IMPROVING WORKER SAFETY AND ENVIRONMENTAL PROTECTION BY UNDERSTANDING CHEMICAL EMISSIONS FROM PLASTIC COMPOSITES DURING MANUFACTURE AND USE

by

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A Dissertation

Submitted to the Faculty of Purdue University

In Partial Fulfillment of the Requirements for the degree of

Doctor of Philosophy

Lyles School of Civil Engineering

West Lafayette, Indiana

May 2020

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This dissertation is dedicated to my mother, Nadiyeh, whose endless love, support and sacrifice enabled me to pursue my dreams. She was a full time nurse for my sick father for so many years while raising her young children all along; to my late father, Ghavam, who taught me hopefulness and patience despite his lingering pain and, to my lovely husband, Reza, who always had my back in difficult times.

ACKNOWLEDGMENTS

First and foremost I would like to express my deepest appreciation to my advisor Dr. Andrew Whelton for accepting me in his research group and mentoring me along. Joining to his research group opened the doors of opportunities, success and cutting-edge research for me. He always explained complex ideas and concepts in a simplified way so I could follow through. There were moments of failure/disappointment during my Ph.D. and it was his encouragement that enabled me to continue. I am evermore grateful to my committee members Dr. Chad Jafvert, Dr. Jeffery Youngblood and Dr. John Howarter for their recommendations and technical inputs on my work.

I would like to thank my family for all their love and encouragement. Thanks to my husband Reza, for being supportive and giving me valuable insights and perspectives. I am truly grateful to my mom's wisdom and support who raised me with love in science.

I would like to thank the following individuals for their technical assistance during this work.

Purdue University

Administration: Jennifer Ricksy

Lyles School of Civil Engineering: Dr. Nadezhda Zyaykina, Dr. Brandon Boor, Dr Maryam Salehi, Kyungyeon Ra, Yoorae Noh, Emily Conkling, Tolu Odimayomi

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LIST OF ABBREVIATION

ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BCHL	Butylcyclohexanol
BCR	Below Calibration Range
BHT	Butylated Hydroxytoluene
CAR	Carcinogenic Compound
CDOT	Colorado Department of Transportation
CIPP	Cured-in-Place-Pipe
CR	Calibration Range
DBP	Dibutyl Phthalate
DSC	Differential Scanning Calorimetry
EC	Exposure Concentration
EDR	Endocrine Disruptors
EPA	Environmental Protection Agency
EPDM	Ethylene Propylene Diene Monomer
ETC	Environmental Test Chamber
GC/MS	Gas Chromatography/Mass Spectrometry
HAP	Hazardous Air Pollutants
^{1}H NMR	Proton Nuclear Magnetic Resonance
HQ	Hazard Quotient
I.D.	Inner Diameter
IQR	Interquartile
IS	Internal Standard
IARC	International Agency for Research on Cancer
IRIS	Integrated Risk Information System
IUR	Inhalation Unit Risk
IDLH	Immediately Dangerous to Life and Health
LD_{50}	Lethal Dose, 50%
LECR	Lifetime Excess Cancer Risk
LLE	Liquid-Liquid Extraction
MDEQ	Michigan Department of Environmental Quality
MTT	3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromidefor
NIOSH	National Institute for Occupational Safety and Health
NOAEL	No-Observed-Adverse-Effect-Level
NQ	Not Quantified
NRC	National Response Center
O.D.	Outer Diameter
OSHA	Occupational Safety and Health Administration
PA DEP	Pennsylvania Department of Environmental Protection
PET	Polyethylene Terephthalate

PID	Photoionization Detector
PFA	Perfluoroalkoxy
ppm_v	Parts Per Million by Volume
RfC	Reference Concentration
PTFE	Polytetrafluoroethylene
TD	Thermal Desorption
TGA	Thermogravimetric Analysis
TMB	Trimethylbenzene
TPGDA	Tripropylene Glycol Diacrylate
TWA	Time-Weighted Average
UGA	University of Georgia
UV	Ultraviolet
VDOT	Virginia Department of Transportation
VOC	Volatile Organic Compound

ABSTRACT

This dissertation focused on cured-in-place-pipe (CIPP) technology, which is being used to repair sewer pipes across the globe. The CIPP process involves the manufacture of a new fiber-reinforced composite plastic pipe inside an existing damaged pipe. By 2022, the global CIPP market will exceed $2.5 billion and constitute 40% of the U.S. pipe rehabilitation market. In recent years, concerns about the type, magnitude, and toxicity of chemical air emissions associated with CIPP installations have markedly increased. CIPP installations in Asia, Europe, Oceania, and North America have been associated with indoor and ambient air contamination incidents, afflicted schools, daycare centers, homes, and offices and prompted building evacuations. This research program was designed to better understand chemical release into the air during CIPP composite manufacture and the human health risks. Principles and techniques from the environmental engineering, air quality, material science, and risk analysis were applied. This dissertation contains three chapters and each chapter is a stand-alone manuscript, with the first chapter already having been published.

Chapter 1 involved the characterization of chemical emissions for steam-cured CIPP installations in Indiana (IN, sanitary sewer) and California (CA, storm sewer). It was discovered that a complex multiphase mixture of organic vapor, water vapor, and particulate (condensable vapor and partially cured resin) was emitted. Chemicals captured included a variety of hazardous air pollutants, carcinogens, endocrine disrupting compounds, and other chemicals with little toxicity data. The materials captured in California during 4 CIPP installations, when normalized against styrene concentration, exhibited different toxicity towards mouse cells. This toxicity indicated that non-styrene compounds were probably responsible for toxicity. Testing revealed significant and previously unreported worker and public safety chemical risks existed with CIPP installations.

Chapter 2 describes experiments conducted to determine which CIPP manufacturing conditions (i.e. curing pressure, temperature, time and ventilation) influenced chemical air emissions during and after composite manufacture. During thermal manufacture, approximately 8.87 wt% volatile organic compounds (VOC) was released into the air at standard pressure. For the CIPP styrene-based resin examined, chemical volatilization during manufacture was influenced by pressure, but temperature and heating time did not influence the composition of

chemical residual inside the new composite. All cured composites, regardless of temperature or heating time, contained approximately 3 wt% VOC. No statistical difference was found for either: (1) VOC loading across cured composites or (2) styrene emission into the air across cured composites despite different curing temperature and heating times. Styrene was the most abundant compound detected in the composite and in air. 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) of the new composite 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.

Chapter 3 includes inhalation health risk assessment due to chemical emission from CIPPs during manufacture and use. Publicly available worksite data for ultraviolet (UV)-light and steam-CIPP installations were utilized and Monte Carlo simulation was applied. Data-gaps were also identified. Health risks associated with newly manufactured (post-cured) chemical emission from lab scale CIPPs were also evaluated. For CIPP resins and post-cured CIPPs 31 chemicals have been quantified among which many are unique volatile organic chemicals VOCs, but only 8 air testing studies were found. At a steam-CIPP worksite, VOCs were found in a condensed multiphase mixture discharged into air, 4 VOCs were detected in the vapor phase, while only styrene vapor phase results could be used for risk assessment. Worksite styrene levels (1,825 ppm_v, 1,070 ppm_v, 220-270 ppm_v, 140 ppm_v) have been reported indicating a health risk can exist. Monte Carlo simulation using literature data revealed that for the single UV-CIPP and single steam-CIPP study negligible styrene HQs were found, while unacceptable styrene LECRs% > 10^{-4} (i.e. 37-38%) were obtained. Monte Carlo simulation on laboratory data showed that post-cured emissions from the composite cured longer increased the unacceptable styrene LECR (from 17.86% to 21.12%) and HQ (0.95% to 8.04%). Whereas curing the composite at greater temperature reduced the styrene LECR and HQ to 0.89%. and 0, respectively. Ventilation also diminished the acceptable LECR% in all composites but did not reduce the carcinogenic health risk to an acceptable level. Health risk can exist as evidenced by limited air testing data. More studies are needed to examine inhalation health risks associated with the CIPP manufacturing process and newly manufactured plastics.

1. WORKSITE CHEMICAL AIR EMISSIONS AND WORKER EXPOSURE DURING SANITARY SEWER AND STORMWATER PIPE REHABILITATION USING CURED-IN-PLACE-PIPE (CIPP)

1.1 Abstract

Chemical emissions were characterized for steam-cured cured-in-place-pipe (CIPP) installations in Indiana (sanitary sewer) and California (storm water). One pipe in California involved a low-volatile organic compound (VOC) non-styrene resin, while all other CIPP sites used styrene resins. In Indiana, the uncured resin contained styrene, benzaldehyde, butylated hydroxytoluene (BHT), and unidentified compounds. Materials emitted from the CIPP worksites were condensed and characterized. An emitted chemical plume in Indiana was a complex multiphase mixture of organic vapor, water vapor, particulate (condensable vapor and partially cured resin), and liquid droplets (water and organics). The condensed material contained styrene, acetone, and unidentified compounds. In California, both styrene and low-VOC resin condensates contained styrene, benzaldehyde, benzoic acid, BHT, dibutyl phthalate, and 1-tetradecanol. Phenol was detected only in the styrene resin condensate. Acetophenone, 4-*tert*-butylcyclohexanol, 4-*tert*-butylcyclohexanone, and tripropylene glycol diacrylate were detected only in the low-VOC condensate. Styrene in the low-VOC condensate was likely due to contamination of contractor equipment. Some, but not all, condensate compounds were detected in uncured resins. Two of four California styrene resin condensates were cytotoxic to mouse alveolar type II epithelial cells and macrophages. Real-time photoionization detector monitoring showed emissions varied significantly and were a function of location, wind direction, and worksite activity.

1.2 Introduction

Cured-in-place-pipe (CIPP) is a popular sanitary sewer, storm water, and drinking water pipe repair technology and was invented in the 1970s [1, 2]. A resin impregnated felt tube is inserted into a damaged pipe and is cured in place with hot water, steam, and/or ultraviolet light [3-9]. In the U.S., styrene based polyester and vinyl ester resin systems are popular because they are less expensive than their alternatives [10]. Non-styrene resin systems such as epoxy are also used [10]. For non-styrene unsaturated polyester or vinyl ester resins, fatty acid-based reactive

monomers are available [11, 12]. Because concentrated chemicals are used and CIPP is manufactured in the field, forced air, pressurized steam, and other activities can release chemicals into the worksite, nearby pipes, and environment during site setup, installation, and cleanup (**Figure 1-1**) [13-25].

CIPP installation activities have caused ambient and indoor air contamination incidents, but the types and magnitude of materials emitted have received little scrutiny. Air contamination has been documented inside (49) and outside (10) the U.S. (see **Table A.1** for details). Persons near CIPP installation sites have reported odors and illness symptoms (i.e., nausea, headache, vomiting, difficulty breathing, eye and nasal irritation, and others). Sometimes buildings were evacuated and emergency services responded. During the past 16 years, only four CIPP chemical air emission studies have been conducted. A 2015 Los Angeles, California study revealed styrene exited three sewer pipe manholes during steam curing (250 to 1,070 ppm_v) and during cool down (3.6 to 76.7 ppm_v) [26]. The styrene 700 ppm_v immediately dangerous to life and health worker exposure limit was exceeded [27] and styrene is expected to be carcinogenic [28]. In 2005, the U.S. Agency for Toxic Substances and Disease Registry (ATSDR) [29] concluded that a CIPP installation caused a public health hazard and contaminated an office building's indoor air. Styrene (0.320 ppm_v) exceeded its minimum acceptable chronic exposure level (0.060 ppm_v). A 2004 CIPP study found chemicals exited two sewer pipe manholes and a photoionization detector (PID) reading indicated a maximum of 110 ppm_v [23]. Steam curing lasted 24 hr. Investigators speculated that styrene caused the PID response. A maximum 3.2 ppm_v styrene level (2.4 hr adsorption onto charcoal sorbent) was found by others [30] in 2001, and buildings with dry plumbing traps were hypothesized to have greater styrene levels compared to buildings with wet traps.

The goal of this study was to better understand the materials emitted into air during CIPP installations. Field work was conducted in Indiana at sanitary sewer sites and California at stormwater sites. Specific study objectives were to: (1) Conduct real-time emission monitoring using PIDs and videotaping, (2) Chemically characterize the uncured resin impregnated tube, and (3) Examine the chemical characteristics and toxicological significance of emitted materials.

1.3 Materials and methods

Seven steam cured CIPP installations were monitored in Indiana and California. Air sampling manifolds were installed to capture materials emitted into the air. PIDs were used for

real-time emission monitoring. Condensate cytotoxicity was evaluated for styrene based CIPP installations in California. The **APPENDIX A** contains a detailed description of the field and laboratory methods: PID devices and calibration, analytical standards, procedures for sample preparation, methylene chloride and hexane solvent extraction for the uncured resin tubes and condensate, gas chromatography/mass spectrometry (GC/MS) methods for uncured resin tube and condensate extracts. Condensate thermal and chemical properties were determined using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. Cell cytotoxicity methods are also described.

1.3.1 Indiana

In July 2016, air sampling was conducted during CIPP installation for two 45.7 cm I.D. vitrified clay sanitary sewer pipes. Manufacturer reported resin information can be found in **A.2**. Chemicals in the uncured resin tube were extracted into methylene chloride and hexane to obtain resin tube extracts that were analyzed by GC/MS.

For site 1, a PID was used to monitor chemical emissions at the refrigerated truck that transported the uncured resin tube, and near the upstream and downstream manholes. For site 2, the PID was used to measure chemical emissions immediately above a section of uncured resin tube cut from the main pipe segment before curing. The PID had a 1 min sampling frequency. An apparatus with a GAST vacuum pump (diaphragm type, ISSACS) was setup and drew exhaust emissions into a polytetrafluoroethylene (PTFE) (64 cm I.D., 0.79 cm O.D.) and perfluoroalkoxy (PFA) (0.32 cm I.D., 0.64 cm O.D.) tubing manifold under vacuum. Emissions flowed through a sealed glass filter flask immersed in an ice bath (condenser) and a vacuum flask. One Tedlar bag sample was collected at a location following the condenser. Condensate captured using the manifold was characterized by TGA, DSC, mixed with chloroform-d and analyzed using ^{1}H NMR.

Air was sampled into Tedlar bags (up to 75% of the total bag volume) using a bag sampler (Model 1060, Xitech Instrument). The bag sample was analyzed within 24 hr after collection. A CIA Advantage-Thermal Desorption Unity Series2 was used with Maverick Bonanza software (version 6.1.0. A, Markes International, Inc.). The cold trap temperature was 10°C. A GC/MS was used to analyze the field and control samples. The GC was equipped with HP-5MS capillary column (length 30 m, diameter 0.25 mm, film 0.25 μm) (Agilent Technologies, Inc.). The oven temperature program was as follow: Oven temperature of 40°C (hold for 2 min), then ramped to

320°C at 15°C/min and hold for 4 min using He carrier gas (5 mL/min) with direct injector mode (hold at 100°C). Purge flow was for 5.0 mL/min and column flow was for 1.5 mL/min.

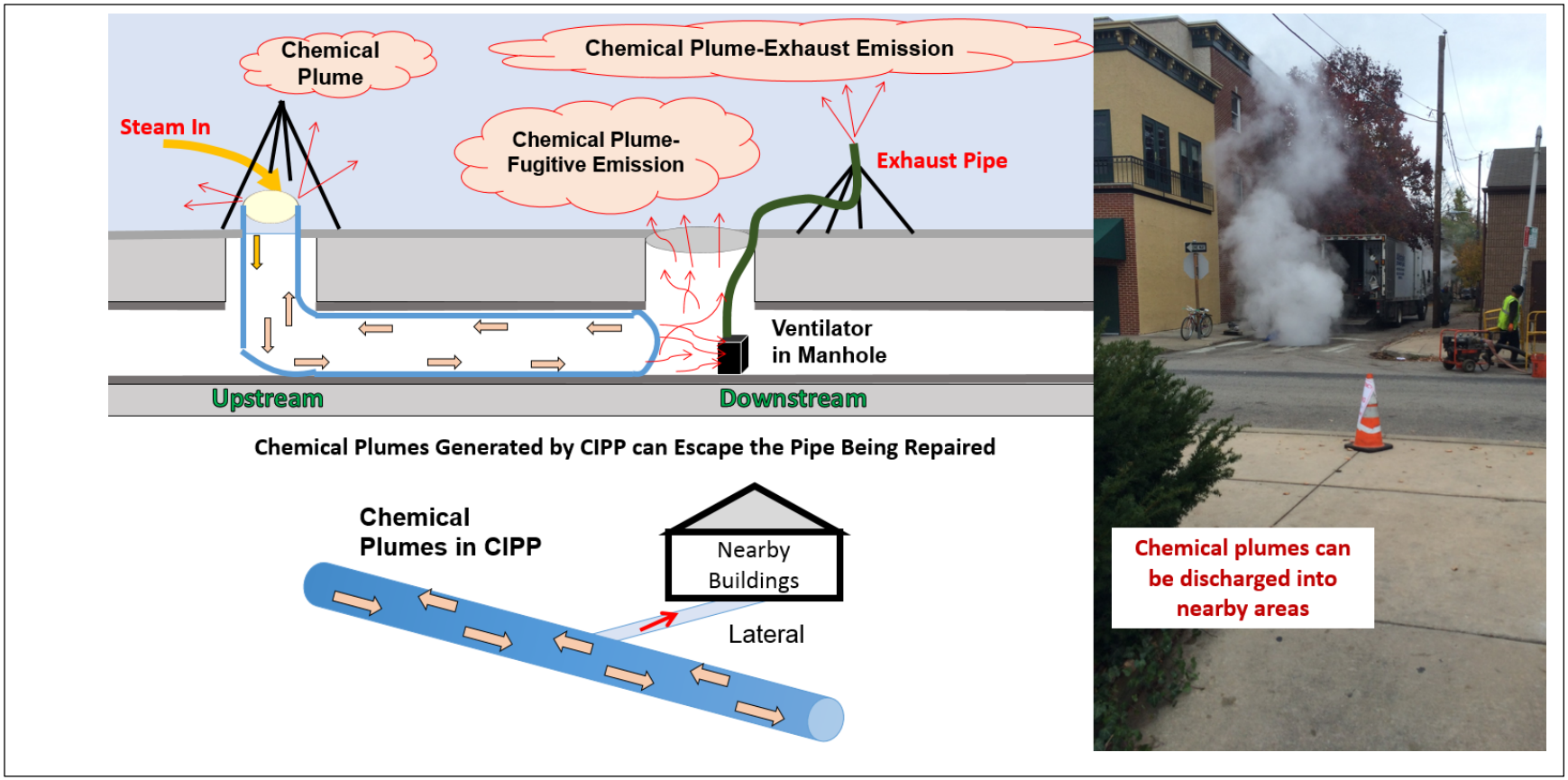


Figure 1-1. Diagram of emissions typical of a sewer CIPP installation. (Left) Steam or hot water is injected in the upstream portion of the uncured resin tube. Chemicals are emitted from the uncured resin tube into the host pipe and annular space between the resin tube and host pipe. Some chemicals can exit buried infrastructure through nearby manholes and pipes. Sometimes contactors add excess resin and it can be squeezed into other nearby pipes, spaces, and cracks during initial tube setup, and does not remain in the resin tube. The process for installing sanitary sewer pipe CIPP is like that required for stormwater pipe CIPP including chemical emission points. (Right) Chemical plume is emitted from a downstream manhole in a residential area in Philadelphia, Pennsylvania.

1.3.2 California

In August 2016, CIPPs were installed in one concrete and four corrugated metal pipes at an outdoor research site. California State University at Sacramento [12] predetermined CIPP design (**Table A.2**) and installation conditions (**Table A.3**). One CIPP was manufactured with a low VOC non-styrene resin and four were manufactured with a styrene-based resin. Manufacturer reported resin information can be found in **A.2**.

At each site, air manifolds were setup at an exhaust and fugitive emission point (**Figures 1-2, A.1-A.3**). These stainless steel manifolds captured and condensed materials from the air. For the exhaust emission point, materials were removed from the air stream by ambient cooling, passage of the air stream through ice chest condensers, and were collected in Pyrex® bottles. Because of equipment damage concerns at the exhaust emission point, the PID was positioned adjacent to the exhaust pipe outlet (**Figure A.2b**). At the fugitive emission point, materials removed from the air by a condenser were collected in Pyrex® bottles. Remaining emissions that continued though the manifold were monitored using a PID. A GAST vacuum pump (0.5 L/min) withdrew air into the manifold. PIDs sampled the air every 2 s at each location. PFA tubing was used to reduce the potential of cross-contamination. Arcodisc filters (0.45 μm PTFE) (Pall Life Sciences) served as humidity filters for each PID and were replaced after each installation.

Captured materials underwent liquid-liquid extraction and chemical sampling flux was reported for condensate samples (mass of compound captured/surface area of stainless steel tube-sample collection time). In preparation for chemical analysis, condensate samples were homogenized by vigorously shaking. Sample (15 g) was added to the separation funnel followed by 20 mL of solvent (hexane or methylene chloride). The mixture was shaken slowly, left for 10 min, and extractant was then collected. The solvent addition and mixing was carried out three times. Next, a rotary evaporator was used to reduce the volume of 60 mL of extractant to 3.7 mL. Finally, 1.5 mL of the sample containing 1 ppm of the internal standard (1,4-dichlorobenzene-d4) was analyzed by GC/MS. The LLE percent recovery of toluene (40 ± 5.0%), naphthalene (76.4 ± 5.8%) and phenanthrene (95.9 ± 3.6%) for methylene chloride and of toluene (20.1 ± 2.4%), naphthalene (70.1 ± 5.1%) and phenanthrene (85.5 ± 3.2%) for hexane were achieved.

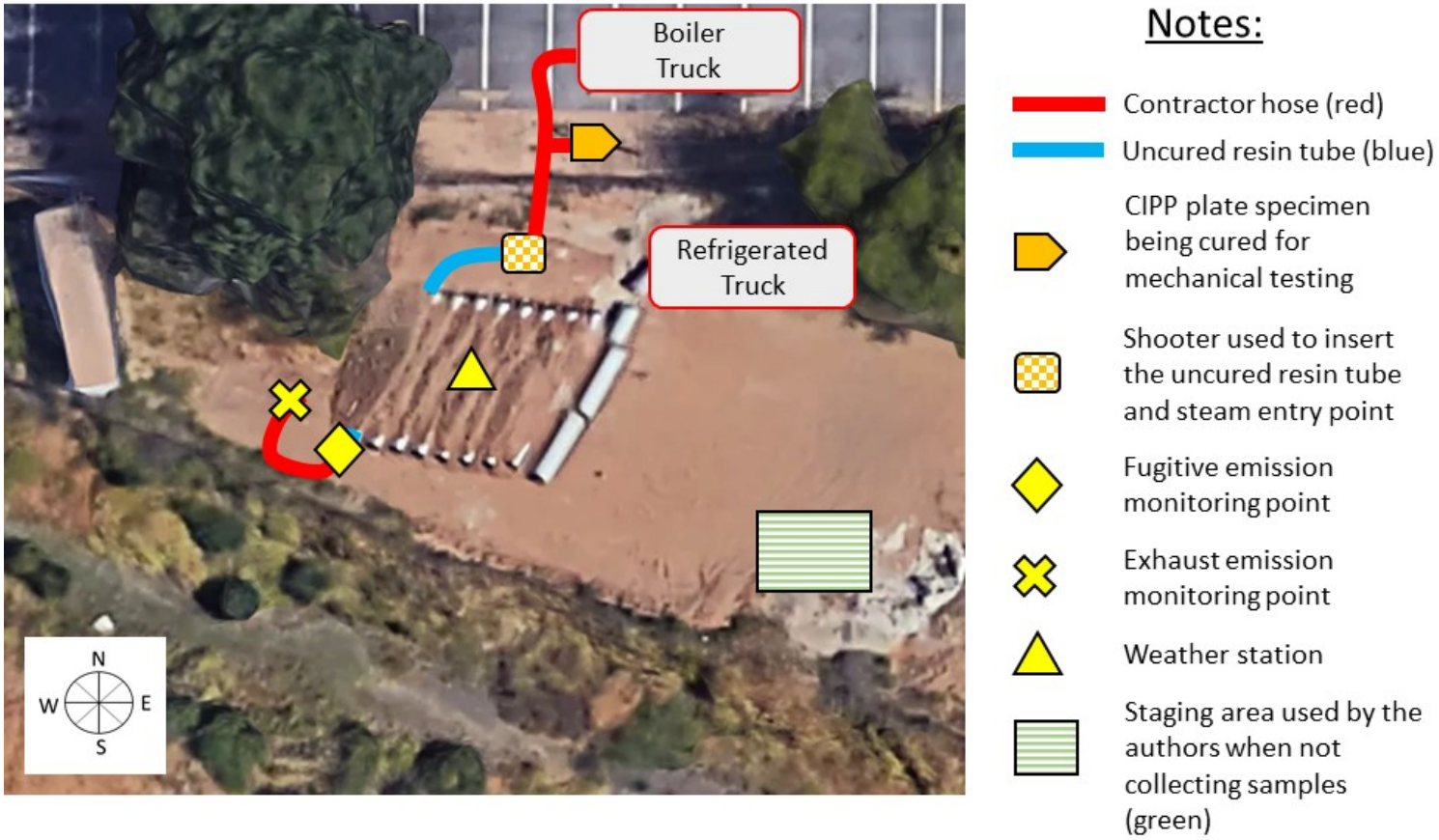


Figure 1-2. Plan view of the California site for a CIPP installation. After an uncured resin tube (blue) was inserted into a target pipe using the shooter, an ethylene propylene diene monomer (EPDM) contractor hose (red) was connected to the boiler truck. An EPDM contractor hose was also connected to the end of the uncured resin tube and extended to the exhaust emission pipe. The boiler truck delivered steam to the "shooter" which then entered the uncured resin tube. Each pipe was approximately 20 ft in length. A weather station was located on the top of the pipes being rehabilitated (**Table A.6**). For each installation, contractors redirected some steam away from the first contractor hose to use for curing a separate uncured resin tube they had removed from the initial uncured resin tube. This small sample was sandwiched between two metal plates, exposed to steam, and was then sent to the laboratory for mechanical testing.

1.4 Results and Discussion

1.4.1 Indiana Investigation of Sanitary Sewer Pipes

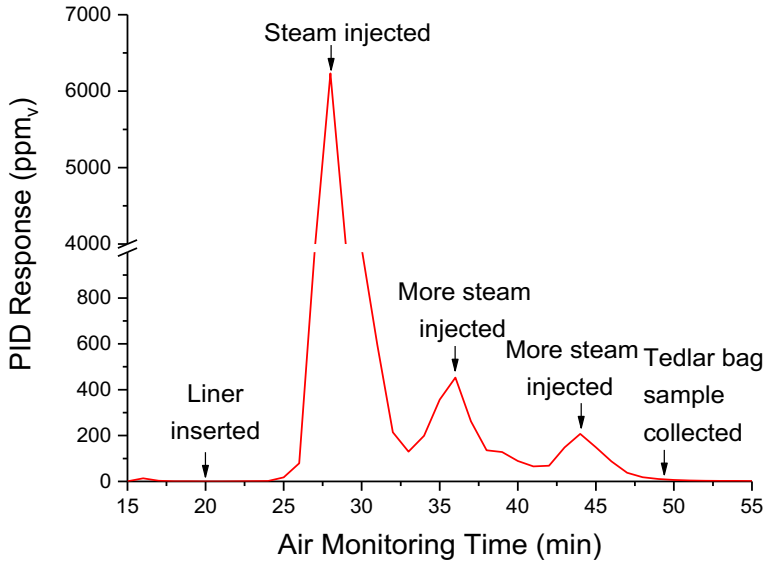
Uncured resin tube samples were extracted using hexane and methylene chloride from site 2. Hexane extractions showed 67.4 ± 19.7 mg styrene per gram of tube. Methylene chloride extractions revealed styrene (40.3 ± 8.6 mg/g), butylated hydroxytoluene (BHT) (22.8 ± 14.0 mg/g), and benzaldehyde (2.2 ± 0.7 mg/g). 1-Dodecanol was also detected, but not quantified.

During CIPP installation, the authors did not see workers using PPE such as respirators and earplugs. One worker sat in a chair inside the white chemical plume emitted from the downstream manhole. This worker monitored a pressure gage to determine when the worker at the boiler needed to inject more steam.

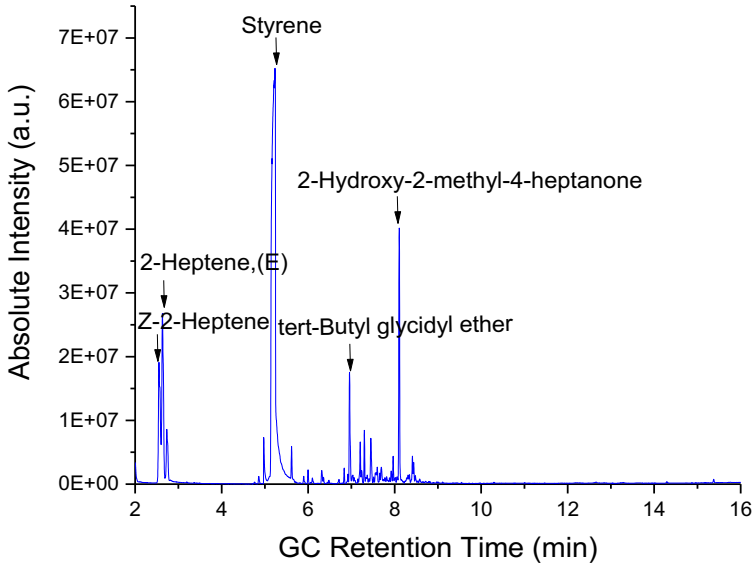
For the two sites, PID measurements ranged from 0 to 6,231 ppm_v and were a function of location, type of CIPP activity taking place (tube insertion, steam injection, curing, venting), wind condition, and vehicle traffic (**Video A.1**, **A.3.1**). Site 1 spot PID measurements ranged from 0 to 514 ppm_v. At site 2, when the PID was located a few centimeters above the uncured tube, a spot reading of 1,361 ppm_v was recorded and white material was emitted into the air (**Video A.2**). Materials were emitted into the air while the uncured resin tube was guided into the sewer manhole (**Video A.3**). Once the tube was inserted into the sewer pipe, the PID was fixed at the exhaust emission point. A PID response of 6,231 ppm_v was detected during the curing process (**Figure 1-3**). The PID signal increase corresponded to forced air introduction into the resin tube, before steam was introduced. A Tedlar bag air sample collected near the end of the curing period confirmed styrene and unidentified compounds were present (**Table A.4**).

The material captured by the condenser was a complex multi-phase mixture. This included organic vapor, water vapor, particulate (condensable vapor and partially cured resin), and liquid droplets (water and organics). At room temperature, the materials partially phase separated into a colorless phase (top) and dense cloudy phase (bottom). The dense cloudy phase was centrifuged (3,500 RPM, 15 min) and separated into a colorless liquid phase and a white waxy phase (the top layer). TGA demonstrated that the waxy phase evaporated fully at 90°C with volatilization occurring immediately at the onset of heating at 30°C. DSC curves showed three characteristic endothermic peaks at 2°C (melting), 42°C (evaporation), and 77°C (evaporation). The waxy phase was likely a mixture of low molecular weight volatile organic material with minimal presence of

water or inorganic materials. ^{1}H NMR revealed styrene monomer, acetone, and multiple unidentified compounds were present in the waxy phase (**Figure 1-4**).



(a)



(b)

Figure 1-3. Exhaust emission point (a) PID air monitoring results for Indiana Site 2, (b) GC chromatogram for the Tedlar bag air sample collected at 49 min. "Liner inserted" refers to the uncured resin tube. The names of compounds with a peak area greater than 24,000,000 are shown. Styrene was confirmed with an analytical standard.

