Environmental Science
Processes & Impacts

# An Emerging Mobile Air Pollution Source: Outdoor Plastic Liner Manufacturing Sites Discharge VOCs into Urban and Rural Areas

| | |
|---|---|
| Journal: | *Environmental Science: Processes & Impacts* |
| Manuscript ID | EM-ART-04-2020-000190.R1 |
| Article Type: | Paper |
| | |

Sewer pipes are being repaired globally by manufacturing a new plastic pipe inside an existing damaged pipe. This increasingly popular technology, cured-in-place-pipe (CIPP), involves the open-air handling of uncured resin that includes VOCs and SVOCs and open-air plastic manufacture. This process poses a significant air pollution risk as contractors create new chemicals during plastic manufacture, and discharge their chemical waste into the air. This study quantitatively characterized how emissions differ across the thermal manufacturing processes in a lab-scale environmental test chamber. Also, the impact of ventilation of the newly created plastic that contains VOC residual was investigated.

# An Emerging Mobile Air Pollution Source: Outdoor Plastic Liner Manufacturing Sites Discharge VOCs into Urban and Rural Areas

*Seyedeh Mahboobeh Teimouri Sendesi[1], Yoorae Noh[2], Md Nuruddin[3], Brandon E. Boor[4], John A. Howarter[5], Jeffrey P. Youngblood[6], Chad T. Jafvert[7], Andrew J. Whelton[8,*]*

[1] Lyles School of Civil Engineering, Purdue University, 550 Stadium Mall Drive, West Lafayette, Indiana USA 47907; steimour@purdue.edu

[2] Lyles School of Civil Engineering, Purdue University, 550 Stadium Mall Drive, West Lafayette, Indiana USA 47907, noh18@purdue.edu

[3] School of Materials Engineering, Neil Armstrong Hall of Engineering, 701 West Stadium Avenue, West Lafayette, IN USA 47907-2045, mnuruddi@purdue.edu

[4] Lyles School of Civil Engineering, Purdue University, 550 Stadium Mall Drive, West Lafayette, Indiana USA 47907; T: (765) 496-0576; bboor@purdue.edu

[5] School of Materials Engineering and Division of Environmental & Ecological Engineering, Purdue University, Neil Armstrong Hall of Engineering, 701 West Stadium Avenue, West Lafayette, IN USA 47907-2045; T: (765) 496-3103; howarter@purdue.edu

[6] School of Materials Engineering, Neil Armstrong Hall of Engineering, 701 West Stadium Avenue, West Lafayette, IN USA 47907-2045; T: (765) 496-2294; jpyoungb@purdue.edu

[7] Lyles School of Civil Engineering and Division of Environmental & Ecological Engineering, Purdue University, 550 Stadium Mall Drive, West Lafayette, Indiana USA 47907; T: (765) 494-2196; jafvert@purdue.edu

[8] Lyles School of Civil Engineering and Division of Environmental & Ecological Engineering, Purdue University, 550 Stadium Mall Drive, West Lafayette, Indiana USA 47907; T: (765) 494-2166; awhelton@purdue.edu

**Corresponding author: Associate Professor, Lyles School of Civil Engineering and Division of Ecological and Environmental Engineering, Purdue University, Purdue University, 550 Stadium Mall Drive, West Lafayette, IN USA 47907-2051; T: (765) 494-2166; F: (765) 494-0395; E:* ajwhelton@gmail.com; awhelton@purdue.edu

## Abstract

The *in-situ* manufacture of cured-in-place-pipe (CIPP) plastic liners in damaged sewer pipes is an emerging mobile source of anthropogenic air pollution. Evidence indicates volatile organic compounds (VOCs) can be released before, during, and after manufacture. The chemical composition of a popular uncured styrene-based CIPP resin was examined, along with the VOCs that remained in the new cured composite. The roles of curing temperature and heating time on waste discharged into the air were examined. Uncured resin contained approximately 39 wt% VOCs. Multiple hazardous air pollutants were present, however, 61 wt% of the uncured resin was not chemically identified. A substantial mass of VOCs (8.87 wt%) was emitted into the air during manufacture, and all cured composites contained about 3 wt% VOCs. Some VOCs were created during manufacture. Curing temperature (65.5-93.3 °C) and heating time (25-100 min) did not cause different composite VOC loadings. High styrene air concentrations inhibited the detection of other VOCs in air. It is estimated that tens of tons of VOCs may be emitted at a single CIPP manufacturing site. Regulators should consider monitoring, and potentially regulating, these growing mobile air pollution and volatile chemical product sources as they are operating in urban and rural areas often in close proximity to residential and commercial buildings.

**Keywords:**

Air Pollution, Mobile Source, VOC, Cured-in-Place Pipe, Resin, Styrene, Composite, Volatile Chemical Products (VCPs)

## 1. Introduction

Cured-in-place-pipe (CIPP) technology is a popular method used for sanitary and storm sewer pipes repair across the U.S.[1-5]. However, this technology constitutes a new mobile source of air pollution. CIPP contractors establish a temporary worksite at the damaged pipe and insert an uncured resin tube inside the pipe. Next, they use steam, hot water, or UV light to polymerize the resin and discharge their process chemicals into the air (see Fig. 1). After the liner hardens, and is cut to allow water to flow, the contractors relocate to their next job site. This plastic manufacturing process is inherently mobile.

It is common practice that contractors discharge their process waste into air, which is a byproduct of manufacture. These pollutants can travel through buried sewer lines and exit nearby manholes and vents, enter into nearby buildings and public spaces, as well as travel aboveground through and off the worksite kilometers away [6-8]. Many of the pollutants are known or suspected carcinogens, acutely toxic at specific concentrations, pose occupational risks to workers, and are substances of concern by the United States Clean Air Action. Regulated hazardous air pollutants (HAPs) have been found discharged to air, though no studies have estimated the magnitude of CIPP-induced air pollution. CIPP-induced air pollution has been detected in more than 130 incidents associated with environmental degradation and risks to the health and safety of workers and the public [9-16] (see Table S1 in ESI). Risk assessments are lacking, and unsubstantiated statements have been found in CIPP industry worker and municipality training courses [17] and textbooks [18-20]. One peer-reviewed CIPP stormwater pipe worksite risk analysis study did not consider worker chemical exposure [21, 22], but instead injuries with manual tasks and equipment use (i.e., mixers, pumps, etc.). Some investigators have stated that CIPP solvent vapors could “pose a health risk”, but also stated “such levels are not typically found in CIPP installations” and the "problem applies only until the resin is cured" [23]. Some CIPP greenhouse gas emission studies have focused on equipment (i.e., trucks, generators), and concluded CIPP use is more 'environmentally' justified than open-cut/pipe replacement [24-27]. Estimates of $CO_2$ emissions, the carbon footprint during CIPP fabrication [28-30] and CIPP installation construction and environmental costs [25, 31] are other examples of such studies.

The scale of pollutant emissions at a single CIPP manufacturing site may be significant because as much as 454,000 kilograms of uncured resin has been brought onsite (see Table S2 in ESI). The uncured resin tube matrix has been either felt or fiberglass matting and contains the resin premixed with monomers, initiators, inhibitors, filler, and other ingredients. Ingredient degradation products have also been found to be present. The HAP styrene is the most popular CIPP resin reactive diluent/monomer [32], but many other contaminants are in the resins, have been discharged into air and water, and extracted from new CIPPs (see Table 1). Air concentrations for only styrene (0.011-1,820 $ppm_v$) [6, 12, 33-36] and another HAP methylene chloride (1.41-1.56 $ppm_v$) [31] have been reported. However, 19 other chemicals were detected in air but were not quantified [36]. In addition, applying forced air or steam, typically with a pressure range of 5-20 psi [37] to inflate the uncured resin tube against the damaged pipe's wall may also contribute to pollutant discharge into the air.

After CIPP manufacture, extractable VOCs can be found in the CIPPs, however, only a few studies on this topic exist. A high of 9.2 wt% VOCs has been reported [38] and these originate from the uncured resin and are created *in-situ* during manufacture. During CIPP manufacture, VOC air concentrations can increase within nearby pipes, manholes, the worksite, and nearby buildings (see Table S1 in ESI). However, no studies were found to monitor chemical air concentrations after CIPP manufacture. Also, the effect of process curing temperature or heating time on the VOC emission profile is presently unknown. For example, for a different application, the styrene flux from a cured styrene-based composite was found to increase by a factor of 8.4 as air temperature increased from 10 to 50 ˚C [39]. To examine the impact of ventilation on styrene air concentration reduction after CIPP manufacture, one study recommended a 24 hr post-CIPP manufacture ventilation period [40]. This ventilation period was chosen because styrene was found in air 24 hr after sewer pipes that had been lined with CIPPs. No similar recommendations have been applied in the U.S., nor have studies been conducted to determine if short-duration ventilation reduces the CIPP's subsequent styrene flux.

The goal of this study was to better understand VOC release into the air during process setup, manufacture, and after CIPP installation. A popular styrene-based CIPP resin was used for the present study. To help identify factors that control CIPP VOC emissions, composites were created in controlled laboratory environment using different curing conditions (pressure, curing temperature, and heating time). In addition, the impact of ventilation on the VOC flux from the cured composite was investigated in a lab-scale environmental test chamber (ETC). Specific objectives were to: (1.) chemically characterize the unsaturated polyester resin, (2.) physically, thermally, and chemically characterize the cured composites, (3.) determine how curing conditions (pressure, temperature, and heating time) influence VOC emissions from new composites, and (4.) examine the effectiveness of ventilation on reducing the VOC emission rate of cured composites.

