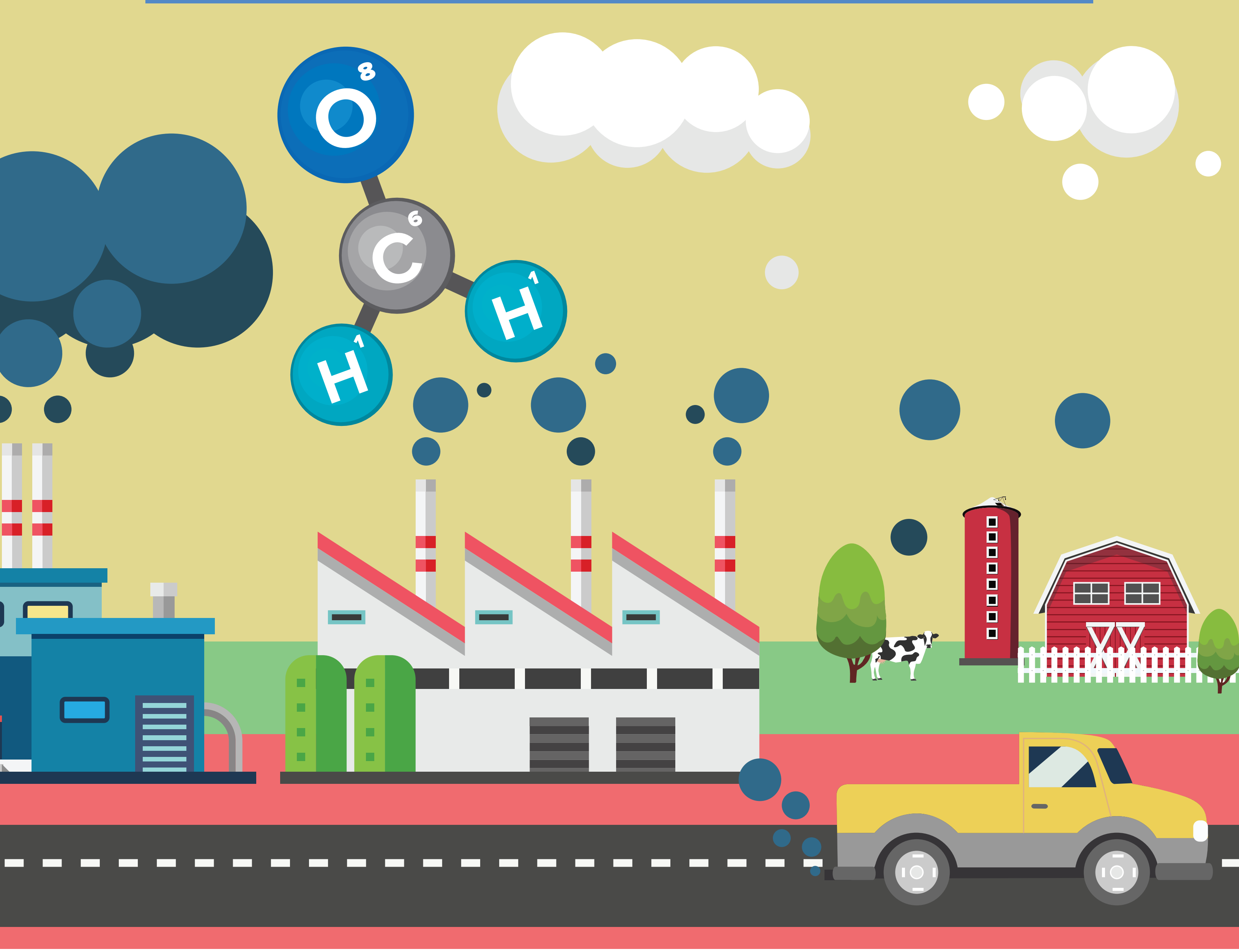

Formaldehyde

A Leading Air Toxic

by Stephen Zemba, Lisa Damiano, Heather Little, Jeffrey Doris, and Matthew Estabrooks

Spotlight on formaldehyde, a strong irritant and a well-known carcinogen, that is used in a variety of consumer products, and is commonly found in both indoor and outdoor air.

Many likely recall the pungent odor of formaldehyde from their high school biology labs as it off-gassed from specimens preserved in formalin (an aqueous solution of 37 percent formaldehyde by mass). The simplest of all aldehydes, with a chemical formula of HCHO, formaldehyde is both a strong irritant and a recognized carcinogen. Despite these well-known hazards, formaldehyde is used in a variety of consumer products, and is commonly found at low µg/m³ levels in outdoor air, and at significantly higher levels indoors in buildings with formaldehyde emission sources.