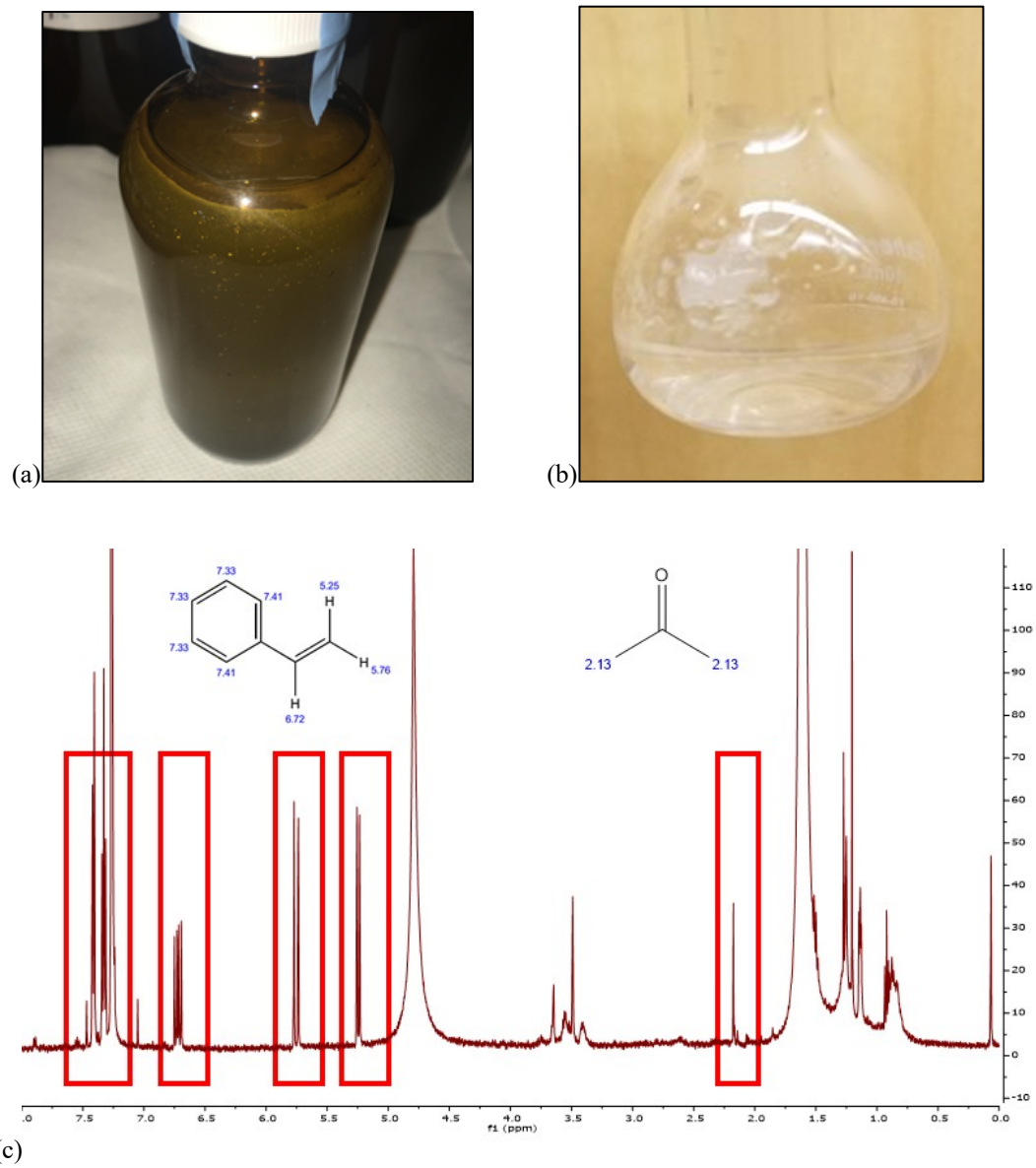


Figure 1-4. (a) Image of the multiphase condensate collected, (b) Image of the white waxy phase material that was separated by centrifugation from the condensate, and (c) NMR spectra of particulate collected from emissions that exited the CIPP exhaust emission point at the Indiana site.

1.4.2 California Investigation of Stormwater Pipes.

Condensate composition. The greatest volume and mass of condensate and number of compounds detected were found at the exhaust emission point (**Video A.4**). Styrene was found in greatest abundance compared to other compounds identified (**Table 1-1**). Some condensate compounds were detected in the uncured resin tubes (**Table A.5**). Non-styrene compounds were likely created during curing and were unreported ingredients in the uncured resin, plastic preliner, plastic coating on interior of resin tube, or the polyethylene terephthalate felt.

Low VOC condensate (site 2) contained a quantifiable amount of styrene. Because the uncured low VOC resin did not contain styrene (**Table A.5**), and Currier [12] found styrene leaching into simulated stormwater from this same CIPP, unintentional contamination by the contractors is suspected. The low VOC non-styrene and styrene based resin tubes were delivered on a refrigerated truck and inserted into the pipes by the same contractor with the same equipment.

Acetophenone, 4-*tert*-butylcyclohexanol, and 4-*tert*-butylcyclohexanone were exclusively found in the low VOC resin condensate. Tripropylene glycol diacrylate (TPGDA) was detected in site 2 and 3 condensates. TPGDA flux was greatest for the low VOC resin site 2 condensate (8.20, 8.99 mg/m^2-s) compared to the styrene-based resin site 3 condensate (1.55, 1.59 mg/m^2-s). 4-*tert*-Butylcyclohexanone and TPGDA were only detected in hexane extracts. Other unidentified compounds were detected in extracts but were not quantified.

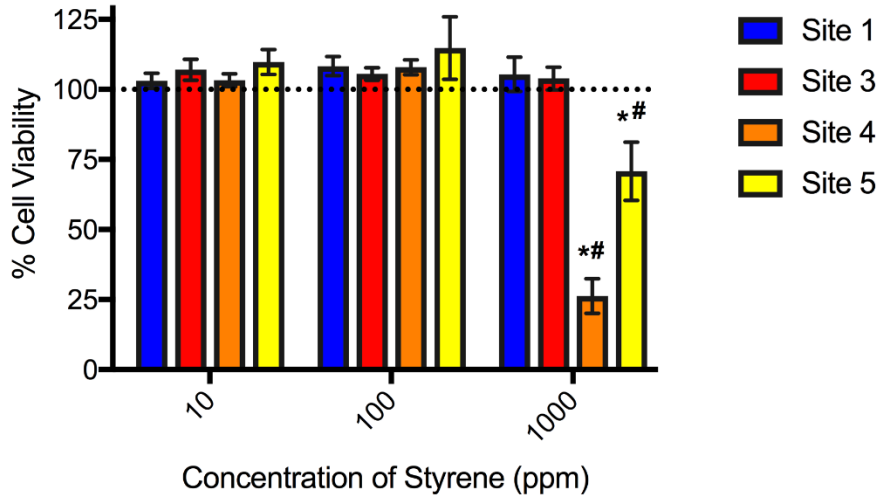
Condensate cytotoxicity. For the styrene-based resin condensates, no cell viability changes were found for mouse alveolar type II epithelial cells or alveolar macrophages exposed to diluted condensate with 10 and 100 ppm styrene, but changes were observed for the 1,000 ppm styrene condensate (**Figure 1-5**). Differential toxicity between sites indicated toxicity due to non-styrene compounds. Site 4 demonstrated enhanced cytotoxicity compared to site 5. These findings support a prior observation that even dilute condensate (styrene below its *D. magna* 48 hr LD_{50}) can be acutely toxic [13].

Evaluation of concentration magnitude and variation. PID readings fluctuated during each CIPP installation (**Figure 1-6**). The lowest maximum PID response was found for the low VOC CIPP installation (9.6 ppm_v), whereas the styrene-based resin CIPP's maximum PID responses ranged from 394 to 757 ppm_v (**Table 1-2**).

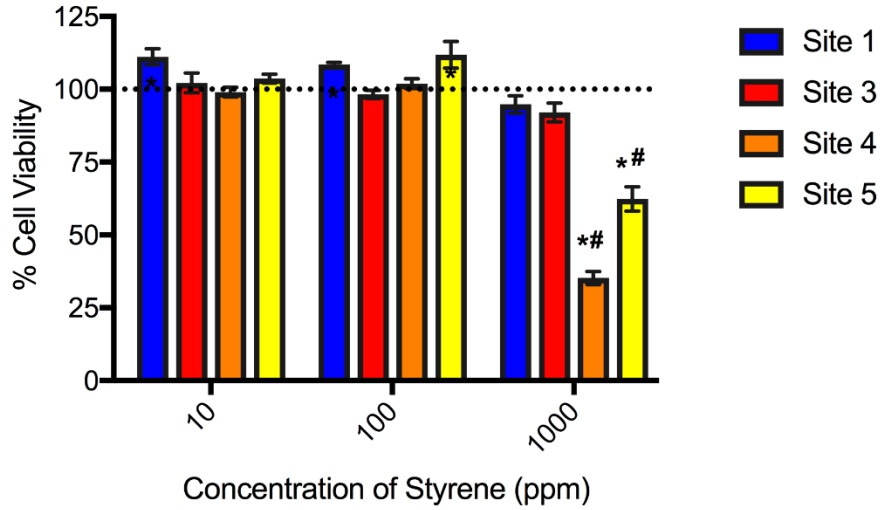
Table 1-1. Maximum exhaust chemical sampling flux for methylene chloride extracted condensates when two different resins were used

Compound	Installation Site (Resin Type) and Chemical Sampling Flux, mg/m^2-s				
	1 (L713)	2 (EcoTek)	3 (L713)	4 (L713)	5 (L713)
Material Captured before the Condensers, Ambient Cooled					
Acetophenone^{HAP}	-	1.65, 1.74$^{\Delta\Delta\Delta}$	-	-	-
Benzaldehyde*‡	0.03, 0.04$^{\Delta}$	0.07$^{\Delta\Delta\Delta}$	0.25, 0.25$^{\Delta}$	-	-
Benzoic acid†	1.12, 1.19$^{\Delta}$	1.84, 1.99$^{\Delta\Delta\Delta}$	1.59, 2.38$^{\Delta}$	0.68$^{\Delta}$	-
BHT*	-	0.08$^{\Delta\Delta\Delta}$	-	-	-
4-*tert*-BCHl	-	1.73, 2.06$^{\Delta\Delta\Delta}$	-	-	-
DBP†‡^{HAP}	0.02, 0.02$^{\Delta}$	0.13$^{\Delta\Delta\Delta}$	-	-	-
Phenol‡^{HAP}	0.06, 0.09$^{\Delta}$	-	0.23, 0.23$^{\Delta}$	-	-
Styrene*^{HAP}	6.17, 7.29$^{\Delta}$	0.63, 0.81 $^{\Delta\Delta\Delta}$	<MRL$^{\Delta}$	13.63, 17.4$^{\Delta}$	<MRL$^{\Delta}$
1-Tetradecanol	-	0.37, 0.37$^{\Delta\Delta}$	-	-	-
Material Captured After Two Cold Condensers					
Acetophenone^{HAP}	-	-	-	-	-
Benzaldehyde*‡	0.26, 0.26	0.04, 0.05	1.16, 1.24	3.76, 4.33	0.56, 0.59
Benzoic acid†	-	-	-	1.88, 2.59	-
BHT*	0.16, 0.18	0.07, 0.12	0.16, 0.17	-	-
4-*tert*-BCHl	-	1.96, 1.99	-	-	-
DBP†‡^{HAP}	0.03, 0.03	0.13	-	-	-
Phenol‡^{HAP}	0.69, 0.76	-	0.89, 1.03	1.34, 1.7	0.63, 0.69
Styrene*^{HAP}	501.4, 853.37	2.62, 2.93	497.68, 683.75	481.23, 715.73	516.75, 530.21
1-Tetradecanol	0.57, 0.68	-	0.47, 0.58	0.92, 1.48	0.13

Two resins were used for CIPP installations: L713-LTA (styrene based resin) and EcoTek (non-styrene based resin); Results shown represent two extractions per single condensate sample collected per condensate collection period. Dash (-) indicates no instrument response for the compound, while MRL indicates the compound was detected, but was present at a concentration less than the minimum calibration curve standard; Triangle ($^{\Delta}$) indicates how many total condensate samples were collected during the entire CIPP curing period at the sampling location before the cold condensers. Samples collected following the cold condensers were collected every 20 min. Condensate samples after the cold condensers reported for sites 1, 3, 4, and 5 represent the first 20 min period of CIPP curing. The condensate sample for site 2 represents the second 20 min period of CIPP curing because styrene was greatest during that period for all the site 2 condensates collected. 4-tert-butylcyclohexanone and TPGDA were detected only in hexane extracts. Site 2 4-tert-butylcyclohexanone was present at a concentration less than the minimum reporting level. Site 2 TPGDA flux was 8.20 and 8.99 mg/m^2-s, site 3 flux was 1.55 and 1.59 mg/m^2-s, and TPGDA was not detected in site 1, 4, or 5 condensates. Acronyms are: BHT: Butylated hydroxytoluene; 4-tert-BCHl: 4-tert-Butylcyclohexanol; DBP: Dibutyl phthalate. Asterix (*) Compound detected in the uncured resin tube; †CDOT (2011) and ‡Tabor et al. (2014) detected compound in their CIPP water impact study; ^{HAP} = Hazardous air pollutant.

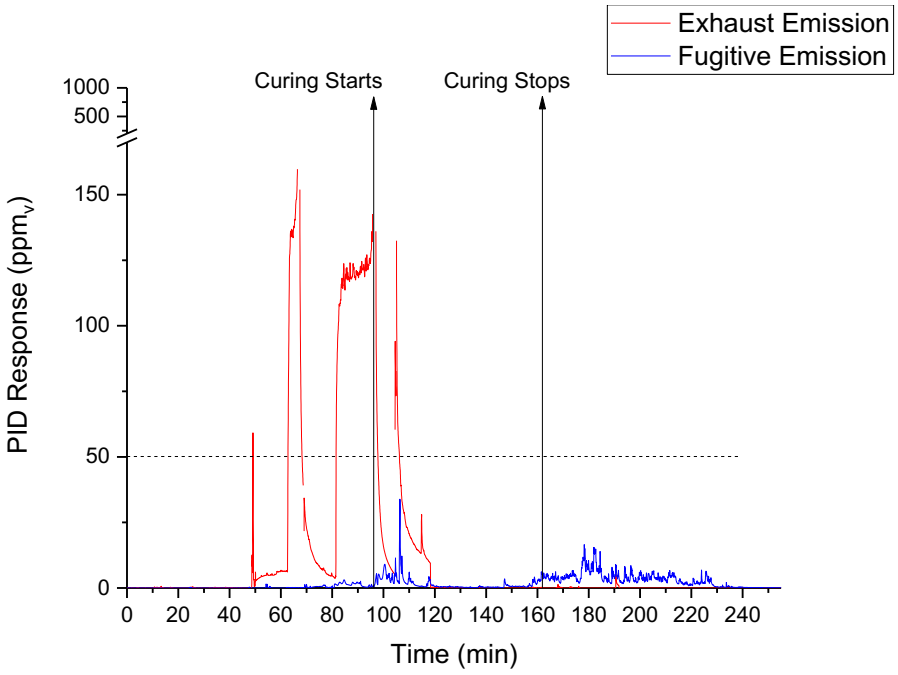


(a)

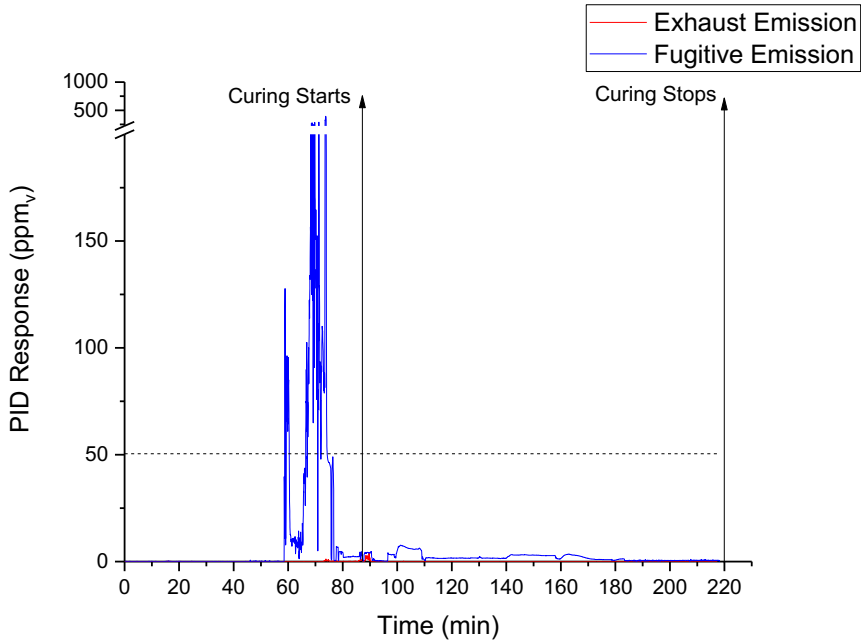


(b)

Figure 1-5. Mouse alveolar type II epithelial cells (a) and macrophages (b) were exposed to styrene based CIPP condensates in serum-free media for 24 hr at styrene concentrations of 10, 100, or 1,000 ppm. Changes in viability were determined via the MTT assay comparing CIPP condensate exposed cells to control (untreated) cells. Dotted line represents control (untreated) cells. Data are presented as mean $\pm$ standard error of the mean (n = 4/group), * denotes statistical significance compared to control cells, # denotes statistical significance compared to all other CIPP condensate exposures at the same concentration ($p \leq 0.05$).



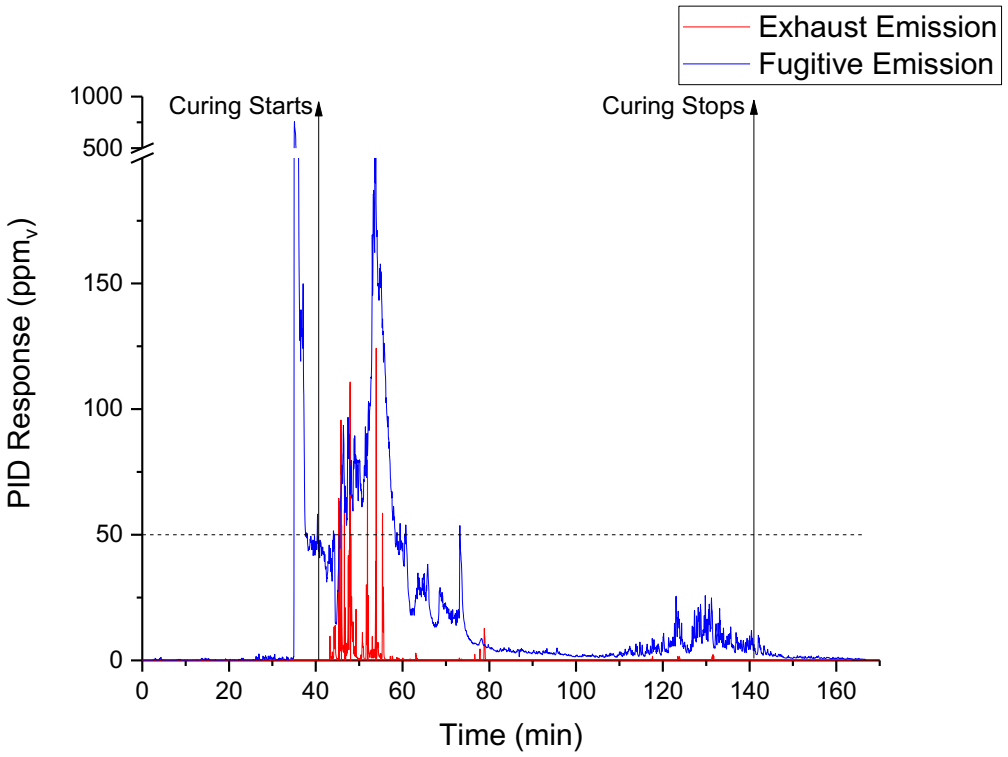
(a)



(b)

Figure 1-6. PID monitoring results for five CIPP installations in California where fixed PID units were located at the fugitive emission point and exhaust emission point for: (a) Site 1, (b) Site 2 [Low VOC], (c) Site 3, (d) Site 4, and (e) Site 5. The horizontal dotted line represents 50 ppm_v. Several "out of range" events were detected when the signal exceeded 9,999 ppm_v and out of range events are not shown in these graphs. Table 2 describes out of range events for each site. The PID at the exhaust emission point was located adjacent to and below the exhaust pipe outlet.

Figure 1-6 continued



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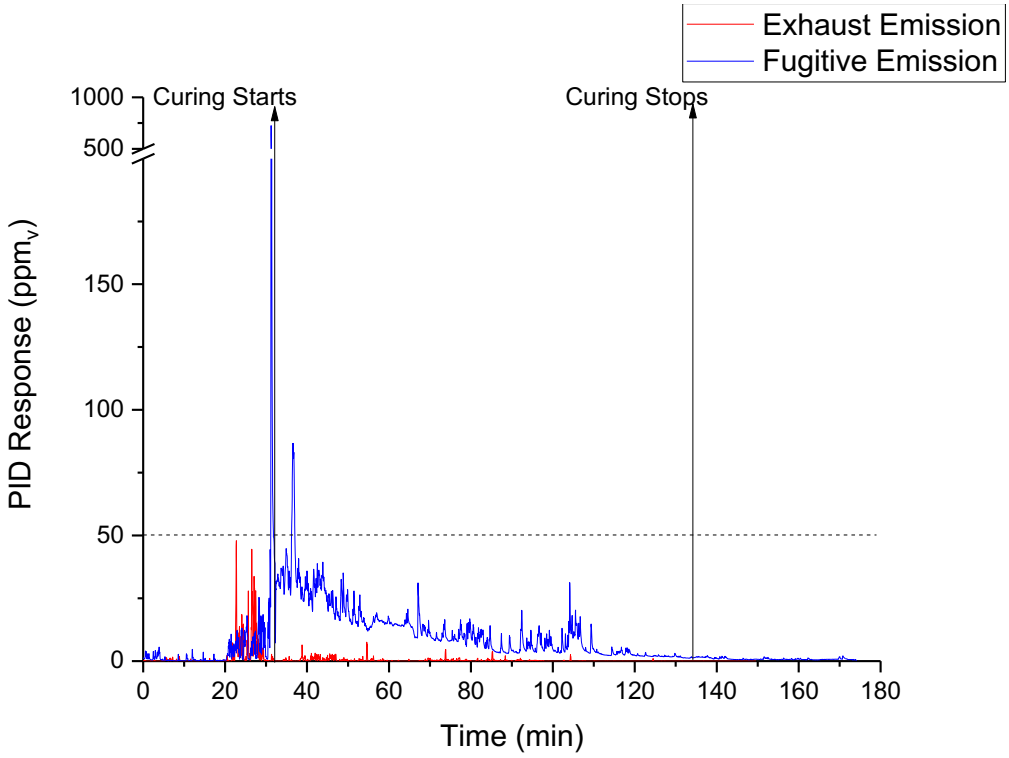
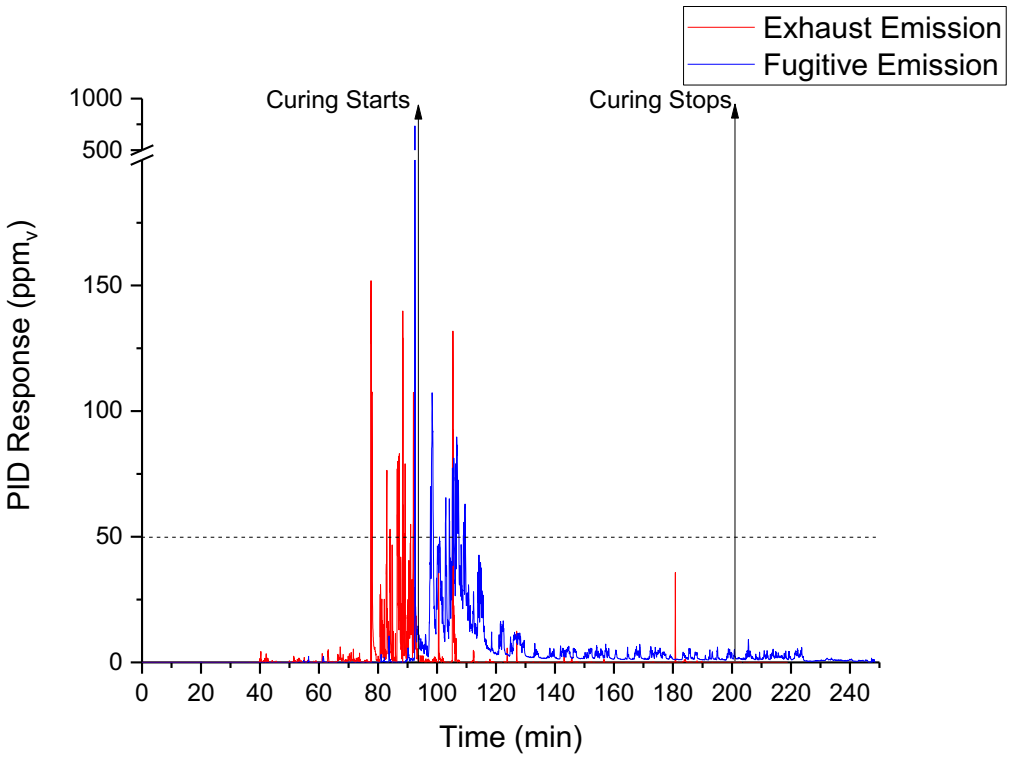


(d)

Figure 1-6 continued



(e)

For the styrene based CIPP's, lower PID levels were likely found at the exhaust emission point compared to the fugitive emission point because the exhaust emission point PID was not located directly in the air stream and greater mixing and dilution with ambient air took place (**Video S3**). PID readings may have been affected by the PTFE filters due to the tendency of filters to adsorb chemicals. Because materials were removed from the manifold prior to PID sampling, observed PID signals may underestimate chemical emissions.

Table 1-2. Maximum PID response at each California CIPP installation, ppm_v

Installation Number (Resin Type)	Fixed PIDs		Out of Range Events	
	Fugitive Emission (ppm_v)	Exhaust Emission (ppm_v)	Total #	Total min.
1 (L713)	394	159	135	4.17
2 (EcoTek)	7.7	9.6	2	0.03
3 (L713)	757	124	15	0.30
4 (L713)	724	47	0	0
5 (L713)	734	151	7	0.17

Two resins were used for CIPP installations: L713-LTA (styrene based resin) and EcoTek (non-styrene based resin); PIDs sometimes recorded "out of range" events and this occurred when the signal exceeded 9,999 ppm_v. The PID at the exhaust emission point was located adjacent to and below the exhaust pipe outlet.

1.5 Implications

The study goal was to better understand the materials emitted into air by steam cured CIPP installation activities. The chemical plume was determined to be a multi-phase chemical mixture including organic vapor, water vapor, particulate (condensable vapor and partially cured resin), and liquid droplets (water and organics). The nature of the partially cured resin captured in the air remains unclear because the extent of polymerization, side reactions, and role of environmental conditions on its formation have not been studied. Compounds that were confirmed in condensates included hazardous air pollutants, a suspected carcinogen, endocrine disruptor compound, along with others that had limited toxicological data. Compounds quantified in condensates included: acetone, acetophenone, benzaldehyde, benzoic acid, BHT, 4-*tert*-butylcyclohexanol, 4-*tert*-butylcyclohexanone, DBP, phenol, styrene, 1-tetradecanol, and TPGDA. Differential cytotoxicity in alveolar cells occurred even when condensate styrene levels were equivalent and indicated non-styrene compounds contributed to chemical toxicity. Styrene emission from the non-styrene resin CIPP installation indicated that contractor equipment handling practices affected the resulting chemical emissions.

Sampling methods and approaches are needed to better characterize chemical emissions, chemical mixture exposures, and short- and long-term health impacts. The high temperature, high velocity, and multi-phase emissions posed a challenge in this study. Emission variability was evident by PID readings and video monitoring. Even when the same CIPP contractor used the same resin on the same diameter and type of pipes, the type and amount of chemicals emitted

differed. To understand worker chemical exposures, the types, and mass of chemicals emitted, their phases, exposure duration, and the mixture's toxicological impacts should be investigated.

Because there are many resins and CIPP installation variables, and because very few studies have been conducted to characterize air emissions, additional investigations are needed. Limited information exists that enables an understanding of chemical exposure risks to CIPP workers, the public, and the environment. During the present investigation, CIPP workers did not use respirators and resided inside and walked through the chemical plumes (**A.3**) and exposures occurred even when plumes were not visible (**Video A.5**). Contractors also sometimes handled the uncured resin tube and CIPP with their bare hands. Until more CIPP air monitoring and chemical toxicity data is available, it is recommended persons at or near CIPP sites (1) lessen dermal and inhalation exposures, (2) monitor emissions, (3) use appropriate personal protective equipment (**A.2**), and (4) capture emissions and confirm this by monitoring

1.6 References

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2. AN EMERGING AIR POLLUTION MOBILE SOURCE: OUTDOOR PLASTIC LINER MANUFACTURING SITES DISCHARGE VOCS INTO URBAN AND RURAL AREAS

2.1 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. The magnitude of volatile organic compound (VOC) release before, during, and after manufacture has gone unstudied. 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% VOC. 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% VOC. 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 was estimated that 10s 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.

2.2 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 (**Figure 2-1**). After the liner hardens, and is cut to allow water to flow, the contractors relocate to their next job site.