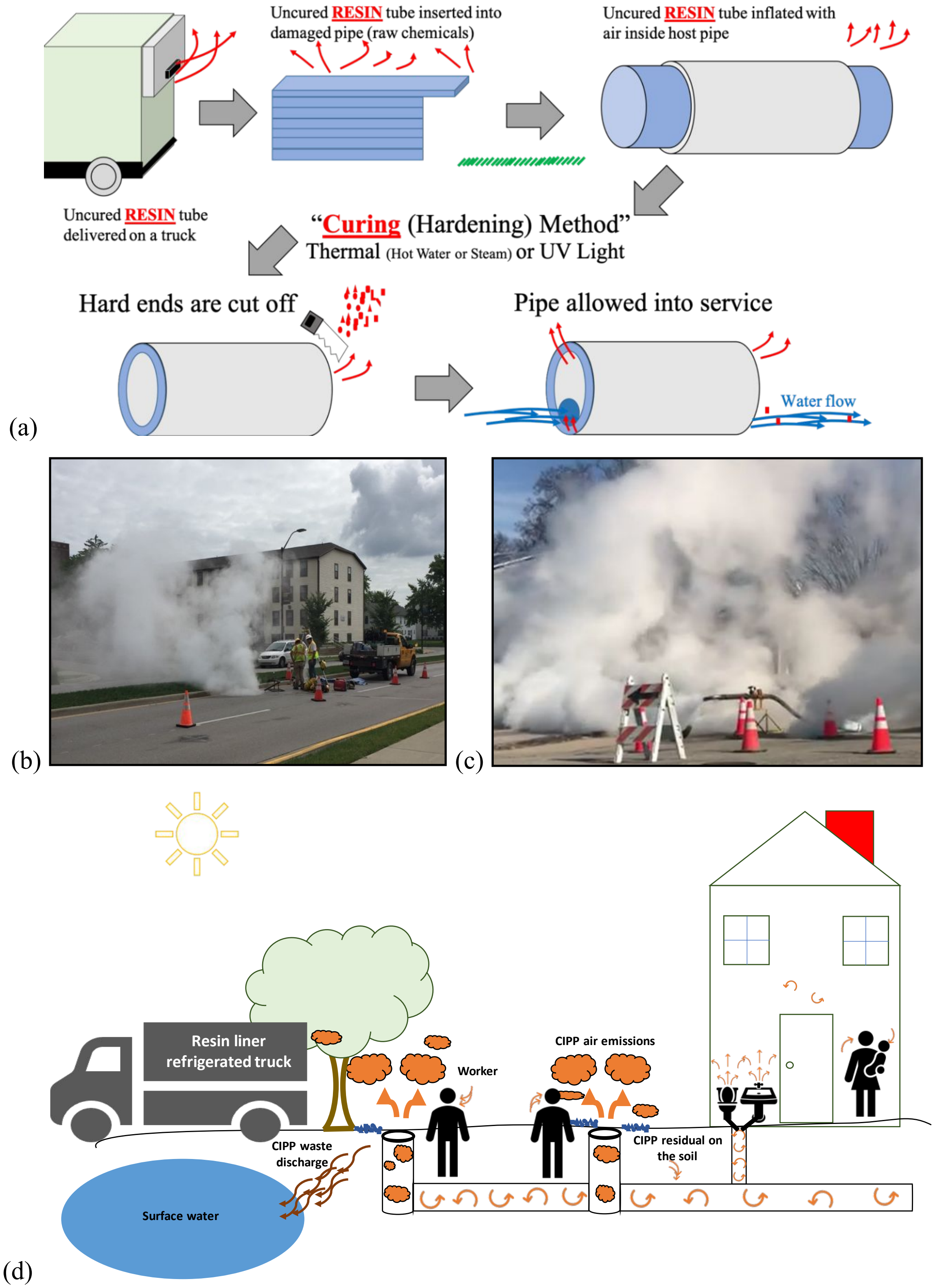


Fig. 1 Chemicals can be released into the air at CIPP manufacturing sites: (a) Illustration of a standard CIPP manufacturing process, (b,c) Chemical plume emitted into air during sanitary sewer CIPP manufacture, (d) Pathways that emissions can travel affecting the environment,

workers, and the public. Uncured resin tubes are delivered or created onsite, tubes are then inserted into the damaged pipe followed by a curing process where chemicals are discharged to the air. Once hardened, the liner is cut and the pipe is often immediately returned to service.

Table 1. List of chemicals detected and reported at past CIPP project sites and in CIPP resins

| **Contaminant** | **Raw Material** | | **Media Where Chemical Found** | | | |
|---|---|---|---|---|---|---|
| | **Uncured CIPP resin** | **Initiator deg. prod.** | **Air** | **New CIPP** | **Water** | **Condensate captured from air** |
| Acetophenone[*+, HAP] | | x | | x | x | x |
| Acetone[θ‡§Δ¶ρ] | | x | | | | x |
| Aniline[β, HAP] | | x | | | | |
| Benzene[θΔ¶β, HAP] | | x | | | x | x |
| Benzaldehyde[Z*] | x | | | x | x | x |
| Benzoic acid[θ* +β] | | x | | x | | x |
| 2(3H)-Benzothiazolone[¶] | | | | | x | |
| Benzyl alcohol[¶] | | | | | x | |
| 1,4-Benzene dicarboxylic acid, bis(2-hydroxyethyl) ester[¶] | | | | | x | |
| Bisphenol a diglycidyl ether[Z] | x | | | | | |
| Bis(*tert*-butylcyclohexyl) peroxydicarbonate[+] | | | | x | | |
| 2-Butanone (Methyl ethyl ketone)[¶β, HAP] | | x | | | | x |
| *tert*-Butyl benzene[ρ] | | | | | | |
| *tert*-Butyl alcohol[§] | | x | | x | | x |
| *tert*-Butyl peroxy-2-ethylhexanoate[+] | | | | | x | |
| Butyl benzyl phthalate (BBP)[#] | | | | | | |
| Butylated hydroxytoluene[*Z] | x | | | x | | x |
| Chloroform[¶, HAP] | | | | | | x |
| Decane[Z] | | | | x | | |
| Di-*n*-butyl phthalate (DBP)[¶$* Z, HAP] | x | | | | x | x |
| Diethyl phthalate (DEP) [θ¶] | | | | | x | |
| Di(2-ethylhexyl) phthalate (DEHP) [θ#¶$, HAP] | | | | x | | |
| Divinylbenzene[§§] | | | x | | | |
| Diisooctyl phthalate (DOP)[¶] | | | | | x | |
| 4-(1,1-Dimethyl) cyclohexanol[¶] | | | | | x | |

| **Contaminant** | **Raw Material** | | **Media Where Chemical Found**[**] | | | |
|---|---|---|---|---|---|---|
| | **Uncured CIPP resin** | **Initiator deg. prod.** | **Air** | **New CIPP** | **Water** | **Condensate captured from air** |
| 4-(1,1-Dimethyl) cyclohexanone[¶] | | | | | x | |
| Dodecanol[Z] | x | | | x | | |
| Ethylbenzene[θ‡Z, HAP] | x | | | x | | |
| 2-Ethylhexanoic acid[ß] | | x | | | | |
| 3-Heptanol[¶] | | | | | x | |
| n-Hexadecanoic acid[¶] | | | | | x | |
| 1-Hydroxymethyl-2-methyl-1-cyclohexene[¶] | | | | | x | |
| Isopropylbenzene[θ‡§Δ¶ΨZ] | x | | | x | | x |
| Irgacure[®Z] | x | | | x | x | |
| Maleic anhydride[Z, HAP] | x | | | | | |
| 4,7-Methano-1H-indenol,hexahydro[¶] | | | | | x | |
| Methyl vinyl ester terephthalic acid[¶] | | | | | x | |
| Methylene chloride[¶Ψ, HAP] | | | x | | | x |
| (4-Methylenecyclohexyl) methanol[¶] | | | | | x | |
| Octadecanoic acid[¶] | | | | | x | |
| Phenol[¶Δ*+, HAP] | | | x | x | x | x |
| 2-Phenyl acetaldehyde[+] | | | | x | | |
| Phenyl ethyl alcohol[¶] | | | | | x | |
| 1-Phenyl-2-propanone1-hydroxy[¶] | | | | | x | |
| Phthalic anhydride[Z, HAP] | x | | | x | x | |
| *N*-Propylbenzene[‡§Δ¶ΨZ] | x | | | x | | x |
| Styrene[¥†‡§θ¶Δρ*Z+, HAP] | x | | x | x | x | x |
| Styrene oxide[Z, HAP] | x | | | x | | |
| Toluene[θΔ] | | | | | | x |
| 1-Tetradecanol[Z+β] | x | x | | x | | x |
| 4-*tert*-Butyl cyclohexanol[+* β] | | x | | x | x | x |

| Contaminant | Raw Material | | Media Where Chemical Found** | | | |
|---|---|---|---|---|---|---|
| | Uncured CIPP resin | Initiator deg. prod. | Air | New CIPP | Water | Condensate captured from air |
| Tripropylene glycol diacrylate[+* β] | x | | | x | | x |
| 1,2,3-Trimethylbenzene[Z] | x | | | x | x | |
| 1,2,4-Trimethylbenzene[θ‡§Δ¶ΨZ] | x | | | x | x | |
| 1,3,5-Trimethylbenzene[θ‡§Δ¶ΨρZ] | x | | | x | x | |
| 3,3-Trimethyl cyclohexanone[¶β] | | | | | x | |
| 2,4,6-Triphenyl-1-hexane [styrene trimer][+] | | | | x | | |
| 1,3,5-Triphenylcyclohexane [styrene trimer][+] | | | | x | | |
| Xylene (total)[ΔZ] | x | | | x | x | |

*NOTES: More than 90 other tentatively identified compounds have been reported that are not shown in the table above. Tentatively identified compounds are chemicals that were detected, but the exact chemical structure/identified was not confirmed. Therefore, the Table above does not list all chemicals that can be released from CIPP processes, but just those that have been confirmed. Blank cell indicates no limit was found for the states surveyed. ** Air samples were collected at the worker's breathing zone. Symbols next to each compound name represent the studies and reports where they were reported and associated with CIPP installations. References for the documents are listed below. Compounds in table were detected by prior investigators who examined CIPP waste or water sampling included [¥]NRC (2010) [41], [θ]CDOT (2011) [42], [‡]CDOT (2012) [43], [Φ]VDOT (2016)[44], [†]Donaldson (2012) [45], [§]Spectrum (2013a-d) [46-49], [¶]Tabor et al. (2014) [50], [ρ]UGA (2016) [51], [Δ]Currier (2017) [52], [*]Teimouri et al. (2017) [11], [H]PA DEP (2019b) [53], [Ψ]Tentatively identified compounds in Tabor et al. (2014) [50], [Z]Li et al. (2019) [38], [+]Ra et al. (2019) [7]. [β]Initiator degradation product reported by Ra et al. (2019) [10], [§§]NIOSH (2019) [12]. HAP is abbreviation for hazardous air pollutant.*

## 2. Methodology

### 2.1 Composite manufacturing in a university laboratory

Styrene-based unsaturated polyester composite plates (7-10 mm thick) were prepared by thermal oven heating inside a fume hood (1.59 m × 1.22 m × 0.58 m) (Model: SafeAire, Hamilton Industries, Inc.). Two felts (10.16 cm × 10.16 cm × 0.381 cm) for each composite manufacture were used. Approximately 100 gr of uncured resin mixture containing unsaturated polyester unfilled CIPP resin, 1.15 wt% of Perkadox® 26 (United Initiators, Inc.) and 0.50 wt% *tert*-butyl peroxybenzoate (CAS # 614-45-9, Sigma Aldrich) were poured on each side of the felt. The resin mixture was spread using a wooden stick and roller. The uncured resin impregnated felts were layered or "laid-up, topped with a perforated Teflon® release film (ACP Composites) and a breather cloth (ACP Composites, Inc.). Next, these were sealed by a Nylon vacuum bag film (ACP Composites, Inc.). The sealed bag was then placed in an oven (Model # 20GCE, Hogentogler and Co., Inc.) and curing was conducted under vacuum using a GAST vacuum pump (diaphragm type, ISSACS). Because the uncured resin mixed with the manufacturer's recommended initiator loading did not harden as per the manufacturer's recommended curing condition (60°C/ 45 min), other conditions were used to obtain hard composites: Condition A: 65.5°C for 50 min, Condition B: 65.5°C for 25 min, Condition C: 65.5°C for 100 min, and Condition D: (a) 93.3°C for 50 min. For each condition, six replicates were manufactured among which 3 replicates underwent liquid-solid extraction and 3 replicates were monitored for VOC air emissions.