The U.S. Environmental Protection Agency's (EPA) 2014 National Air Toxics Assessment (NATA) has identified formaldehyde as the hazardous air pollutant (HAP) that contributes more than half of the U.S. average estimate of incremental cancer risk (see Figure 1) and roughly one third of the respiratory effects hazard quotient (see Figure 2), making it arguably the leading air toxic that is regulated under Section 112 of the U.S. Clean Air Act.[1]

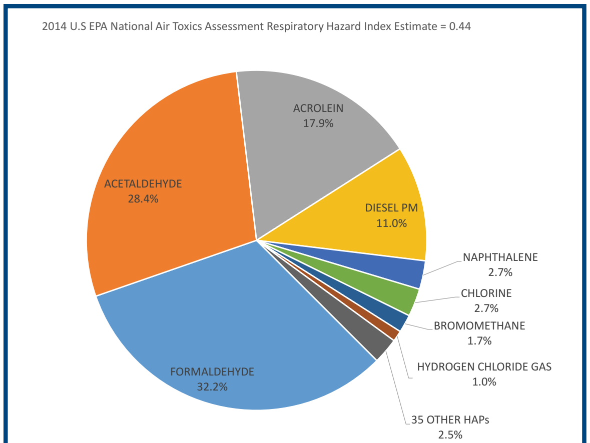

Figure 1. HAP Attribution to the 2014 NATA U.S. Average Respiratory Hazard Index of 0.44.

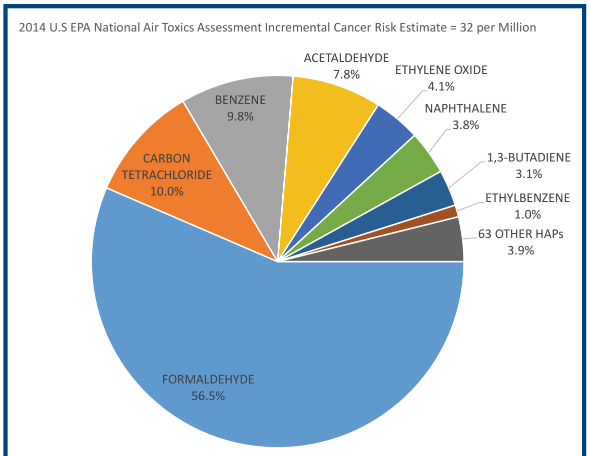

Figure 2. HAP Attribution to the 2014 NATA U.S. Average Incremental Cancer Risk Estimate of 32 per million.

Properties

Formaldehyde is a colorless gas at room temperature and pressure, but readily dissolves and remains in water. The reported odor thresholds for formaldehyde range from 62 µg/m³ to 1,200 µg/m³.[2,3] Formaldehyde is both created and destroyed through photolysis and chemicals reactions in the atmosphere, with typical half-lives estimated to be of the order of hours to days depending on solar intensity and the availability of hydroxyl radicals.[2,4]

Emission Sources

The sources that contribute to ambient formaldehyde levels are complex and involve both direct releases and indirect formation via atmospheric chemistry (see Figure 3). As discussed further on, indirect sources are now thought to be of greater overall importance, and of the formaldehyde released directly to air, biogenic emissions are estimated to dominate on a regional basis. For historical and regulatory reasons, though, anthropogenic emissions receive greater attention, and hence are discussed first. Numerous industries release formaldehyde directly to the atmosphere,[5] including:

- Formaldehyde synthesis/production;
- Resin (binder) production and applications/use in manufactured products, such as:
  - Urea-formaldehyde (e.g., particleboard, fiberboard, indoor plywood, foam insulation, textiles, paper, surface coatings, adhesives),
  - Phenol-formaldehyde (e.g., outdoor plywood, molding compounds, insulations, foundry molds, laminates, particle board, friction materials, abrasives),
  - Polyacetal (e.g., plumbing fixtures, hardware, sporting goods), and
  - Melamine-formaldehyde (e.g., countertops, dinnerware, surface coatings);
- Synthesis of more complex organic chemicals (e.g., hexamethylenetetramine, pentaerythritol, 1,4-butanediol, trimethylolpropane, 4,4-methylenedianiline, phthalic anhydride);
- Production of solid urea and ureaform fertilizers;
- Preservation, embalming, and disinfection uses;
- External and internal combustion of hydrocarbon-based fuels;
- Oil refineries; and
- Asphaltic concrete production and use.