It is common practice that contractors discharge their process waste into air, which is a byproduct of manufacture. Regulated hazardous air pollutants (HAPs) have been found discharged

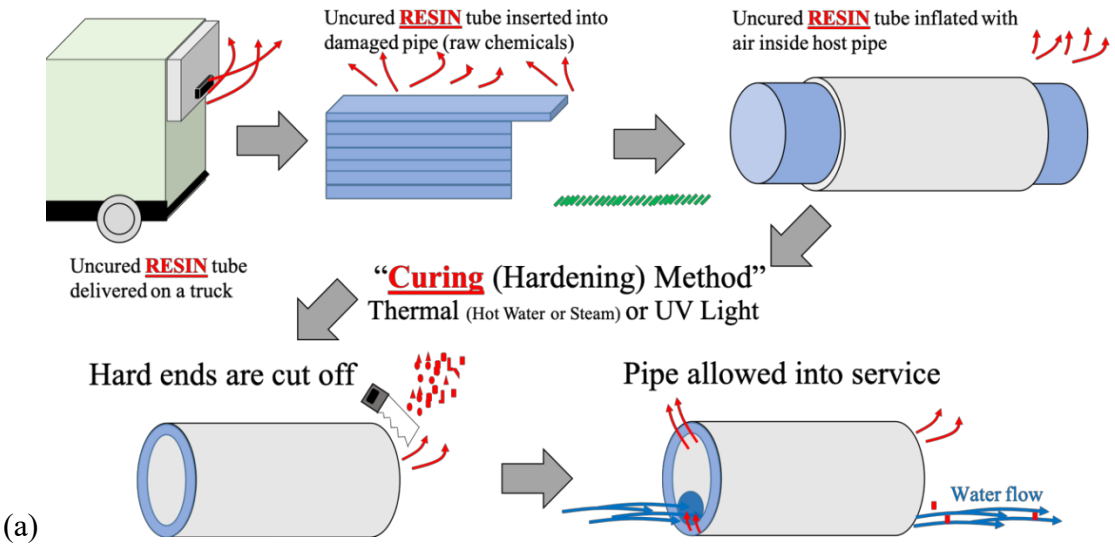
to air, though no studies have estimated the magnitude of CIPP-induced air pollution. CIPP-induced air pollution has been detected in more than 130 incidents associated with environmental degradation and risks to the health and safety of workers and the public [6-14] (**Table B.1**). However, CIPP risk assessments are lacking and unsubstantiated statements have been propagated into CIPP industry worker and municipality training courses [15] and textbooks [16-18]. For example, one peer reviewed CIPP stormwater pipe repair worksite risk analysis study did not consider worker chemical exposure [19, 20], but instead injuries with manual tasks and equipment use (i.e., mixers, pumps, etc.). Others acknowledged that CIPP solvent vapors could "pose a health risk", but stated without evidence, "such levels are not typically found in CIPP installations" and the "problem applies only until the resin is cured" [21]. Some CIPP greenhouse gas emission studies have been conducted, but focused on equipment (i.e., trucks, generators), and often concluded CIPP use is more 'environmentally' justified than open-cut/pipe replacement [22-24]. Estimates of CO_2 emission during CIPP fabrication [25] and CIPP installation construction and environmental costs [26] 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 can be brought onsite (**Table B.7**). The uncured resin tube matrix is either felt or fiberglass matting and contains the resin premixed with monomers, initiators, inhibitors, filler, and other ingredients. Ingredient degradation products can also be present. The HAP styrene is the most popular CIPP resin reactive diluent/monomer [27], but many other contaminants are in the resins, have been discharged into air and water, and extracted from the new CIPPs (**Table 2-1**). Air concentrations for only styrene (0.011-1,820 ppm_v) [9, 13, 28-32] and another HAP methylene chloride (1.41-1.56 ppm_v) [29] were reported. However, 19 other chemicals were detected in air but were not quantified [13, 29]. In addition, applying forced air or steam, typically with a pressure range of 5-20 psi [33] to inflate the uncured resin tube against the damaged pipe's wall may also contribute to resin discharge into the air and more pollutant emission.

After CIPP manufacture, extractable VOCs can be found in the CIPPs. A high of 9.2 wt% VOC has been reported [34] and these originate from the uncured resin and are created *in-situ* during manufacture; it is likely these compounds can volatilize into the air. During CIPP manufacture, VOC air concentrations can increase within nearby pipes, manholes, the worksite, and nearby buildings (**Table B.1**). No studies were found where chemical air concentrations were

monitored after CIPP manufacture. Also unstudied is whether the process curing temperature or heating time would alter the new CIPP's VOC emission profile. For a different application, 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 [35]. To reduce styrene air concentration after CIPP manufacture, one study recommended a 24 hr post-CIPP manufacture ventilation period [36]. 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 lab environment using different curing conditions (pressure, curing temperature, and heating time). In addition, the impact of ventilation on 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.



(a)

(b)

(c)

Figure 2-1. 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. 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 2-1. 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	

Table 2-1 continued

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

Table 2-1 continued

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. 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) [37], [θ]CDOT (2011) [38], [‡]CDOT (2012) [39], [Φ]VDOT (2016) [40], [†]Donaldson (2012) [41], [§]Spectrum (2013a-d) [42-45], [¶]Tabor et al. (2014) [46], [ρ]UGA (2016) [47], [Δ]Currier (2017) [48], [*]Teimouri et al. (2017) [8], [H]PA DEP (2019b) [49], [Ψ]Tentatively identified compounds in Tabor et al. (2014) [46], [Z]Li et al. (2019) [34], [+]Ra et al. (2019) [29]. [β]Initiator degradation product reported by Ra et al. (2019) [7], [§§]NIOSH (2019) [9]. HAP is abbreviation for hazardous air pollutant.

2.3 Methodology

2.3.1 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 & 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.

2.3.2 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. [29]. Prior to extract analysis by gas chromatography mass spectrometry (GC/MS), the methylene chloride and hexane extracts of cured composites were diluted 100 and 10 times, respectively to avoid contamination of the instrument. For uncured resin extracts, extracts were first diluted 10,000 times for methylene chloride extracts and 1,000 times for hexane extracts to quantify styrene since enormous level of styrene was anticipated in the uncured resin. Such a massive dilution could eliminate the existence of other compounds. Therefore, the resin extracts were injected into and analyzed by GC/MS once again, but with no dilution while styrene with 6.7 min retention time was excluded from 6.6 to 7.3 min in MS program to 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.

2.3.3 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 (**Figure B.1**) according to ASTM D 6670–01 [50]. 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 (**Figures B.1 & 2-2**). Among the nine 50-hr chemical air monitoring events from 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.

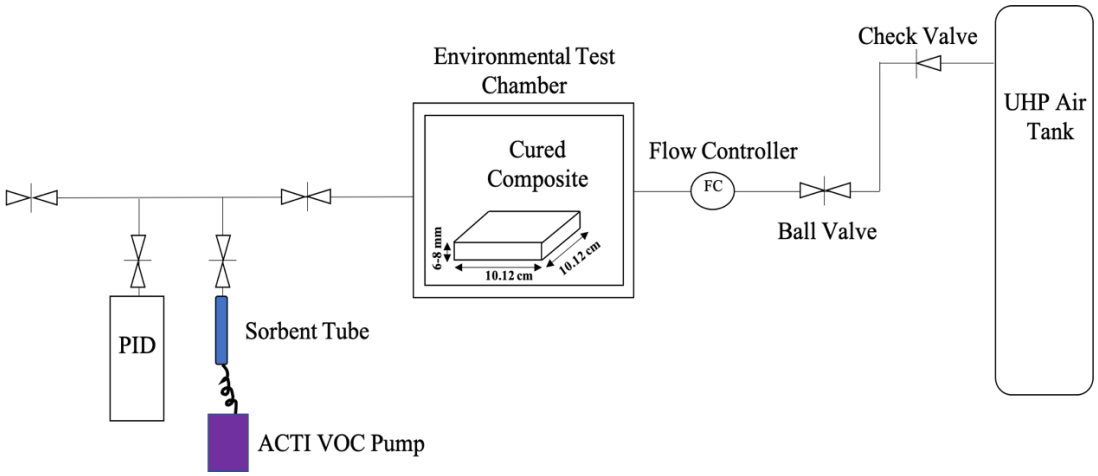


Figure 2-2. Experimental setup for capturing post-cured chemical air emissions from cured composites

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.

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

The first step of chemical emission monitoring for cured composites 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.

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, Θ = 42 s) over the same cured composite used in static I. 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.

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 chemical removal from the confined ETC. In this step, both valves were closed again to mimic static conditions in the confined ETC. The vacuum pump, air flowrate and sampling duration were similar to static 1. The time intervals to capture sorbent tube air samples were: initial, 2, 4, 6, 8, 10, 12 and 24 hr. 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.

2.3.4 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 gas chromatograph (GC) (Shimadzu, Inc., 2010-Plus) and mass spectrometer (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.

2.3.5 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.

2.3.6 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.

Density of cured composite was determined according to ASTM D792–00 [51]. Similar to porosity, two cured composite replicates (out of three) at each curing condition were cut by waterjet to obtain density 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.

2.4 Results and Discussion

2.4.1 The uncured resin contained chemicals beyond just styrene

TGA revealed that the uncured resin contained approximately 39 wt% VOCs. The uncured resin SDS reported only styrene monomer as a hazardous component [52]. Styrene (290,839 $\pm$ 20,154 mg/kg) was found in most abundance and was approximately 29.1% of resin weight. More than 60 other compounds were tentatively identified in the uncured resin (**Table B.2**), and 8 were confirmed (**Table 2-2**). 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 (**Tables 2-2 & B.2**). 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 analyses [29, 34], 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 [34]. 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 2-2. 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	$(1.04\times10^{4}$ - $1.44\times10^{5})$ [36]
Styrene oxide [CAR, HAP]	Not detected	Detected	$(4.70\times10^{1}$ - $1.38\times10^{2})$ [36]
1,3,5-TMB	$7.12\times10^{1} \pm 6.84$	Detected	$(4.40$ - $5.60\times10^{1})$ [36]
N-Propylbenzene	$1.03\times10^{2} \pm 9.49$	Detected	$(5.90$ - $5.80\times10^{1})$ [36]
2-Propenylbenzene	$6.81 \pm 7.70\times10^{-1}$	Not examined	Not reported
Hydroquinone [CAR*, HAP]	$2.15\times10^{2} \pm 5.32\times10^{1}$	Not examined	Not reported
3-Ethyl-1-methylbenzene	> CR	Not examined	Not reported
2-Ethylhexanoic acid	$1.64\times10^{2} \pm 2.42\times10^{1}$	Detected	Not reported
BHT	$4.30\times10^{1} \pm 4.78$	Not examined	$(5.33$ - $2.37\times10^{2})$ [17, 36]
Sum	2.92×10^{5}	-	$(1.58\times10^{3}$ - $1.52\times10^{5})$ [36]

Not examined = authors did not search for this compound in the analytical result; 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 [8, 9, 13, 28-31], water [34, 38-49] and CIPP condensate [8, 46]; 1,3,5-TMB: in water [34, 38, 39, 43-47] and CIPP condensate [46]; BHT: in CIPP condensate [8].*

2.4.2 Chemical volatilization was influenced by the manufacturing condition

Chemical volatilization was influenced by pressure, while temperature and heating time did not influence the final chemical composition of cured composite. 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% (**Table B.3**). This lost material was emitted into the air. 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 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 exceed the melting temperature of those films (29). 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. Air temperature (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) (**Table 2-3**).

Table 2-3. 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	**Condition C**	**Condition D**
	50 min, 65.5˚C	**100 min, 65.5˚C**	**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.

2.4.3 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 reported by others (1.07 to 1.20 g/cm^3) [29, 53], while the observed porosity was significantly lower than the porosity range of 3.41 to 17.75% reported from CIPPs manufactured in the field [53, 54] (**Table B.4**). 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 [55]. 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 (**Section APPENDIX B, Fig. B.2**).

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-1methylbenzene, and *N*-propylbenzene were detected and quantified. The chemical loading of styrene, 1,3,5-TMB, 1,2,4-TMB, benzoic acid and *N*-propylbenzene in the composite cured at ambient pressure was statistically significantly lower than the chemical loadings of the same compounds obtained from the composites cured under vacuum. No statistically 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 temperature or heating time were varied (**Tables 2-4 & B.5**).

Styrene was detected in most abundance across cured composites (14,518 to 20,691 mg/kg), but was present at a much lesser loading than in the uncured resin (**Table 2-2**). 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 (**Table 2-2**) (**Figure B.3**). 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. Results of the present study, however, do not explain the significant residual chemical loading differences found for CIPPs manufactured in the field, sometimes even when using the same resin, the same contractor, and manufactured within 2 days of one another at the same location: styrene (1-13x), benzaldehyde (1-7x), 1-tetradecanol (1-7x), benzoic acid (2-4x), *N*-propylbenzene (1-3x), 1,3,5-TMB (1-19x), 1,2,4-TMB (1-2x), styrene oxide (1-5x), BHT (1-3x) [29, 49].

2.4.4 VOC emissions from newly manufactured composites

Styrene was the only compound detected and quantified in the air during chemical emission monitoring, but analytical method limitations in the present study were significant. These limitations were similar to those also encountered by NIOSH (2019). NIOSH found that a newly manufactured CIPP caused a high styrene air concentration (5,100 ppm_v/g_{sample}) and made identifying other VOCs present in the air unsuccessful. In the present study, the author's chemical analysis of the uncured resin and cured composites themselves indicates that other VOCs were present and were likely emitted to the air.

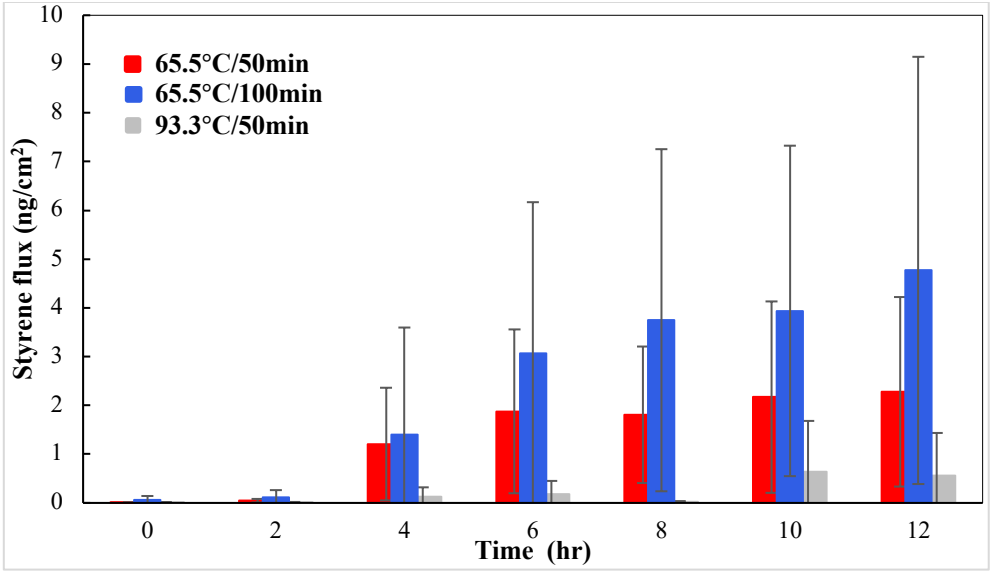
The time needed to achieve ETC styrene equilibrium in air differed across cured composites (**Figure 2-3**), even though composite styrene loadings were not different (**Table 2-4**). The time to achieve equilibrium was about 10 hr for the Composite A (65.5˚C/50 min) and no equilibrium was achieved for either Composite B (65.5˚C/100 min) or Composite C (93.3˚C/50 min). The highest 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 highest 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, it was hypothesized that the observed styrene emission was a surface phenomenon. Because these 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.

2.4.5 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 air concentrations were below the 8 hr-TWA 50 ppm$_v$ occupational exposure limit, but above the limit at which odor can be detected (0.04 to 0.32 ppm$_v$) [57, 58]. According to both the PID and sorbent tube results (**Figure B.4, Table B.6**), air ventilation (Θ = 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 (**Table 2-4**). The ratio of inlet air flowrate/exposed surface area used in this study (9.9 m/hr) was approximately 3 to 11 times less than the ratio recommended from field CIPP study in the Netherlands (30-107 m/hr). The ratio was also less than the velocity headspace obtained by Roghani et al. (396-1,872 m/hr) [59]. This 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.

(a)



(b)

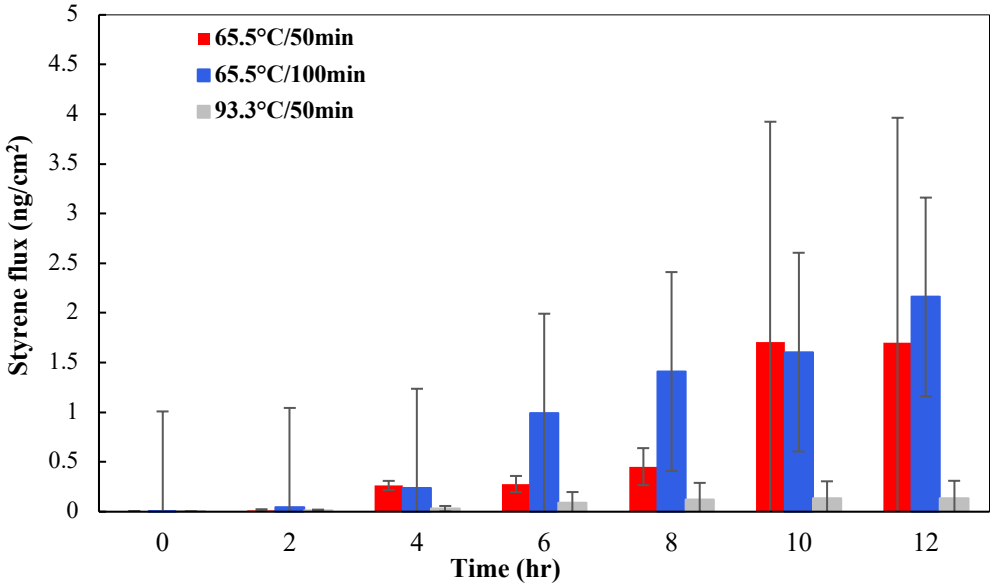


Figure 2-3. Normalized styrene emitted from composites manufactured under different conditions for: (a) static I air monitoring experiments and (b) static II air monitoring experiments. Between each experiment, air flow was flushed through the ETC for 2 hr and air monitoring was conducted before and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

Table 2-4. Chemical mass loading (mg/kg) for the new composites manufactured under different conditions when extracted using methylene chloride

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]	9.74×10^{3} ± 1.09×10^{3}	1.45×10^{4} ± 4.82×10^{3}	1.98×10^{4} ± 2.43×10^{3}	1.92×10^{4} ± 4.40×10^{3}	2.07×10^{4} ± 3.06×10^{3}	(8.60×10^{1} - 1.67×10^{4}) [17, 36]
Styrene oxide [CAR, HAP]	1.04×10^{2} ± 5.62×10^{1}	1.25×10^{2} ± 5.63×10^{1}	5.69×10^{2} ± 4.83×10^{2}	2.69×10^{2} ± 6.70×10^{1}	1.56×10^{2} ± 2.30×10^{1}	(1.90×10^{1} - 9.50×10^{1}) [36]
Benzaldehyde	5.74×10^{2} ± 5.72×10^{2}	1.39×10^{2} ± 5.49×10^{1}	3.00×10^{2} ± 2.34×10^{2}	2.94×10^{2} ± 1.26×10^{2}	4.05×10^{2} ± 3.82×10^{2}	(2.70×10^{1} - 3.64×10^{2}) [17, 36]
1,3,5-TMB	3.00×10^{1} ± 3.35	6.06×10^{1} ± 2.51×10^{1}	8.18×10^{1} ± 8.56	7.51×10^{1} ± 3.74	6.71×10^{1} ± 7.84	(1.40 - 2.60×10^{1}) [36]
1,2,4-TMB	2.02×10^{2} ± 1.20×10^{1}	3.39×10^{2} ± 1.12×10^{2}	4.46×10^{2} ± 1.69×10^{1}	4.21×10^{2} ± 4.38×10^{1}	3.95×10^{2} ± 3.86×10^{1}	(7.50×10^{1} - 8.60×10^{1}) [36]
Benzoic acid	3.40×10^{3} ± 2.48×10^{2}	4.76×10^{3} ± 1.09×10^{3}	5.87×10^{3} ± 6.75×10^{2}	6.23×10^{3} ± 5.17×10^{2}	5.88×10^{3} ± 6.10×10^{2}	(4.70×10^{2} - 1.80×10^{3}) [17]
1-Tetradecanol	1.36×10^{3} ± 1.44×10^{2}	1.80×10^{3} ± 4.90×10^{2}	1.95×10^{3} ± 2.73×10^{2}	2.18×10^{3} ± 4.72×10^{2}	1.95×10^{3} ± 4.69×10^{2}	(3.94×10^{2} - 2.65×10^{3}) [17]
N-Propylbenzene	2.96×10^{1} ± 1.35	4.57×10^{1} ± 1.10×10^{1}	5.47×10^{1} ± 3.40	5.32×10^{1} ± 3.12	5.27×10^{1} ± 5.80	(1.50×10^{1} - 3.80×10^{1}) [36]
2-Propenylbenzene	-	2 replicates shown <5.00×10^{4} - SIM<90	2 replicates shown <5.00×10^{4} - SIM<90	1 replicate shown <5.00×10^{4} - SIM<90	3 replicates shown <5.00×10^{4} - SIM<90	-

Table 2-4 continued

Hydroquinone CAR*, HAP	-	-	-	-	-	-
3-Ethyl-1-methylbenzene	5.20×10^{1} ± 1.42	9.03×10^{1} ± 5.13×10^{1}	9.55×10^{1} ± 5.71×10^{1}	9.35×10^{1} ± 1.47×10^{1}	2.48×10^{2} ± 2.81×10^{2}	-
2-Ethylhexanoic acid	1.26×10^{3}	1.40×10^{3}	1.52×10^{3} ± 1.52×10^{1}	1.45×10^{3} ± 1.85×10^{1}	1.43×10^{3} ± 4.26×10^{1}	-
BHT	-	-	-	-	-	(1.50×10^{1} - 4.40×10^{1}) [36]
Sum	1.44×10^{4}	2.19×10^{4}	2.92×10^{4}	2.88×10^{4}	2.98×10^{4}	(2.26×10^{3} - 1.73×10^{4}) [36]

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 [8, 9, 13, 28-31], benzaldehyde in water [50] and CIPP condensate [8]; benzoic acid: in CIPP condensate [8]; water [34, 38-49] and CIPP condensate [8, 46]; 1,3,5-TMB: in water [34, 38, 39, 43-47] and CIPP condensate [46]; 1,2,4-TMB in water [34, 43-47] and CIPP condensate [46]; BHT: in CIPP condensate [8]; 1-tetradecanol: in CIPP condensate [8].*

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

Because CIPP 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 mobile source pollutant air emissions. Based on the present study and information publicly available, the VOC emitted into the air during CIPP manufacture may be on the order of ten to thousands of tons for some CIPP projects (**Table B.7**). Public records indicated 61,000 to 454,000 kg of resin has sometimes been used per CIPP 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 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 [59]. Using that result, roughly, 10,863,083 kg [~12,000 tons] of VOCs could have been discharged to the air. In 2017, chemical discharge may have been made more significant as

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 [60]. 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 [61]. Because of the magnitude of CIPP VOC emission and potential that includes HAPs (styrene, styrene oxide, methylene chloride, dibutyl phthalate, ethylbenzene, maleic anhydride, phthalic anhydride, and *N*-propylbenzene), work is needed to understand the environmental implications. It may be that CIPP emissions exceed the limits of fixed composite manufacturing facilities. While prior studies claim CIPP manufacture is an environmentally friendly technique [62], VOC emissions like those described here have not been developed for their consideration. Not included in this study were the partially cured resin and oligomers and water saturated with VOCs [8].

This study provides new knowledge associated with CIPP VOC emissions, but 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 to examine CIPP emission reactivity with atmospheric ozone, the hydroxyl radical, and the nitrate radical, as reactions can form other compounds and particulate matter [63]. The role of filler 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 [9], 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 (**Table B.8**).

2.5 Conclusion

The study goal was to better understand VOC release before, during, and after styrene-based composite manufacture using an uncured CIPP resin. Specific objectives were to (1) chemically characterize the unsaturated polyester resin, (2) manufacture composites at different temperature and time conditions, (3) conduct post-cure chemical emission monitoring from cured

composites in an ETC with and without ventilation, and (4) physically, chemically, and thermally characterize the cured composites. No prior studies were found that utilized an ETC to examined chemical emissions with CIPP resin.

The uncured resin contained approximately 39 wt% VOC, and chemical volatilization was influenced by pressure, but temperature and heating time did not influence final chemical composition of cured composite. Hazardous air pollutants (styrene, styrene oxide, and hydroquinone) were detected in the uncured resin (29.1 wt%). 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) found, emission toxicity was styrene-independent [63]. The presence of water, steam, 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 10s 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 [6, 8, 27].

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 industry has captured the chemical emissions to comply with environmental regulations. Such a practice is more helpful during the ozone season when VOCs can react with NOx to form the pollutant ground level ozone [65]. 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.

2.6 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.

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3. HEALTH RISK ASSESSMENT: RESEARCH NEEDS FOR BETTER UNDERSTANDING OCCUPATIONAL INHALATION RISKS ASSOCIATED WITH THE CURED-IN-PLACE-PIPE PROCESS

3.1 Abstract

The cured-in-place-pipe (CIPP) sewer repair process is increasingly being used globally, but no quantitative health risk assessments were found. In this study, a quantitative health risk assessment for inhalation exposure was conducted. This study utilized publicly available worksite data for ultraviolet (UV)- light and steam-CIPP installations, applied Monte Carlo simulations, and data-gaps were identified. Health risks associated with chemical emission from newly manufactured lab-scale CIPPs (post-cured) were also evaluated. In CIPP resins and post-cured CIPPs (31) chemicals have been quantified among which many are unique volatile organic chemicals (VOC), but only 18 air testing studies were found. Among these air testing studies, only 9 studies quantified styrene concentrations. At a steam-CIPP worksite, 5 VOCs were found in a condensed multiphase mixture discharged into air, 4 VOCs were detected in the vapor phase, while only styrene vapor phase results could be used for risk assessment. Worksite styrene levels (1,825 ppm_v, 1,070 ppm_v, 220-270 ppm_v, 140 ppm_v) have been reported indicating a health risk can exist. Monte Carlo simulation over literature data revealed that for the single UV CIPP and single steam-CIPP study negligible styrene HQs were found, while unacceptable styrene LECRs% > 10^{-4} (i.e. 37-38%) were obtained. Monte Carlo simulation on laboratory data showed that post-cured emissions from the composite cured longer increased unacceptable styrene LECR (from 17.86% to 21.12%) and HQ (0.95% to 8.04%). Whereas for the composite cured at greater temperature styrene LECR and HQ caused by post-cured emissions reduced to 0.89%. and 0, respectively. Ventilation also decreased the acceptable LECR% for all composites but did not reduce the carcinogenic health risk to an acceptable level.

3.2 Introduction

The cured-in-place pipe (CIPP) process has become increasingly popular across the U.S., but presents unique occupational and public health risks. The CIPP process involves the manufacture of new plastic liners inside damaged sanitary sewer, storm sewer, and drinking water

pipes. The process polymerizes a resin into a hard plastic using either thermal methods (steam or hot water), ultraviolet (UV) light, or less popular ambient temperature cure. By 2023 the global CIPP market will exceed $2.6 billion, and 40% of the U.S. pipe rehabilitation market [1].

Chemical exposures to workers and the nearby public have been documented in the U.S., Canada, and the U.K. prompting several government agencies to formally investigate [2-6]. The authors have cataloged more than 130 outdoor and indoor air contamination incidents and occupational chemical exposures [5-7]. Reported adverse health effects include acute injuries and one fatality where blood styrene levels implied a CIPP worker had been exposed to 220–270 ppm_v for four hours [4]. Chemical exposure symptoms have been reported by members of the public and medical professionals in vicinity of outdoor CIPP manufacturing (i.e., headaches, nausea, vomiting, loss of consciousness, eye irritation, abdominal pain, aching joints, nostrils burning, dizziness, shortness of breath, gastroenterological problems, tightness of chest, inflamed tonsils & throat, lethargy, inhalation injury, faint, gagging, loss of hearing, confusion) [6, 8] as well as erythema and eczema for CIPP workers as a result of dermal exposure [9]. CIPP condensed materials have prompted mouse alveolar epithelial and alveolar macrophage cell line protein changes to pathways involved in cell damage, immune response, and cancer [10]. An environmental toxicity study demonstrated that condensate dissolved daphnia magna organisms within 24 hours at room temperature [11]. Unlike other composite manufacturing processes, the CIPP processes lacks occupational health risk assessments [12-22]. Unique to the CIPP practice is that public health risk assessments are also needed the proximity of the activity and lack of capturing emissions has caused public exposures for children, adults, and immunocompromised persons. While attempts have been made to understand occupational risk, they have not explicitly considered chemical exposures [16] which is a notable concern for CIPP manufacture. A risk-based occupational safety decision process is lacking for this widely used process.

Chemical exposure risks associated with composite manufacture are not new, but the unique factors associated with the CIPP process make these exposures significant. First, CIPPs are manufactured in neighborhoods and outdoors where emissions are routinely vented at the worksite sometimes into public spaces and into nearby buildings (**Figure 3-1**). Substandard worker safety posture has been documented such as a lack of personal protective equipment for dermal and respiratory protection [3, 5, 23]. In contrast, other composites (i.e., boats, turbine blades) are typically manufactured in engineered ventilated buildings. These processes may involve VOC

capture or destruction and include personal protective equipment such as gloves and respirators [24]. Chemical emission into air during CIPP projects can occur (1) when uncured resin is being removed from the delivery truck [5, 25], (2) when the uncured resin tube is inserted and positioned inside the damaged pipe [26], (3) when emissions are discharged to air or directed to an exhaust stack sometimes placed downstream [3, 5, 6, 8, 25], (4) when contractors cut the newly manufactured plastic [3, 26], and (5) after the new CIPP is placed into service [23]. A task by task list of chemical air emission potential for steam- and UV-CIPP installations can be found in elsewhere [27].

(a)  (b) 

Figure 3-1. (a) Chemicals can be released into air at CIPP manufacturing sites, (b) Worker exposed to chemical emissions during sanitary sewer CIPP manufacture.

Many decades ago, VOC occupational exposures in the U.S. fiberglass reinforced plastic industry were found to exceed occupational exposure limits, and this prompted the adoption of engineered and administrative controls. In 1985, Crandall et al. [28] examined occupational exposure to styrene monomer during fiberglass reinforced plastic boat manufacture in 7 fabrication plants. Styrene exposure exceeded the National Institute for Occupational Safety and Health (NIOSH) recommended time-weighted average (TWA) standard of 50 ppm_v in 59% of the samples from which 24% of samples exceeded the OSHA eight-hour TWA permissible exposure limit of 100 ppm_v. Job category was considered as the main parameter for styrene exposure level, among which, hull lamination (78 ppm_v as mean value) and deck lamination (73 ppm_v as mean value) were recognized as highest exposure job category. Health risk analysis for this sector has helped better quantitatively assess potential VOC exposure health effects. Malherbe et al. [29] assessed inhalation health risk due to VOC exposure during outdoor ship painting and found maximum

VOC concentration of 278 mg/m^3 for shipyard repair site and 26.5 mg/m^3 for shipyard construction. For the repair shipyard, the maximum hazard quotient (HQ) was determined to be 0.81 for acute exposure and 0.9 for chronic exposure. HQs were found to be 0.038 for maximum acute exposure and 0.09 for chronic exposure. Since all HQ values were less than 1, this indicated shipyard repair did not have notable noncarcinogenic inhalation health risks.

Numerous statements about CIPP emission safety have been found in industry documents, municipal documents, and public press releases but lack supporting data. No quantitative approach has been applied to express chemical exposure health risks associated with chemical exposure of workers and public in worksites [30-37]. Existing air testing data is limited (Table 3-3), and much of it only focuses on styrene. For example, AirZone Inc. reported finding a maximum styrene concentration of 3.2 ppm_v [38] but was much lower than Ajdari [39] who detected a maximum concentration of 1070 ppm_v in downtown Los Angeles, CA during CIPP curing. This level exceeded the NIOSH immediately dangerous to life or health (IDLH) limit of 700 ppm_v [40]. In 2019, NIOSH found 140 ppm_v at a UV CIPP worksite which exceeded the 15-minute short-term exposure limit (STEL) of 100 ppm_v [3]. Others reported in 2019 finding styrene concentration greater than 1,825 ppm_v inside the uncured resin truck and greater than 300 ppm_v exiting exhaust pipes during steam-CIPP installation [25]. Ra et al. [7] reported that styrene air concentrations likely exceeded 86.5 ppm_v onsite during steam-CIPP manufacture. Other investigators have conducted air testing in Europe and the U.S. as explained in **Table 3-1**.

In the present study, the CIPP manufacturing and emission literature as well as occupational exposure literature were reviewed. Next, HQ and lifetime excess cancer risk (LECR) were estimated over limited publicly available chemical air emissions data from CIPP activities in bench and field-scale. The objectives of this study were to (1) compile and review existing CIPP practices from publicly reported data; (2) conduct quantitative health risk assessments from CIPP related practices for workers in lab and field scale; and (3) provide guideline for better occupational and public health protection.