## 2.2 Liquid-solid extraction of uncured resin, cured composites, and analysis

The uncured styrene-based CIPP resin and cured composite replicates were chemically extracted at room temperature using methylene chloride and hexane. Each replicate was first drilled into spiral shapes. Next, 3 g of drilled material and 3 g of uncured resin were separately immersed headspace-free in solvents. The samples were stored in 20 mL amber glass vials with PTFE caps for three days in darkness. This approach was determined to achieve equilibrium between the cured composite-solvent pair by Ra et al. [7]. Prior to extract analysis by gas chromatography mass spectrometry (GC/MS), the cured composite methylene chloride and hexane extracts were diluted 100 and 10 times, respectively to avoid contamination of the instrument. For uncured resin extracts, extracts were first diluted 10,000 times (methylene chloride) and 1,000 times (hexane) to quantify styrene since a very high styrene loading was anticipated in the uncured resin. Such a significant dilution could eliminate the existence of other compounds. Therefore, the resin extracts were again injected into and analyzed by GC/MS, but with no dilution while styrene with 6.7 min retention time was excluded from 6.6 to 7.3 min in the MS program. This exclusion helped prevent styrene instrument contamination while detecting other chemicals. Chlorobenzene-d5 dissolved in methylene chloride with 1 mg/L concentration was added as an internal standard to the samples with the same solvent, while the internal standard for hexane extracts was 2 mg/L chlorobenzene-d5. Controls (i.e. solvents without cured composites) were also created and analyzed by GC/MS.

Chemical detection and confirmation were conducted using GC/MS and H NMR. A GC (Shimadzu, Inc., 2010-Plus) and MS (Shimadzu, Inc., TQ8040) was used to analyze the extract samples. The GC/MS was equipped with a HP-5MS capillary column (length 30 m, diameter 0.25 mm, film 0.25 μm) (Agilent Technologies, Inc.) to separate different compounds in the samples. The oven temperature program for GC was as follows: oven temperature of 40°C (hold for 4 min), then ramped to 210°C at 12 °C/min (hold for 4 min) using He carrier gas (5 mL/min) with split injection of 1:10 at 280 °C. Purge flow and column flow were 5.0 mL/min and 1.5 mL/min, respectively. The samples were analyzed for 18 min. For nuclear magnetic resonance (NMR) spectroscopy, uncured resin sample and cured composites chips were dissolved in deuterated chloroform. $^1$H NMR spectra were collected using 32 scans on a 500MHz Bruker spectrometer (Bruker Bio Spin, Fremont, CA) equipped with Top Spin software. The Supporting Material section includes a detailed description of analytical standards and equipment.

### 2.3 Chemical air monitoring of cured composites placed in an ETC for a total time of 50 hr

An electropolished stainless steel environmental test chamber (ETC) was constructed (see Fig. S1 in ESI) according to ASTM D 6670–01 [54]. The ETC was designed based on a CIPP culvert with 45.72 cm diameter (i.e., 8.75 $m^2/m^3$ loading factor) and 6 m length. An air monitoring setup for the ETC was placed in a fume hood (see Fig. 2 & S1 in ESI). Among the nine 50-hr chemical air monitoring events conducted for cured composites, four background air samples from an empty

ETC were collected. A similar approach was applied for the 50-hr chemical air monitoring events for both chemical air monitoring from cured composites and background air sampling.

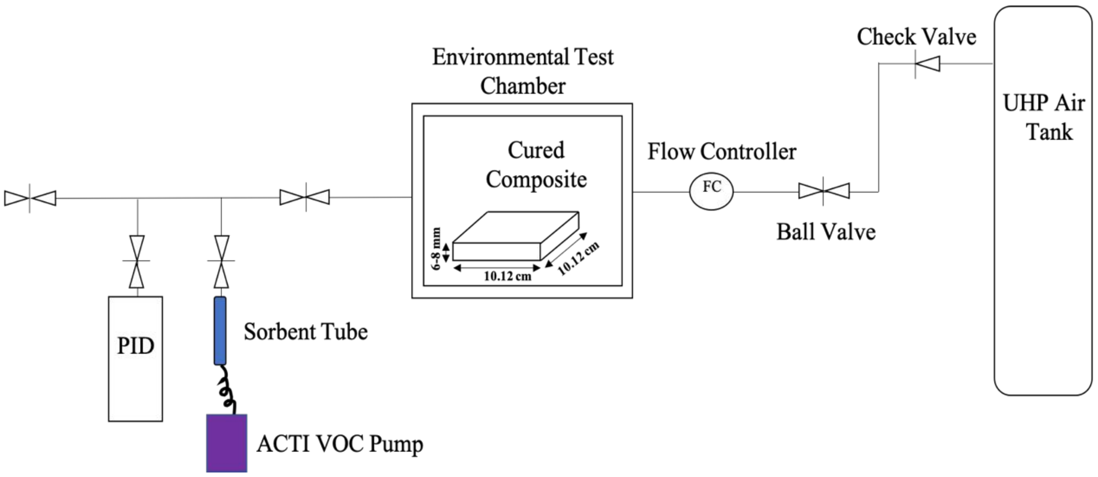


Fig. 2 Experimental setup for capturing post-cured chemical air emissions from cured composites

Prior to each experiment, the stainless steel setup was disassembled and rinsed with high purity methylene chloride (CAS# 75-09-2, Sigma Aldrich) and acetone (CAS# 67-64-1, Sigma Aldrich) at least three times. The rinsed pieces were then flushed with high pressure air for 2 min, and then dried in a vacuum oven (model 3608, Thermo Fisher Scientific) at 200°C for 4 days followed by drying at ambient temperature for 2 days. After assembling the setup, ultra-high purity (UHP) air with 0.3 L/min flowrate was flushed through overnight to remove possible contaminant/solvents residuals. Eventually, the cured composite plate was placed in the ETC to undergo 50 hr of air monitoring following the three consecutive steps listed below.

### 2.3.1. Chemical air monitoring from cured composites in a confined ETC with zero air exchange rate for 24 hr: the static I experiment

The first step of chemical emission monitoring was conducted in the ETC at ambient temperature for 24 hr. Two on-off valves (Parker) upstream and downstream of the ETC were closed to mimic static conditions. Air samples with 25 ml volume were collected using an ACTI VOC vacuum pump (Markes International, Inc.) with 50 ml/min flowrate and sorbent tubes (Markes International, Inc.) packed with quartz wool, TenaxTA and Carbograph 5 TD. Sampling from emissions inside the enclosed ETC was performed without replacement, causing slight decrease in pressure. However, the pressure change across the ETC was considered negligible. Different intervals were used to collect the air samples: initial, 2, 4, 6, 8, 10, 12, 14, and 24 hr.

### 2.3.2. Chemical air monitoring during ventilation of the ETC for 2 hr: the dynamic experiment

Immediately after the 24 hr static test, a dynamic test was performed at room temperature by ventilating the ETC for 2 hr. Experiments involved ETC flushing with ultra-high purity air (1.7 L/min flowrate, $\Theta = 42$ s) over the same cured composite used in the static I experiment. During the entire ventilation period, continuous emission monitoring was conducted using a ppbRae 3000 photon ionization detector (PID) (RAE Systems, 10.6 eV lamp). The device had a 10.6 eV lamp and was calibrated with isobutylene at $10 \pm 0.03$ ppm$_v$. PID monitoring was performed using a styrene correction factor of 0.43 and firmware v2.13 was used. An external filter (PALL Life Science, Acrodisc CR 25 mm Syringe Filter) was also connected to PID to protect the PID detector from saturation by styrene. Sorbent tube air samples with 25 ml sample volume were also collected in different intervals: initial, 5, 10, 20, 40, 60, 80, 100, and 120 min. The vacuum pump and flowrate were the same as the static I experiment.

### 2.3.3. Additional chemical air monitoring from the confined ETC with zero exchange rate for 24 hr: the static II experiment

An additional 24 hr static emission monitoring period was performed right after the 2 hr dynamic test to estimate the effectiveness of ventilation in removing chemicals from the ETC. In this step, both valves were closed again to mimic static conditions in the ETC. The vacuum pump, air flowrate and sampling duration were similar to the static 1 experiment. Sorbent tube air samples were captured when the experiment began and then at the 2, 4, 6, 8, 10, 12 and 24 hr periods. Due to a lack of consistency in sampling intervals during the static 1 and static 2 experiments, the results of sorbent tube samples for the first 12 hr were presented and compared.

### 2.4 Air sample collection and analysis

For sorbent tube analysis, chlorobenzene-d5 (CAS# 3114-55-4, Sigma Aldrich), dissolved in methylene chloride was injected to sorbent tube air samples as internal standard (IS). An IS solution with 11.57 mg/L concentration (1 µL) was injected into the samples anticipated to have low concentrations of chemicals, while for the air samples expected to have high concentrations, 115.7 mg/L (1µL) was added. To analyze the sorbent tube samples, a multi-tube thermal desorption (TD) autosampler (Ultra) Unity 2 series running on Maverick Tubes software (version 5.2.0, Markes International, Inc.) and connected to a GC (Shimadzu, Inc., 2010-Plus) and MS (Shimadzu, Inc., TQ8040) were used to thermally desorb the samples. The cold trap temperature in the TD was held at 25°C and then ramped to 300°C at 20 °C/min. Desorbed compounds from the TD cold trap were then injected into a GC/MS equipped with HP-5MS capillary column (length 30 m, diameter 0.25 mm, film 0.25 µm) (Agilent Technologies, Inc.). The oven temperature program for the GC was as follows: oven temperature of 40°C (hold for 2 min), then ramped to 210°C at 15°C/min using He carrier gas (5 mL/min) with direct injector mode (hold at 100°C). The purge flow and column flow were 5 mL/min and 1.5 mL/min, respectively. The samples were analyzed for 13 min. To quantify styrene, calibration curves with coefficient of determinations of 0.999, 0.998, 0.997, 0.993, 0.991, 0.9781 and 0.9635 were developed. After analysis by GC/MS, a tube conditioner (TC-20, Markes International, Inc.) was used to decontaminate the sorbent tubes. Decontamination was performed at 320°C for 12 hr while UHP He at 100 ml/min was passed through the sorbent tubes.