Industrial sources emitted an estimated 4.6 million tons of formaldehyde in the United States in 2006.[6] Formaldehyde is also produced inadvertently as a byproduct of incomplete combustion of hydrocarbon fuels, which encompasses numerous stationary and mobile sources.

However, anthropogenic sources account for only a small fraction of direct formaldehyde emissions to the atmosphere. As indicated in Figure 4, the U.S. EPA 2014 NATA estimates

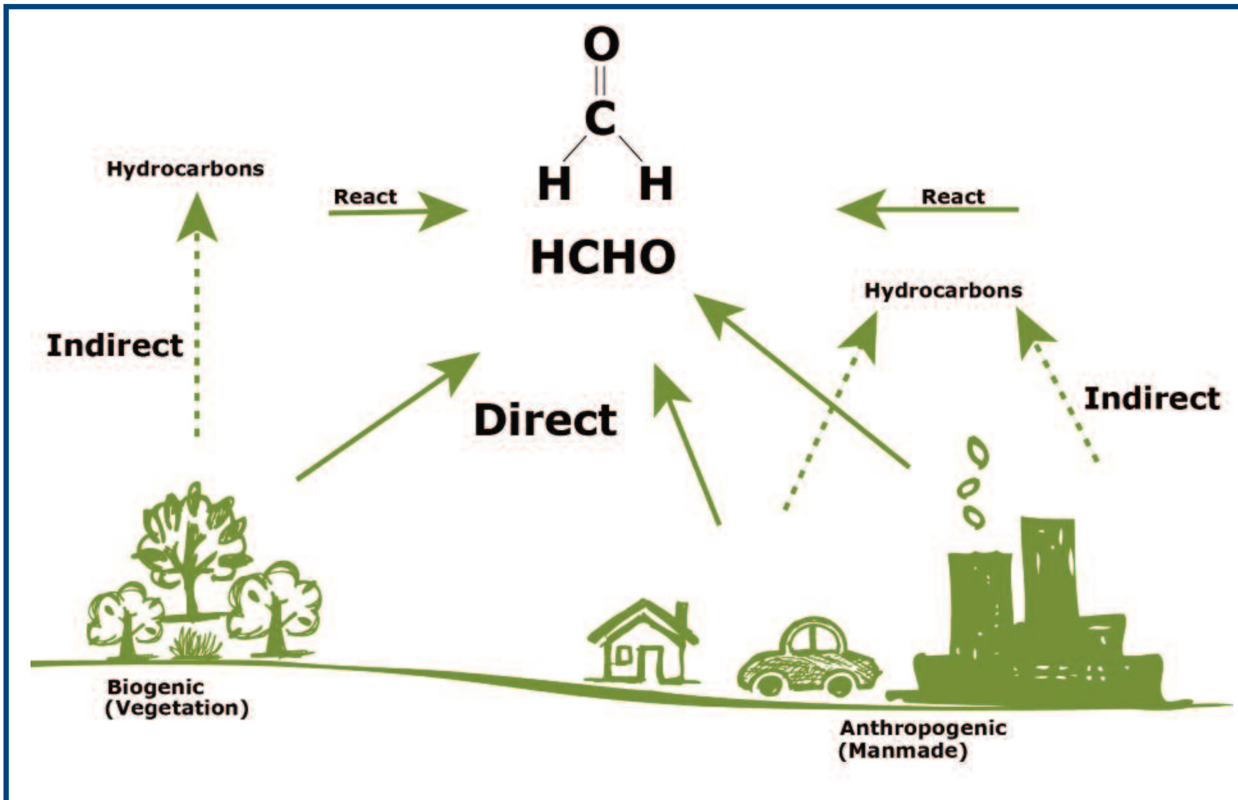

Figure 3. Sources of Formaldehyde in Ambient Air.

that biogenic sources (from vegetation) and fires account for 89 percent of the 1.3 million tons of aggregate emissions in the United States. Traditional point and non-point sources contribute only 4 percent of emissions, while on-road and non-road mobile sources account for 7 percent. The portion of non-anthropogenic emissions varies regionally, with western states such as California and Arizona exceeding 90 percent, and eastern states such as Connecticut less than 60 percent.