Table 3-1. Reported styrene and methylene chloride air concentrations air exposure in existing associated with CIPP field practices.

Date	Project Details				Monitoring and Analysis Methods	Chemicals Detected	Air Conc. (mg/m^3)			Ref
	Country	Method	Resin	CIPP						
2019	USA	Thermal, Oven	Styrene	9 lab composites	Sorbent tube - GCMS	Styrene	Before ventilation	65.5°C/50 min	$2.75\times10^{-2} \pm 4.58\times10^{-2}$ - 12.59 ± 10.80	Present study
								65.5°C/100 min	$3.34\times10^{-1} \pm 4.31\times10^{-1}$ to 25.92 ± 24.02	
								93.3°C/50 min	$3.38\times10^{-2} \pm 5.86\times10^{-2}$ to 3.51 ± 5.42	
							After ventilation	65.5°C/50 min	$7.38\times10^{-3} \pm 9.02\times10^{-3}$ to 9.64 ± 12.33	
								65.5°C/100 min	$4.79\times10^{-2} \pm 5.60\times10^{-2}$ to 11.73 ± 9.85	
								93.3°C/50 min	$4.56\times10^{-3} \pm 5.59\times10^{-3}$ to $7.77\times10^{-1} \pm 8.74\times10^{-1}$	

Table 3-1 continued

2019	USA	Thermal, Steam	Styrene	7	Canister, HAPSITE® ER/n.r.	Styrene	Liner transport truck	Site 1/ Shreveport	2.31	25
								Site 2/ Shreveport	175.8	
								Site 3/ Shreveport	115.8	
								Site 4/ St. Louis, MO	156.9	
								Site 5/ St. Louis, MO	95.5	
								Site 6/ Aurora, Co	315.7, 1.82×10^{3}	
							Emission stack	Site 1/ Shreveport	1.21	
								Site 2/ Shreveport	107.5	
								Site 3/ Shreveport	5.12×10^{-2}	
								Site 4/ St. Louis, MO	8.45	
								Site 5/ St. Louis, MO	110.6, 292.7	
								Site 6/ Aurora, Co	1.57×10^{-3}, 25.4	
							Worker exposure	Site 1/ Shreveport	2.11, 4.37	
								Site 2/ Shreveport	8.82	
								Site 3/ Shreveport	2.68×10^{-2}, 2.01×10^{-1}	
								Site 4/ St. Louis, MO	1.86-2.66	
								Site 5/ St. Louis, MO	4.92×10^{-1} to 16.9	
								Site 6/ Aurora, Co	4.40×10^{-2} to 1.6	

Table 3-1 continued

2019	USA	UV	Styrene	4	Sorbent tubes, evacuated canisters/GCMS	Styrene & divinylbenzene; but only styrene was quantified due to high abundance	Worker exposure (February)		4.58×10^{-1} - 6.32×10^{-2}	3
							Worker exposure (June)		4.28×10^{-1} - 1.44×10^{-2}	
							Area monitoring		4.30×10^{-1} - 2.31×10^{-2}	
2019	USA	Thermal, Steam	Styrene	5	PID; Tedlar bags/GCMS	Methylene chloride	Site 1	Fugitive emission point	-	7
								Exhaust emission point	NC	
							Site 2	Fugitive emission point	-	
								Exhaust emission point	-	
							Site 3	Fugitive emission point	-	
								Exhaust emission point	5.14	
							Site 4	Fugitive emission point	-	
								Exhaust emission point	5.07	
							Site 5	Fugitive emission point	4.90	
								Exhaust emission point	5.42	
						Styrene	Site 1	Fugitive emission point	1.43 - 368	
								Exhaust emission point	NC	
							Site 2	Fugitive emission point	BCR	
								Exhaust emission point	BCR	
							Site 3	Fugitive emission point	2.19 – 14.0	
								Exhaust emission point	1.98 – 31.21	
							Site 4	Fugitive emission point	2.89 – 79.5	
								Exhaust emission point	2.35 – 16.4	

Table 3-1 continued

							Site 5	Fugitive emission point	9.80×10^{-1} - 151	
								Exhaust emission point	3.46 - 155	
2018	USA	Thermal, Steam	Styrene	3	PID; Charcoal sorbent tubes - GC/FID	Styrene	Sampling at: 10/05/2017		5.26, 26.9	41
							Sampling at: 10/16/2017		<0.056 - 1.1	
							Sampling at: 03/22/2018		0.67, <0.74	
							Sampling at: 04/20/2018		<0.046, 7.3	
2018	USA	Thermal, Hot water	n.r.	2	Passive badges - GC/FID	Styrene	186.2 m of sewer piping		2.10-190	42
							65.8 m sewer piping		1.00 - 4.90	
2017	USA	Thermal, Steam	n.r.	2	Passive badges - GC/FID	Styrene	Worker exposure in Insituform project		< 2*	43
							Worker exposure in AM-Liner project		< 1*	
2015	USA	Thermal, Steam	Resin	3	Tedlar bag - GC/MS	Styrene	Site 1	During curing	1.23×10^{3}	39
								During cooling	22.4	
							Site 2	During curing	4.56×10^{3}	
								During cooling	327	
							Site 3	During curing	1.06×10^{3}	
								During cooling	15.4	
2001	CAN	Thermal, Hot water	n.r.	n.r.	Charcoal sorbent tubes - GCMS	Styrene	Manhole 1		1.90×10^{-4} - 9.80×10^{-2}	38
							Manhole 2		7.00×10^{-5} – 1.60×10^{-2}	
							Manhole 3		9.00×10^{-5} – 1.49	

Table 3-1 continued

							Manhole 4	1.60×10^{-4} – 3.19	

*BCR: below calibration range (< 2.99 mg/m^3); -: not detected; NC: no Tedlar bag air sample was captured; n.r.: not reported; *: the authors considered values 1 & 2 mg/m^3 to better examine health risks and to provide more prudent assessment. In addition to styrene, 3 more chemicals in air and 18 more chemicals in CIPP condensate captured from air were found. Chemicals found in air were: divinylbenzene, phenol and methylene chloride. Chemicals found in the CIPP condensate were: acetophenone, acetone, benzene, benzaldehyde, benzoic acid, 2-butanone (methyl ethyl ketone), tert-butyl alcohol, butylated hydroxytoluene, chloroform, dibutyl phthalate (DBP), isopropylbenzene, methylene chloride, phenol, n-propylbenzene, toluene, 1-tetradecanol, 4-tert-butyl cyclohexanol, tripropylene glycol diacrylate.*

3.3 Methodology

A literature review was conducted to identify the chemicals and their magnitudes emitted into air associated with CIPP installations. Peer-reviewed journal articles, state government agency reports, NIOSH health hazard evaluation reports, conference proceedings, and a webinar presentation available as of February 2020 were reviewed. Uncured resin tube constituents, initiators and their degradation products, as well as chemicals detected inside CIPPs after manufacture and released to the air and nearby water were compiled. Next, air monitoring data was sought but little was found. While five chemicals have been detected in the vapor phase (styrene, methylene chloride, phenol, divinylbenzene) at CIPP worksite, 8 other chemicals have been found when condensed from the chemical plume (acetophenone, benzaldehyde, benzoic acid, butylatedhydroxy toluene, 4-*tert*-butylcyclohexanol, dibutyl phthalate, 1-tetradecanol). In December 2019 it was reported that styrene and 18 other chemicals were detected at steam-CIPP worksites in air, but only styrene concentrations were reported [25]. Among detected compounds in vapor phase, however, styrene and methylene chloride were quantified. Due to the scarcity of air monitoring results of methylene chloride, estimation of a proper distribution function and subsequently, health risk assessment of this compound was not possible. Therefore, only available styrene (a common CIPP resin monomer) air concentration data were included in this study. The health risk assessment was developed to examine: (1) styrene emissions captured during CIPP installation – field scale and (2) post-chemical emissions captured after CIPP manufacturing-bench scale. CIPP styrene concentrations collected from literature review are presented in **Table 3-1**. Air concentrations originally reported as ppm_v in the literature were converted to mg/m^3 for use in the risk assessment.

3.3.1 Risk assessment

Hazard identification

Hazard identification is determining whether a specific compound causes a particular health effect. Due to the observed transient nature and dispersion of CIPP chemical plumes, inhalation was considered as the main route of worker exposure. Subsequently, worker inhalation exposure risks were investigated. Because of limited available data, only styrene, as human carcinogen, was selected for the health risk assessment.

Dose-response assessment

Dose-response assessment involves evaluating the critical concentration such as reference concentration (RfC) of a target compound for toxicity in a critical organ. RfC is an estimate with uncertainty and defined as the daily air concentration of a target chemical with no human health effect. The styrene RfC calculated by Mutti et al. [44] used no-observed-adverse-effect-level (NOAEL) value of 34 mg/m^3 in workers to find central nervous system effects in workers exposed to >22 ppm. An uncertainty factor of 30 was then applied to NOAEL value of 34 mg/m^3 to obtain styrene RfC of 1 mg/m^3 [45]. Inhalation unit risk of 5.7×10^{-7} for styrene was also used to evaluate carcinogenic risk [46].

Exposure assessment

USEPA formulas (Eq. 1-5) were used to conduct non-carcinogenic and carcinogenic health risk assessment of CIPP associated styrene exposure [47]. Exposure concentration (EC) of pollutant was obtained using Eq. 3-1 (**Table 3-2**). CA is the pollutant concentration in the air (μg/m^3), ET is the exposure time (hours/day), EF is the exposure frequency (days/year), ED is the exposure duration (year), and AT is the averaging time ($lifetime\ in\ years \times 365\frac{days}{year} \times 24 hours/day$). The range of each input/exposure factor is presented in **Table 3-3**.

Risk characterization

Non-carcinogenic health risk

To determine the non-carcinogenic inhalation health risk of the target compound, styrene hazard quotients (HQ) were estimated [47]. This was accomplished considering the styrene exposure concentration (EC) and compound reference concentration (RfC) using Eq. 3-2 (**Table 3-2**). HQ of less than 1 is considered safe as it indicates the concentration of inhaled pollutant is less than its reference concentration and no adverse health effects could be probably observed. HQ greater than 1 indicates the potential for an adverse health effect.

Carcinogenic health risk

To estimate the carcinogenic inhalation health risk, the lifetime excess cancer risk (LECR) of target compounds [47] were calculated using equation (3-3) (**Table 3-2**). IUR is the inhalation

unit risk $(\mu g/m^3)^{-1}$ and illustrates cancer risk for a 70-year exposure per 1 μg pollutant/m^3 air. According to USEPA [47], LECR higher than 1×10^{-6} is considered a definite risk for humans.

Table 3-2. Equations used for health risk assessments

Formula	Equation number
$EC = \frac{CA \times ET \times EF \times ED}{AT}$	$3-1$
$HQ = \frac{EC}{RfC} = \frac{EC\,\frac{\mu g}{m^3}}{(RfC\,\frac{mg}{m^3} \times \frac{1000 \mu g}{mg})}$	$3-2$
$LECR = EC \times IUR$	$3-3$

3.3.2 Monte Carlo simulation - Stochastic risk assessment

Due to data scarcity and variability in environmental systems, risk assessment is always linked with uncertainties. Neglecting these uncertainties may cause impractical decision-making regarding environment and human health protection. In this study, Monte Carlo simulation with 10,000 iterations was performed to estimate noncarcinogenic and carcinogenic expected risks (**Figures 3-2 & 3-3**) caused by styrene only inhalation. For this simulation statistical software R was used.

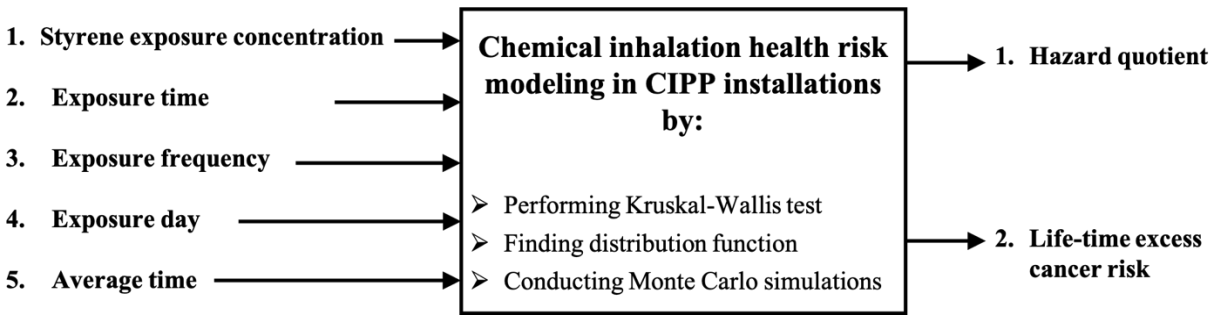


Figure 3-2. General concept of risk modeling for chemical inhalation during and after CIPP activities

Monte Carlo simulation on data obtained from field studies review

A Monte Carlo simulation on field data was conducted to better understand the inhalation health risks associated with CIPP manufacture. A challenge however was that each air testing

study contained different sites and/or days for chemical monitoring and collecting data. Therefore, prior to Monte Carlo simulation, Kruskal-Wallis analysis was performed on the data within each study to examine if multiple studies could be combined as a single data set. To combine data sets, no statistically significant difference between sets could be detected (i.e. $p>0.05$). This practice could also help increase the number of records analyzed in order to find better distribution function and subsequently, more precise risk predictions.

Monte Carlo simulation on data obtained from lab study review

A detailed description of laboratory-scale experiments can be found in Chapter 2 and **APPENDIX B**. In brief, three replicate composites were first manufactured in the laboratory at different curing conditions (i.e. temperature and time). Then, the composites were placed in an environmental test chamber (ETC) for 24 hr and air sampling was conducted. Immediately after 24 hr, the composites underwent 2 hr ventilation by ultra-high purity air (Θ=42s). For post-cured chemical air monitoring of the composites [6], the aim was to investigate the effect of different curing conditions as well as ventilation on workers' health risks. Three replicates were monitored for each curing condition and therefore, the results of them were combined as a single data set. According to Chapter 2 results, styrene was the only compound captured and quantified in air for composites cured at different conditions [6]. Therefore, after finding the best distribution function for combined styrene concentration, Monte Carlo was then conducted. Simulation results were then compared.

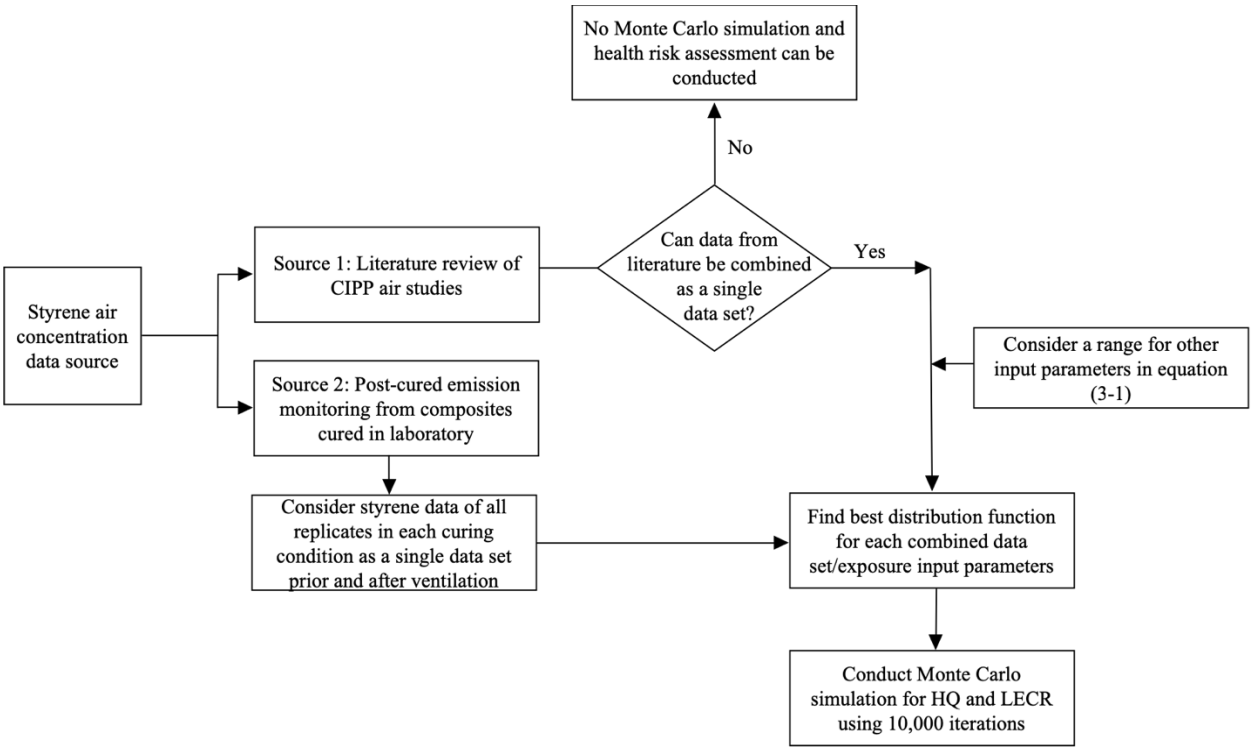


Figure 3-3. Procedure of risk assessment framework for chemical exposures caused by CIPP emissions into atmosphere

3.4 Results

3.4.1 Literature Review

While the CIPP process has been used for more than 30 years, little quantitative information was found about the chemicals present in the uncured resin, chemicals created during the manufacturing process, and those emitted into the environment. **Table 2-1** describes the chemicals that have been associated with CIPP manufacture as of February 2020. In 2019, a CIPP resin SDS listed styrene, phenyl bis(2,4,6-trimethylbenzoyl)-phosphine oxide (Irgacure® 819), and Irgacure® 651 as its ingredients, but characterization revealed more than 70 other chemicals that were not listed [6, 26]. Many of the unlisted chemicals were VOCs and are known carcinogens such as isopropylbenzene, styrene oxide, and styrene. A variety of different initiators have also been used for CIPP manufacture, and these can decompose into a multitude of VOCs and include carcinogens [48]. The Perkadox®, Trigonox® and Butanox® class initiators decomposed into 24 different compounds. Based on the literature review, SDSs cannot be used to fully understand which chemicals workers may come into contact with during a CIPP project.

During manufacture, a variety of materials can be emitted into air. This includes organic vapors, particulates, partially polymerized oligomers, and water vapor, depending on the CIPP manufacturing method. To identify what chemicals may be produced or subsequently volatilize into air or leach into water, newly manufactured CIPPs have undergone liquid-solid extraction. These chemicals included: acetophenone, benzaldehyde, benzoic acid, bis(*tert*-butylcyclohexyl) peroxydicarbonate, *tert*-butyl alcohol, butylated hydroxytoluene, decane, di(2-ethylhexyl) phthalate, dodecanol, ethylbenzene, isopropylbenzene, Irgacure, phenol, 2-phenyl acetaldehyde, phthalic anhydride, *n*-propylbenzene, styrene, styrene oxide, 1-tetradecanol, 4-*tert*-butyl cyclohexanol, 4-*tert*-butyl cyclohexanone, tripropylene glycol diacrylate, 1,2,3-trimethylbenzene (TMB), 1,2,4-TMB, 1,3,5-TMB, 2,4,6-triphenyl-1-hexane [styrene trimer], 1,3,5-triphenylcyclohexane [styrene trimer] and xylene. Among these compounds, benzaldehyde, di-n-butyl phthalate, Irgacure®, phthalic anhydride, styrene, 1,2,3-TMB, 1,2,4-TMB, 1,3,5-TMB and xylene were also found in CIPP resins. A challenge with much of the existing air testing data is that many studies only applied the use of PIDs, not chemical identification and quantification. Also, Ra et al. [7] found that PID concentration signals (when calibrated for styrene) at 5 steam-CIPP worksites were 10s- to 1000s-fold different than the actual styrene air concentration. LeBouf et al. [3] also has reported PIDs can over and underestimate responses. It is likely that PIDs cannot accurately estimate styrene air concentration at CIPP manufacturing sites, and PID results were not included in the risk assessments. Chemical emissions are also possible after the curing process where the ends of the new plastic are mechanically cut where organic vapors and composite dust enter the air [26].

Air testing data from CIPP worksites indicates that three compounds have been confirmed in air sample vapor phase [3, 7] while 17 other chemicals found in the condensed phase at CIPP worksites [5]. Although, the vapor concentration of only two compounds have been quantified, in another study, 18 more chemicals in addition to styrene were detected, but their names were not reported [25]. Ra et al. [7] found styrene (>86.5 ppm_v) and methylene chloride (1.56 ppm_v). In a 2015 Los Angeles, California study [39] styrene exited manholes from 250 to 1,070 ppm_v at three sanitary sewer pipe sites during steam curing and 3.6 to 76.7 ppm_v during cool down, exceeding the 700 ppm_v immediately dangerous to life and health (IDLH) worker exposure limit [40]. NIOSH found styrene and divinylbenzene in air for during UV CIPP activities [3]. Occupational exposure to styrene was obtained 140 ppm_v which exceeded 15-minute short-term exposure limit of 100

ppm_v. In Alaska, an exposure study on workers during hot water cured CIPP installations found styrene in the range of <0.3 to 45 ppm_v [42]. PBS Engineering and Environmental, Inc. in Oregon detected styrene (<0.011 to 6.32 ppm_v) monitored chemical emissions from steam cured CIPPs in sewer pipe rehabilitation sites and surrounding area. and represented public exposure in downwind outside the work area [41]. In 2005, Agency for Toxic Substances and Disease Registry (ATSDR) responded to an office building in Milwaukee in which CIPP chemical emissions was entered and caused contamination [2]. After investigation, the incident was declared as a 'public health hazard' since styrene with 0.320 ppm_v concentration exceeded its minimal acceptable chronic exposure level of 0.060 ppm_v. In 2001, AirZOne Inc. Reported a high of 3.2 ppm_v styrene in Toronto/Canada during CIPP lining of sanitary sewer [38]. As additional studies are conducted additional chemicals may be identified and quantified associated with CIPP manufacture.

To the author's knowledge, only limited studies conducted VOC emission monitoring after CIPPs have been manufactured [3, 6, 23]. CIPP specimens from two installations were examined using 1 g of sample placed in a micro-chamber/thermal extractor. The results indicated styrene as the only compound identified with headspace concentration of 1,300 ppm_v and 5,100 ppm_v per gram. However, due to analytical method limitations, the presence of other compounds known to be released during CIPP manufacture into air could not be detected.

3.4.2 Stochastic risk assessment

Risk assessment for chemical emissions during CIPP installations/ Field scale

Kruskal-Wallis analysis indicated that only two of the eight studies contained usable data for risk assessment: (1) UV curing CIPP study performed by NIOSH et al. *(p*=0.072) [3] and (2) steam curing CIPP study conducted by Ra et al. (*p*=0.539) [7]. However, among 5 different CIPP sites in Ra et. al (2019) study, styrene concentrations captured in site 2 (non-styrene based CIPP installation) were not quantitated as they were below the researcher's analytical calibration range. Hence, all the usable styrene concentrations from different sites/days presented in each study were pooled and consider as a single data set. For UV curing and steam curing CIPP studies, median concentrations of styrene were 12.44 and 9.11 mg/m^3, respectively (**Figure 3-4**). Probability distribution functions for styrene concentrations in these studies as well as other input parameters presented in Eq. 3-1, were selected after distribution optimization using R (**Table 3-3**). While there

are clear differences between UV- and steam-CIPP manufacture as explained elsewhere [5, 7, 26, 27], this approached enabled the application of a health risk assessment.

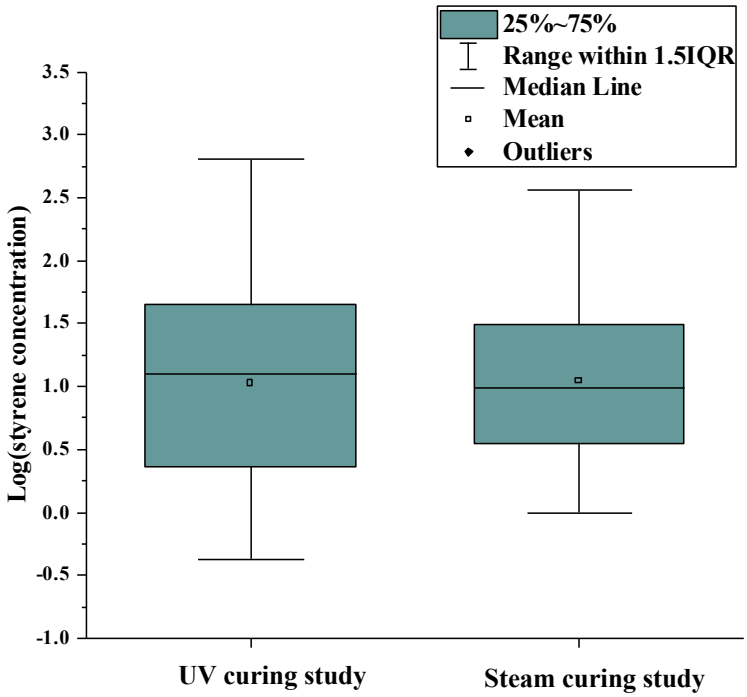


Figure 3-4. Styrene air concentration box plot for the two CIPP air testing studies used for the inhalation health risk assessment. The studies were conducted by the NIOSH (2019) [3] and Ra et al. (2019) [7]. In this graph, for visualizations purposes the concentration in log scale was used while arithmetic scale was used for Monte Carlo modeling. IQR is and abbreviation for interquartile and equals to third quartile (Q3)- first quartile (Q1).

Table 3-3. Distribution function selected for exposure factors

Exposure factors	Unit	Minimum	Maximum	Distribution
Styrene concentration [7]	mg/m^3	9.80×10^{-1}	3.68×10^{2}	Lognormal
Styrene concentration [3]	mg/m^3	4.29×10^{-1}	6.37×10^{2}	Lognormal
Styrene concentration (Static I, 65.5 °C/50min) [6]	mg/m^3	0	23.9	Exponential
Styrene concentration (Static I, 65.5 °C/100min) [6]	mg/m^3	1.45×10^{-3}	4.89×10^{1}	Lognormal
Styrene concentration (Static I, 93.3 °C/50min) [6]	mg/m^3	0	9.77	Exponential
Styrene concentration (Static II, 65.5 °C/50min) [6]	mg/m^3	2.17×10^{-3}	23.9	Lognormal
Styrene concentration (Static II, 65.5 °C/100min) [6]	mg/m^3	1.45×10^{-3}	1.78×10^{1}	Lognormal
Styrene concentration (Static II, 93.3 °C/50min) [6]	mg/m^3	0	1.79	Exponential
Exposure time	hr/day	1.70×10^{-2}	3	Uniform
Exposure frequency	day/year	30	365	Uniform
Exposure duration	year	5	30	Uniform
Averaging time	year	20	70	Uniform

Monte Carlo simulation results revealed that styrene inhalation during CIPP activities in both UV curing and steam curing studies posed negligible noncarcinogenic health risks whereas worker carcinogenic health risks were high. For the UV curing CIPP study only 14.48% of the HQs were greater than 1 (**Figure 3-5**). The minimum and maximum HQs were 4.76×10^{-6} and 192.15, respectively. For the carcinogenic health risk, LECR, EPA [49] considered 1×10^{-6} to 1×10^{-4} as the acceptable carcinogenic risk level by unconditionally acceptable risk level below 10^{-6} [50, 51]. LECRs greater than 10^{-4} require protective measures and remediation. In this study, 95.10% of styrene LECR exceeded the unconditionally acceptable risk of 10^{-6} among which 56.78% was in the range of 1×10^{-6} to 1×10^{-4} and 38.32% was below 10^{-4}. The lowest and highest LECR values caused by styrene inhalation were calculated 2.72×10^{-9} and 1.10×10^{-1}, respectively.

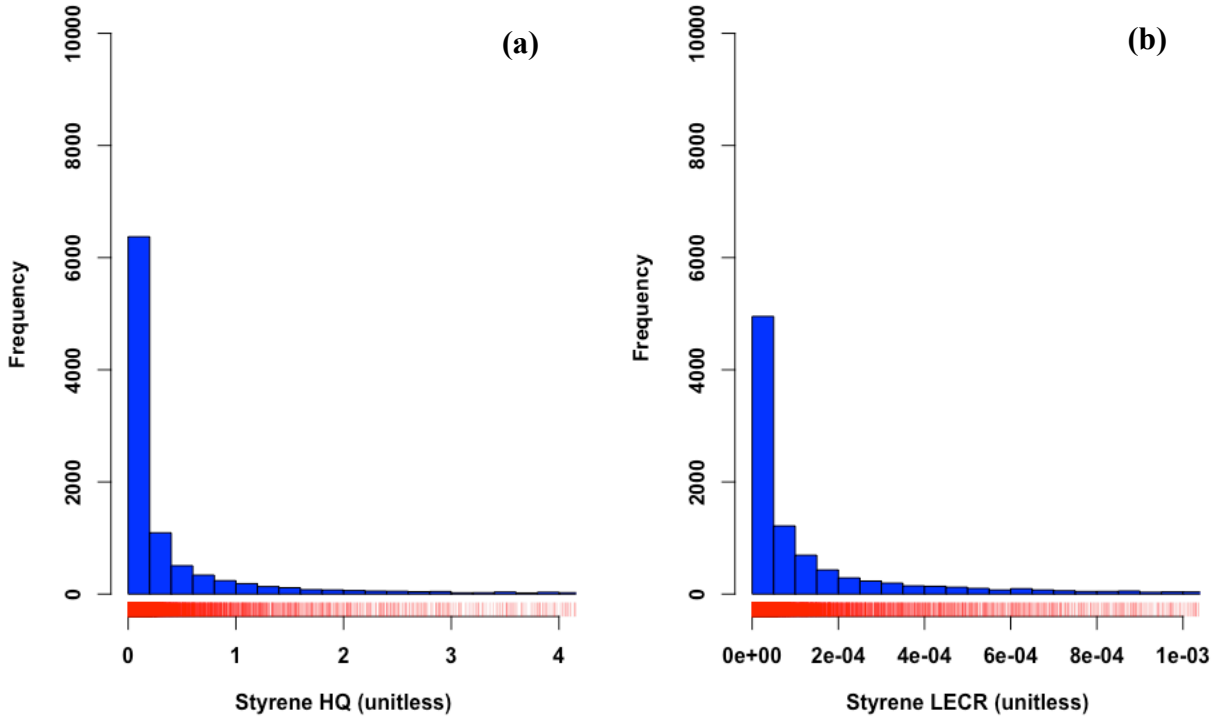


Figure 3-5. (a) Noncarcinogenic HQ and (b) carcinogenic LECR health risks caused by workers styrene inhalation from UV curing CIPP activities obtained by Monte Carlo simulation

For the steam curing CIPP study, only 9.83% of styrene air concentrations showed HQs greater than 1 meaning negligible significant noncarcinogenic risks were found during installation (**Figure 3-6**). Compared to UV curing, noncarcinogenic health risks caused by steam curing was lower. Approximately, 60.43% of LECRs were in the acceptable range of 1×10^{-6} to 1×10^{-4} and 37.14% of them were above 10^{-4} (**Figure 3-6**). Unacceptable LECR% > 10^{-4} in both studies were considerable and similar.