## 2.5. Thermal characterization of cured composites

Composite thermal characteristics were determined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Prior to analyses, samples were drilled from the surface (1-2 mm) and the bulk (7-10 mm) by a drill press equipped with 1/8-inch bit. For TGA (Q-500, TA Instruments, Inc., New Castle, DE), 11-13 mg of drilled material was placed in a platinum pan, heated at 10°C/min to 160°C under nitrogen atmosphere (60 ml/min) and held for 120 min to determine VOC evaporation. A DSC Q-2000 (TA Instruments Inc., New Castle, DE) was used to investigate if unreacted initiator remained in the cured composites. Approximately 10-11 mg of drilled material was placed in aluminum crucibles and were hermetically sealed by aluminum lids. Scans were performed at 10°C/min from 25°C to 200°C. TGA results were analyzed using a two-way ANOVA with a significance level of 0.05 to determine if curing conditions caused differences in the amount of VOC remaining in each cured composite after manufacture measured as weight loss. This was also applied based on composite depth.

## 2.6. Physical characterization of cured composites

Optical microscopy, as well as Adobe Photoshop and ImageJ, were used to calculate composite porosity. Adobe Photoshop was then applied to select the pore regions in each image using the selection tool. Selected pores were copied and pasted in ImageJ to apply a threshold. Percent porosity (percent area) was calculated by dividing the total area obtained by the ‘‘analyze particles’’ feature in ImageJ to image size. For each curing condition, two cured composite replicates underwent waterjet cutting to obtain porosity samples (50 mm × 12 mm × 6-8 mm). For conditions 65.5˚C/50 min and 65.5˚C/100 min, 2 porosity samples per replicate and for condition 93.3˚C/50 min 1 porosity sample per replicate was achieved. The samples were then polished by water for more clear images. Using an AmScope stereo microscope and an AmScope image capture software, 8-12 images were captured from two different sides of each sample.

The density of cured composites was determined according to ASTM D792–00 [55]. Similar to porosity, two cured composite replicates (out of three) at each curing condition were cut by waterjet to obtain replicate cubes (12 mm ×12 mm × 6-8 mm). The number of replicate cubes was as follows: for composite replicates cured at 65.5°C/50 min/: 3 replicate cubes for replicate 1 and 2 replicate cubes for replicate 2; for composite replicates cured at 65.5°C/100 min: 3 replicate cubes for replicate 1 and 3 replicate cubes for replicate 2; for composite replicates cured at 93.3°C/50 min: 3 replicate cubes for replicate 1 and 1 replicate cube for replicate 2. Replicate cubes were kept at room temperature for 48 hr prior to density measurement. The weight of the replicates was measured in air and after water immersion. Samples were shaken slowly during submersion in water to remove the entrapped water from the specimens. Specific gravity was calculated by using the difference between sample weight in air and water of a replicate. The density of each replicate was obtained by multiplying the specific gravity to water density at ambient temperature.

## 3. Results and Discussion

### 3.1. The uncured resin contained chemicals beyond styrene

TGA revealed that the uncured resin contained approximately 39 wt% VOCs. The uncured resin SDS reported only styrene monomer as a hazardous component [56]. Styrene (290,839 ± 20,154 mg/kg) was found in most abundance and was approximately 29.1% of the total resin weight. More than 60 other compounds were tentatively identified in the uncured resin (see Table S3 in ESI), and 8 were confirmed (see Table 2). Confirmed compounds were HAPs, as well as known and suspected carcinogens, endocrine disruptors and/or had high signal intensity. These confirmed compounds constituted approximately 29.2 wt% of the uncured resin while the composition of the remaining 70.8 wt% of the uncured resin was not identified (see Table 2 & S2 in ESI). The unidentified material using the GC/MS approach may include the low molecular weight polyester of isophthalic or orthophalic acid polymerized with a diol and fumaric acid. Like prior styrene-based CIPP resins analyzed [7, 38], the monomer styrene and antioxidant butylated hydroxytoluene (BHT) were found. *N*-Propylbenzene, 1,3,5-trimethylbenzene (TMB), and 1,2,4-TMB were also found in the resin and by others in CIPP resins [38]. Four compounds were found in the present study but were not reported by others: 3-ethyl-1-methylbenzene (monomer), 2-ethylhexanoic acid (Trigonox® initiator degradation product), 2-propenylbenzene (unknown) and hydroquinone (polymerization inhibitor).

Table 2. Chemical mass loading (mg/kg) for the uncured resin

| **Chemical Detected** | **Present Study** | | **Range Reported in the Literature** |
|---|---|---|---|
| | **GC/MS** | **H NMR** | |
| Styrene [CAR, EDR, HAP] | $2.91\times10^{5} \pm 2.02\times10^{4}$ | Detected | $(1.04\times10^{4} - 1.44\times10^{5})$ [38] |
| Styrene oxide [CAR, HAP] | Not detected | Detected | $(4.70\times10^{1} - 1.38\times10^{2})$ [38] |
| 1,3,5-TMB | $7.12\times10^{1} \pm 6.84$ | Detected | $(4.40 - 5.60\times10^{1})$ [38] |
| *N*-Propylbenzene | $1.03\times10^{2} \pm 9.49$ | Detected | $(5.90 - 5.80\times10^{1})$ [38] |
| 2-Propenylbenzene | $6.81 \pm 7.70\times10^{-1}$ | ne | nr |
| Hydroquinone [CAR*, HAP] | $2.15\times10^{2} \pm 5.32\times10^{1}$ | ne | nr |
| 3-Ethyl-1-methylbenzene | > CR | ne | nr |
| 2-Ethylhexanoic acid | $1.64\times10^{2} \pm 2.42\times10^{1}$ | Detected | nr |
| BHT | $4.30\times10^{1} \pm 4.78$ | ne | $(5.33 - 2.37\times10^{2})$ [7, 38] |
| Sum | $2.92\times10^{5}$ | - | $(1.58\times10^{3} - 1.52\times10^{5})$ [38] |

*Not examined (ne) = authors did not search for this compound in the analytical result; Not reported (nr); A dash indicates the chemicals detected by HNMR were not quantified; CAR = carcinogenic compound; EDR = endocrine disruptors; HAP = hazardous air pollutant; NQ = not quantified; CR: calibration range (57.67 mg/L ~ 28.4 mg/kg, loading calculation was based on 3 g uncured resin); TMB = trimethylbenzene, BHT = butylated hydroxytoluene; CAR*: suspected carcinogen; some of the chemicals presented here were also found in different media: styrene in air [6, 11, 12, 33-35], water [38, 42-53] and CIPP condensate [11, 50]; 1,3,5-TMB: in water [38, 42, 43, 47-51] and CIPP condensate [50]; BHT: in CIPP condensate [11].*

### 3.2. Chemical volatilization was influenced by the manufacturing condition

Chemical volatilization was influenced by air pressure, while temperature and heating time did not influence the final chemical composition of cured composites. At ambient pressure, the weight difference between the initial uncured material and final hardened composite for composite A (*50 min at 65.5˚C*) was 8.87 ± 1.67 wt% (see Table S4 in ESI). This lost material was emitted into the air as a waste product. In contrast, when composites were manufactured for the same and different conditions, under vacuum, a 21-27 wt% VOC loss was detected. Because a vacuum is not known to the authors of being applied at CIPP manufacturing sites, it is suspected that actual VOC loss to the air may more closely mimic the ambient condition. Also, uncured resin tubes often have a thin film (i.e., polyethylene, polyvinylchloride) on their inner surface covering the PET felt and fiberglass, which may help to reduce VOC loss. Though, some temperatures previously documented in the field exceeded the melting temperature of those films [7], and this allows the resin to be directly exposed to the air or steam. A film was not used for the present study. In the field, forced air and steam are commonly blown down the length of uncured resin tubes during CIPP manufacture, whereas composites were cured in an oven for the present study. The air temperature during curing (65.5-93.3 °C) and heating time (25-100 min) did not significantly influence the amount of VOC that remained inside the cured composites after their manufacture ($p$ =0.59) (see Table 3).

Table 3. The weight of volatile material found in new composites based on curing conditions

| Parameter | Curing condition and weight of volatile material detected, wt% | | |
|---|---|---|---|
| | **Condition A**<br>**50 min, 65.5˚C** | **Condition C**<br>**100 min, 65.5˚C** | **Condition D**<br>**50 min, 93.3˚C** |
| ***After Manufacture, No vacuum*** | | | |
| Surface | 2.76 ± 0.46 % | - | - |
| Depth | 3.07 ± 0.43 % | - | - |
| ***After Manufacture, Vacuum applied*** | | | |
| Surface | 2.90 ± 0.12 % | 2.77 ± 0.25 % | 2.90 ± 0.11 % |
| Depth | 2.94 ± 0.17 % | 2.46 ± 0.24 % | 2.98 ± 0.07 % |

*Initial volatile content of the uncured resin was 39 ± 1.74 %; A hyphen (-) indicates no sample was manufactured at that condition to measure weight loss.*

### 3.3 Physical, thermal, and chemical characteristics of the new composites

Different curing temperature and heating conditions resulted in composites with different density (1.10 to 1.19 g/cm$^3$) and porosity (0.25 to 1.27 %) characteristics. The densities observed were similar to CIPPs exhumed from the field by others (1.07 to 1.20 g/cm$^3$) [7, 57], while the observed porosity was significantly lower than the porosity range of 3.41 to 17.75% reported from CIPPs manufactured in the field [57, 58] (see Table S5 in ESI). Such a difference might be due to use of steam curing CIPP field installations. In the lab, the higher temperature curing condition caused more porosity and lower density, which might be due to increasing void pressure [59]. The first heating scan of DSC thermograms revealed a small endothermic peak at 55-65°C and an exothermic peak at 140-160°C for all composites cured under vacuum. This implied the presence of unreacted VOCs, uncured resin, and/or initiator (see Fig. S2 in ESI).

For the composite cured at ambient pressure, styrene, styrene oxide, 1,3,5-TMB, 1,2,4-TMB, benzaldehyde, benzoic acid, 1-tetradecanol, 3-ethyl-1-methylbenzene, and *N*-propylbenzene were detected and quantified. The chemical loading of styrene ($p = 0.022$) in the composite cured at ambient pressure was significantly lower than the chemical loadings of the same compounds obtained from the composites cured under vacuum. No significant difference, however, was observed for styrene oxide and 1-tetradecanol loadings by changing curing pressure. Among different quantified compounds, styrene constituted the highest portion ($9.74 \times 10^3 \pm 1.09 \times 10^3$ mg/kg) in the cured composite, which was 3-fold greater than other compounds. No statistical difference in the amount of each compound extracted from the cured composites was found when either air temperature during curing or heating time were varied (see Tables 4 & S5 in ESI).