Note, however, that even though biogenic emissions may dominate source inventories at the state level, anthropogenic emission sources tend to concentrate in urban areas and can contribute substantially to formaldehyde concentrations at the local level. The source distribution for the District of Columbia is indicative of this urbanization effect, as it is the only state/district that does not have biogenic emissions as its largest source, instead being dominated by mobile source emissions.

Formaldehyde also has indirect sources as it is produced in the atmosphere through oxidation of various hydrocarbons released from emission sources. This secondary formaldehyde formation, which is tied to the emissions of precursor hydrocarbon species, is in fact estimated to account for most of the formaldehyde present in outdoor air (as discussed below). Hence, formaldehyde shares a parallel characteristic with particulate matter in that secondary formation can contribute significantly to ambient levels.

Concentrations in Air

Formaldehyde is ubiquitous in both outdoor and indoor air, in part because of its numerous emission sources, and also due to its role in hydrocarbon chemistry and oxidation. Observations in outdoor air range from a few µg/m^3 in rural areas to 10 µg/m^3 and higher in urban areas due to the increased density of local emission sources (despite the general dominance of biogenic emission sources at the regional level). Although this article focuses on formaldehyde in outdoor air, indoor air often contains levels of formaldehyde an order of magnitude or more higher than found in outdoor air due to off-gassing from building materials (e.g., pressed board and similar products that incorporate formaldehyde-based resins) and emissions from indoor combustion sources such as woodstoves, fireplaces, and cooking. Salthammer[7] summarizes reported concentrations, which for indoor environments with significant formaldehyde sources (e.g., mobile homes) are typically 30–100 µg/m^3, and in some cases as high as 1,000 µg/m^3.

Figure 5 depicts a national map of the concentrations of formaldehyde in ambient air modeled in the 2014 NATA study. It shows that 99.9 percent of the formaldehyde concentrations modeled across individual census tracts are less than 2.7 µg/m^3. The NATA estimates indicate a geographic dependence, with higher formaldehyde concentrations predicted at southern latitudes due to greater biogenic emissions and secondary formaldehyde formation (both of which increase with temperature).