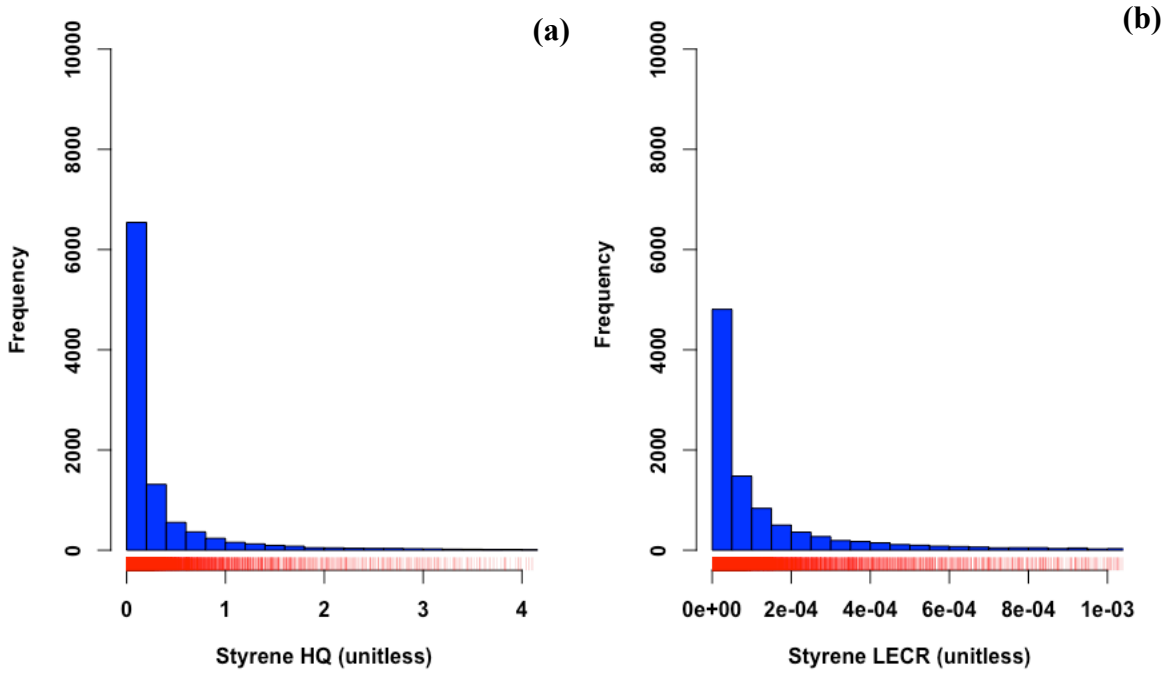


Figure 3-6. (a) noncarcinogenic HQ and (b) carcinogenic LECR health risks caused by workers styrene inhalation from steam curing CIPP activities obtained by Monte Carlo simulation

Risk assessment for post-cured chemical emissions after CIPP manufacture/ Lab scale

Despite similar CIPP resins and initiators being used for composite manufacture, a slight change in curing conditions caused significant difference in unacceptable carcinogenic health risks as well as HQs. (**Table 3-4 & Figure 3-7)**. The results of health risk assessment on 12 hr post-cured styrene emission monitoring data revealed that a longer curing duration caused an increase in unacceptable LECR% from 17.86% for 65.5 °C/50 min to 21.12% for 65.5 °C/100 min whereas a greater curing temperature the LECR% from 17.86% to 0.89% for 93.3 °C/50 min condition. The same trend was observed for noncarcinogenic health risks. Post-cured styrene emission from composite cured for extended time caused higher HQ, from 0.95% to 8.04%, while it reached to 0 by post-cured styrene emission from the composite manufactured at higher temperature.

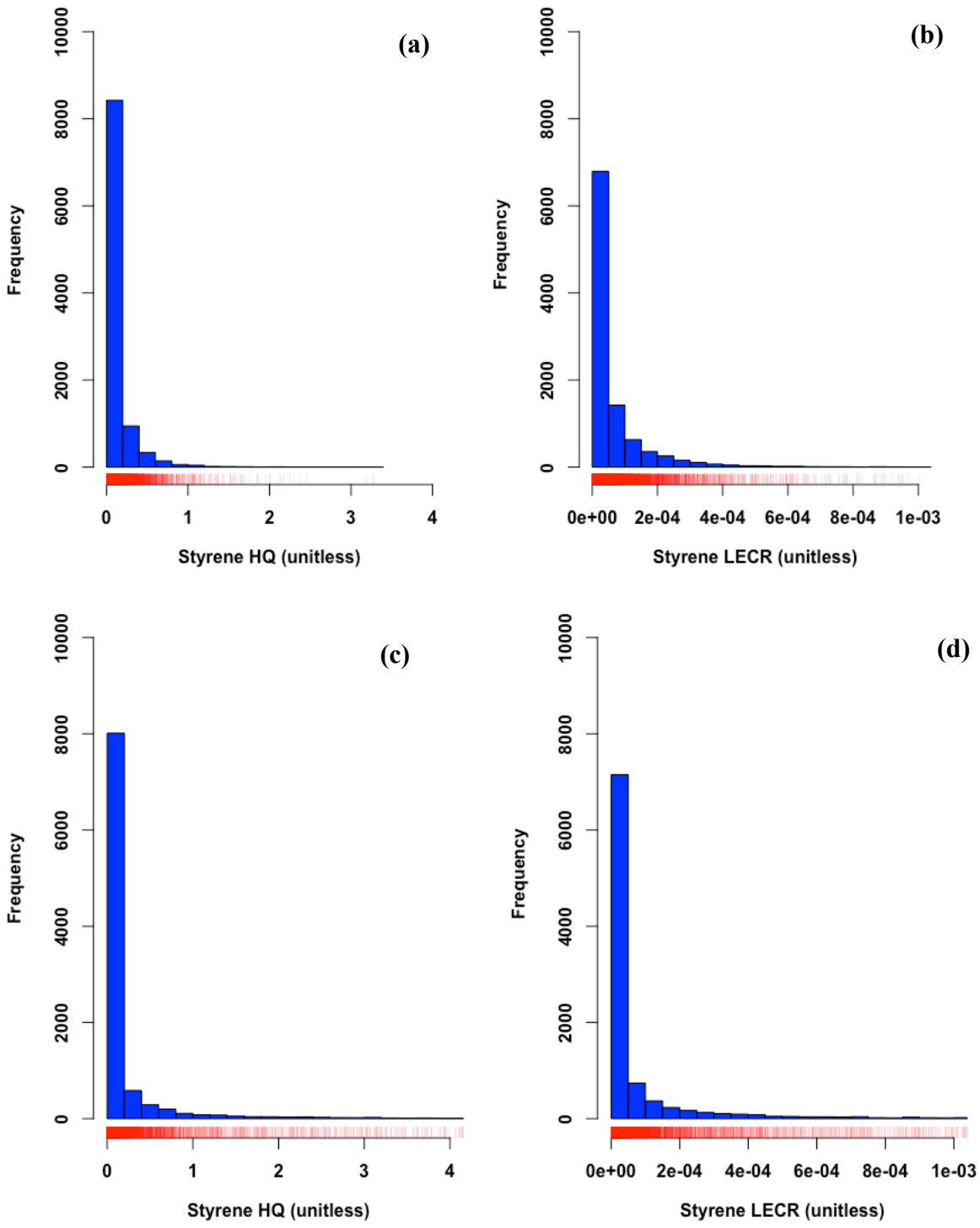
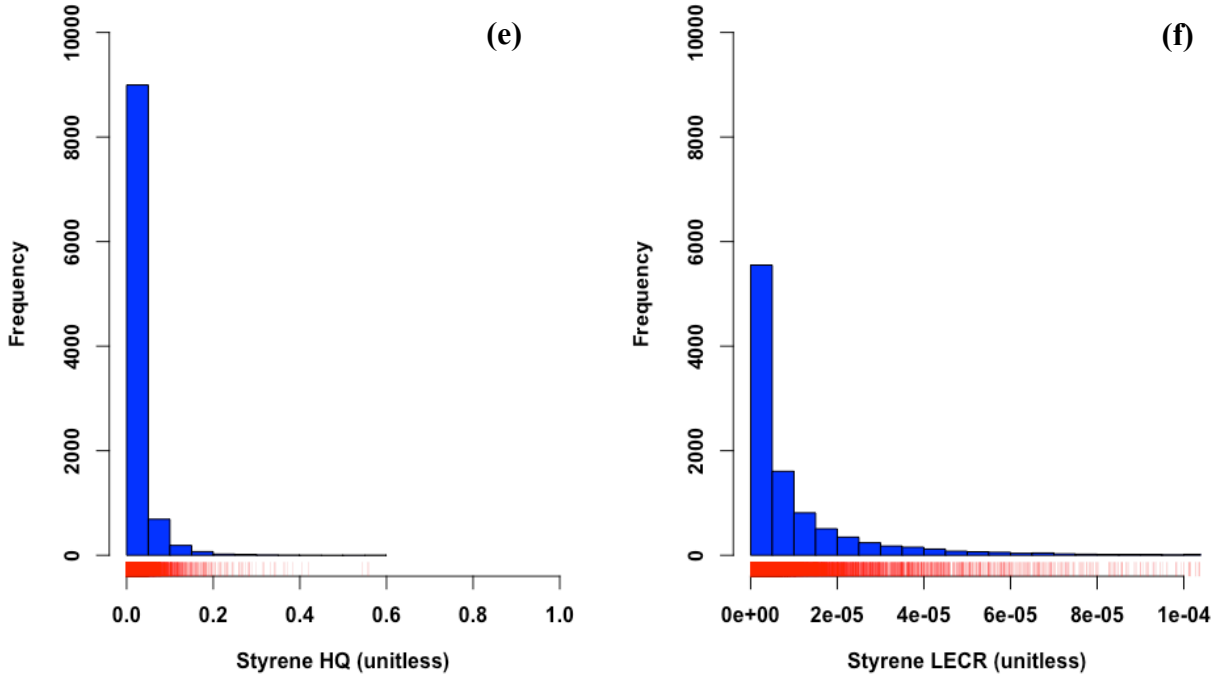


Figure 3-7. Risk assessment for post cured styrene emission: (a) HQ estimation for composite cured at 65.5°C/50 min composite, (b) LECR estimation for composite cured at 65.5°C/50 min composite, (c) HQ estimation for composite cured at 65.5°C/100 min, (d) LECR estimation for composite cured at 65.5°C/100 min, (e) HQ estimation for composite cured at 93.3°C/50 min and (f) LECR estimation for composite cured at 65.5°C/50 min

Figure 3-7 continued



The effect of ventilation on stochastic health risks associated with the inhalation of post-cured styrene emissions after composite manufacture/ Lab scale

Ventilation of post-cured styrene emissions reduced the unacceptable LECR% in all curing conditions compared with the corresponding values prior ventilation. Unacceptable LECR% values were achieved for 65.5 °C/50min [10.66%], 65.5 °C/100 min [12.37%], and 93.3 °C/50 min [0.03%]. A longer curing duration increased unacceptable LECR% while approximately no unacceptable carcinogenic health risk was acquired due to higher curing temperature. Unlike HQ obtained for 65.5 °C/50 min before ventilation, noncarcinogenic HQ% greater than 1 increased to 3.01% which reached to 3.43% by higher curing duration. No noncarcinogenic HQ risk greater than 1 was observed by inhalation of post-cured styrene emission for 93.3 °C/50 min.

Table 3-4. LECR and HQ risk percentage caused by styrene inhalation from composites cured at different conditions prior and after ventilation.

	Risk Range	Risk percentage obtained from Monte Carlo simulation (%)		
		65.5 °C/50min	**65.5 °C/100min**	**93.3 °C/50min**
Prior ventilation	**10^{-6} <LECR**	93.9	78.5	77.1
	10^{-6}<LECR < 10^{-4}	76.1	57.4	76.2
	10^{-4} <LECR	17.9	21.1	0.89
	1 <HQ	0.95	8.04	0.00
After ventilation	**10^{-6} <LECR**	65.8	70.4	56.9
	10^{-6}<LECR < 10^{-4}	55.2	58.0	56.8
	10^{-4} <LECR	10.7	12.4	0.03
	1 <HQ	3.01	3.43	0.00

Risk percentage obtained in this Table is calculated based on 10,000 iterations.

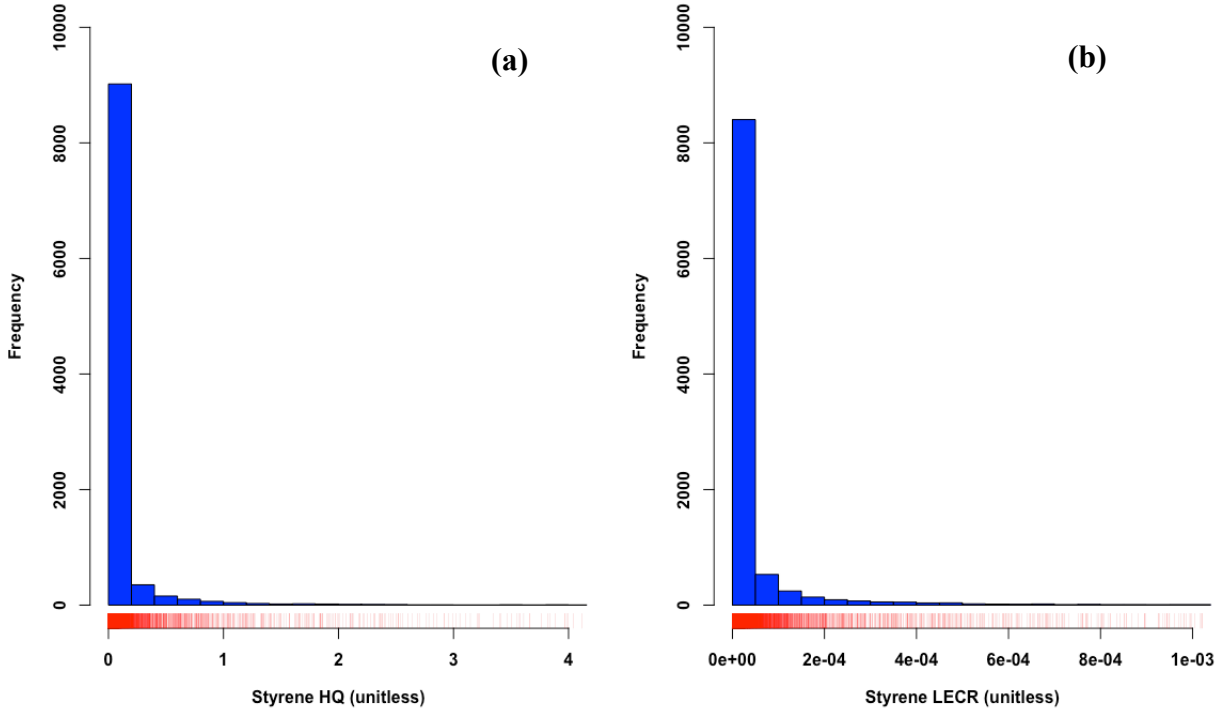
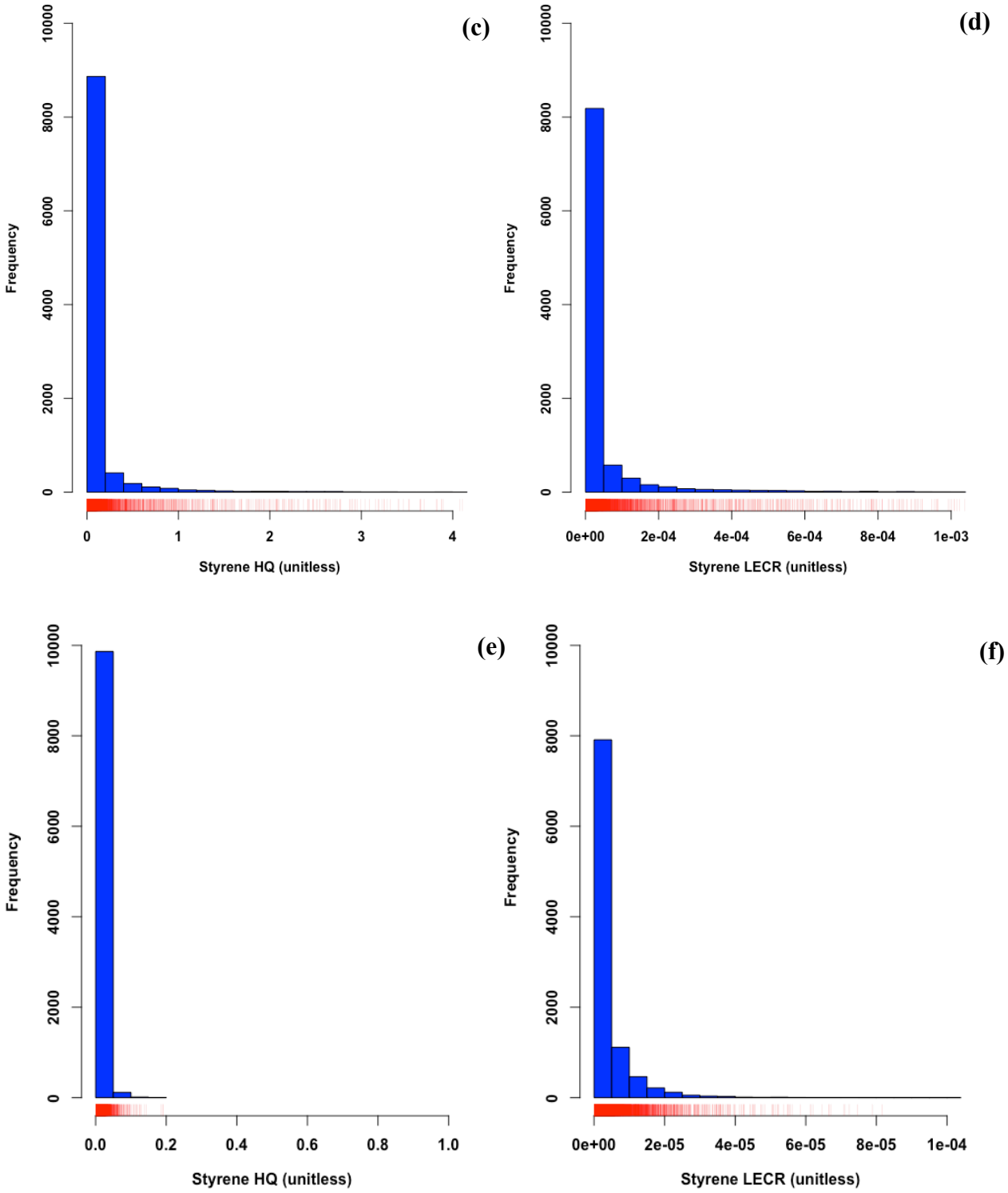


Figure 3-8. Risk assessment for post cured styrene emission: (a) HQ estimation for composite cured at 65.5°C/50 min composite, (b) LECR estimation for composite cured at 65.5°C/50 min composite, (c) HQ estimation for composite cured at 65.5°C/100 min, (d) LECR estimation for composite cured at 65.5°C/100 min, (e) HQ estimation for composite cured at 93.3°C/50 min and (f) LECR estimation for composite cured at 65.5°C/50 min

Figure 3-8 continued



3.5 Implications

The goal of this study was to better understand health risks associated with occupational chemical inhalation during CIPP manufacture/installation and use and identify data-gaps. The objectives were to (1) compile and review existing CIPP practices from publicly reported data; (2) conduct quantitative health risk assessments from CIPP related practices for workers in lab and field scale; and (3) provide guideline for better occupational and public health protection.

Limited chemical air testing data exists for CIPP worksites which inhibited generalizations about worksite health risks. Evidence indicates while styrene has been commonly detected at CIPP worksites, more chemicals are discharged into the air. From 18 air testing studies found, 6 studies only quantified styrene concentration in air, and the 2 most recent studies confirmed the existence of another organic vapor compound at CIPP installation sites by air sampling: divinylbenzene and methylene chloride. In one study, in addition to styrene, 18 other compounds were tentatively identified. A multiphase mixture of organic vapors, water vapor, particulates, and partially cured resin also found discharged into air at steam-CIPP worksites which this risk assessment did not consider. The chemical plume contained a variety of additional chemicals that were not considered in this study, where the condensed phase contained up to 4,300 ppm_v of styrene. Statistical analysis (i.e. Kruskal Wallis analysis) showed that styrene air concentrations of only two of the nine studies, captured at different sites/days, could be pooled and analyzed for the risk assessment, further limiting data available. These studies used were a: UV curing CIPP study conducted by NIOSH [3] and steam curing CIPP studies conducted by Ra et al. [7]. Therefore, the concentration data of different sites/days in each study were combined and considered as a single data set. Monte Carlo simulation was then conducted over them, separately.

For both the UV and steam CIPP studies, negligible noncarcinogenic health risks were found, but worker carcinogenic health risks were determined to be considerable. For UV curing, approximately 14% of HQs were greater than 1 and 10% of the HQs exceeded 1 for this number for steam curing was around 10%. Around 95% and 98% of the styrene LECR values in for the UV and steam curing studies, respectively were considered within the acceptable carcinogenic risk level.

After a composite was manufactured from the laboratory CIPP resin, post-cured styrene emission monitoring data also indicated that higher curing duration increased to an unacceptable LECR% from 17.86% to 21.12% while post-cured styrene emission from the composite

manufactured at greater temperature reduced it to 0.89%. For non-carcinogenic risks, post-cured styrene emission from the composite heated from longer duration increased HQs greater than 1 from 0.95% by roughly 7% and reached to 0 by post-cured styrene concentrations emitted from the composite cured at higher temperature. Ventilation also diminished the unacceptable LECR% in all composites but did not reduce the carcinogenic health risk to an acceptable level. HQ% greater than 1 increased after ventilation for 65.5°C/50 min while for 93.3°C/50 min all HQ were less than 1.

Study results are important as they indicate occupational exposure risks to workers and the lack of available air testing data that inhibited a more thorough understanding of health risks. NIOSH [3] has conducted one UV CIPP health hazard evaluation, and additional studies are recommended. Additional occupational testing studies should involve chemical identification and quantification during and after CIPP manufacture. In addition to inhalation exposures during the curing process, inhalation exposures also can occur inside resin delivery trucks, when handling materials onsite, cutting the new CIPP, and cleaning up. Identification of non-styrene components present in a chemical mixture workers are exposed to when styrene has an overwhelming analytical signal is also needed. Kobos et al. (2019) found the non-styrene compounds present can prompt inhalation toxicity for CIPP chemical plumes. Also needed are risk assessments to consider other components of the multi-phase chemical plume such as water vapor, particulates, partially cured resin. Post-CIPP manufacture, work is needed to determine if ventilation of newly installed CIPPs can reduce the overall risk to workers should they enter or work near the end of those pipes. Chemical exposure associated with dermal pathway as well as the significance of clothing contamination is also recommended. The 2017 documented CIPP worker fatality, discovery that styrene levels exceed IDLH levels at multiple worksites when so few have been tested underscores the need for occupational safety officials to better engage this industry. Until additional air testing data and risk assessments are available, workers should avoid areas associated with chemical fallout, wear respiratory and dermal protection, and not permit emissions to exit the CIPP manufactured by chemical capture. CIPP companies are also advised to contact NIOSH for a free health hazard evaluation. Regulators are also encouraged to consider examining worker safety.

3.6 Acknowledgement

This research was funded by National Institute of Environmental Health Sciences grant ES030783, Purdue University and Ohio State University.

3.7 Declaration of Interest

AJW, 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 technologies for capturing, identifying, analyzing, and addressing emissions that are potentially hazardous to the environment and humans. The invention was developed with support from rom US National Science FoundationCBET-1624183 Grant.

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APPENDIX A

A.3.2 California Investigation of Stormwater Pipes

A.4. REFERENCES SPECIFIC TO THE SUPPORTING INFORMATION

A.1. INTRODUCTION

Table A.1. List of reported CIPP caused air contamination incidents found by the authors and styrene concentration reported in air

Information presented in the table is verbatim or summarized from the references; Table Notes: nr = Not reported in the reference; PERSONAL COMMUNICATION indicates the source contacted co-author Dr. Whelton individually; FOIA indicates records were obtained from a utility by a Freedom of Information Act (FOIA) records request. Information obtained from that request, where applicable, was described. FOIA requests were submitted to the following organizations based on input from CIPP industry representatives and author contacts: Bureau of Engineering, City of Los Angeles, CA; Orange County Sanitation District, Orange County, CA; St. Louis Metropolitan Sewer District, St. Louis, MO; Citizens Energy Group, Indianapolis, IN; City of Chicago Division of Water Management, Chicago, IL; DC Water, Washington, DC; Washington Suburban Sanitation Commission, Laurel, MD. Citizens Energy Group did not provide documents to the authors in response to their January 2017 FOIA request by the time this manuscript was submitted.

Incident Location (Year)	Styrene	Description of events from reference
West Lafayette, IN (2016) [1]	nr	Fumes entered a University campus office building through floor drains; chemicals were generated by a nearby CIPP sewer pipe repair activity; building inhabitants complained to the University safety department and onsite CIPP contractor about odors; doors were opened to ventilate building before the safety department representative arrived to investigate; fire department was not called; University safety department conducted spot PID testing after building ventilation; contractor stated there was no health risk just an unpleasant odor.
Good Hope, IL (2016) [2]	nr	Report that ‘steam’ filled the post office four different times; no fire department called; lateral not plugged allowed chemical plume to enter building; "It blew the water out of the toilet," Town Manager said. "It blew the wax seal out because steam was coming out between the floor and the toilet, and steam was coming out of the toilet….and it was coming out of the roof vent. I came up here six times." I got phone calls from the post office out of Bloomington, out of La Harpe, out of Galesburg and like three times up here...The first time, it ruined their computer, and they had to replace their computer inside. It was so wet, there was water dripping from the ceiling. Everything in there was just covered, and the floors were just sopping wet.”
Madison, WI (2016) [3]	nr	Hazardous materials team responded; odor-permeating basements of local businesses and exiting storm drains; The reporter stated, “A white haze that was unidentifiable on monitoring equipment was seen coming out of a storm sewer drain, so firefighters called in the hazardous incident team. Chemical identified was styrene.” "An employee of the CIPP company said they used styrene and the chemical had been disposed of in a drain about four blocks away," per the fire department.

Table A.1 continued

Bethlehem, NY (2016) [4]	nr	Reported stated that there was a foul smell up and down the street where cured in place pipe installation for sewer repair was occurring; Insituform hired by town for sewer work; Residents were asked to cover toilets.
Cheetowaga, NY (2016) [5]	nr	Resident complained “it automatically takes your breath away. You're like what is that smell?” The Cheektowaga resident said it's coming from a silvery liquid that settled in her basement sump pump. It stems from sewer work performed by a company called Insituform last week. The letter also said homeowners might experience an odor. Resident said “I woke up in the middle of the night sick to my stomach from it.” Resident said she contacted Insituform and they did come and check out the problem. But, she said it hasn't been resolved. Resident worries what kind of effect the smell might have on her health. “… What is causing that smell?” The Town of Cheektowaga said they've received a handful of complaints. It said the gas is coming through a faulty trap or an illegal sump pump. The town recommends running water through the trap to fix it. But, it is on the homeowner to fix a faulty trap or an illegal sump pump.
Cornwall, UK (2016) [6]	nr	Resident claimed, “Suffered from burning eyes, abdominal pain, aching joints and memory loss at their home”; Water utility stated, "No evidence their work caused the family's ill health. As a gesture of goodwill, they were paying for the family to stay in a B&B.” In a letter, specialist doctor at hospital said, “resident presented with symptoms of styrene poisoning and was advised not to enter the house until it had been cleared of the chemical.” Water utility stated, “styrene is widely used across the country to line water mains and sewers and there is no regulatory requirement to wear respiratory masks whilst working with the substance.”
Alexandria, VA (2016) [7,8]	nr	FOIA: Fire department responded to a resident complaint; collected dräeger tube air sample; RK&K, Inc. contractor took them to the downstream manhole. Later, someone with a baby came by and said they called the fire department; fire department told her to open her windows and pour water down her basement drain. RK&K, Inc. contractor told person to additionally put a wet rag over the opening. RK&K, Inc. contractor thinks some people are more sensitive to styrene than others or their house somehow captures more odors due to their lateral location. Contractor recommends set up a fan “even if it is for show.” Per RK&K, Inc., “There was no visible steam or odor from the manhole although [fire department] took their reading about 4 inches from the bags' end which will/may result in a high reading. They did not return for further discussions.”

Table A.1 continued

Alexandria, VA (2016) [9]	0 ppm	FOIA: City spoke with resident who filed odor complaint April 14, 2016 to report styrene odor; RK&K, Inc. contractor visited home and used PID, which stated "0.0 ppm at all times when they were in the house. "Homeowner called again on April 27, 2016, 13 days after the lining cool down, to report the styrene odor again. RK&K went to the home again and this time there was a reading as they entered the front door. RK&K, Inc. walked outside, went back in and the reading was 0.0 both at the door and at the basement trap; Homeowner called May 16, 2016 (today) to request another reading; City explained to him that the work was accomplished over 3 weeks ago and that if there was an odor it was not caused by the sewer lining.
North Tonawanda, NY (2016) [10]	nr	Reporter stated "For about a month, noses have been picking up a distinctive smell near the site of the former Durez Corp. plastics and chemical plant that was torn down in 1997." Sewer pipes were being repaired with cured in place pipe and the odor was suspected to be caused by the construction activity per the City Engineer. The reporter stated that community air monitoring was performed throughout the project.
Québec, CN (2015) [11]	nr	PERSONAL COMMUNICATION: Fumes stayed in building for 1 month; installers claimed styrene trapped underground and drifted into house; installers installed blowers; after the 2nd month (1 month of ventilation) odor went away.
Picayune, MS (2015) [12]	nr	Calls to utility during weeks and typically with older homes; Utility suspects most residents that notice a smell may be living in a home with inadequate vent or trap which is allowing the odor to enter the home from the wastewater lines; CIPP contractor recommends residents add water to sewer traps and if smell intrudes home they should open windows for a short time; CIPP contractor assures the smell is not harmful and cites a 2001 study to determine the levels of styrene concentration during the installation and a worst case scenario; Contractor states during testing the concentration detected with a working trap was 0.0002 ppm while faulty vents had 0.1 and 0.2 ppm; Claimed person standing over a manhole would experience 3.2 ppm styrene; Contractor reported that if odor does enter house it could remain for up to two days.
Lincoln, NB (2015) [13]	nr	Several homes evacuated; fire department called and stated "The readings in one of the houses was significantly high, higher than expected levels or safe levels;" Fire department chief stated "When they inject steam into the sewer line and in that steam is a chemical called styrene." City health specialist stated, "Our assumption is it pushed a bunch of this odor through the sewer line, on down stream of where they were working." Fire department opened windows in the affected homes and set fans up to help aerate them, and residents were allowed back inside later that day.
Ottawa, CN (2015) [14]	nr	Residents and businesses complained about chemical exposures: "The smell was so intense that I had to let my secretary go home because she was ready to vomit." The city paid for one family to be put up into a home; the city stopped CIPP work to investigate; city recommended work only be conducted in summer when buildings can be better aired out.