Styrene was detected in most abundance across cured composites (14,518 to 20,691 mg/kg), but was present at a much lower loading than in the uncured resin (see Table 2). Other compounds detected in the cured composites were present at a loading 3-fold less than styrene. Several compounds were likely created during manufacture as they were detected in the cured composites, but not the uncured resin, such as benzaldehyde, benzoic acid, styrene oxide, and 1-tetradecanol. Several compounds found in the uncured resin were not detected in the cured composites: hydroquinone, BHT, and 2-ethylhexanoic acid. H NMR results confirmed the existence of styrene (monomer), styrene oxide (styrene oxidation product), 2,4-diphenyl-1-butene (styrene dimer), 1,3,5-TMB, phthalic anhydride (suspected monomer), *N*-propylbenzene and 2-ethylhexanoic acid in cured composites and styrene, styrene oxide and 1,3,5-TMB in uncured resin (see Table 2 & Fig. S3 in ESI). 2,4-Diphenyl-1-butene (styrene dimer) was the only compound detected in cured composites by H NMR and not by GC/MS extract analysis. No styrene dimer was found by H NMR analysis of the uncured resin. Most, but not all, of the chemicals extracted from the cured composites were previously confirmed in other studies focused on CIPP styrene-based resins, newly manufactured CIPPs, and released into in air and water at CIPP manufacturing sites. For the present study, the variability of compound magnitude in the composites was minimal. CIPPs removed from the field however by others, and extracted using the same methods as the present study, found significant chemical loading differences. In some cases, variability was up to 19 times greater in magnitude even when CIPPs were manufactured using the same resin, by the same contractor, and manufactured within 2 days of one another at the same location. [7, 53] As a result, this indicates the existence of unknown factors influencing CIPP chemical loading that requires additional investigation.

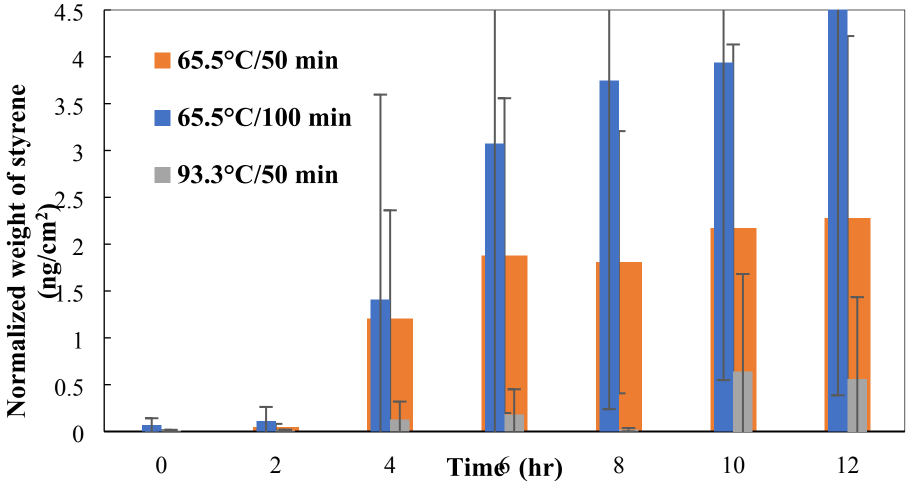
### 3.4 VOC emissions from newly manufactured composites

Styrene was the only compound detected and quantified in the air during chemical emission monitoring. The authors encountered similar analytical method limitations as those encountered by NIOSH (2019). The high styrene air concentration prevented the identification and quantification of other VOCs with lower abundance in air samples. In the present study, the author's chemical analysis of the uncured resin and cured composites themselves indicated that other VOCs were present and were likely also emitted to the air.

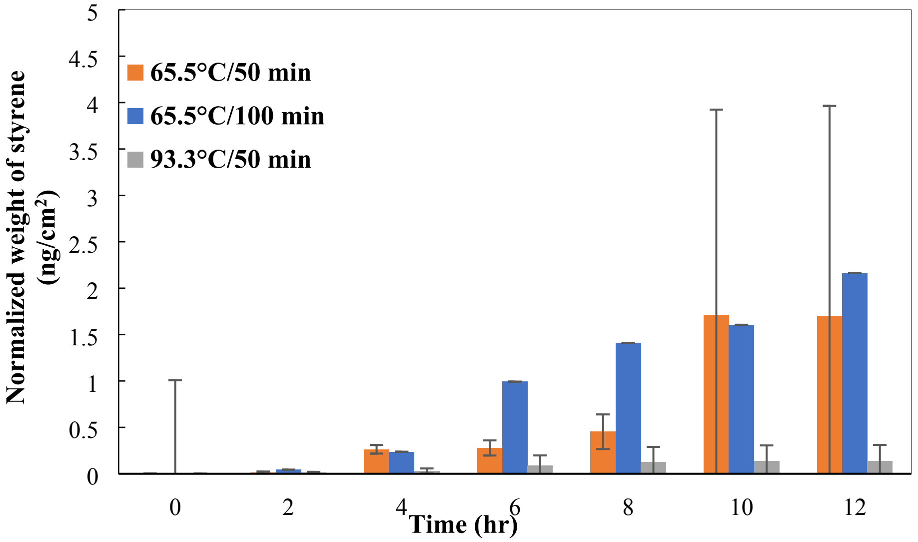
The time needed to achieve ETC styrene equilibrium in air differed across cured composites (see Fig. 3), even though composite styrene loadings were not different (see Table 4). The time to achieve equilibrium was about 10 hr for the Composite A (65.5˚C/50 min) and no equilibrium was achieved for either Composite B (65.5˚C/100 min) or Composite C (93.3˚C/50 min). The greatest normalized styrene weight ($mg/cm^2$) (and air concentration) was obtained for Composite A (65.5˚C/50 min) and Composite B (65.5˚C/100 min) after 12 hr which were 4.77 ± 4.38 $ng/cm^2$-12 hr (i.e., 6.08 ± 5.64 $ppm_v$) and 2.28 ± 1.94 $ng/cm^2$-12 hr (i.e., 2.95 ± 2.53 $ppm_v$), respectively. Composite C (93.3˚C/50 min), which was manufactured at the greatest temperature, had a noticeably lower normalized weight and air concentration than other composites: 0.56 ± 0.87 $ng/cm^2$-12 hr (i.e., 0.71 ± 1.08 $ppm_v$). No relationship was found between normalized styrene weight, composite porosity, and density. Because the composite cured at higher temperature exhibited the lowest normalized styrene weight, greatest porosity and lowest density, the authors hypothesize that the observed styrene emission was a surface phenomenon. Therefore, the styrene loading measurement for a composite sample through the entire wall could not detect this factor. Since the cured composites were prepared under vacuum, styrene and other VOCs that could be present after CIPP manufacture may have been removed and thus were not detectable during the ETC experiment that was not conducted under vacuum.

### 3.5 Air ventilation of new composites and VOC rebound

Immediately before air ventilation, average normalized styrene weight (and air concentration) were found to be 0.62 ± 0.37 ng/cm$^2$ (i.e. 1.20 ± 0.69 ppm$_v$) for Composite A (65.5˚C/50 min), 2.99 ± 2.69 ng/cm$^2$ (i.e. 3.82 ± 3.46 ppm$_v$) for Composite C (65.5˚C/100 min) and 0.22 ± 0.28 ng/cm$^2$ (i.e. 0.27 ± 0.35 ppm$_v$) for Composite D (93.3 ˚C/50 min). The styrene air concentrations were below the styrene 8 hr-TWA 100 ppm$_v$ OSHA occupational exposure limit [60], but above the limit at which odor can be detected (0.04-0.32 ppm$_v$) [61, 62]. Concentrations were also below the level California established for a 1 hr exposure of the general public, 4.9 ppm$_v$ [14]. But, exceeded the USEPA acute residential inhalation indoor air target of 0.244 ppm$_v$[63]. According to both the PID and sorbent tube results (see Fig. S4 & Table S7 in ESI), air ventilation ($\Theta$ = 42 s) reduced styrene air concentration rapidly to almost 0 ppm$_v$ in 10 min. Although, levels rebounded back to the initial concentration when ventilation was halted, which is likely due to the substantial loading of residual styrene in the cured composites (see Table 4). The ratio of inlet air flowrate/exposed surface area used in this study (9.9 m/hr) was approximately 3- to 11-fold less than the ratio recommended from a field CIPP study in the Netherlands (30-107 m/hr). The ratio was also less than the headspace velocity obtained by Roghani et al. (396-1,872 m/hr) [64]. This experimental condition was due to a lab scale flow controller limitation. Because of the significant amount of VOC residual found in the cured composite and very limited amount of styrene volatilized into air during a 12 hr period (for example 0.0007 % for Composite A) it is likely that a similar rebound effect will occur for new CIPPs.



431 (a)



432 (b)

433 Fig. 3 Normalized weight of styrene from composites that were manufactured under different conditions for: (a) static I air monitoring experiments and (b) static II air monitoring experiments. Between each experiment, air flow was flushed through the ETC for 2 hr and air monitoring was conducted before and after ventilation using sorbent tubes and a PID

Table 4. Chemical mass loading for the new composites manufactured under different conditions when extracted using methylene chloride, mg/kg