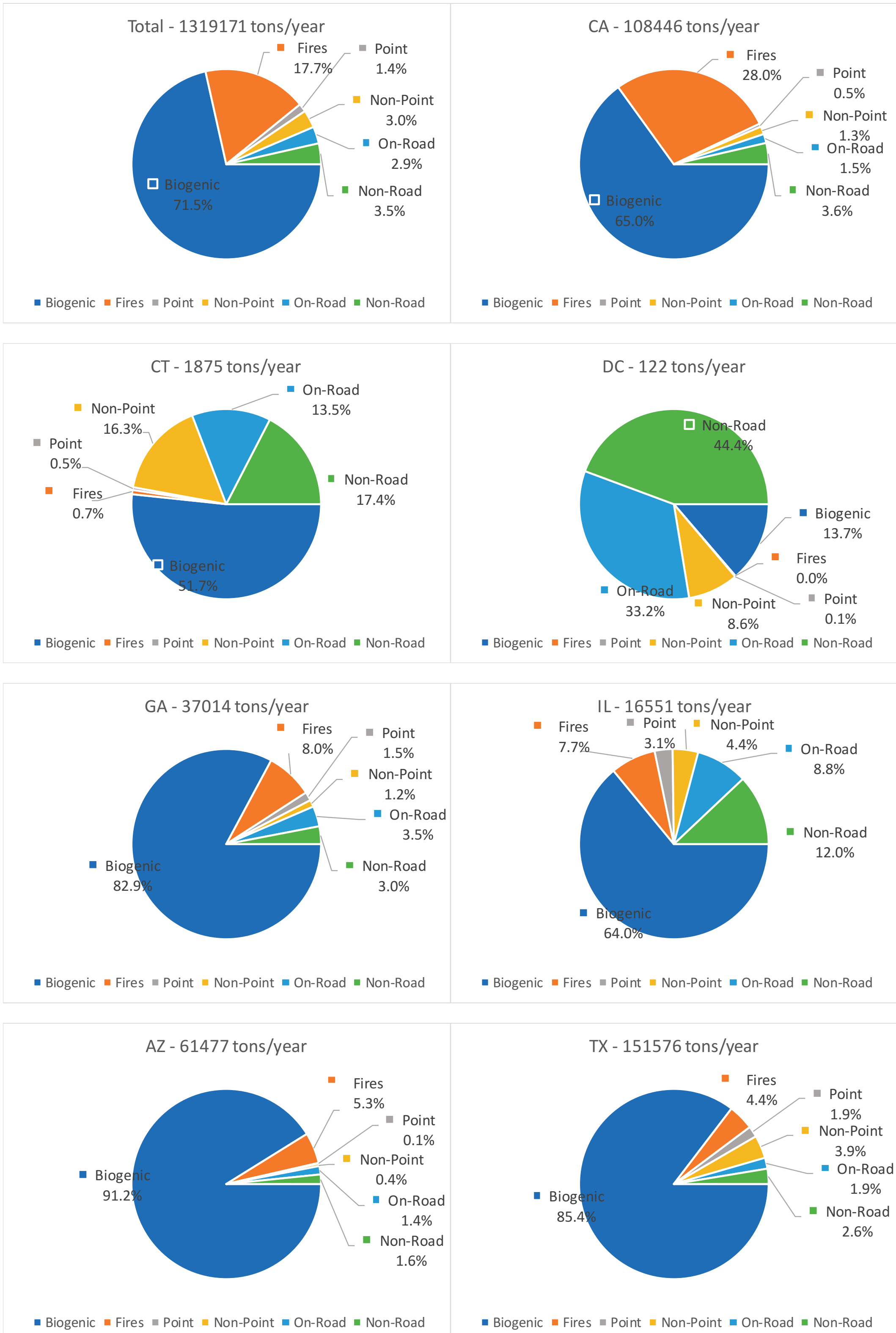

Figure 4. Formaldehyde Emissions and Source Attribution in the 2014 National Emission Inventory Used in 2014 NATA.

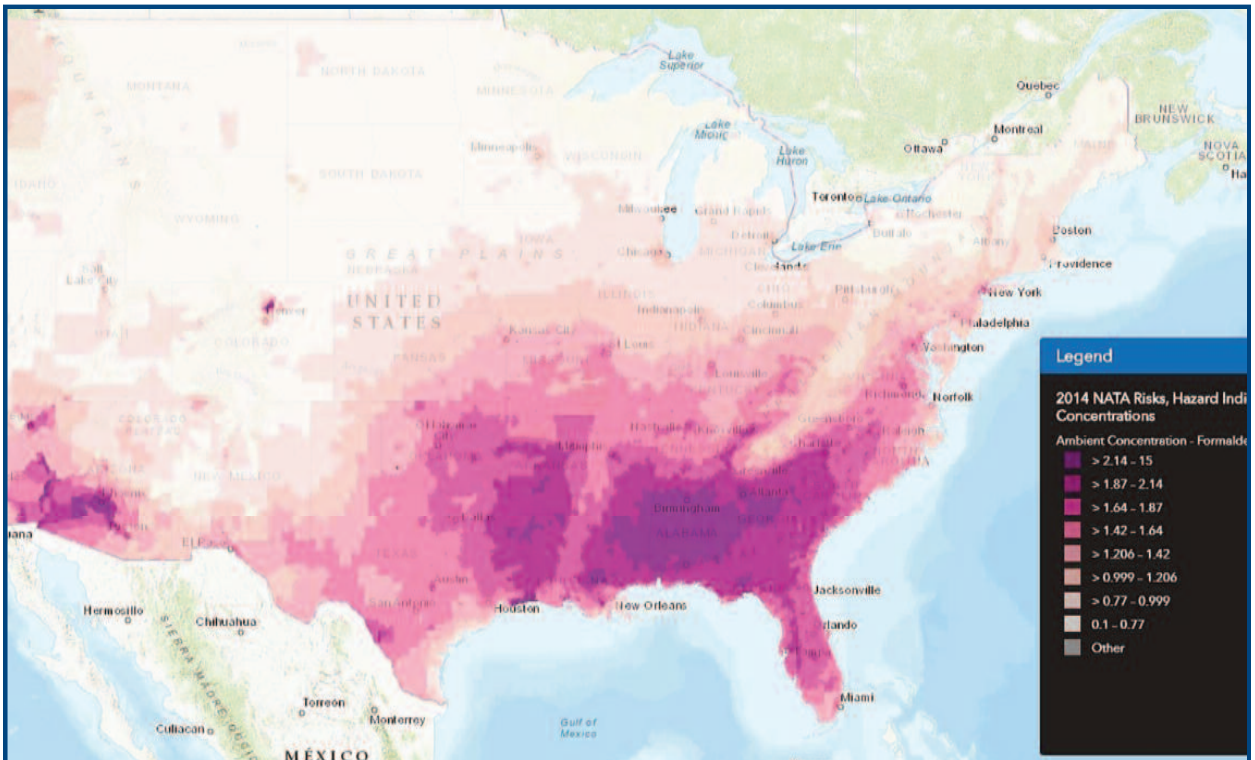

Figure 5. Modeled Concentrations of Formaldehyde in Outdoor Air (μg/m^3), NATA Map Application.

