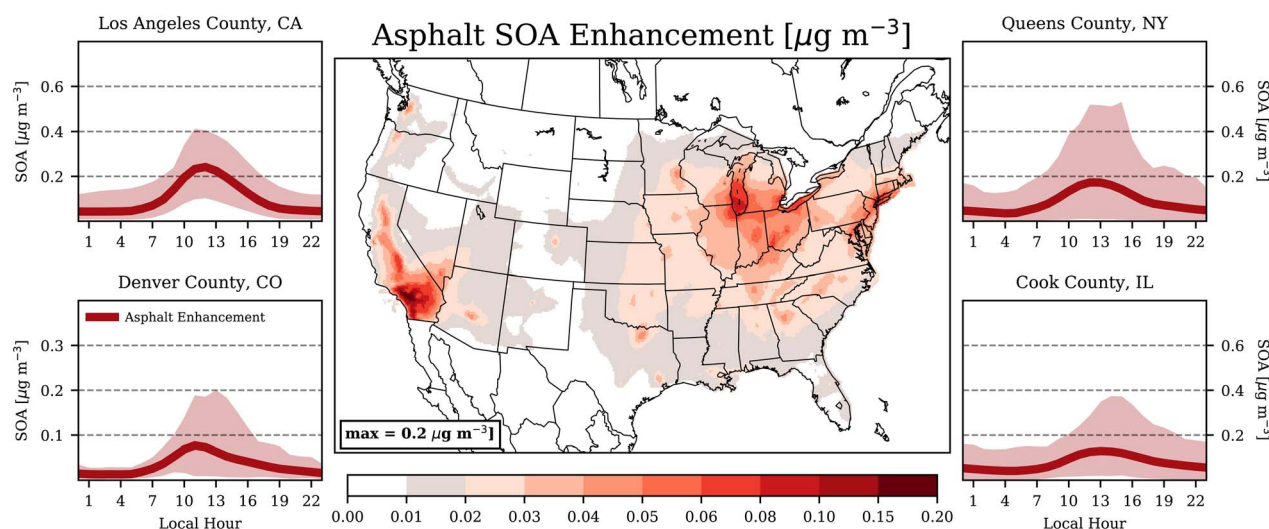


Fig. 3 Summertime-average SOA enhancements from asphalt-related emissions (center). Diurnal, population-weighted SOA enhancements from asphalt-related emissions for select counties (side panels) where the lines indicate the average asphalt-related enhancements for each hour of the day and shading represents the asphalt-related enhancements for 95% of all days. Note: Chicago is in Cook County, Illinois.



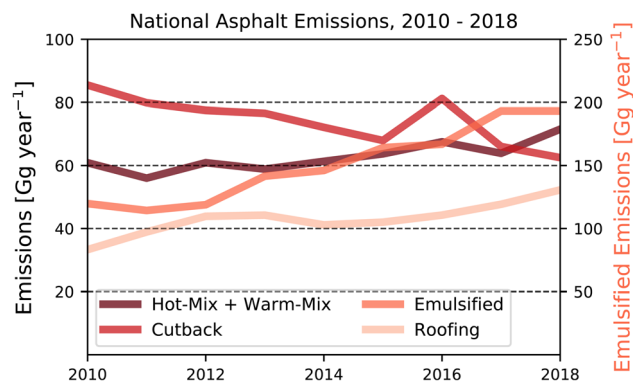


Fig. 4 Estimated 2010–2018 national-scale emissions for all asphalt processes. Note that emissions from emulsified asphalt utilize the secondary (right) y-axis.

2010–2018, liquid asphalt usage increased roughly 3% per year. Most processes featured increases over this period, including hot-mix asphalt paving (2.7% per year), warm-mix asphalt paving (7.2% per year), emulsified paving (6.4% per year), and roofing asphalt products (6.0% per year). As hot-mix asphalt paving is the dominant usage process (~60% of all asphalt usage), its trajectory drives the overall usage patterns. In contrast, cutback asphalt paving featured a decrease of ~3.5% per year.

Since cutback asphalt paving features the largest emissions potential (Fig. 1), the usage reduction between 2010 and 2018 continues a decades long decline in overall asphalt-related emissions, both from cutback asphalt and asphalt paving more broadly. In 1975, national VOC emissions from cutback asphalt paving were estimated to be ~600 Gg,<sup>36</sup> which is ~8× higher than present day emissions from cutback asphalt paving and ~2× higher than all present-day asphalt paving emissions. All other liquid asphalt processes feature increases in estimated emissions since 2010, driven by increased activity. Heated paving emissions (*i.e.*, hot-mix and warm-mix) have grown, with warm-mix asphalt emissions, which have less emissions per mass of asphalt applied (Fig. 1), outpacing the relative emissions growth from hot-mix asphalt paving. The sustained substitution of emulsified asphalt in place for cutback asphalt for ambient paving applications has driven emulsified asphalt emissions to be the dominant emissions source from liquid asphalt. Similar conclusions were presented in prior National Emission Inventories<sup>8</sup> and this trend continues in the present analysis. Emissions from roofing asphalt have also increased since 2010 but are estimated to emit less organics than all other liquid asphalt usage processes.