| **Chemical detected** | **Newly manufactured composites** | | | | | **Range reported for CIPPs in the literature** |
|---|---|---|---|---|---|---|
| | **Without vacuum** | **Under vacuum** | | | | |
| | ***50 min at 65.5˚C*** | ***50 min at 65.5˚C*** | ***25 min at 65.5˚C*** | ***100 min at 65.5˚C*** | ***50 min at 93.3˚C*** | |
| Styrene $^{CAR, EDR, HAP}$ | $9.74\times10^{3} \pm 1.09\times10^{3}$ | $1.45\times10^{4} \pm 4.82\times10^{3}$ | $1.98\times10^{4} \pm 2.43\times10^{3}$ | $1.92\times10^{4} \pm 4.40\times10^{3}$ | $2.07\times10^{4} \pm 3.06\times10^{3}$ | $8.60\times10^{1}$ to $1.67\times10^{4}$ [7, 38] |
| Styrene oxide $^{CAR, HAP}$ | $1.04\times10^{2} \pm 5.62\times10^{1}$ | $1.25\times10^{2} \pm 5.63\times10^{1}$ | $5.69\times10^{2} \pm 4.83\times10^{2}$ | $2.69\times10^{2} \pm 6.70\times10^{1}$ | $1.56\times10^{2} \pm 2.30\times10^{1}$ | 1.90 to $9.50\times10^{1}$ [38] |
| Benzaldehyde | $5.74\times10^{2} \pm 5.72\times10^{2}$ | $1.39\times10^{2} \pm 5.49\times10^{1}$ | $3.00\times10^{2} \pm 2.34\times10^{2}$ | $2.94\times10^{2} \pm 1.26\times10^{2}$ | $4.05\times10^{2} \pm 3.82\times10^{2}$ | 2.70 to $3.64\times10^{2}$ [7, 38] |
| 1,3,5-TMB | $3.00\times10^{1} \pm 3.35$ | $6.06\times10^{1} \pm 2.51\times10^{1}$ | $8.18\times10^{1} \pm 8.56$ | $7.51\times10^{1} \pm 3.74$ | $6.71\times10^{1} \pm 7.84$ | 1.40 to $2.60\times10^{1}$ [38] |
| 1,2,4-TMB | $2.02\times10^{2} \pm 1.20\times10^{1}$ | $3.39\times10^{2} \pm 1.12\times10^{2}$ | $4.46\times10^{2} \pm 1.69\times10^{1}$ | $4.21\times10^{2} \pm 4.38\times10^{1}$ | $3.95\times10^{2} \pm 3.86\times10^{1}$ | 7.50 to $8.60\times10^{1}$ [38] |
| Benzoic acid | $3.40\times10^{3} \pm 2.48\times10^{2}$ | $4.76\times10^{3} \pm 1.09\times10^{3}$ | $5.87\times10^{3} \pm 6.75\times10^{2}$ | $6.23\times10^{3} \pm 5.17\times10^{2}$ | $5.88\times10^{3} \pm 6.10\times10^{2}$ | $4.70\times10^{2}$ to $1.80\times10^{3}$ [7] |
| 1-Tetradecanol | $1.36\times10^{3} \pm 1.44\times10^{2}$ | $1.80\times10^{3} \pm 4.90\times10^{2}$ | $1.95\times10^{3} \pm 2.73\times10^{2}$ | $2.18\times10^{3} \pm 4.72\times10^{2}$ | $1.95\times10^{3} \pm 4.69\times10^{2}$ | $3.94\times10^{2}$ to $2.65\times10^{3}$ [7] |
| *N*-Propylbenzene | $2.96\times10^{1} \pm 1.35$ | $4.57\times10^{1} \pm 1.10\times10^{1}$ | $5.47\times10^{1} \pm 3.40$ | $5.32\times10^{1} \pm 3.12$ | $5.27\times10^{1} \pm 5.80$ | 1.50 to $3.80\times10^{1}$ [38] |
| 2-Propenylbenzene | - | 2 replicates shown $<5.00\times10^{4}$ - SIM<90 | 2 replicates shown $<5.00\times10^{4}$ - SIM<90 | 1 replicate shown $<5.00\times10^{4}$ - SIM<90 | 3 replicates shown $<5.00\times10^{4}$ -SIM<90 | - |
| Hydroquinone $^{CAR*, HAP}$ | - | - | - | - | - | - |
| 3-Ethyl-1-methylbenzene | $5.20\times10^{1} \pm 1.42$ | $9.03\times10^{1} \pm 5.13\times10^{1}$ | $9.55\times10^{1} \pm 5.71\times10^{1}$ | $9.35\times10^{1} \pm 1.47\times10^{1}$ | $2.48\times10^{2} \pm 2.81\times10^{2}$ | - |
| 2-Ethylhexanoic acid | $1.26\times10^{3}$ | $1.40\times10^{3}$ | $1.52\times10^{3} \pm 1.52\times10^{1}$ | $1.45\times10^{3} \pm 1.85\times10^{1}$ | $1.43\times10^{3} \pm 4.26\times10^{1}$ | - |
| BHT | - | - | - | - | - | 1.50 to $4.40\times10^{1}$ [38] |
| *Sum* | *$1.44\times10^{4}$* | *$2.19\times10^{4}$* | *$2.92\times10^{4}$* | *$2.88\times10^{4}$* | *$2.98\times10^{4}$* | *$2.26\times10^{3}$ to $1.73\times10^{4}$* [38] |

*CAR = carcinogenic compound; EDR = endocrine disruptors; HAP = hazardous air pollutant; TMB = trimethylbenzene, BHT = butylated hydroxytoluene; hyphen symbol (-) means not detected; CAR*: suspected carcinogen; some of the chemicals presented here were also found in different media: styrene in air [6, 11, 12, 33-35], benzaldehyde in water [54] and CIPP condensate [11]; benzoic acid: in CIPP condensate [11]; water [38, 42-53] and CIPP condensate [11, 50]; 1,3,5-TMB: in water [38, 42, 43, 47-51] and CIPP condensate [50]; 1,2,4-TMB in water [38, 47-51] and CIPP condensate [50]; BHT: in CIPP condensate [11]; 1-tetradecanol: in CIPP condensate [11].*

### 3.6 VOC loss during and after manufacture, study limitations, and recommendations

The mobility of the CIPP manufacturing process, where contractors move from site to site, sometimes multiple times per day, poses a challenging measurement issue. These mobile contractors discharge their waste into the environment and do not conduct chemical air monitoring to determine which and how much VOC is discharged, the authors estimated pollutant air emissions. Further, the variety of resin compositions, initiator packages, curing practices, and environmental conditions also poses a challenge for making broad statements about waste discharged into local environment at these CIPP installations. There is a lack of quantitation of the pollutants generated and discharged from these mobile sources.

Based on the present study and publicly available information, VOCs emitted into the air during manufacture may be on the order of tens to thousands of tons for some projects (see Table S2 in ESI). Public records indicated 61,000 to 454,000 kg of resin has sometimes been used per project (where multiple CIPPs have been installed in series along a single sewer line and the resin is considered about 50% styrene by weight). These projects involved thermal manufacturing methods (steam/hot water). If 8.87 wt% VOC loss (observed during the present study) occurred for the resin brought to a CIPP worksite, an estimated 5,400 to 30,000 kg [6 to 33 tons] of VOCs could have possibly been discharged into the air. As of 2013, one resin manufacturer reported providing 122,469,940 kg [135,000 tons] of uncured resin for CIPP for over 25 years and their main resin lines support thermal CIPP manufacture [64]. Using that result, roughly, 10,863,083 kg [~12,000 tons] of VOCs could have been discharged to the air. In 2017, CIPP installers were directed to consider “maximizing the flow of air through the curing CIPP for the site-specific conditions” to minimize the amount of condensate waste that remains after the CIPP is manufactured [65]. Under section 112 of the Clean Air Act, the plastic pipe and pipe fitting manufacturing industry [North American Industry Classification System code of 326122] has been categorized to follow a permit limit of less than 100 tons per year of HAP emission [66]. Because the magnitude of CIPP VOC emission and that the waste includes HAPs (styrene, styrene oxide, methylene chloride, dibutyl phthalate, ethylbenzene, maleic anhydride, phthalic anhydride, and *N*-propylbenzene), work is needed to document actual emissions and understand the environmental and human health implications. It may be that CIPP emissions for a single worksite or contractor (mobile source, moving site to site) exceed the limits of fixed plastic composite manufacturing facilities. While prior studies claim CIPP manufacture is an environmentally friendly technique [67], VOC emissions like those described here have not been documented for their consideration. Not included in this pollutant estimation are the composition and magnitude of partially cured resin, oligomers, and water saturated with VOCs that can also be emitted in addition to organic vapors [11].

This study provides new knowledge associated with CIPP VOC emissions, and additional work is needed. First, the introduction of the different curing variables (steam, hot water, UV light) may increase the complexity of chemicals produced during manufacture. It is important to first understand VOC emission in the absence of these factors and then additional work can examine their impact. Also needed is an examination of CIPP emission reactivity with atmospheric ozone, the hydroxyl radical, and the nitrate radical, as reactions can form other compounds and particulate matter [68]. The role of fillers, diluents added to resins, and a wide curing temperature range may impact chemicals produced. Variability may occur across resins, with different initiators and/or loadings. Also unclear is whether slight differences in resin batch chemical composition influences the type and magnitude of chemicals released. Similar to observations reported by NIOSH [12], the magnitude of styrene's air concentration prevented the authors from detecting other compounds in air. Cured composite characterization however revealed that other VOCs were present and these likely volatilized into the air (see Table S9 in ESI).

## 4. Conclusion

The study goal was to better understand VOC release before, during, and after styrene-based composite manufacture using an uncured CIPP resin. The uncured resin contained approximately 39 wt% VOC and composites also contained some resin composites but other pollutants that were generated during manufacture. Hazardous air pollutants (styrene, styrene oxide, and hydroquinone) were detected in the uncured resin (29.1 wt%). More than 60 compounds were tentatively identified in the uncured resin among which 8 chemicals including HAPs, suspected carcinogens and endocrine disrupters were confirmed. Several compounds were detected only in the cured composites likely created during manufacture: benzaldehyde, benzoic acid, styrene oxide and 1-tetradecanol. The presence of styrene can be an "indicator" that other VOCs are present, but have yet to be fully characterized in CIPP emissions.

Chemical volatilization was influenced by pressure, but temperature and heating time did not influence final chemical composition of cured composite. During manufacture, approximately 8.87 wt% VOC was discharged to the air at standard pressure. All cured composites, regardless of temperature or heating time, contained approximately 3 wt% VOC. No statistical difference for VOC loading was found across cured composites and styrene was the most abundant compound for a pipe with 45.7 cm diameter and 6 m length. No statistical difference was found for styrene emission into the air across cured composites despite different curing temperature and heating times. High styrene air concentration signals inhibited the author's ability to determine if other non-styrene compounds were emitted into the air. Short-term ventilation (2 hr) reduced styrene air concentration to near zero in 10 min, but styrene levels rebounded when ventilation was halted. Due to the high styrene loading in the cured composite, it is expected that ventilation will only temporarily reduce VOC air levels in pipes, manholes, and other affected spaces. To reduce the amount of VOC in the cured composite and potentially reduce the VOC emission rate, modifying the uncured resin, using different initiators, initiator loading, curing with a higher temperature range, or post-installation CIPP treatment (i.e., a fluid, high temp air) should be investigated.

Advancements in air sampling and analytical methods are needed. An analytical method is needed for detecting non-styrene VOCs when styrene air concentration is high. Understanding the other constituents is needed as Kobos et al. (2019) [69] found, emission toxicity was styrene-independent [68]. The presence of water, steam, particulates, and reactive air pollutants on VOC fate and degradation requires scrutiny. Chemical risk assessments for occupational and public health decisions are also needed.

Evidence suggests that air pollutant emissions from these mobile sources are likely significant, but have received little scrutiny. Potentially tens of tons of VOCs may be emitted into the air during a single CIPP project. The greatest air pollutant discharge seems to be when the uncured resin tube is undergoing curing. Emission capture at CIPP worksites has been previously recommended to reduce air pollution and reduce occupational and public safety risks [9, 11, 15, 32]. Evidence from the present study indicates that environmental protection professionals should consider monitoring, regulating, and potentially implement restrictions. The most immediate reduction in mobile source air pollution could likely be resin encapsulation coupled with capturing materials generated instead of discharging them into the environment. For example, boat manufacturers have previously instituted controls to capture chemical emissions to comply with environmental regulations. Such a practice may be more environmentally helpful during the ozone season when VOCs can react with NOx to form the pollutant ground level ozone [70]. The *in-situ* manufacture of CIPP plastic liners is a new mobile source of air pollution that is growing in popularity but lacks appropriate environmental regulatory controls and oversight. Reductions in technology environmental impacts may also help reduce health risks to workers and members of the general public nearby, including inside buildings.