Source: www.epa.gov/national-air-toxics-assessment/2014-nata-map.

Figure 6 illustrates the breakdown of point source categories contributing to the national average formaldehyde concentration of 1.3 μg/m^3 (as weighted by census tract populations). Secondary formaldehyde formed from atmospheric chemistry makes up 74 percent of the estimate, while direct anthropogenic sources contribute only 10 percent across the point, non-point, on-road, and non-road categories. One caveat, however, regarding the 2014 NATA estimates is that they tend to under-predict monitored formaldehyde concentrations.

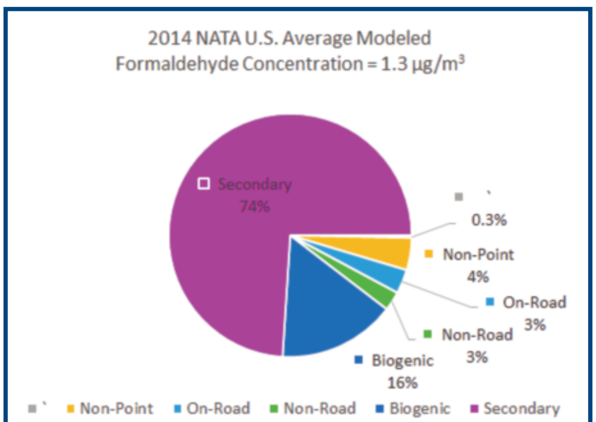

Figure 6. Point Source Attribution to the 2014 NATA U.S. Average Modeled Concentration of Formaldehyde in Outdoor Air.

Figure 7 is a scatter plot of modeled vs. monitored formaldehyde concentrations at 111 locations across 31 states. The average monitored median concentration (2.32 μg/m^3) exceeds the average modeled concentration (1.38 μg/m^3) by about 68 percent. Additionally, the range of monitored concentrations is more than twice as large as the range modeled in the NATA study. These differences may not reflect inaccuracy, however, as air monitoring stations are frequently located near significant emission areas where the highest ambient concentrations are anticipated, and hence may reflect a high bias with respect to averages across census tracts (which are reflected by the NATA modeled estimates).

Toxicity and Exposure Guidelines

At sufficient concentrations, formaldehyde is a strong respiratory and ocular irritant. Additionally, the Agency for Toxic Substances and Disease Registry (ATSDR) and the International Agency for Research on Cancer (IARC) have concluded that formaldehyde is a human carcinogen.

Nationally, the Occupational Safety and Health Administration (OSHA) 8-hr average permissible exposure limit is