Table A.1 continued

Ottawa, CN (2015) [15]	nr	Residents state that odors come through drains and circulate in the building through air vents and started about a month ago, "Using incense to cover the smell"; Ottaway Public Health monitored air; City Hall recommends that residents open their windows until the smell goes away; the business owner interviewed however did not have windows that can be opened.
St. Petersburg, FL (2015) [16]	nr	Resident filed complaint to city that "For two days having some strong chemical (epoxy or glue-like odor) coming from drains periodically. The smell has resulted in irritation to the back of our nasal passages in just a short period of time breathing it."
Antigo, WI (2015) [17]	nr	Illness symptoms reported by child; pregnant woman concerned about the exposure; firefighters responded to homes; firefighters said, "According to the MSDS sheet it was not safe to just be breathing those inhalants." Resident explained, "The basement was incredibly full of fumes, and whatever they're shooting into the pipes was shooting up out of our drain pipe into our basement so forcefully it was actually whistling."
Alexandria, VA (2015) [18-21]	nr	FOIA: City tells residents, "Higher ambient temperatures have a tendency to exacerbate odors associated with the relining." Homeowner association representative stated, "Different homes very near to one another have been affected to widely varying degrees. Just speaking in my home, the basement and main floors were worse than the second floor. Some houses were not affected. In addition, when all windows were opened, fumes dissipated fairly well and resident thought the threat was over. When resident closed windows, and turned on air conditioning, and left to go to the store, fumes became bad again. The fumes were also bad last night even though the crew finished work about 5:30pm the day before, albeit not nearly as bad as while they were working." City declared, "People and Pets are safe because the contractors are not working with enough styrene to be dangerous. Styrene is only dangerous in large quantities."
Kensington, MD (2015) [22,23]	nr	FOIA: Resident called utility and left message about complaint and claimed he and several neighbors who were ill due to the smell exposure that caused a nose bleed; utility CIPP contractor was lining a 30 inch diameter sewer pipe in the area with steam curing and utility suspects that would cause the styrene odor; utility spoke with one resident who claimed that there was a shift in the wind causing the odor to linger about his house and his neighbors causing temporary illness; utility staff explained they are working to figure out what chemicals were used; follow up by utility indicates that, "Customers contacted WSSC regarding the resin odor which is typical when lining sewers." CIPP contractor installation failed (400 linear feet of the 500 linear foot liner) and contractor has been cutting/removing the failed liner.
Rensselaer, NY (2015) [24]	nr	Chemical entered homes from sewer CIPP lining; one resident taken to hospital; city paid for hotel rooms for 5 homes impacted. Resident claimed, "Styrene permeated the clothing in their drawers, closets, and couches."
Botany Village, NJ (2015) [25]	nr	Resident reported strong and fragrant sewer odor pervaded the neighborhood; yearlong project.

Table A.1 continued

St. Louis, MO (2014) [26]	nr	Residents report odors in homes; Described them as “toxic, permanent-marker-type smell.” Sewer utility [Metropolitan St. Louis Sewer District] spokesperson stated: The heating/curing process is known to release smells that, while gross and annoying, don't pose a health risk, says LeComb. "Odors do come off sometimes, and we certainly apologize for the inconvenience. This is a very large sewer, so it'll have more of an odor impact than we usually see," says LeComb. However, Lacomb adds, it is possible for the smell to emanate from inside a home, likely through dried-out sink traps or basement drains. If you start to smell something funky indoors, he suggests pouring two or three cups of water in the sink or down the drain to seal those smells away.”
Prairie Village, KS (2014) [27]	nr	PERSONAL COMMUNICATION: Resident reported the smell of superglue in house, headaches and nostrils burning; utility contacted and told resident vapors nontoxic; windows and doors opened for ventilation, but odor remained; county did not investigate and told resident chemicals were nontoxic.
Manchester, UK (2014) [28]	nr	Steam cured CIPP was installed; residents complained about odor, and health effects such as headaches and nausea. “A number of households were relocated to stay with relatives or in hotels. Subsequent investigations indicated that a small breach occurred in the liner during the early curing process. This allowed chemicals to escape and enter nearby properties, most likely through connections to the culvert.”
Baltimore, MD (2014) [29]	nr	PERSONAL COMMUNICATION: Resident evacuated house after detecting odor caused by CIPP sewer pipe repair activity nearby and experienced chemical exposure symptoms; sought medical attention; fire department responded conducted air testing but discrepancy between resident observed results [400 ppm styrene on draeger tube] and fire department filed report [nothing found]; moved out of house for 1 month; odors got stronger when it rained.
Illinois (2014) [30]	nr	PERSONAL COMMUNICATION: Resident claimed fumes from CIPP sanitary sewer installation backed-up into private residences and residents reported chemical exposure symptoms.
Kensington, MD (2014) [31]	nr	FOIA: Resident called utility and filed a complaint, chemical odor from nearby sewer work happening behind his house; utility staff recommended borrowing language provided to them by the CIPP when responding to the resident. The contractor language stated, but not limited to, “Don’t be alarmed. The CIPP industry is a worldwide 100 billion dollar industry that installs more than one million feet a year and thousands of people are involved with no diverse effects.”
Nashville, TN (2014) [32]	nr	Complaints from residents about chemicals emitted during CIPP activities; “We're having a hard time breathing, getting dizzy," Zach Shedd said. "Pretty much have to leave the house. It's got a very think, pungent smell, like burning plastic. When you inhale or breathe it, it literally coats the back of your throat." Utility stated “There is no research or studies showing that this is hazardous, styrene is actually in things we use every day. It's in certain foods, like strawberries or coffee. It's in automobile exhaust."

Table A.1 continued

Philadelphia, PA (2013) [33]	nr	PERSONAL COMMUNICATION: Resident took 4 month old baby to a medical center after exposure to fumes inside a house generated during nearby CIPP sanitary sewer repair.
Fayetteville, NY (2012) [34]	nr	Odors permeated into nearby residences; residents complained and evacuated their homes; city engineer stated odor "Is not toxic, not dangerous"; contractor stated, "Odor from it is not harmful. There is no health risk. The contractor's personnel are trained in handling the liner properly, and once it hardens, there is no residual left. There is no exposure other than an odor blown off the material. It's no different than smelling turpentine or gas."
Brisbane, AUS (2012) [35]	nr	PERSONAL COMMUNICATION: Resident reported that odors were detected and exposure lasted 5 days in home; person hospitalized; health department investigated and demanded home be decontaminated; resident reported his and his neighbor's pets died.
Ontario, CN (2012) [36]	nr	Odors detected kilometers from worksite and within nearby private residences; exhaust fans used for manholes.
Ontario, CN (2012) [37]	nr	CIPP wastewater discharged to sanitary sewer; odors reported near worksites.
Worcester, MA (2011) [38]	60 - 70	Fumes caused daycare center evacuation; headaches reported; emergency responders called to site; Fire chief reported, "For the styrene to be dangerous, it needs to be 10 times that amount."
Minnesota (2011) [39-41]	nr	Odor caused by resin spill prompted building evacuations; residual remained for five months.
Port Huron, MI (2011) [42]	nr	Daycare owner sent children home early and remained closed; claimed odors made staff and children sick and dizzy; residents reported strong odors in homes; firefighters responded and said no toxic or flammable fumes in homes; officials told residents to pour water in their traps to keep odors out of homes.
Port Huron, MI (2011) [43]	nr	Firefighters responded to reports of a strong odor; resident claimed it smelled like turpentine, started puking, removed her three dogs, and opened house windows.

Table A.1 continued

Southfield, MI (2011) [44-46]	nr	Five students and one staff member at high school transported to hospital after becoming nauseated; 20-25 classrooms affected; fire fighters responded with local HAZMAT unit; odor reportedly entered building day before and students were moved by teachers to different part of building; Oakland County Water resources (water utility) manager stated, "At levels present in the resin, neither the styrene nor the other chemicals were toxic." Civil Engineer at water utility stated, "It's not uncommon to have people complain about the odor, and we have had complaints (about the odor) from the public before, but we've never had people go to the hospital until this incident. Up to this point, it's really just been about odor. We have had complaints about eye irritation and gastroenterological problems, but nothing worse than that. It's never really been a public health concern…..the process only produces one to three parts per million when you're exposed."
Saugus, MA (2011) [47,48]	nr	Firefighters ordered evacuation of elementary school because of strong odor; dizzy and light-headed symptoms reported; the following day, after the building had been evacuated, the state health agency conducted air testing using a PID; odor detected outside above a manhole cover but PID did not respond; PID did not respond for VOCs in the in-building locations.
Pittsburgh, PA (2011) [49]	nr	Two schools evacuated; elementary and high school students evacuated for fear of gas leak, but odors turned out to be caused by nearby CIPP operation; theory was "The wind was blowing in such a way that the smell drifted to the schools, where windows were open." Utility stated, "Did not believe chemicals used in the process would cause any danger to people in the schools, especially since schools were not in close proximity to the work and the contractors doing the work aren't required to wear masks or other breathing apparatus."
Clear Creek, CO (2011) [50-52]	nr	"Source Type: Culvert Lining. Cause Information: Styrene was released to the water of Clear Creek after it had been used on 2/4/11 by CDOT [Colorado Department of Transportation] as part of the process of lining a culvert near the water intake on Clear Creek for the Loveland Valley Ski Area. The ski area noted the smell on 2/7/11 and did a test that showed the presence of styrene." It had contaminated their drinking water. "…February 7, 2011 at 1125 a.m. the Clear Creek County Environmental Health Dept received information of a possible contamination of the waterway of Clear Creek at the Loveland Ski Area. An elevated, but unknown amount of styrene has been detected, and is suspected to be at the CDOT culverts …" Investigation discovered unknown amount of uncured resin was discharged to creek and styrene as well as other compounds known to be present in resin or produced during CIPP manufacture were detected in downstream waterways. Community affected by drinking water contamination was provided alternate drinking water supply followed by actions to remediate the affected area and wide area environmental sampling.

Table A.1 continued

Birmingham, UK (2011) [53]	15 - 200	Odor complaints reported by residents; residences evacuated homes at contractor's recommendation; one resident claimed, "My 3 children (6yrs, 4yrs, 17 mths) have all been sick during the night and we have all suffered headaches, dizziness, tight chests and nausea. My baby has swollen & inflamed tonsils & throat which the GP feels is due to the irritation caused by styrene." 3 days after, reported styrene above 20 ppm in one home still; 8 days after incident 100 ppm styrene measured in one home and resident reporting chemical exposure symptoms; responders theorized there was a leak in the lining used for styrene CIPP sewer pipe repair; building ventilation conducted; health department did not conducted testing, relied on contractor results to make safety decisions; contractor did not disclose styrene present in homes above health limits until days after health agency involved.
Williams Co. Village, OH (2010) [54]	nr	Residents complained, "Smelling a glue-like odor inside their houses for the last two weeks, and have suffered from severe headaches, nausea, and dizziness." Some claimed, "They only began to link their symptoms to the fumes this week after the odor intensified." Family began experiencing upset stomachs, diarrhea, severe headaches, dizziness, and lethargy about 2.5 weeks ago. Residents moved out of house and afraid to return home; some went to emergency room to seek help, hospital told them they do not have facilities to test for the chemicals. Village manager evacuated 19 families from their homes and put them up in a hotel for 2 nights at a total cost of about $3,000. Town manager stated, "There's flu going around. I can't tell you why they were sick." Town manager said, "Smell came from a chemical called styrene which was used as a sealant for the sewer pipeline… odor got into people's homes through floor drains." Reporter stated other substances - acetone, a polyester resin and chemical products named "Perkadox 16" and "Trigonox 42S" - also were used during the project.
Helena, MT (2010) [55]	nr	Fire department evacuated affected building because of complaints of strong odors, nausea, and headaches.
Helena, MT (2010) [56]	nr	Workers at local businesses left the office after smelling the CIPP causing odor. Businesses opened doors to ventilate their buildings; city hired contractor to test air, but was unaware of complaint by business interviewed by reporter; the prior week firefighters evacuated an area due to odors; businesses filed insurance claims due to lost business.
Helena, MT (2010) [57]	nr	Businesses closed; residents reported chemical exposure symptoms to include headaches; part of the old sewer pipe being repaired was exposed in a building's basement, making it easier for the chemicals to escape. Complaints about the smell of paint thinner or glue caused firefighters to evacuate the building 3 days ago; at that time a peak of 67 ppm in the building's basement was detected; following day, it was 10.2 ppm on average, and 3 days later, the level was 2.5 ppm. City workers set fans to pump fresh air into the building, which made the problem worse by pushing gases into other areas.

Table A.1 continued

Lorain County, OH (2010) [58]	nr	Residents claimed, “They became nauseated or dizzy last week from 8 days ago from an overpowering chemical smell coming from their toilets or floor drains.” CIPP contractor stated, “Styrene odor can be irritating to some people but that rarely does anyone become ill.” 5 days after odor, engineering contractor conducted testing per residents; resident claimed, “Went in the bathroom and the pressure had shot up water out of the toilet -- and the smell just about knocked you over…couldn't breathe right and got a headache from it….felt confused, groggy, like I was drunk or slurring my speech."
Arlington, VA (2010) [59]	nr	Nearby CIPP installation caused odor; residents called, fire department responded; city publicly claimed, “The resin is not harmful to pets or people.” City claims pouring water in sewer traps “prevents sewer odors from entering the home.”
Willemette River, OR (2012) [60]	nr	Contractor discharged steam cured CIPP waste to Willamette River; “Styrene levels were so high that the responder had to wear a respirator to collect samples.”
Bellevue, WA (2010) [61,62]	nr	CIPP storm water pipe cured by steam; plug failed and released waste to local waterway including styrene two different days; odors detected; city closed area to the public near spill to prevent exposures; odor remained for more than 14 days after the spill.
Pittsburgh, PA (2009) [63]	nr	Firefighters evacuated apartment buildings; initially suspected cyanide gas, but styrene was ultimately detected from nearby CIPP.
Des Moines, IA (2009) [64]	nr	Odor inside government building caused by CIPP nearby caused building inhabitants to evacuate twice; downtown workers and residents also noted the odor. Fire department stated, “Smell is harmless and will dissipate quickly.”
Cambridge, MA (2008) [65]	nr	Contractor released contaminated process water down sewer line which exited downstream manhole; fans were used to divert fumes away from a neighborhood; cease and desist order issued by utility to contractor.

Table A.1 continued

Snellville, GA (2007) [66]	nr	Resident contacted health department about chemicals entering homes during a recent storm sewer rehabilitation project and reportedly caused neighbors to experience headaches. Health department contacted the contractor who installed in-place polymer liners. The process involved running a polyester resin tube inside existing storm pipe, then filled with 180 degree water. A styrene based thermoset resin and catalyst system was used to cure the resin in place when the 180 degree water was added. According to the contractor, during this process, all the styrene was gassed off. Upon complaint by the resident, the contactor discovered an illegal drain pipe coming from the home that was connected to the storm pipe. Resident ventilated the house during the day, which health department told him was the right thing to do. Four days after the incident, the resident stated that the smell had diminished, but was still present. The health department informed the resident that the NIOSH relative exposure limit was set at a TWA of 50 ppm. Without measuring the actual indoor air concentration, the health department reported that there was no way of knowing whether his family was exposed to styrene gas above the REL. The resident continued to ventilate the home and the health department informed the resident that this was all that could be done and that the styrene gas would eventually dissipate.
Somerset, UK (2007) [67]	nr	Foul CIPP styrene odor permeated into residence through drain because of nearby installation; resident stated odor persisted for 12 days and rejected the offer of a masking spray. Utility (Wessex Water) stated, “The smell of styrene is not harmful and is generally short-lived.”
Brooklyn, NY (2007) [68]	nr	Foul CIPP styrene odor permeated into buildings through drain because of nearby installations; Department of Environmental Protection adds pine deodorizer at the site cover the smell; odors first detected in 2006.
Boston, MA (2007) [69]	nr	CIPP installation prompted chemicals to enter the basement of a nearby restaurant.
Ottawa, CN (2004) [70]	20, 115	Venting determined to be helpful to prevent air backup into nearby residences/ buildings.

Table A.1 continued

Alexandria, VA (2004) [71]	500	HAZMAT team responded because of styrene vapor backup into nearby buildings; illness symptoms reported by residents and residents evacuated homes. Police officer stated he felt nauseated, light-headed, short of breath and his eyes were burning, like they were on fire. Went to urgent-care center and was diagnosed with an inhalation injury. Another resident who worked at the World Bank said, "The smell was so strong that he was afraid to return to his home with his 19-month-old son.". He reported vomiting repeatedly the next day, and thought he had food poisoning. City officials said yesterday, "That the toxic fumes might have affected more residents than they initially disclosed." Hose left behind by contractor was emitting 500 ppm of styrene; public works conducted tests in sewer and homes and declared styrene was "within acceptable levels"; city recommended residents fill "dry pipe traps with water to prevent fumes from entering through pipes. Workers also planned to ventilate manholes and flush sewer lines with water. Contractor stated, "On rare occasions, we've had people overreact, as we've had in this situation, and go to the hospital as a result of smelling the styrene . . . which can cause your eyes to burn and your nose to run, much like smelling ammonia."
Milwaukee, WI (2004) [72]	0.01 - 0.32; 30 ppm_v for total VOC	An office building became contaminated; building evacuated for 2 days. Occupants complained about irritant symptoms and strong odor. US federal health agency investigated; styrene and other VOCs detected; 4 months required to reduce styrene levels to background; greatest styrene levels detected in basement; ASTDR declared the exposures a public health hazard due to styrene levels exceeding acceptable ATSDR chronic (long-term) exposure levels. Recommendations made to ventilate the building basement to reduce exposure and odor. A temporary exhaust system was installed in the building basement near the point of vapor entry.

A.2. MATERIALS AND METHODS

A.2.1 Photoionization detectors (PID)

RAE system ppbRae 3000 PIDs (10.6 eV lamp) were calibrated with isobutylene at 10 ± 0.03 $ppm_{v.}$ PIDs were operated with a styrene correction factor of 0.43 and firmware v2.13.

A.2.2 Analytical standards

A variety of analytical standards were used to examine GC/MS results. They include 1,4-dichlorobenzene-d4 (CAS# 3855-82-1, Supelco), butyl hydroxytoluene (BHT) (CAS# 128-37-0, Supelco), benzaldehyde (CAS# 100-52-7, Sigma-Aldrich), acetophenone (CAS# 98-86-2, Sigma-Aldrich), benzoic acid (CAS# 65-85-0, Supelco), phenol (CAS#108-95-2, ARCOS Organics), 1-tetradecanol (CAS#112-72-1, Sigma-Aldrich), EPA phthalate esters mix (CRM48805, Supelco), 4-*tert*-butylcyclohexanol (CAS# 98-52-2, ACROS Organics), 4-*tert*-butylcyclohexanone (CAS# 98-53-3, ACROS Organics), tripropylene glycol diacrylate (TPGDA) ≥90% stabilized with MEHQ (CAS# 42978-66-5, TCI America), naphthalene-d8 (CAS# 1146-65-2, Supelco), toluene-d8 (CAS# 2037-26-5, Sigma-Aldrich), phenanthrene (CAS# 85-01-8, Supelco), chlorobenzene-d5 (CAS# 3114-55-4, Supelco), and styrene ≥99% that contained 4-*tert*-butylcatechol stabilizer (CAS# 100-42-5, Sigma-Aldrich).

Calibration curves were also created for methylene chloride extracts. These were for styrene (R^2=0.998 for medium range (240 ppb to 2.5 ppm) and R^2 for the high range (R^2=0.995, 0.997 & 0.998 for concentration in the range of 120.8 ppb to 7.25 ppm), benzaldehyde (R^2=0.995, 0.998 for concentration in the range of 69.9 ppb to 20.88 ppm) and BHT (R^2=0.995 & 0.996 for the concentration in the range of 43.5 ppb to 4 ppm), benzoic acid (R^2=0.996, for the concentration range of 3.7 ppm to 11.2 ppm), phenol (R^2=0.999, for the concentration in the range of 22 ppb to 17.6 ppm, 1-tetradecanol (R^2=0.996, for the concentration in the range of 246.7 ppb to 5.18 ppm), 4-*tert*-butylcyclohexanol (R^2=0.998 for the concentration in the range of 1.22 ppm to 31.22 ppm), DBP (R^2=0.994, for the concentration in the range of 80 ppb to 2.4 ppm) and acetophenone (R^2=0.997, for the concentration in the range of 412 ppb to 10.99 ppm) were developed.

Calibration curves were also developed for hexane extracts. These were for styrene (R^2= 0.994, 0.998 & 0.999 for concentration in the range of 120.8 ppb to 30.2 ppm), TPGDA (R^2 = 0.992 & 0.994 for concentration in the range of 1.24 ppm to 44.66 ppm), benzaldehyde (R^2=0.991

& 0.999 for concentration in the range of 139.2 ppb to 48.72 ppm), 1-tetradecanol (R^2=0.993, for concentration in the range of 400 ppb to 30 ppm), acetophenone (R^2=0.997, for concentration in the range of 137.33 ppb to 13.73 ppm), 4-*tert*-butylcyclohexanol (R^2=0.999, for concentration in the range of 1.04 ppm to 31.23 ppm, BHT (R^2=0.994, 373.3 ppb to 23.33 ppm).

A.2.3 Site safety and equipment cleaning

To minimize chemical exposure and at the recommendation of Purdue University Radiological and Emergency Management (REM) industrial hygiene staff, the authors wore long-pants, closed toe shoes, hardhats, safety glasses, shirts, and safety vests. Nitrile gloves were worn by the authors when handling samples. Neoprene gloves on top of a double layer of nitrile gloves were worn to handle the uncured resin. A few times, contractors handed uncured resin sample to the authors using their bare hands. Air testing results obtained from the Indiana CIPP sites resulted in the authors and Purdue University industrial hygienists concluding that full-facemask respirators with carbon filters should be used for field work in California. The authors were fit tested and used full face respirators (3M 6800, North 5400) with organic vapor carbon filter cartridges (3M 6610, N75001). A site safety plan was prepared by the authors for the California field work, was reviewed by Purdue University industrial hygienists, and provided to California State University Sacramento for informational purposes. The California field work was conducted on the California State University campus.

In Indiana, the air sampling manifold was used only one time. In California, after each CIPP installation sampling event, equipment was cleaned to include the stainless steel air sampling manifolds and respiratory protection. Decontamination activities were conducted in a nearby wet chemistry laboratory fume hood using high purity acetone. Stainless steel manifold pieces were rinsed at least three times with acetone, exposed to high-pressure air purging for 5 min, and then air dried. Stainless steel caps and PTFE stoppers were used to cap the end of manifold tubing during acetone rinsing.

A.2.4 Material SDS of resin impregnated tube in Indiana

A material SDS described that resin impregnated felt contained: ITI 191024 CTDFelt 15 mil 69 (11% wt. to 29% wt.), polyester/vinyl ester resin (38% wt. to 47% wt.), amorphous fumed silica

(0% wt. to 2% wt.), styrene (15% wt. to 31% wt.), various organic peroxides (0.5% wt. to 0.7% wt.), fiber glass (0% wt. to 20% wt.), and proprietary filler (0% wt. to 22% wt.) [73]. A high molecular weight isophthalic unsaturated polyester resin, 102T/TA, with unreported composition was used for the installation [74].

A.2.5 Material SDS of resin impregnated tube in California

Vipel® isophthalic based polyester resin was used for styrene based CIPP installations [75, 76]. The material SDS indicated this resin included 0.5% Trigonox® KSM and 1% di-(4-*tert*-butylcyclohexyl) peroxy dicarbonate initiators. The resin was L713-LTA-12 and was reported to contain: Styrene (32.0% wt.) and Talc (20% wt. to 30% wt.). For the low VOC CIPP installation, EcoTek™ L040-TNVG-33 vinyl ester resin was used and the initiators were not disclosed[77].

A.2.6 Potential contractor application of a lubricant when the air inverted resin impregnated tubes were inserted into California target pipes

For the uncured resin tubes inserted by air inversion, a small amount of Crisco® may have been used by the contractors to help lubricate the tube so that it could be initially inserted into the shooter. The shooter was used to invert the uncured resin tubes using forced air into the target pipes. The degree and how much Crisco® was added was not documented by the contractors and they did not describe how much they applied. Uncured resin tube lubrication is common when tubes are inserted using air inversion. Crisco® and vegetable oil have been seen at other sites.

A.2.7 Method for extracting uncured resin tube and analyzing extracts for the Indiana and California sites

Samples of felt tube impregnated with uncured resin were obtained for each CIPP site, immersed in hexane and dichloromethane (1.69 ± 0.25 g sample / 22.87 ± 0.53 mL solvent) and stored at 4°C for four months. Extracts were filtered, diluted 10,000x and analyzed in scan mode with a GC/MS-TQ8040 (Shimadzu). The temperature program of the GC-2010 Plus started at 40°C, was held for 4 min, was ramped at 12°C/min to 250°C and held for 3 min. Purge flow and column flow (Helium) were 3.0 mL/min and 1.5 mL/min, respectively. Samples were injected in split mode (ratio 1:10) at 280°C. Quantification was performed based on response of 1,4-dichlorobenzene-d4 (internal standard, 1 ppm).

A.2.8 Method for assessment of pipe condensate cytotoxicity

Changes in cell viability for mouse alveolar macrophages and alveolar type II cells were observed for condensates collected from California CIPP installations. Mouse alveolar macrophages (RAW 264.7) and mouse alveolar type II (C10) cells were cultured individually in dulbecco's modified eagle's media containing 10% FBS and maintained under standard conditions of 37°C and 5% CO_2. Experiments to evaluate cytotoxicity were performed at 90% confluency, in 48 well plates, and in serum-free media conditions. Cells were exposed to condensates diluted to 10, 100, or 1,000 ppm of styrene, serum-free media only (controls), or 400 µg/mL of zinc oxide nanoparticles (positive control). Condensate captured from the exhaust emission point of site 2 was not evaluated for cytotoxicity due to styrene levels being too low compared to other condensate samples during the first 20 min capture period. Following a 24 hr exposure to the diluted condensates, changes in cell viability were assessed via the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay (Sigma-Aldrich, St. Louis, MO) via the instructions of the manufacturer using a spectrophotometer (Molecular Devices, Sunnyvale, CA). Briefly, following the 24 hr exposure, the condensates were removed from the cells and the cells were washed with phosphate buffered saline. Cells were then incubated with MTT at 37°C. Dehydrogenase enzymes in viable cells reduce MTT to generate purple formazan salt crystals. These salt crystals are then solubilized by dimethyl sulfoxide and transferred to a new plate. The absorbance was then quantified using a spectrophotometer at a wavelength of 570 nm. The absorbance (generation of salt crystals) is proportional to the number of viable cells present. The absorbance values from exposed cells were compared to control (untreated) cells to determine alterations in cell viability. Control cells were considered 100% viable. Exposure to the positive control (zinc oxide nanoparticles) resulted in cell viability of 23.27 $\pm$ 6.87% in macrophages and 17.12 $\pm$ 2.70% in epithelial cells (data not shown). Data are presented in the graphs as mean $\pm$ standard error of the mean and an n = 4/group, with each sample consisting of three technical replicates. Data were analyzed by two-way analysis of variance (ANOVA) with differences between groups assessed by Tukey's post hoc tests. All graphs and analysis were performed using Graph Pad Prism 6 software (Graph Pad, San Diego, CA). Statistical significance was determined when p was found to be less than or equal to 0.05 between groups. Cytotoxicity for condensate collected from the low VOC CIPP installation was not examined.

A.2.9 Method for the analysis of particulate captured and condensed from the chemical plume at the Indiana site

Three different techniques were applied to examine particulate captured and condensed from the chemical plume. Thermal stability was studied using thermogravimetric analysis (TGA) on a Q500 from TA Instruments, Inc. (New Castle, DE). Platinum pans were used with samples weight maintained between 10 mg to 15 mg, while scans were performed at 10°C/min from 30°C to 200°C. TGA was performed under nitrogen environment with a purge flow rate of 60 mL/min. Differential scanning calorimeter (DSC) analysis was performed using Q2000 from TA Instruments, Inc. (New Castle, DE). Aluminum pans were used with sample weight approximately 10 mg to 15 mg. Two heating and cooling scan were performed at a heating rate of 5^{o}C/min across a temperature range of -100°C to 200°C. Nuclear magnetic resonance (NMR) spectroscopy was performed and ^{1}H NMR spectra were collected using 32 scans on a 500MHz Bruker spectrometer (Bruker Bio Spin, Fremont, CA) equipped with Top Spin software; specimens were analyzed in deuterated chloroform.