## Conflicts of interest

AJW, JAH, BEB, and SMTS are named in a patent application (PCT/US18/28173) filed April 18, 2018 by the Purdue Research Foundation. The patent application pertains to the capture and treatment of materials released during closed molding processes. The invention was developed with support from a National Science Foundation CBET-1624183 grant.

## Acknowledgement

This research was funded by National Science Foundation RAPID Grant CBET-1624183, Purdue University, and the U.S. Federal Highway Administration pooled fund project TPF-5(339)”. The CIPP resin company is thanked for their assistance. Dr. Nadezhda Zyaykina (Purdue University) is also acknowledged for her help.

## References

1 U.S. Environmental Protection Agency, *The Clean Water and Drinking Water Infrastructure Gap Analysis*, *EPA-816-R-02-020*, Environmental Protection Agency, Washington, DC, 2002, https://nepis.epa.gov/Exe/ZyPDF.cgi/901R0200.PDF?Dockey=901R0200.PDF.

2 ASCE (American Society of Civil Engineers), *Report Card for America's Infrastructure,* Reston, VA, 2013.

3 American Water Works Association, *Buried No Longer: Confronting America's Water Infrastructure Challenge*, 2012, http://www.climateneeds.umd.edu/reports/American-Water-Works.pdf.

4 National Research Council of the National Academies, *Drinking Water Distribution Systems: Assessing and Reducing Risks*, The National Academies Press, Washington, D.C., 2006.

5 A. Whelton, M. Teimouri, K. Ra, E. Conkling, B. Boor, J. Howarter, C. Jafvert, J. Youngblood, N. Zyakayina, M. Townsend, Water Pipe Repair Can Cause Toxic Air, Association of Environmental Engineering and Science Professors, Ann Arbor, Michigan, June, 2017.

6 U.S. Agency for Toxic Substances and Disease Registry, *Health Consultation: Schlitz Park Office Building, Milwaukee, Milwaukee County*. Atlanta, GA, 2005, https://www.atsdr.cdc.gov/HAC/pha/Schlitz%20Park%20Office%20Building/SchlitzParkHC091305.pdf.

7 K. Ra, S.M. Teimouri Sendesi, M. Nuruddin, N. Zyaykina, E. N. Conkling, B.E. Boor, C. T. Jafvert, J. A. Howarter, J. P. Youngblood, A. J. Whelton, Considerations for emission monitoring and liner analysis of thermally manufactured sewer cured-in-place-pipes (CIPP), *J. Hazard. Mater.*, 2019, **371**, 540-549.

8. A. Sullo, King Street sewer rehab and water quality impacts. *Presentation at Underground Infrastructure Research Int. Conf. and Trenchless Technology Road Show, Center for Advancement of Trenchless Technologies*, Waterloo, ON CAN, 2012.

9 A. J. Whelton, K. Ra, S. M. Teimouri Sendesi, M. Nuruddin, X. Li, J. A. Howarter, J. P. Youngblood, C. T. Jafvert, N. N. Zyakyina, Contaminant Release from Storm Water Culvert

Rehabilitation Technologies: Understanding Implications to the Environment and Long-Term Material Integrity. U.S. Federal Highway Administration Transportation Pooled Fund (TPF)-5(339), 2019, DOI: 10.5703/1288284317089.

10 K. Ra, S. M. Teimouri Sendesi, J. A. Howarter, C. T. Jafvert, B. M. Donaldson, A. J. Whelton, Critical Review: Surface Water and Stormwater Quality Impacts of Cured-In-Place Pipe Repairs, *J. Am. Water. Works. Ass*. 2018, **110**, 15-32.

11 S. M. Teimouri Sendesi, K. Ra, E. N. Conkling, B. E. Boor, M. Nuruddin, J. A. Howarter, J. P. Youngblood, L. M. Kobos, J. H. Shannahan, C. T. Jafvert, A. J. Whelton, Worksite Chemical Air Emissions and Worker Exposure during Sanitary Sewer and Stormwater Pipe Rehabilitation Using Cured-in-Place-Pipe (CIPP), *Environ. Sci. Technol. Lett*., 2017, **4**, 325–333.

12 R.F. LeBouf and D. A. Burns, *Health Hazard Evaluation Report: Evaluation of Exposures to Styrene During Ultraviolet Cured-in-Place-Pipe Installation, NIOSH HHE Report No. 2018-0009-3334*, Centers for Disease Control and Prevention, U.S. National Institute of Occupational Safety and Health, Morgantown, WV, 2019, https://stacks.cdc.gov/view/cdc/70136.

13 U.S. Occupational Safety and Health Administration, *Citation and Notification of Penalty Inspection Number 1274028*, U.S. Department of Labor, Des Plaines, IL, April, 2018, https://engineering.purdue.edu/CIPPSafety/resources/OSHA-Region5-CIPP-Fatality-Notification-of-Penalty-2018.pdf.

14 CDPH (California Department of Public Health—Division of Environmental and Occupational Disease Control), https://engineering.purdue.edu/CIPPSafety/resources/CDPH-CIPP-Safety-Alert-2017.pdf, (Accessed: 1 September 2017).

15 California Department of Public Health, *Cure-in-Place Pipe (CIPP) Additional Considerations for Municipalities*, www.cdph.ca.gov/Programs/CCDPHP/DEODC/CDPH%20Document%20Library/CIPP%20additional%20considerations.pdf#search=CIPP%20alert, (accessed November 2017).

16 Finger lakes Times, https://www.fltimes.com/news/illnesses-cause-new-policy-for-seneca-falls-sewer-pipe-repairs/article_411a3c3d-da94-55b7-86b6-b822d789319a.html, (assessed October 2019)

17 NASSCO, Inc. Manual for Inspector Training and Certification Program (ITCP) for the Inspection of Cured in Place Pipe Installation, Version 3.0, *Chapter 4 Specifications- The Inspectors Instructions and Guidelines,* Marriottsville, MD, 2011.

18 M. Najafi, Trenchless Technology: Pipeline and Utility Design, Construction, and Renewal, ISBN: 9780071422666, McGraw-Hill Education, 1st edn., 2005.

19 M. Najafi, Trenchless Technology Piping: Installation and Inspection, ISBN :978-0-07-148928-7, McGraw-Hill Education, 1st edn., 2010.

20 M. Najafi, Trenchless Technology: Planning, Equipment, and Methods, ISBN10: 0071762450, McGraw-Hill Education, 1st edn., 2013.

21 S. Syachrani, H. S. Jeong, V. Rai, M. J. Chae, T. Iseley, A risk management approach to safety assessment of trenchless technologies for culvert rehabilitation, *Tunn. Undergr. Sp. Tech.*, 2010, **25**, 681-688.

22 A. Pinto, I. L. Nunes, R. A. Ribeiro, Occupational risk assessment in construction industry – Overview and reflection, Saf. Sci*.,* 2011, **49**, 616-624.

23 M. Hastak, S. Gokhale, V. Thakkallapalli, Decision model for assessment of underground pipeline rehabilitation options, *Urban Water J*., 2004, **1**, 27 – 37.

24 H. Lu, J. Matthews, T. Iseley, How Does Trenchless Technology Make Pipeline Construction Greener? A Comprehensive Carbon Footprint and Energy Consumption Analysis, J. Clean. Prod., 2020, **261**, 121215.

25 V. Kaushal, M. Najafi, R. Serajiantehrani, Comparative Analysis of Environmental and Social Costs of Trenchless Cured-in-Place Pipe Renewal Method with Open-Cut Pipeline Replacement for Sanitary Sewers, J. Pipeline. Syst. Eng. Pract, 2020, **11** (4): 04020037.

26 V. Kaushal, M. Najafi, Comparative Assessment of Environmental Impacts from Open-Cut Pipeline Replacement and Trenchless Cured-in-Place Pipe Renewal Method for Sanitary Sewers, Infrastructures 2020, **5** (48); doi:10.3390/infrastructures5060048.

27 A. A. Alsadi, J. C. Matthews, Evaluation of Carbon Footprint of Pipeline Materials during Installation, Operation, and Disposal Phases, J. Pipeline Syst. Eng. Pract., 2020, **11**(2): 04020005

28 A. Alsadi, J. C. Matthews, E. Matthews, Environmental Impact Assessment of the Fabrication of Pipe Rehabilitation Materials, *J. Pipeline. Syst. Eng.,* 2020, **11**, DOI:10.1061/(asce)ps.1949-1204.0000395.

29 H. Lu, J. Matthews, T. Iseley, How Does Trenchless Technology Make Pipeline Construction Greener? A Comprehensive Carbon Footprint and Energy Consumption Analysis, *J. Clean. Prod.*, 2020, **261**, DOI: https://doi.org/10.1016/j.jclepro.2020.121215.

30 V. Kaushal, M. Najafi, R. Serajiantehrani, Environmental Impacts of Conventional Open-Cut Pipeline Installation and Trenchless Technology Methods: State-of-the-Art Review, *J. Pipeline Syst. Eng. Pract*., 2020, **11**, DOI: 10.1061/(ASCE)PS.1949-1204.0000459.

31 R. Serajiantehrani, Development of a Machine Learning-based Prediction Model for Construction and Environmental Costs of Trenchless Spray-applied Pipe Linings, Cured-in-

place Pipe, and Sliplining Methods in Large Diameter Culverts, Ph.D. Thesis, University of Texas at Arlington, 2020.

32 G. Muenchmeyer, personal communication.

33 E. Bourbour Ajdari, Volatile Organic Compound (VOC) Emission during Cured-in-Place-Pipe (CIPP) Sewer Pipe Rehabilitation, Ph.D. Thesis, University of New Orleans, 2017.

34 AirZone, Inc, *A Report on the Monitoring of Styrene in Toronto Homes During the Cured in Place Pipe (CIPP) Process for Sewer Pipe Rehabilitation by Insituform*, *Project 041-6742*, Toronto, 2001.

35 G. Bauer, Styrene: an overview - an awareness, Underground Infrastructure Research International Conference and Trenchless Technology Road Show, ON, CAN, 2012.

36 J. Matthews, NASSCO CIPP Emissions Phase 2: Evaluation of Air Emission from Polyester Resin CIPP with Steam Cure, Webinar by the National Association of Sewer Service Companies, December 17, 2019.

37 SAK Pipeline Infrastructure. Solved.™, CIPP submittal for CA, 2016.

38 X. Li, M. Nuruddin, K. Ra, S. M. Teimouri Sendesi, J. A. Howarter, C. T. Jafvert, J. P. Youngblood, A. J. Whelton, Outdoor Manufacture of UV-Cured Plastic Linings for Storm Water Culvert Repairs: Chemical Emission and Residual, Environ. Pollut., 2019, **245**, 1031-1040.

39 S. Crawford, C. T. Lungu, Influence of temperature on styrene emission from a vinyl ester resin thermoset composite material, *Sci. Total Environ.*, 2011, **409**, 3403–3408.

40 RIVM (Rijksinstituut voor Volksgezondheid en Milie, Netherlands National Institute for Public Health and the Environment), *Sewer renovation with stocking methods: backgrounds in the information sheet, Report Number 609021038/2006*, Amsterdam, Netherlands,2006.