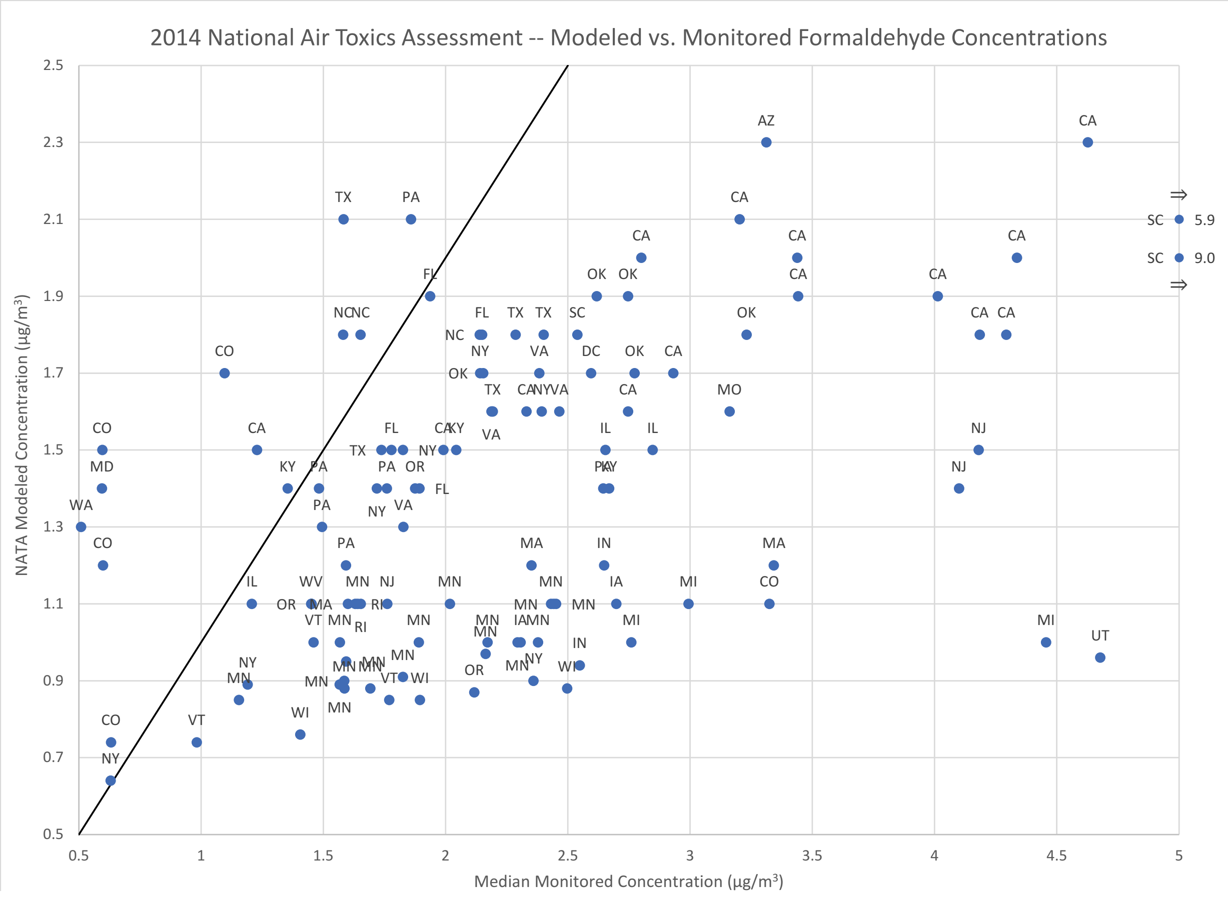

Figure 7. Comparison of Modeled versus Measured Formaldehyde Concentrations (µg/m³), 2014 NATA.

920 µg/m³ and 15-minute average short-term exposure limit is 2,460 µg/m³. In consideration of formaldehyde's carcinogenicity, the National Institute for Occupational Safety and Health (NIOSH) has established an 8-hr average recommended exposure limit of 20 µg/m³. Public health guidelines are considerably more protective than workplace standards. The current EPA regional screening levels (RSLs) for airborne formaldehyde exposure to a resident are 10 µg/m³ (based on ATSDR's minimum risk level) to protect against irritation effects and 0.22 µg/m³ based on a 1 per million incremental cancer risk over a long-term (26 year) exposure period.[8]

Formaldehyde toxicity is under reevaluation,[9] as the current Integrated Risk I System (IRIS) summary dates back to 1990. A 2010 draft IRIS toxicological review stirred considerable controversy from its proposed increase in cancer potency.[10] The American Chemistry Council and other industry groups continue to question the scientific underpinnings of EPA's 2010 draft report, pointing out that humans produce formaldehyde as part of their normal metabolic processes, exhaling formaldehyde in our breath at concentrations of a few µg/m³.[11]

Evaluating potential irritation effects caused by formaldehyde is perhaps less controversial, though exposure guidelines and standards vary considerably. Uncertainties in evaluating scientific evidence translate to varying degrees of protectiveness among regulatory agencies. Table 1 summarizes relevant values of various standards or recommended guidelines for formaldehyde. Guidelines typically are based on lowest or no observed adverse effects levels (LOAELS or NOAELs) found in toxicity studies, with safety factors added to derive protective levels. A recent comprehensive literature review determined 123 µg/m³ (or 100 parts per billion, ppb) of formaldehyde is a level low enough to likely protect people from irritation (even individuals sensitive to air pollutants). Both the World Health Organization and Health Canada recommend this value as a generally protective short-term exposure limit. The value is also within or below the typical range of reported odor thresholds for formaldehyde (a point at which irritation effects might be noticed). Even so, some agencies have chosen to be even more protective in establishing irritation-based exposure guidelines. For example, ATSDR has chosen to add in additional safety factors in its minimum risk levels (MRLs).