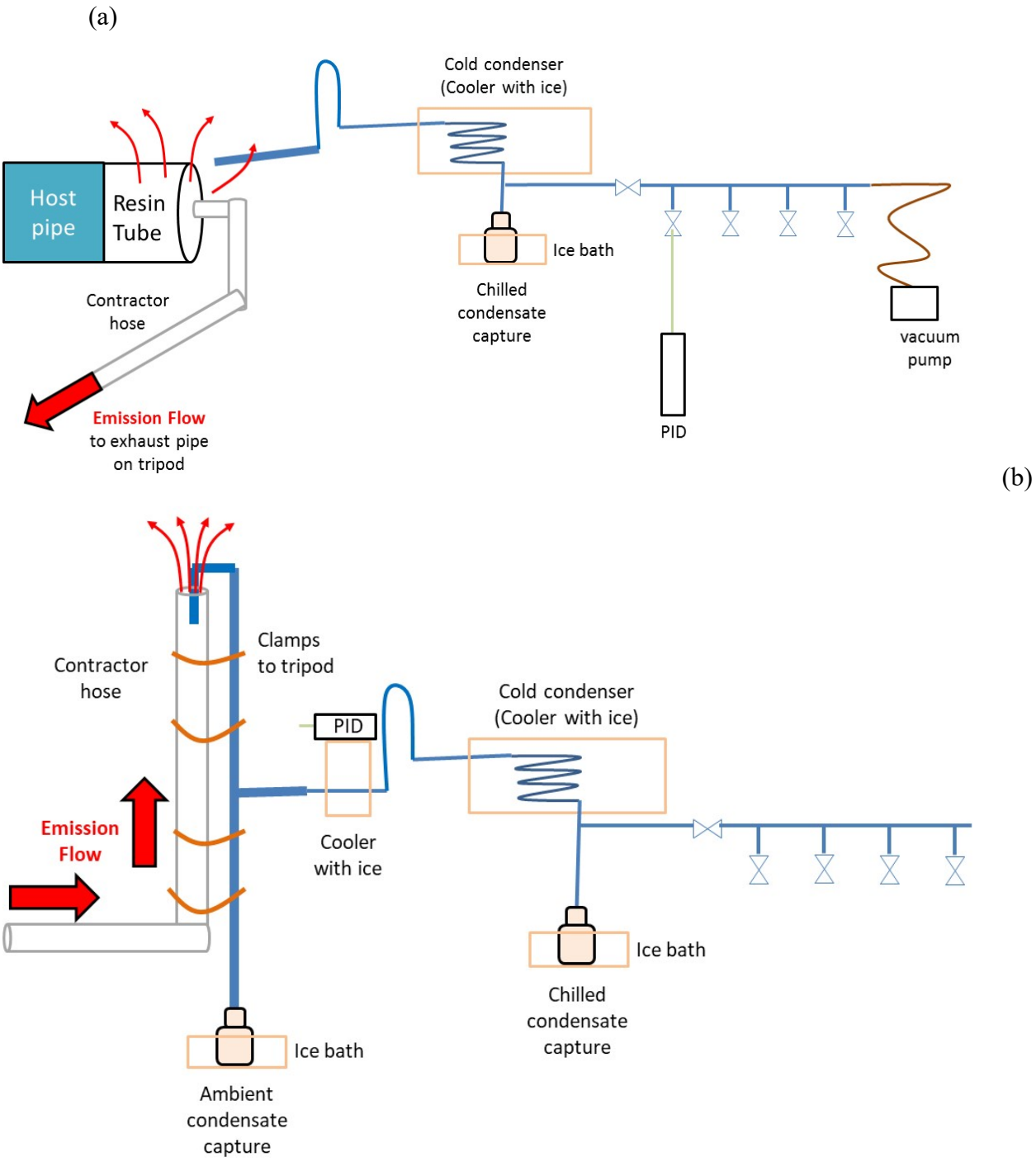
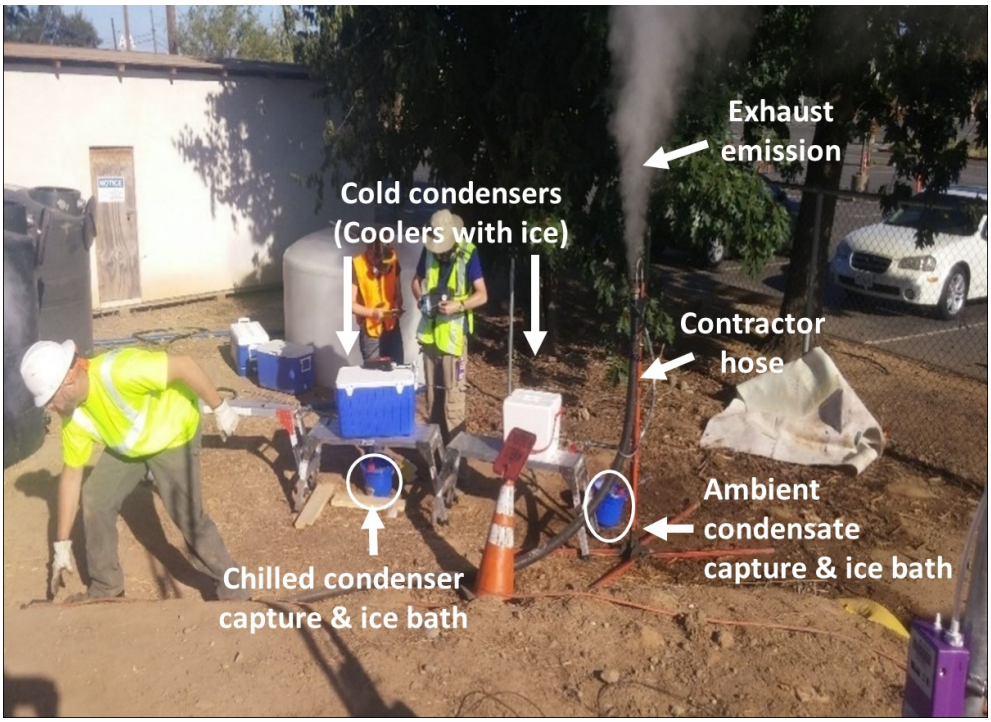


Figure A.1. Schematic diagram of California site (a) fugitive and (b) exhaust emission capture system

(a)



(b)

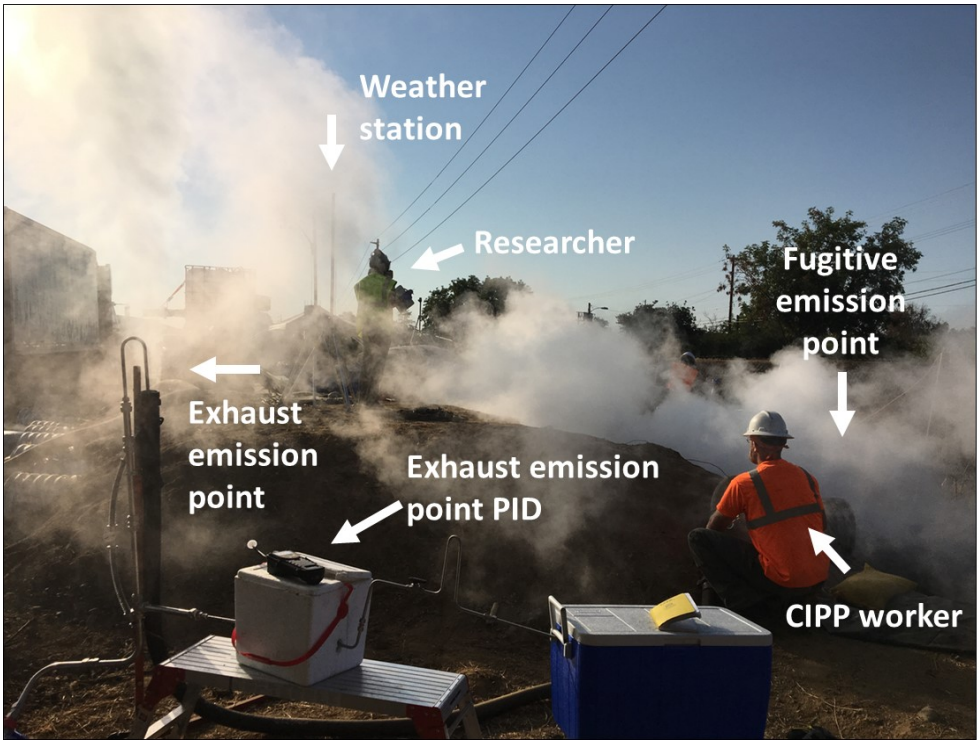


Figure A.2. Images of the California site (a): exhaust emission capture system, (b) exhaust emission and fugitive emission points for one CIPP installation. The black hose used by the contractor connecting the uncured resin tube to the exhaust emission point was ethylene propylene diene monomer (EPDM).

Table A.2. Design characteristics of each CIPP installation in Sacramento, California

Install. Number	Host pipe (Length-m, Diameter-cm)	Used Preliner, Number Used	Resin Type	Cool down Method	Liner Insertion Method
1	CSP (6,45.7)	Yes, 1	L713	Ambient Air	Air inversion
2	CSP (6,48.2)	No, 0	EcoTek	None	Air inversion
3	CSP (6,45.7)	Yes, 2	L713	Hot Air	Air inversion
4	RCP (6,45.7)	Yes, 1	L713	None	Air inversion
5	CSP (6,45.7)	No	L713	None	Pull-in

CSP = Corrugated Steel Pipe; RCP = Reinforced Concrete Pipe; According to the contractor's submittal the target thickness of the uncured liner wall was to be 9 mm and after curing the CIPP wall thickness was to be no less than 7.62 mm; Design conditions were predetermined by Currier[11]who examined water quality impacts of the CIPP installations. Two AOC, LLC resins were used for CIPP installations: L713-LTA (styrene based resin) and EcoTek (non-styrene based resin).

Table A.3. Operational conditions for each CIPP installation in Sacramento, California

Install. Number	Cure Time (min)	Interface Range Temperature (°C)	Steam Range Temperature (°C)
1	130	14.4 to 93.3	115.5 to 121.1
2	150	14.4 to 80.5	115.5
3	165	18.3 to 117.7	110 to 121.1
4	175	15.5 to 76.6	110 to 121.1
5	155	15.5 to 137.7	120 to 121.1

Contractors reported that pressure inside the uncured resin tube for each installation was 34.4 kPa.

A.2.10 Meteorological Condition Monitoring

Meteorological conditions were monitored using a Davis Vantage Pro 2 wireless weather station. Measurements monitored included: wind speed, wind direction, rainfall, temperate, humidity, and barometric pressure. Additionally, the weather station was programmed with Sacramento's latitude and longitude, altitude, rainy season, and time zone. Every minute, data was logged and sent to the wireless monitor, which was downloaded at the end of each day. The weather station was placed roughly 1 m off the ground, while the anemometer was roughly 1.8 m off the ground.

A.3 RESULTS AND DISCUSSION

A.3.1 Video A.1. Video of white chemical plume movement due to local conditions and nearby vehicle movement

Video uploaded to ACS Manuscript submission system

Text Posted: This video was recorded as part of a National Science Foundation RAPID response research project (CBET-1624183) in July 2016. Cured-in-place-pipe (CIPP) technology is used to repair damaged sewer, storm water, and drinking water pipes. As part of the repair, a new plastic pipe is chemically manufactured onsite, inside the existing damaged pipe. The video above was recorded at a CIPP sewer pipe installation site where, after contractors inserted an uncured resin tube into the host pipe, steam was added to cure or harden the CIPP in place. Contractors injected steam into one end of the pipe and this material exited the latter end of the pipe and exiting the manhole shown above where it entered the environment/worksite. Environmental conditions and nearby traffic influenced the direction and size of the white chemical plume that was emitted.

A.3.2 Video A.2. Video of chemical emission into the air from an uncured resin tube (used for CIPP) before curing

Video uploaded to ACS Manuscript submission system

Text Posted: This video was recorded as part of a National Science Foundation RAPID response research project (CBET-1624183) in July 2016. Cured-in-place-pipe (CIPP) technology is used to repair damaged sewer, storm water, and drinking water pipes. As part of the repair, a new plastic pipe is chemically manufactured onsite, inside the existing damaged pipe. The blue material seen in the video is an uncured resin tube. The video above was recorded at a CIPP installation site and shows a white substance being emitted from an uncured resin tube. The uncured resin tube is then inserted into a damaged pipe and then cured or hardened in place.

A.3.3 Video A.3. Video of the uncured resin tube guided from a refrigerated truck into a sewer manhole for CIPP

Video uploaded to ACS Manuscript submission system

Text Posted: This video was recorded as part of a National Science Foundation RAPID response research project (CBET-1624183) in July 2016. Cured-in-place-pipe (CIPP) technology is used to repair damaged sewer, storm water, and drinking water pipes. As part of the repair, a new plastic pipe is chemically manufactured onsite, inside the existing damaged pipe. The blue material seen in the video is an uncured resin tube. The video above was recorded at a CIPP installation site and shows a substance emitted into the air while the uncured resin tube is removed from a refrigerated truck and guided into a sewer manhole below. Once inserted into the sewer pipe and positioned, the uncured resin tube was then cured or hardened in place.

A.3.4 Video A.4. Video of a CIPP exhaust pipe emitting materials into the environment and worksite

Video uploaded to ACS Manuscript submission system

Text Posted: This video was recorded as part of a National Science Foundation RAPID response research project (CBET-1624183) in August 2016. Cured-in-place-pipe (CIPP) technology is used to repair damaged sewer, storm water, and drinking water pipes. As part of the repair, a new plastic pipe is chemically manufactured onsite, inside the existing damaged pipe. The video above was recorded at a CIPP installation site where, after contractors inserted an uncured resin tube into the host pipe, steam was added to cure or harden the CIPP in place. Contractors injected steam into one end of the pipe and this material exited the latter end of the pipe and then traveled through this EPDM plastic hose to where it entered the environment/worksite. This discharge point is located at the worksite.

A.3.5 Video A.5. Video where a researcher walked by a CIPP exhaust pipe and his PID detected chemical exposure

Video uploaded to ACS Manuscript submission system

Text Posted: This video was recorded as part of a National Science Foundation RAPID response research project (CBET-1624183) in August 2016. Cured-in-place-pipe (CIPP) technology is used to repair damaged sewer, storm water, and drinking water pipes. As part of the repair, a new plastic pipe is chemically manufactured onsite, inside the existing damaged pipe. The video above was recorded at a CIPP installation site where, after contractors inserted an uncured resin tube into the host pipe, steam was added to cure or harden the CIPP in place. Contractors injected steam into one end of the pipe and this material exited the latter end of the pipe and then traveled through a plastic hose to where it entered the environment/worksite. A CIPP worker is stationed at the Exhaust Pipe monitoring the installation. The photoionization detector (PID) affixed to a Purdue researcher is shown at the bottom of the screen. As the Purdue researcher approaches the worker and Exhaust Pipe location where emissions are occurring, the Purdue researcher's PID signal increases. The signal represents the magnitude of chemical exposure experienced by the person as the person was wearing a real-time air monitoring device. The device readings and video footage have been linked to one another using EVADE video exposure monitoring software (http://www.cdc.gov).

A.3.6 Indiana Investigation of Sanitary Sewer Pipes

PID readings. Spot PID readings at the open refrigerated truck's back door were 72.4 ppm_v and 79.3 ppm_v. When the PID was placed on the pavement approximately 1.82 m from the manhole while the uncured resin tube was installed a maximum 77.7 ppm_v PID reading was observed. During steam curing, when a white chemical plume exited the downstream manhole, spot PID readings at nearby active sidewalks reached 19.5 ppm_v, but wind shifted and rapidly reduced this maximum signal to 0 ppm within 2 min. A spot PID reading of 514 ppm_v was recorded in the breathing zone about 4.5 m from the exhaust pipe during curing. When contractors started venting the CIPP, the PID signal from a location approximately 3.0 m from the downstream manhole (2.2ppm_v) increased to 52.8 ppm_v.

Table A.4. Styrene (Confirmed) and List of Tentatively Identified Compounds Detected in the Tedlar Bag Sample Collected at the Indiana Site

RT, min.	Tentatively Identified Compound (TIC)	Similarity Index	Area	m/z	Area*, %
2.55	(Z)-2-Heptene	94	53,945,944	41	7.2
2.63	2-Heptene, (E)-	97	66,143,075	56	8.8
2.73	2-Heptene	97	18,821,568	56	2.5
2.81	2-Heptene	92	299,946	41	<0.1
3.19	1-Hexanol, 2-ethyl-	86	230,025	57	<0.1
3.36	3-Octene, (E)-	88	173,703	41	<0.1
3.42	Toluene	81	83,670	91	<0.1
3.49	Octanal	87	146,754	43	<0.1
4.46	2,4-Dimethyl-1-heptene	88	86,730	43	<0.1
4.76	Benzene, ethyl-	91	522,913	91	0.1
4.86	Heptane, 3-ethyl-	95	1,736,566	57	0.2
4.97	*N,N*-Dimethylacetamide	98	9,923,726	44	1.3
5.23	Styrene (confirmed with standard)	89	419,446,197	104	55.8
5.62	Benzene, (1-methylethyl)-	95	5,569,848	105	0.8
5.71	1,3,5,7-Cyclooctatetraene	88	122,212	104	<0.1
5.89	Benzene, 1-propenyl-	95	1,583,939	117	0.2
6.00	Benzene, propyl-	98	2,413,702	91	0.3
6.06	Heptane, 2,2,4,6,6-pentamethyl-		149742		<0.1
6.23	Pentane, 3-ethyl-2,2-dimethyl-		66886		<0.1
6.31	Phenol	93	2,861,046	94	0.4
6.36	Benzene, (1-methylethenyl)-	94	646,193	118	0.1
6.44	Undecane, 2,2-dimethyl		214,994		<0.1
6.48	Benzene, 1-propenyl-	93	561,691	117	0.1
6.55	Dodecane	82	70,657	43	<0.1
6.71	Benzene, (1-methylpropyl)-	88	1,054,450	105	0.1
6.83	Octane, 2,2-dimethyl-	94	2,522,918	57	0.3
6.92	Heptane, 2,2,4,6,6-pentamethyl-	95	1,334,137	57	0.2
6.96	*tert*-Butyl glycidyl ether	88	24,415,516	57	3.2
7.03	2,4-dimethyl-3-pentanol	88	1,486,567		0.2
7.06	Cyclohexanone, 3,3,5-trimethyl-	95	866,071	83	0.1
7.15	Dodecane, 4,6-dimethyl-	91	552,667	71	0.1

Table A.4 continued

7.20	Pentane, 2,2,3,4-tetramethyl-	91	8,297,266	57	1.1
7.92	Pentane, 2,2,3,4-tetramethyl-	89	2,236,912	57	0.3
7.24	Hexane, 2,2,5-trimethyl-	91	2,784,190	57	0.4
7.30	Undecane, 2,6-dimethyl-	92	8,405,959	57	1.1
7.34	Undecane, 2,2-dimethyl-	86	856,447	57	0.1
7.37	Undecane, 2,6-dimethyl-	90	1,138,972	57	0.2
7.41	Undecane,5-methyl-	92	403,215	57	0.1
7.45	Dodecane, 4,6-dimethyl-	92	11,121,542	71	1.6
7.51	Undecane, 2,6-dimethyl	91	804,680	57	0.1
7.57	Dodecane, 2,6,11-trimethyl-	92	3,329,807	71	0.4
7.69	Dodecane, 4-methyl-	92	3,310,417	71	0.4
7.77	Decane, 3-methyl-	92	648,003	57	0.1
7.81	Octane, 2,2-dimethyl-	90	1,081,405	57	0.1
7.88	Dodecane, 2,6,11-dimethyl	93	586,989	57	0.1
7.92	Pentane,2,2,3,4-tetramethyl	89	2,236,912		0.3
7.97	Undecane, 2,2-dimethyl-	92	3,851,513	57	0.5
8.11	2-Hydroxy-2-methyl-4-heptanone	82	55,034,610	71	7.3
8.31	Undecane, 3-methyl-	92	558,061	57	0.1
8.34	Decane, 2,2,3-trimethyl-	91	865,423	57	0.1
8.41	Octane, 3,6-dimethyl-	92	4,975,979	57	0.7
8.44	Octane, 2,2-dimethyl-	91	3,321,016	57	0.4
8.48	Decane, 1-iodo	90	1,121,860	85	0.1
8.71	Heptadecane	91	451,982	57	0.1
8.79	Undecane, 3-methyl-	92	190,060	57	<0.1
8.89	Undecane, 3-methyl-	92	144,370	57	<0.1
8.98	Undecane, 3-methyl	88	239,103	57	<0.1
9.01	3-Methyl tetradecane	88	189,352	57	<0.1
9.55	Hexadecane	90	197,902	71	<0.1
9.72	Tetradecane	87	67,601	57	<0.1
9.97	Dotriacontane	87	94,790	71	<0.1
14.29	Nonadecane	90	405,287	57	0.1
15.38	Nonasocane	92	803,372	57	0.1
16.27	Nonasocane	88	683,126	57	0.1
17.03	Heptasocane	82	577,602	207	0.1

Table A.4 continued

17.71	Heptasocane	64	339,712	207	<0.1

** Results shown only represent chromatogram signals greater than 50,000 a.u.; The total area for the signals shown is 739,409,490; The total area of unidentified compounds is 12,843,661 implying 1.71% of their proportion in the chromatograph; Styrene peak on the chromatogram was confirmed with an analytical standard.*

A.3.7 California Investigation of Stormwater Pipes

Site safety. The authors did not see CIPP workers using PPE such as respirators and earplugs. Some workers crouched or sat next to the white chemical plume emitted from the fugitive emission and also exhaust emission points. Contractors also walked through the plumes periodically. Workers monitored a pressure gage to determine when the workers at the boiler needed to inject more steam. Also observed was that contractors carried the uncured resin tube and cured CIPP with their bare hands.

Composition of uncured resin tubes. Compounds extracted from sites 1, 3, 4, and 5 were similar (**Table A.5**). Methylene chloride extracted a greater number of compounds than hexane. The low-VOC uncured resin tube did not have a detectable amount of styrene, while styrene was present in all styrene based uncured resin tubes. Tripropylene glycol diacrylate (TPGDA), a known reactive acrylic diluent, was found in the low-VOC resin tube. Butyl hydroxyltoluene (BHT), an antioxidant, was found in a few uncured resin tubes, and benzaldehyde was only found in styrene based uncured resin tubes.

Table A.5. Loading of compounds present in each uncured resin tube from Sacramento, California

Compound	Installation Site (Resin Type), mg Compound / g Resin				
	1 (L713)	2 (EcoTek)	3 (L713)	4 (L713)	5 (L713)
Methylene chloride extracts					
Styrene	52.85 ± 6.72 [b]	-	72.91 ± 4.39 [c]	66.23 ± 7.53 [c]	45.27 ± 9.47 [c]
BHT	5.33 [a]	>HCL	7.3 [a]	-	-
Benzaldehyde	1.65 [a]	-	1.69 ± 0.68 [c]	-	1.41 [a]
Hexane extracts					
Styrene	44.51 ± 6.69 [b]	<MRL [b]	61.35 ± 5.25 [c]	53.72 ± 3.63 [c]	49.26 ± 2.8 [c]
TPGDA	-	319.63 ± 24.29 [c]	-	-	-

Two resins were used for CIPP installations: L713-LTA (styrene based resin) and EcoTek (non-styrene based resin); Three replicate extractions were conducted for each uncured resin tube. Sometimes compounds were detected in some, but not all, replicates. The number of replicates where compounds were detected are denoted by the use of roman numerals: a: 1 replicate; b: 2 replicates; c: 3 replicates. Lowest concentration minimum reporting level (MRL) on calibration curve: styrene (in hexane): 1.208 ppm, styrene (in methylene chloride): 0.241 ppm, Benzaldehyde: 20.88 ppb, BHT: 43.52 ppb, Highest concentration maximum reporting level (HCL) on calibration curve: Styrene (methylene chloride) = 2.47 ppm, BHT: 195.8 ppb. For the installation 1 hexane extraction, one replicate resulted in zero compounds detected.

Meteorological conditions. Meteorological conditions during the CIPP heat up, curing, and cool down periods are described in **Table A.6**. The wind speed was greatest at sites 3 and 4. The highest detected wind speed on this day was 7 mph, while the highest wind speed overall was 8 mph, which occurred at site 2 (low VOC CIPP). As an overall trend, both humidity and temperature increased during the day, while pressure decreased slightly. The average value of the period is found within the cell. The values in the parentheses represent the minimum and maximum values within that same period.

(a)

(b)

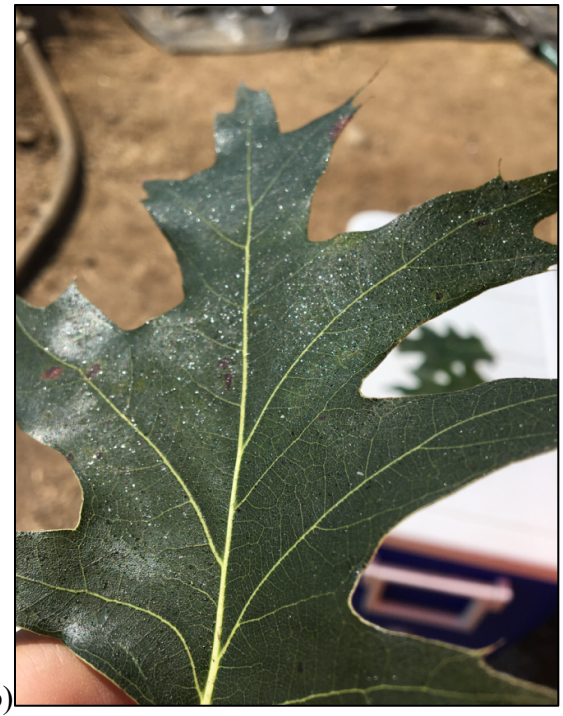


Figure A.3. Images of (a) exhaust emission point and (b) Oak tree leaf directly above the exhaust emission hose that was exposed the white chemical plume at the California site. White material seen on the leaf surface and was not found on unexposed leaves.

Table A.6. Overview of average meteorological conditions at CIPP installation sites

Site (Resin Type) and Date	Sampling Period (Time)	Temp (°F)	Temp (°C)	Humidity (%)	Barometric Pressure (Hg)	Barometric Pressure (Torr)	Predominant Wind Direction	Wind Speed (mph)	Number of Data Points
1 (L713) 8/9/2016	heat up (8:26-10:12)	70.254 (66.5 - 74.4)	21.252 (19.167- 23.556)	59.99 (52-68)	29.774 (29.77 - 29.777)	756.261 (756.160 - 756.337)	E	2.430 (0 - 5)	106
	curing (10:12- 11:44)	79.263 (74.5 - 83.7)	26.257 (23.611 - 28.722)	46.94 (37 - 61)	29.776 (29.772 - 29.78)	756.312 (756.210 - 756.414)	NNW	1.848 (0 - 4)	92
	cool down (11:45- 12:29)	85.740 (83.8 - 87.3)	29.856 (28.778 - 30.722)	35.53 (34 - 38)	29.767 (29.762 - 29.772)	756.083 (755.956 - 756.210)	NNW	2.044 (1 - 5)	44
	overall (8:26- 12:29)	**76.507 (66.5 - 87.3)**	**24.726 (19.167 - 30.722)**	**50.56 (34 - 68)**	**29.773 (29.762 - 29.78)**	**756.236 (755.956 - 756.414)**	**ENE**	**2.139 (0 - 5)**	242
2 (EcoTek) 8/9/2016	heat up (13:12 - 14:12)	90.677 (88.9 - 92.1)	32.598 (31.611 - 33.389)	27.93 (25 - 32)	29.744 (29.733 - 29.753)	755.499 (755.220 - 755.728)	NNW	2.333 (0 - 5)	60
	curing (14:12 - 16:03)	94.622 (91.3 - 96.6)	34.790 (32.944 - 35.889)	23.96 (19 - 31)	29.714 (29.695 - 29.733)	754.737 (754.255 - 755.220)	NW	2.473 (1 - 8)	81
	cool down (16:03 - 17:19)	96.575 (95.3 - 97.9)	35.875 (35.167 - 36.611)	18.18 (16 - 24)	29.689 (29.684 - 29.699)	754.102 (753.975 - 754.356)	SW and NW*	2.658 (0 - 7)	76
	overall (13:12 - 17:19)	**94.266 (88.9 - 97.9)**	**34.592 (31.611 - 36.611)**	**23.15 (16 - 32)**	**29.714 (29.684 - 29.753)**	**754.737 (753.975 - 755.728)**	**NW**	**2.496 (0 - 8)**	217
3 (L713) 8/10/2016)	heat up (7:12 - 8:34)	66.742 (64 - 69.1)	19.301 (17.778 - 20.611)	65.9 (62 - 71)	29.809 (29.796 - 29.822)	757.150 (756.820 - 757.480)	S	3.988 (2 - 6)	82
	curing (8:34 - 10:17)	72.630 (69.2 - 75.8)	22.572 (20.667 - 24.333)	60.55 (54 - 76)	29.822 (29.82 - 29.826)	757.480 (757.430 - 757.582)	S	3.786 (2 - 6)	103
	cool down (10:17 - 10:44)	76.956 (76 - 78.1)	24.976 (24.444 - 25.611)	50.85 (49 - 55)	29.829 (29.825 - 29.832)	757.658 (757.557 - 757.734)	SW	3.037 (1 - 5)	27

Table A.6 continued

	overall (7:12 - 10:44)	**70.884 (64 - 78.1)**	**21.602 (17.778 - 25.611)**	**61.41 (49 - 71)**	**29.818 (29.796 - 29.832)**	**757.379 (756.820 - 757.734)**	**S**	**3.770 (1 - 6)**	212
4 (L713) 8/10/2016	heat up (12:04 - 12:53)	86.342	**30.190**	**37.48**	**29.820**	**757.430**	SW	**3.813**	49
		(83.9 - 88.7)	**(28.833 - 31.5)**	**(33 - 41)**	**(29.814 - 29.826)**	**(757.277 - 757.820)**		**(1 - 7)**	
	curing (12:53 - 14:33)	91.236	**32.909**	**30.91**	**29.806**	**757.074**	SW	**3.733**	100
		(88.3 - 93.9)	**(31.278 - 34.389)**	**(26 - 45)**	**(29.793 - 29.815)**	**(756.744 - 757.303)**		**(0 - 6)**	
	cool down (14:33 - 15:30)	94.753	**34.863**	**25.39**	**29.787**	**756.591**	SW	**3.263**	57
		(93.2 - 96.2)	**(34 - 35.667)**	**(24 - 29)**	**(29.779 - 29.791)**	**(756.388 - 756.693)**		**(1 - 7)**	
	overall (12:04 - 15:30)	91.068	**32.816**	**30.91**	**29.804**	**757.023**	**SW**	**3.621**	206
		(83.9 - 96.2)	**(28.833 - 35.667)**	**(24 - 45)**	**(29.779 - 29.826)**	**(756.388 - 757.820)**		**(0 - 7)**	
5 (L713) 8/11/2016	heat up (8:00 - 8:16)	63.956	17.753	71.69	**29.920**	**759.970**	SW	**2.313**	16
		(63.6 - 64.5)	(17.556 - 18.056)	(71 - 72)	**(29.917 - 29.923)**	**(759.893 - 760.046)**		**(0 - 4)**	
	curing (8:16 - 10:00)	68.920	20.511	68.17	**29.930**	**760.224**	SSW	**2.375**	104
		(64.6 - 72.9)	(18.111 - 22.722)	(59 - 87)	**(29.923 - 29.934)**	**(760.046 - 760.325)**		**(0 - 4)**	
	cool down (10:00 - 10:17)	73.724	23.180	58.41	**29.929**	**760.198**	SSE and SSW*	**2.765**	17
		(73.1 - 74)	(22.833 - 23.333)	(56 - 71)	**(29.928 - 29.932)**	**(760.173 - 760.274)**		**(1 - 4)**	
	overall (8:00 - 10:17)	**68.936 (63.6 - 74)**	**20.520 (17.556 - 23.333)**	**67.37 (56 - 87)**	**29.929 (29.917 - 29.932)**	**760.198 (759.893 - 760.274)**	**SSW**	**2.416 (0 - 4)**	137
Daily Averages at	Day 1 - 08/09/2016	76.00	24.444	51.00	29.770	756.160	SSW	**5**	
Sacramento Airport according	Day 2 - 08/10/2016	75.00	23.889	52.00	29.820	757.430	SSW	**7**	
to Weather Underground	Day 3 - 08/11/2016	75.00	23.889	55.00	29.920	759.970	SSW	**6**	

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APPENDIX B

B.1. INTRODUCTION

B.2. MATERIALS AND METHODS

B.3. RESULTS AND DISCUSSION

B.4. REFERENCES SPECIFIC TO THE SUPPORTING INFORMATION

B.1. INTRODUCTION

Table B.1. List of CIPP associated air contamination incidents found by authors not included in the 59 incidents reported by Teimouri et al. (2017) and 45 incidents reported by Ra et al. (2019) in their Supplementary Information files.

Incident Location (Year)	Styrene	Description of events from reference
Philadelphia, PA (2020) [1]	nr	PERSONAL COMMUNICATION: A resident found her house filled with CIPP fumes which entered to the building through the basement. She left the house and contacted the water department and contractors. A water department inspector came to her house but only prepared a report. The resident was a cancer survivor with neuropathy, and that became worse after the incident.
Harrisburg, PA (2020) [2, 3]	nr	PERSONAL COMMUNICATION: A resident noticed a strong glue-like smell in his basement coming from an underground work in the neighborhood. The resident asked the workers the cause of such smell and they assured him that the smell would vanish and not be as strong as it cures. The resident was concerned because: 1) the incident happened during the winter and they expect residents to open windows to ventilate; 2) it affected those who may be elderly, working remotely or children who may be home schooled or in cyber school; 3) nobody in the City of Harrisburg Codes was too concerned. They also said that there was no oversight from the City government of the process or possible health, safety, welfare of residents; 4) With the population being 25% under the age of 18, any type of chemicals can adversely affect brain development up until 25 years of age; 5) With older houses, many times there are floor drains that may not have a functioning trap as in the case of our house. However, the Capital Region Water released a notice in which they claimed that "the smell released in sewer rehabilitation process is in such small quantities that it does not pose a significant risk to human health, the environment, or the workers who are working on our behalf. It exists briefly in the environment and is destroyed rapidly in the air, disappearing quickly."
Chicago, IL (2020) [4]	nr	MEDIA REPORT: Sewer pipe repair construction caused a very strong chemical smell adversely impacted business at a bakery in Chicago.
Seneca Falls, NY (2019) [5]	nr	MEDIA REPORT: A teacher and several middle school students in a classroom became sick because of inhalation of odors caused by sewer pipe rehabilitation work at nearby area. Windows of the classroom were opened when the rehabilitation work was taking place. Nine students went home sick at the incident day. Eight students felt better and returned school the next day while one student still felt sick two days later. Styrene, as a volatile organic compound, was mixed with the resin to help it cure. An engineer for the project from Barton & Loguidice Engineers told the reporter that curing of the resin impregnated liner causes odors. He also mentioned that results of some studies showed that even though odors are a common occurrence in CIPP practices, styrene concentrations are less than exposure guidelines and do not lead to health risk. He said that individuals have different sensitivities towards styrene odors and can be inconvenient to those who are not used to working around it. After investigation it was concluded that a combination of weather conditions (i.e. breeze and air movement at the incident day) and opened windows resulted in increased odors from the CIPP process.