## Discussion & conclusions

Nationwide, liquid asphalt-related emissions contributed an estimated ~380 Gg of organic emissions (95% CI: 317 Gg – 447 Gg) in 2018. This is ~12% the mass of known emissions from volatile chemical products (VCPs),<sup>37</sup> a separate and increasingly important evaporative source of anthropogenic organic emissions. However, asphalt-related emissions are of lower volatility

and have high SOA yields on average. Compared to the 2017 NEI (~158 Gg),<sup>8</sup> the asphalt-related emissions derived here are ~222 Gg higher. This is due to the inclusion of new sources (*i.e.*, hot-mix, warm-mix, and roofing asphalt emissions) and better reflecting the present-day usage patterns of cutback and emulsified asphalt (see Fig. 4). Here, 2018 usage statistics are applied for all emission calculations, whereas the 2017 NEI relied upon usage statistics from a 2008 survey.

Emissions from asphalt-related processes undergo oxidation in the atmosphere and form both SOA and O<sub>3</sub>. The magnitude of both pollutants are highest in the summertime and in the middle of the day when photochemistry peaks, which may also coincide with enhancements in temperature (or solar) dependent emissions of in-use asphalt materials. In several major cities (*e.g.*, Los Angeles, New York City) and in the upper Midwest, asphalt-related emissions increase the summertime population-weighted concentration of anthropogenic SOA, on average, by 0.1–0.2 µg m<sup>-3</sup>, and can reach up to 0.5 µg m<sup>-3</sup> at noontime on select days. In these regions, such concentrations account for 2–4%, on average, of the modelled SOA. In contrast, the influence of asphalt-related emissions on O<sub>3</sub> were more localized and generally small. Several major cities feature enhancements of summertime MDA8 O<sub>3</sub> on the order of 0.1–0.2 ppb (0.1–0.4% of the modelled MDA8 O<sub>3</sub>), whereas much of the remaining CONUS features enhancements <0.01 ppb. Interestingly, several states feature sizable quantities of asphalt-related emissions (*e.g.*, Texas and Florida) that do not translate into much asphalt-related SOA due to lower concentrations of oxidants, highlighting the importance of chemistry on SOA formation.

Variability in the magnitude of emissions from asphalt-related materials during application, in-use, and other parts of their complete lifecycle are expected, and may be due to several variables. These variables include, but are not limited to, feedstock composition, production processes, final binder chemical composition, application methods and conditions, pavement or roofing material physical properties, environmental conditions, and aging/weathering. The emission estimates and uncertainty analysis used here, in concert with spatially resolved usage data and photochemical modeling, are intended to contextualize the potential contributions of asphalt-related emissions to air quality, relative to ambient pollutant concentrations and other sources. While uncertainty in the results presented here are reflected in the Monte Carlo analysis, key areas of further research that could better constrain these estimates include future updates to application-related or in-use emission factors for cutback and emulsified asphalt, analysis of potential application-related or in-use emissions from a range of other roofing asphalt products, including those applied at near-ambient temperatures using solvents, allocation of emissions from the state-level to the county-level, temporal allocation of emissions, and chemical aging of the highly functionalized species following emission in photochemical modeling mechanisms. Quantification of application-related emissions from emulsified asphalt would be especially useful since asphalt usage for this process are growing in magnitude (Fig. 4). It is possible the application emission factor adopted



here and used in the 2017 NEI is biased high,<sup>36</sup> however, given the speciation of emulsified asphalt (predominantly  $C^* > 3 \times 10^5 \mu\text{g m}^{-3}$ ), variation in these emissions should not affect the anthropogenic SOA predictions presented here. In addition, quantification of emissions from production and storage facilities were not specifically included in the sensitivity simulations performed here; both of which may include SOA precursor emissions. Experiments also indicate that emissions from asphalt are amplified following exposure to increased solar irradiance, often with a rise in the fraction of SVOCs ( $3 \times 10^{-1} \mu\text{g m}^{-3} < C^* < 3 \times 10^2 \mu\text{g m}^{-3}$ ).<sup>7</sup> These dependencies were not considered here and could lead to an increased enhancement of SOA on sunny, clear sky days, especially when coupled with high surface temperatures.

Nationally, the emissions presented here ( $\sim 380$  Gg) have an estimated effective SOA yield of  $\sim 22\%$ , resulting in an estimated SOA potential of  $\sim 85$  Gg. Following photochemical transport modeling, this leads to a summertime SOA average of  $\sim 0.1\text{--}0.2 \mu\text{g m}^{-3}$  in the most densely populated cities of the United States. While modest in magnitude, if on-road tailpipe emissions continue their multidecade decline,<sup>18,38,39</sup> the contribution of urban SOA from evaporative sources and other non-traditional sources will grow in relative proportion in the coming years-to-decades.<sup>18</sup> Furthermore, while the scale of the modeling implemented here (12 km resolution) is appropriate for estimating the contributions of asphalt emissions to regionally distributed SOA and  $\text{O}_3$ , asphalt-paving activities should not be overlooked when considering the potential impacts of direct emissions at the community-scale. Finally, it should be noted that asphalt application is an intermittent process and the temporal profile of emissions applied in the photochemical modeling performed here likely smoothes the day-to-day enhancements to  $\text{PM}_{2.5}$  and  $\text{O}_3$  from asphalt-related processes.

## Author contributions

K. M. S. designed the research scope. All authors participated in data/measurement curation, model development, and/or analysis. K. M. S. drafted the initial manuscript and all authors contributed to subsequent drafts. All authors have given approval to the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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