Table 1. Irritation-based recommendations for residential guideline concentrations for formaldehyde.

Averaging time	Concentration (µg/m³)	Effect	Point of Departure (µg/m³)	Adjustment/ safety factor	Study type
Agency for Toxic Substances and Disease Registry Minimum Risk Levels (MRLs) (1999)					
Acute 1 – 14 days	49	Nasal and eye irritation and the cellular makeup of nasal discharge in occupationally exposed patients with skin hypersensitivity to formaldehyde	490	9	Lowest Observed Adverse Effects Level (LOAEL), human study
Intermediate 15–364 days	37	Clinical signs of nasopharyngeal irritation (hoarseness and nasal congestion and discharge) and lesions in the nasal epithelium (squamous metaplasia and hyperplasia)	1215	30	LOAEL, animal study
Chronic ≥ 1 year	9.8	Mild irritation of the eyes and upper respiratory tract and mild damage to the nasal epithelium	297	30	LOAEL
-	620 to 1200	Odor threshold			
World Health Organization Air Quality Guidelines (2nd Edition) (2001)					
30 min	123	Odor threshold			
1-hour	123	Eye, nose and throat irritation	490	9	Human study, 1/5th of the NOAEL and no observable adverse 1/10th of the LOAEL for eye irritation
8-Hour and longer	50	Respiratory symptoms in asthmatic children	1215	30	Lower end of the exposure category associated with no significant increase of asthma hospitalization
Golden, R. (2011), Critical Reviews in Toxicology 41(8):672-721 (review paper)					
Any	123	Odor detection and sensory irritation			Other review studies indicate 472 µg/m³ will provide protection from eye irritation for virtually everyone. 124 µg/m³ is a weight-of-evidence recommendation to protect all individuals for odor detection and sensory irritation.

In developing air toxics programs, various states have addressed either or both of the irritation and cancer concerns associated with formaldehyde, often basing short-term guidelines on potential irritation effects and long-term exposure guidelines on incremental cancer risk. Table 2 summarizes the values that have been adopted in some states. Note that many formaldehyde exposure guidelines, especially those based on long-term exposure, are below typical background levels in outdoor air.

Impacts from Specific Sources and Implications for Air Permitting

The breakdown of sources that contribute to the average NATA formaldehyde concentration in ambient air (Figure 6) suggests that impacts from individual point sources may be small. However, our recent experience indicates that certain sources, such as large stationary internal combustion engines that potentially release significant amounts of formaldehyde near ground-level, when assessed through dispersion modeling may produce predicted concentrations of formaldehyde that exceed state guidelines. A lack of published emission factors may be the reason behind delayed regulatory recognition of formaldehyde, but we have recently noticed increased state awareness in source permitting and have applied project-specific risk assessments to better evaluate formaldehyde impacts.

To our knowledge, secondary formaldehyde production from precursor volatile organic compound emissions has not yet been examined in source permitting, but research on reactive plume dynamics suggests the possibility of significant near-source contributions to localized atmospheric

Table 2. State air toxics standards and guidelines.

State	Short-Term Standard or Guideline		Annual Average Standard or Guideline (µg/m³)
	Averaging Period	Concentration (µg/m³)	
CA	1 hr 8 hr	55 9	9
CT	30 min 8 hr	60 12	None
GA	15 min	245	0.077
LA	None		7.69
MA	24 hr	2	0.08
MI	24 hr	30	0.08
NH	24 hr	1.3	0.88
NY	1 hr	30	0.06
NC	1 hr	0.15	None
ND	1 hr	7.37	None
OK	24 hr	8	None
TX	1 hr	15	3.3
SC	24 hr	15	None
VA	1 hr	62.5	2.4
VT	None		0.078
WA	None		0.167

formaldehyde concentrations.[12] On a regional basis, concerns over formaldehyde transcend individual source impacts due to the large fraction of biogenic emissions. Additionally, public health concerns over formaldehyde should focus on indoor sources, as indoor air can contain concentrations of formaldehyde many times greater than found outdoors. There is considerable debate ongoing, however, regarding formaldehyde toxicity, particularly its carcinogenicity at typical atmospheric concentrations. **em**

Stephen G. Zemba, Lisa Damiano, Heather Little, Jeffrey Doris, and **Matthew Estabrooks** are all with Sanborn Head and Associates, Inc. E-mail: szemba@sanbornhead.com.

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