41 U.S. NRC, Incident Report. 957007, 2010.

42 T. Weldon, M. Morton, Report of CDOT I-70 Culvert Repair Project Styrene Release, Response, and Mitigation at Clear Creek County, Colorado, *Colorado Department of Transportation*, 2011.

43 CDOT (Colorado Department of Transportation), FY 2012-13 Joint Budget Committee Hearing Agenda, *Colorado Department of Transportation*, 2012, https://www.codot.gov/business/budget/legislative-reports-information/previous-legislative-reports-and-information/CDOT%20JBC%20Hearing%20responses%201-3-2012.pdf.

44 VDOT (Virginia Department of Transportation), Special Provision for Pipe Rehabilitation. SP302-000140-01, *Virginia Department of Transportation*, 2016.

45 B. M. Donaldson, A. J. Whelton, Water Quality Implications of Culvert Repair Options: Cementitious and Polyurea Spray-on Liners (No. FHWA/VCTIR 13-R3), *Virginia Center for Transportation Innovation and Research,* 2012, https://trid.trb.org/view.aspx?id=1243674.

46 Spectrum Analytical Inc., *2013a. Laboratory Report - Project No. 08-220953.00, Weathersfield, VT*, 2013.

47 Spectrum Analytical Inc., *2013b. Laboratory Report - Project No. 08-220953.00, Weathersfield, VT*, 2013.

48 Spectrum Analytical Inc., *2013c. Laboratory Report - Project No. 08-220953.00, Weathersfield, VT*, 2013.

49 Spectrum Analytical Inc., *2013d. Laboratory Report - Project No. 08-220953.00*, *Weathersfield, VT*, 2013.

50 M. L. Tabor, D. Newman, A. J. Whelton, Stormwater Chemical Contamination Caused by Cured-in-Place Pipe (CIPP) Infrastructure Rehabilitation Activities, *Environ. Sci. Technol.*, 2014, **48**, 10938−10947.

51 UGA (University of Georgia), Water Testing VOC Analysis for 9/16/2016 and 9/21/2016. College of Agriculture and Environmental Services, Athens, GA, 2016.

52 B. Currier, *Water Quality of Flow Through Cured-In-Place Pipe (CIPP)*, Final Report, Office of Water Programs, California State University Sacramento, Sacramento, CA, 2017.

53 Commonwealth of Pennsylvania Department of Environmental Protection (PA DEP), 2019b Notice of Violation: Sewage- 3A, Carlisle STP, NPDES Permit No. PA0026077, Carlisle, PA, August, 2019.

54 American Society of Testing and Material (ASTM), Standard Practice for Full-Scale Chamber Determination of Volatile Organic Emissions from Indoor Materials/Products, ASTM D6670 − 18, 2007.

55 American Society of Testing and Material (ASTM), Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement, ASTM D792 – 13, 2013.

56 Interplastic Incorporation. *COR72-AA-451 Unsaturated Polyester Resin, Material Safety Data Sheet.* St. Paul, MN. 2001.

57 E. Allouche, S. Alam, J. Simicevic, R. Sterling, W. Condit, J. Matthews, A. Selvakumar, A pilot study for retrospective evaluation of cured-in-place pipe (CIPP) rehabilitation of municipal gravity sewers, *Tunn Undergr Sp Tech*., 2014, **39**, 82–9.

58 S. Alam, J. Matthews, R. Sterling, E. Allouche, A. Selvakumar, W. Condit, E. Kampbell, D. Downey, Evaluation of testing methods for tracking CIPP liners' life-cycle performance, *Cogent Eng.*, 2018, **5**, DOI:10.1080/23311916.2018.1463594.

59 H. Koushyar, S. Alavi-Soltani, B. Minaie, M. Violette, Effects of variation in autoclave pressure, temperature, and vacuum-application time on porosity and mechanical properties of a carbon fiber/epoxy composite, *J. Compos. Mater.*, 2011, **46**, 1985–2004.

60 Occupational Safety and Health Administration (OSHA), *Annotated OSHA Z-2 Table*, https://www.osha.gov/dsg/annotated-pels/tablez-2.html#osha_pel1.

61 National Institute for Occupational Safety and Health (NIOSH), *Styrene, Immediately Dangerous to Life and Health (IDLH) Concentration*, Atlanta, 1994, https://www.cdc.gov/niosh/idlh/100425.html, (accessed July 2017).

62 Interplastic Corporation Thermoset Resins Division, *Cured-in-place pipe (CIPP) resin COR72-AT-470HT,* Saint Paul, Minnesota, 2013, ftp://ftp02.portlandoregon.gov/BES/E10531%20NW%20Northrup%20and%2019th/CONSTRUCTION/Submittals/SUB%20007.00%20Mainline%20CIPP%20Liner/Submittal%20d.pdf.

63. U.S. Environmental Protection Agency, *Integrated Risk Information System. (IRIS). 2020. Styrene.,* Washington, DC., 2020, https://www.epa.gov/iris

64 M. Roghani, Investigation of Volatile Organic Compounds (VOCs) Detected at vapor Intrusion sites, Ph.D. Thesis, University of Kentucky, 2018.

65 National Association of Sewer Service Companies (NASSCO), *Guidelines for the Safe Use and Handling of Styrene Based Resins in Cured-In-Place-Pipe*, Marriottsville, MD, 2017, https://www.nassco.org/sites/default/files/Styrene%20Guideline%2004Jan2018-2018Logo.pdf.

66 U.S. Environmental Protection Agency, *National Emissions Standards for Hazardous Air Pollutants: Reinforced Plastic Composites Production (40 CFR Part 63), Federal Register/Vol.*

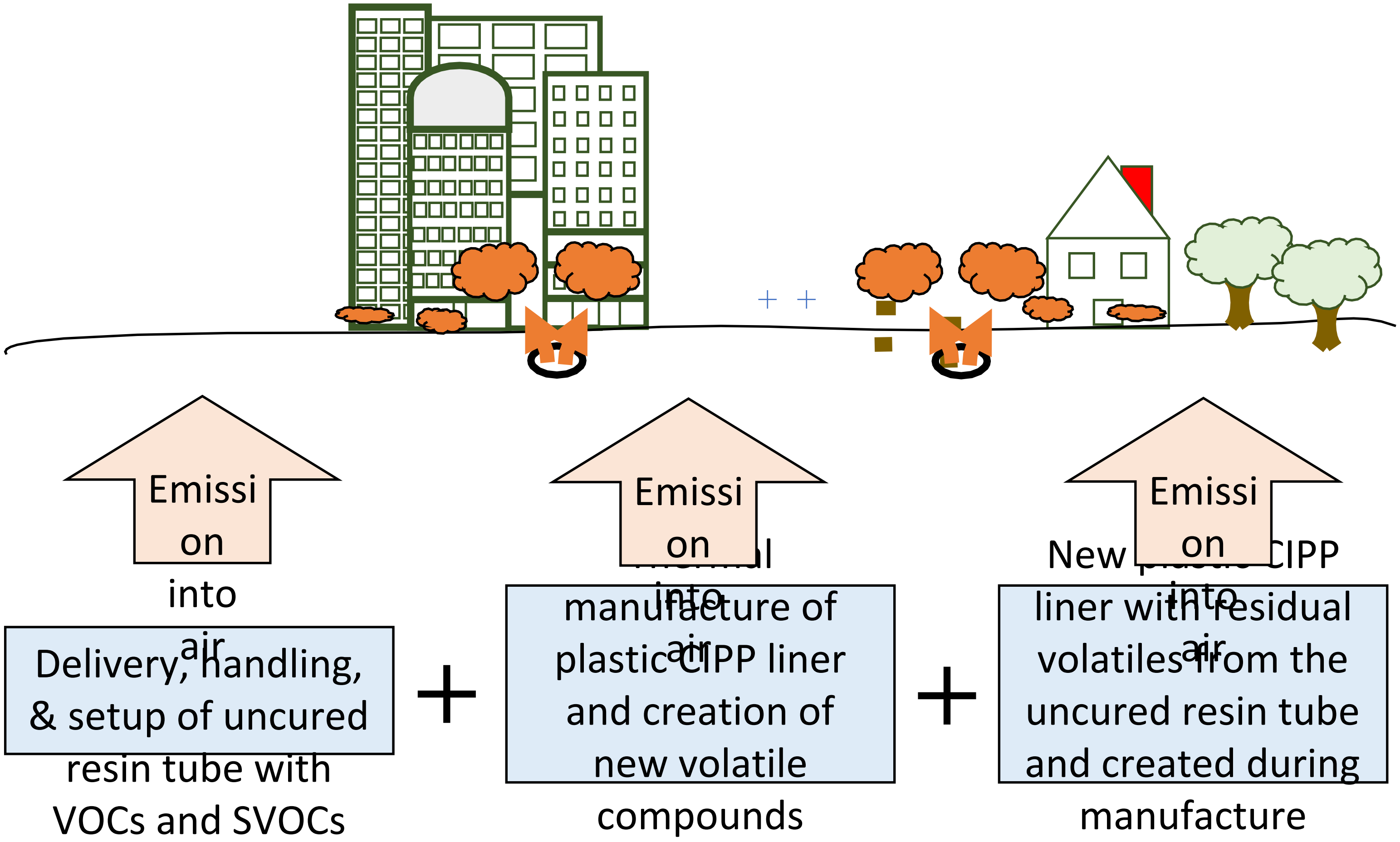
*70, No. 164, OAR–2003–0003; FRL–7957–7, RIN 2060–AM23*, 2005, 50118-50136, https://www.govinfo.gov/content/pkg/FR-2005-08-25/pdf/05-16701.pdf#page=10.

67 J. C. Matthews, A. Selvakumar, R. L. Sterling, W. Condit, Innovative rehabilitation technology demonstration and evaluation program, *Tunn Undergr Sp Tech*., 2014, **39**, 73–81.

68 M. S. Waring, J. R. Wells, Volatile organic compound conversion by ozone, hydroxyl radicals, and nitrate radicals in residential indoor air: Magnitudes and impacts of oxidant sources, *Atmos. Environ*., 2015, **106**, 382-391.

69 L. Kobos, S.M. Teimouri Sendesi, A.J. Whelton, B.E. Boor, J. A. Howarter, J. Shannahan J, In vitro toxicity assessment of emitted materials collected during the manufacture of water pipe plastic linings, *Inhal. toxicol*., 2019, **31**, 131-1.

70 J. Quinn, T. Aburn, R. Mosier, D. Franks, Air Quality Control Advisory Council Agenda, Baltimore, Maryland, March, 2015.



Emission into air

Delivery, handling, & setup of uncured resin tube with VOCs and SVOCs

+

Emission into air

Thermal manufacture of plastic CIPP liner and creation of new volatile compounds

+

Emission into air

New plastic CIPP liner with residual volatiles from the uncured resin tube and created during manufacture