Festus, MO (2019) [6]	nr	MEDIA REPORT: Public Works director Matt Clemens announced that while fabric lining in sewer lines was conducting in Festus, residents may notice a strange odor. He said that this process has been conducted every other year on a rotating basis and nothing harmful exists in this procedure.
Regina, CAN (2019) [7]	nr	MEDIA REPORT: One of the residents found going outside impossible because of massive maintenance project being conducted nearby her house. The noise and fumes from the project have disrupted her daily life. Some residents noticed sewer gas smell after steaming the pipe. said some people have been put as a result of the project, but only Residents directly affected by the noise and fumes were put in hotels while contractor decided when a house should be evacuated.
Regina, CAN (2019) [8]	nr	PERSONAL COMMUNICATION: Explosion in a basement in sump pit occurred as a result of fume accumulation during sewer pipe lining. CIPP was installed a few months prior the incident. The pit was connected to sanitary sewer. During CIPP installation styrene residue settled in pit for 4 months and the spark was from the pump and ignited gas.
Herndon, VA (2019) [9]	nr	PERSONAL COMMUNICATION: Residents were concerned about a strong smell assumed to originate from chemical reaction to the epoxy in the sewer pipe. The chemical odor became worse in the past 30 minutes of incident report. It was advised that the odor would dissipate by the morning and was not harmful.
Pitcairn, PA (2019) [10]	nr	MEDIA REPORT: Three students and three teachers felt ill after breathing emissions from a sewer project near school. It caused nausea and watery eyes for students and staff. 280 students and staff were vacated from the school and students were sent home an hour later.
Rochelle, IL (2019) [11]	nr	MEDIA REPORT: Aldi evacuated the building and stayed closed for several hours as a result of smoke coming from restrooms. A strong odor was also noticed in the building and parking area. Sewer pipe rehabilitation work near the area was the reason for smoke and strong smell. Rochelle fire chief explained that they monitored the air nothing harmful, flammable or explosive was found.
Evanston, IL (2019) [12]	nr	MEDIA REPORT: City officials announced a sewer repair work will be conducted and advised nearby residents not to distress by unpleasant odors caused by heated styrene. The chemical has been commonly used in fiberglass industry and is not dangerous. They also asked the residents to pour a gallon of water into drains to avoid the odor in their home and repeat the process when the water evaporates.
Festus, MO (2019) [13]	nr	MEDIA REPORT: In March, Instituform was awarded $130,124 by Festus City Council to repair city sewer pipes by CIPP installations. There’s no need to worry about steam rising from Festus streets, Public Works Matt Clemens said.
Moncton, CAN (2019) [14]	nr	MEDIA REPORT: An unpleasant glue-like odor came from sewer lining activities and permeated homes in the city's north end. The city declared the smell isn’t a public-health risk. However, some residents developed headaches and felt nauseous. One resident rented an industrial fan to force the smell out of his building. A few of them smelt the odor on their cloths, furniture and even bottled water.
Norwalk, CT (2019) [15, 16, 17]	nr	MEDIA REPORT: All students’ after school activities were canceled due to an odor from an adjacent construction. The students left the building by local Fire Department personnel "out of an abundance of caution".

Pitcairn, PA (2019) [18]	nr	MEDIA REPORT: Students were sent home after several were sickened by an odor from a nearby sewer lining project. A 5th grade student was among the six people taken to the hospital after inhaling the odor.
Ontario, CAN (2019) [19]	nr	PERSONAL COMMUNICATION: A resident found their house saturated with a peculiar chemical smell came from sewer pipes working in the neighborhood. The odor got into the house through sewer pipes of toilets. The house was also filled with a high roaring sound that came from some violent action in the toilet bowls. The resident alerted the authorities. A group of inspectors/engineers arrived at the incident place and after investigation they ordered the residents leave the house as the gas concentrations were beyond an acceptable level. The residents stayed at hotel overnight until the house is properly ventilated. In the incident place, windows were opened, and a large number of fans were installed to ventilate. Project engineers claimed that this has never happened before and then modified to a chance of one in a million.
Warsaw, IN (2019) [20]	nr	PERSONAL COMMUNICATION: Several residents were concerned and complained about glue like odor in their homes as a result of sewer pipe lining conducted in their neighborhood. Wastewater Treatment Utility Plant responded to the residents by saying that the odor is not toxic and residents can avoid it by pouring water to their plumbing traps.
Deerfield beach, FL (2019) [21]	nr	MEDIA REPORT: Individual reported that emissions entered a single-family home during sanitary sewer CIPP installation in front of the house. When she arrived, she opened the door, smelled a glue-like odor in the house, and found 2 adults unconscious. The individual then called 911.
Jersey City, NJ (2019) [22]	nr	PERSONAL COMMUNICATION: The resident found the CIPP odor overwhelming and noticeable in his second floor apartment. The city never notified residents of this project.
Warrnambool, AU (2018) [23]	nr	MEDIA REPORT: Warrnambool residents were told that a strong plastic-like smell originating from an innovative sewer repair project and persisting in parts of the city was not toxic and disappeared very quickly.
Decatur, IL [24]	nr	Cancer Care Center of Decatur was evacuated due to an odor caused by city sewer projects. Decatur Fire Department responded to the incident but did not find anything unsafe.

nr = not reported in the reference

B.2. MATERIALS AND METHODS

Analytical standards for liquid-solid extraction samples

Different analytical standards were used to confirm and quantify some compounds identified by GC/MS. They include: butyl hydroxytoluene (BHT) (CAS# 128-37-0, Supelco), benzaldehyde (CAS# 100-52-7, Sigma-Aldrich), benzoic acid (CAS# 65-85-0, Supelco), 1-tetradecanol (CAS#112-72-1, Sigma-Aldrich), , chlorobenzene-d5 (CAS# 3114-55-4, Supelco), styrene oxide 97% (CAS# 96-09-3, Sigma-Aldrich), hydroquinone (CAS# 123-31-9, Sigma-Aldrich), 3-ethyl-1-methylbenzene (CAS# 620-14-4, Sigma-Aldrich), 2-ethylhexanoic acid

(CAS# 149-57-5, Supelco), 2-propenylbenzene (CAS# 300-57-2, Sigma-Aldrich), *N*-propylbenzene (CAS# 103-65-1, Supelco), 1,3,5-trimethylbenzene (CAS# 108-67-8, Supelco), 1,2,4-trimethylbenzene (CAS# 95-63-6, Sigma-Aldrich) and styrene ≥99% that contained 4-tert-butylcatechol stabilizer (CAS# 100-42-5, Sigma-Aldrich).

Calibration curves were developed for methylene chloride extracts: styrene (R^2 = 0.991, 0.992) benzaldehyde (R^2 = 0.998), 1,3,5-trimethylbenzene (R^2 = 0.985, 0.998), 1,2,4-trimethylbenzene (R^2 = 0.991), benzoic acid (R^2 = 0.998), 1-tetradecanol (R^2 = 0.995), *N*-propylbenzene (R^2 = 0.999, 0.998), 2-propenylbenzene (R^2 = 1), styrene oxide (R^2 = 0.997), 3-ethyl-1-methylbenzene (R^2 = 0.999, 0.980), 2-ethylhexanoic acid (R^2 = 0.999, 0.961), hydroquinone (R^2 = 0.998) and BHT (R^2=0.995).

Calibration curves were also created for hexane extracts and were for: styrene (R^2= 0.996, 0.999), benzaldehyde (R^2 = 0.999, 0.998), 1,3,5-trimethylbenzene (R^2 = 0.999, 0.991, 0.980) , 1,2,4-trimethylbenzene (R^2 = 0.998, 0.997), benzoic acid (R^2 = 0.980, 0.950), 1-tetradecanol (R^2 = 0.982), *N*-propylbenzene (R^2 = 0.999, 0.997), 2-propenylbenzene ((R^2 = 0.999), styrene oxide (R^2 = 0.995), 3-ethyl-1-methylbenzene (R^2 = 0.994), 2-ethylhexanoic acid (R^2 = 0.996), hydroquinone (R^2 = 0.999) and BHT (R^2 = 0.999).

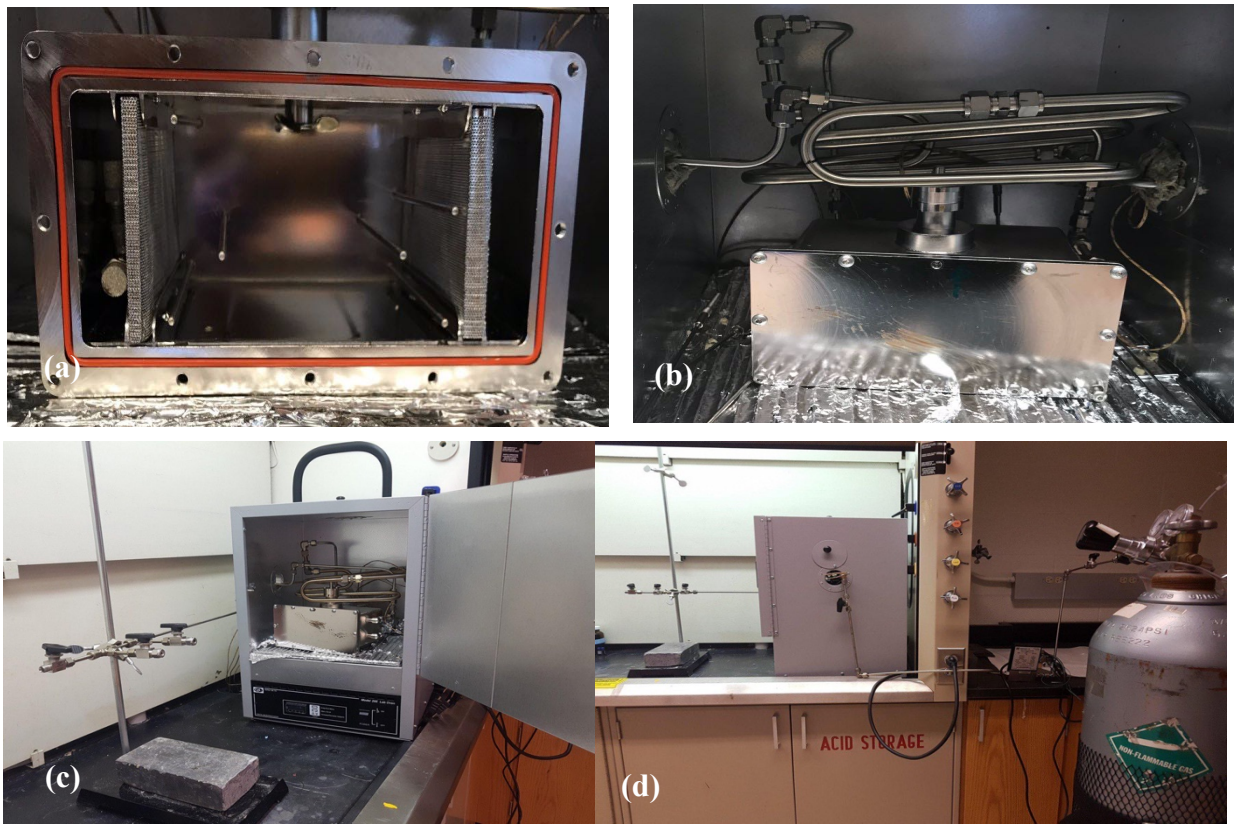


Figure B.3-9. Experimental setup for capturing post-cured chemical air emissions from cured composites: (a) inside the ETC; (b) enclosed ETC; (c) sampling ports connected to the ETC; (d) entire set-up

B.3. RESULTS AND DISCUSSION

Table B.2. List of some tentatively identified compounds detected in uncured resin dissolved in methylene chloride with no dilution

Retention Time	Tentatively identified compound	IM	m/z	%Area (Average, STDEV)	
				Methylene chloride	Hexane
3.929, 3.933	Benzene, methyl-	3	1	3 replicates shown intensity < 5.00×10^{4}	2.85×10^{-2}, 1.20×10^{-1} 1 replicate shown intensity < 5.00×10^{4}
4.415, 4.418, 4.20, 4.395, 4.396, 4.397	1,3-Dioxolane, 2-ethyl-4-methyl-	5	7	$1.26\times10^{-1} \pm 7.64\times10^{-3}$	$2.70\times10^{-1} \pm 1.80\times10^{-1}$
4.617, 4.618, 4.621, 4.636, 4.638, 4.639	1,3-Dioxolane, 2-ethyl-4-methyl-	3	7	$9.81\times10^{-2} \pm 8.61\times10^{-3}$	$1.90\times10^{-1} \pm 1.20\times10^{-1}$
6.176, 6.177, 6.179, 6.192	Benzene, ethyl-	9	1	$5.76\times10^{-1} \pm 3.43\times10^{-2}$	1.68 ± 1.12
6.381	o-Xylene	4	1	3 replicates shown intensity < 5.00×10^{4}	2.82×10^{-1}, 5.90×10^{-2}
6.44, 6.449, 6.467	Maleic anhydride	5	4	$2.06\times10^{-1} \pm 1.25\times10^{-1}$	3 replicates shown intensity < 5.00×10^{4}
7.526, 7.528, 7.529, 7.54, 7.546, 7.551	Benzene, (1-methylethyl)-	7	05	1.30 ± 1.43	1.92 ± 1.21
7.785, 7.793. 7.797	Cyclooctane, ethyl-	4	9	$1.26\times10^{-1} \pm 1.11\times10^{-2}$	2 replicates shown intensity < 5.00×10^{4}
7.906, 7.907, 7.909, 7.912, 7.919, 7.923	Benzene, 2-propenyl-	6	17	$2.87\times10^{-1} \pm 2.84\times10^{-2}$	$5.30\times10^{-1} \pm 3.40\times10^{-1}$
8.04, 8.043, 8.044, 8.046, 8.054, 8.057	Benzene, propyl-	8	1	$2.57 \pm 3.09\times10^{-1}$	4.74 ± 2.97
8.182, 8.185, 8.186, 8.189, 8.196, 8.2	Benzene, 1-ethyl-3-methyl-	7	05	12.8 ± 1.93	22.6 ± 14.1
8.297, 8.301,8.303, 8.311, 8.314	Mesitylene	7	05	$3.54 \pm 4.60\times10^{-1}$	4.33 ± 2.74
8.494, 8.499, 8.5, 8.507, 8.51	Benzene, 1-ethyl-3-methyl-	6	05	$3.20 \pm 3.02\times10^{-1}$	4.19 ± 2.62
8.534, 8.535, 8.539, 8.547, 8.549	Benzene, (1-methylethenyl)-	7	18	$6.53\times10^{-1} \pm 1.38\times10^{-1}$	$1.17 \pm 7.2\times10^{-1}$

Table B.2 continued

8.589, 8.597, 8.599	Cyclohexane, 1-methyl-4-(1-methylethyl)-, trans-	4	5	$3.14\times10^{-2} \pm 4.33\times10^{-3}$	3 replicates shown intensity < 5.00×10^{4}
8.723, 8.728, 8.729, 8.73, 8.738, 8.741	Mesitylene	7	05	13.5 ± 1.99	21.9 ± 13.7
8.824, 8.829, 8.83, 8.837	Decane	3	7	2.75×10-1 ± 6.34×10-2	3.10×10-1 ± 2.0×10-1
8.959, 8.964, 8.965, 8.971, 8.973	Benzene, (2-methylpropyl)-	1	1	1.07×10-1 ± 1.78×10-2	1.30×10-1 ± 8.00×10-2
9.013, 9.018, 9.019, 9.025, 9.027	Benzene, (1-methyl-4-propyl)-	0	05	9.53E×10-2 ± 1.56×10-2	1.20×10-1 ± 8.00×10-2
9.199, 9.203, 9.204, 9.205, 9.211, 9.214	Benzene, 1,3,5-trimethyl-	4	05	2.89 ± 4.43×10-1	3.53 ± 2.21
9.354, 9.355	Cyclohexane, butyl-	8	3	2.28×10-2, 2.83×10-2, 1 replicate shown intensity < 5.00×104	3 replicates shown intensity < 5.00×104
9.412, 9.417, 9.418, 9.419, 9.424, 9.427	Indane	5	17	3.50×10-1 ± 5.11×10-2	6.60×10-1 ± 4.20×10-1
9.654, 9.659, 9.666, 9.668	Benzene, 1-methyl-3-propyl-	4	05	4.91×10-1 ± 7.46×10-2	6.30×10-1 ± 4.0×10-1
9.764, 9.769, 9.77, 9.776, 9.778	Benzene, 1-ethyl-3,5-dimethyl-	4	19	2.50×10-1 ± 4.13×10-2	2.10×10-1 ± 1.40×10-1
9.840	Decane, 2-methyl-	8	7	4.44×10-2 ± 1.13×10-2	3 replicates shown intensity < 5.00×104
9.875	Oxirane, phenyl-	4	1	2.95×10-2 ± 4.47×10-3	2.46×10-1, 2 replicates shown intensity < 5.00×104
9.968, 9.978	1,2-Propanedione, 1-phenyl-	4	05	3.56×10-2, 7.45×10-2, 1 replicate shown < 5.00×104	3 replicates shown intensity < 5.00×104
10.052, 10.058, 10.061	Benzene, 2-ethyl-1,4-dimethyl-	9	19	1.13×10-1 ± 8.07×10-2	9.49×10-2, 9.69×10-2

Table B.2 continued

10.167, 10.172, 10.173, 10.179, 10.181	Benzene, 1-ethyl-3,5-dimethyl-	3	19	1.68×10-1 ± 3.49×10-2	1.90×10-1 ± 1.10×10-1
10.351,10.355, 10.361, 10.363	Undecane	0	7	8.10×10-2 ± 3.72×10-3	2.76×10-2, 2 replicates shown < 5.00×104
10.568, 10.572, 10.575 10.657, 10.688, 10.689	Hexanoic acid, 2-ethyl-	5	3	3.02 ± 2.96×10-1	5.20×10-1 ± 3.30×10-1
10.74, 10.769, 10.786	Phosphoric acid, triethyl ester	5	9	2.90×10-2 ± 7.86×10-3	1 replicate shown intensity < 5.00×104
11.14, 11.16, 11.182, 11.21	Benzoic acid	6	05	3.47×10-2 ± 2.01×10-2	3 replicates shown intensity < 5.00×104
12.29	Ethanedione, diphenyl-	9	05	6.00×10-2 ± 1.00×10-2	3 replicates shown intensity < 5.00×104
12.565, 12.654, 12.706	Hydroquinone	3	10	5.05×10-1 ± 1.46×10-1	3 replicates shown intensity < 5.00×104
12.76, 12.763	4,7-Methano-1H-indenol, hexahydro-	1	6	3.96×10-2, 3.06×10-2	3 replicates shown intensity < 5.00×104
13.035, 13.064, 13.084	1,2-Ethanediol, 1-phenyl-	9	07	7.32×10-2 ± 1.12×10-2	3 replicates shown intensity < 5.00×104
13.214, 13.224, 13.231	1,2-Benzenedicarboxylic acid	4	04	4.99 ± 5.59×10-1	3 replicates shown intensity < 5.00×104
15.294, 15.306, 15.318	p-tert.-Butylcatechol	9	91	1.41×10-1 ± 2.12×10-2	3 replicates shown intensity < 5.00×104
15.313, 15.314	2,4-Di-tert-butylphenol	0	91	1.57×10-1	9.77×10-2 ± 6.58×10-2
15.37, 15.379, 15.38, 15.382, 15.384	2,6-bis (1,1-dimethylethyl)-4-methyl-phenol	2	05	1.51 ± 1.70×10-1	1.80×10-1 ± 1.20×10-1

**Results shown only represent chromatogram signals greater than 50,000 a.u.; Styrene is not mentioned because it was excluded from MS program to protect MS from saturation and contamination due to very high concentration in the solution.*

Volatile content in the cured composite cured at 65.5°C for 25 min

For the composite cured at Condition B (65.5°C / 25 min), the amount of volatile residual remained on the surface (2.63 ± 0.24 %) and in the depth (2.96 ± 0.13 %) was statistically similar to volatile content existed on the surface and in the depth of composites cured at Conditions A, C and D.

Table B.3. The magnitude of volatile material that was released from cured composites during manufacture

Material description	**Volatile material emitted during manufacture**			
Composite manufacture conditions	**Condition A** **50 min, 65.5 ˚C**	**Condition B** **25 min, 65.5 ˚C**	**Condition C** **100 min, 65.5 ˚C**	**Condition A** **50 min, 93.3 ˚C**
	Weight loss due to manufacture[†], wt%			
Manufacture [†], No vacuum [††]	8.87 ± 1.67			
Manufacture, Vacuum applied	26.43 ± 1.73	25.87, 11.56*	21.95 ± 8.85	23.55 ± 3.77

*[†] Weight loss due to manufacture is equal to the difference between weight of resin mixture and two felts prior to curing and weight of composite obtained from the same materials after curing; * Weight loss was conducted for three replicate cured composites except for this condition where two replicates were measured; [††] Weight loss at ambient conditions (no vacuum) was only measured at 65.5˚C for 50 min.*

Table B.4. Density and porosity results of cured composites

	Curing conditions (Average ± STD)		
	50 min at 65.5˚C	***100 min at 65.5˚C***	***50 min at 93.3 ˚C***
Density (g/cm^3)	R_1: 1.19 ± 1.00×10^{-2}, R_2: 1.16, 1.17[£]	R_1: 1.15 ± 5.38×10^{-3}, R_2: 1.17 ± 7.44×10^{-3}	R_1: 1.14 ± 4.04×10^{-2}, R_2: 1.10[§]
Porosity (%)	R_1: 3.44×10^{-1} ± 2.03×10^{-1}, R_2: 2.52×10^{-1} ± 1.56×10^{-1}	R_1: 3.14×10^{-1} ± 1.63×10^{-1}, R_2: 5.70×10^{-1} ± 3.40×10^{-1}	R_1:6.04×10^{-1} ± 5.51×10^{-1}, R_2: 1.27 ± 4.79×10^{-1}

R is replicate; STD = standard deviation; [£] Each cured composite replicate (i.e. R_1 and R_2) contained three replicate cubes to undergo density measurements except for this condition where two replicate cubes were measured; [§]Each cured composite replicate (i.e. R_1 and R_2) contained three replicate cubes to undergo density measurements except for this condition where one replicate cube was measured.

The single composite cured at ambient pressure showed no exothermic peak on the surface. No endothermic or exothermic peak was found on the second heating scan exhibiting no volatile residual and resin/initiator remained.

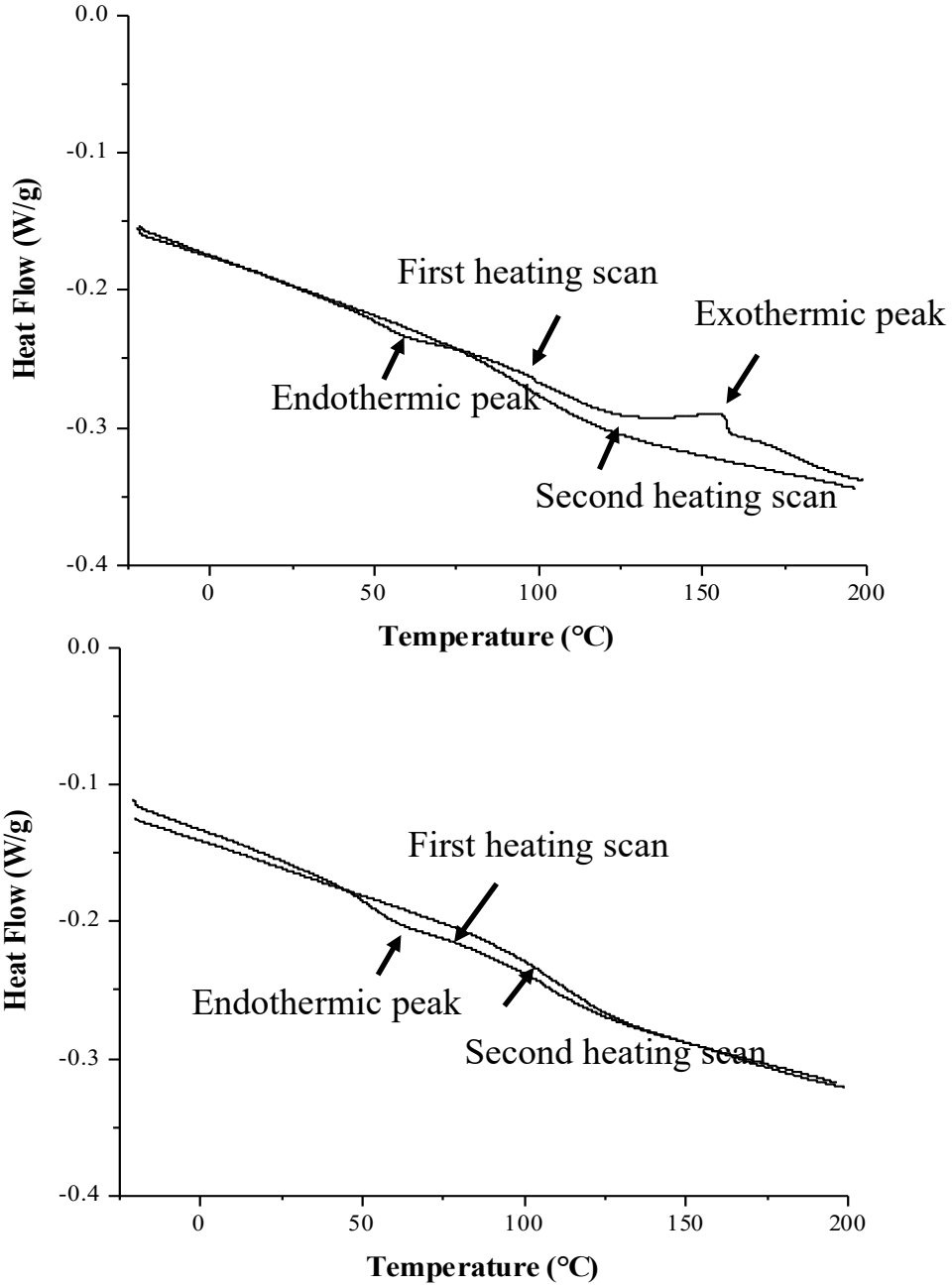


Figure B.2. DSC thermograms of cured composites cured at: (a) 65.5°C/50 min from surface; and (b) 93.3°C/50min from depth.

Table B.5. Chemical Mass Loading (mg/kg) for the resin and new cured composites manufactured under different conditions in hexane

Chemical Detected	**Resin**	**Under Vacuum**				**No Vacuum**	**Studies in the Literature**	
		25 min at 65.5˚C	***50 min at 65.5˚C***	***100 min at 65.5˚C***	***50 min at 93.3˚C***	***50 min at 65.5˚C***	***CIPP***	***Resin Tube***
Hexane								
Styrene [CAR, EDR, HAP]	$2.34\times10^{5} \pm 2.91\times10^{4}$	$1.02\times10^{4} \pm 2.20\times10^{2}$	$1.20\times10^{3} \pm 2.73\times10^{2}$	$1.06\times10^{3} \pm 4.41\times10^{2}$	$1.26\times10^{3} \pm 3.05\times10^{2}$	$5.22\times10^{2} \pm 1.81\times10^{2}$	$(5.63\times10^{2}$ -$1.47\times10^{4})$ [19], $(3.20\times10^{1}$ – $9.30\times10^{1})$ [20]	$(5.72\times10^{3}$-$1.68\times10^{5})$ [19], $(4.45\times10^{4}$ – $6.14\times10^{4})$ [20]
Styrene oxide [CAR, HAP]	-	$3.45\times10^{1} \pm 2.24\times10^{1}$	$1.61\times10^{1} \pm 0.94$	$2.05\times10^{1} \pm 7.55$	$1.68\times10^{1} \pm 4.93$	$4.40\times10^{1} \pm 3.65\times10^{1}$	$(1.10\times10^{1}$ -$3.90\times10^{1})$ [19]	$(2.20\times10^{1}$ -$5.50\times10^{1})$ [19]
Benzaldehyde	-	$4.91\times10^{1} \pm 3.32\times10^{1}$	$3.18\times10^{1} \pm 3.34\times10^{1}$	$7.58\times10^{1} \pm 2.89\times10^{1}$	$2.06\times10^{1} \pm 2.45\times10^{1}$	$1.14\times10^{1} \pm 8.54\times10^{1}$	$(1.40\times10^{1}$ – $9.40\times10^{1})$ [20]	-
1,3,5-TMB	$2.27\times10^{1} \pm 4.00$	3.35 ± 0.87	2.96 ± 0.48	3.61 ± 1.06	3.26 ± 0.58	7.13×10^{1}	(1.70-2.40) [19]	$(5.10\text{-}5.40\times10^{1})$ [19],
1,2,4-TMB	$1.07\times10^{2} \pm 2.52\times10^{1}$	$1.54\times10^{1} \pm 4.44$	$1.83\times10^{1} \pm 3.15$	$1.94\times10^{1} \pm 5.86$	$1.70\times10^{2} \pm 5.16$	9.08 ± 4.11	$(2.30\text{-}1.20\times10^{1})$ [19]	$(1.10\times10^{1}$ -$1.88\times10^{2})$ [19]
Benzoic Acid	1 replicate shown<5.00×10^{4} & SIM<90	$1.51\times10^{2} \pm 5.37\times10^{1}$	$1.41\times10^{2} \pm 1.25\times10^{1}$	$1.80\times10^{2} \pm 2.17\times10^{1}$	$1.68\times10^{2} \pm 2.74\times10^{1}$	$1.10\times10^{2} \pm 2.59\times10^{1}$	-	-
1-tetradecanol	-	$2.88\times102 \pm 2.93\times101$	$3.14\times102 \pm 2.99\times101$	$3.49\times102 \pm 1.30\times102$	$3.38\times102 \pm 5.26\times101$	$3.04\times102 \pm 6.07\times101$	(4.33×102 - 8.72×102) [20]	

Table B.5 continued

N-Propylbenzene	2.03×101 ± 5.19	3.48 ± 0.80	3.69 ± 0.42	4.03 ± 0.99	3.58 ± 0.94	3.40 ± 0.57	(0.43-1.20×101) [19]	(2.40×101 - 4.90×101) [19]
2-Propenylbenzene	2.31 ± 5.39×101	-	-	-	-	-	-	-
Hydroquinone [CAR*, HAP]	-	-	1 replicate shown<5.00×104 & SIM<90	-	-	2 replicates shown<5.00×104 & SIM<90	-	-
1-Ethyl-3-methylbenzene	1.27×102 ± 2.84×101	3 replicates shown> 5.00×104 & SIM>90	3 replicates shown> 5.00×104 & SIM>90	3 replicates shown> 5.00×104 & SIM>90	3 replicates shown> 5.00×104 & SIM>90	3 replicates shown> 5.00×104 & SIM>90	-	-
2-Ethylhexanoic acid	1.23×101 ± 2.43	2 replicates shown<5.00×104 & SIM<90	3 replicates shown<5.00×104 & SIM<90	3 replicates shown<5.00×104 & SIM<90	3 replicates shown<5.00×104 & SIM<90	3 replicates shown<5.00×104 & SIM<90	-	-
BHT	1.41 ± 0.24	-	-	-	-	-	(4.90-9.40) [19]	(3.10×101 - 8.90×101) [19]
Sum	2.34×105	1.57×103	1.73×103	1.72×103	1.82×103	1.07×103	(6.22×102 - 1.47×104) [19], (8.37×102 - 1.57×103) [20]	(5.98×103 - 1.69×105) [19], (4,45×104 - 3.20×105) [20]

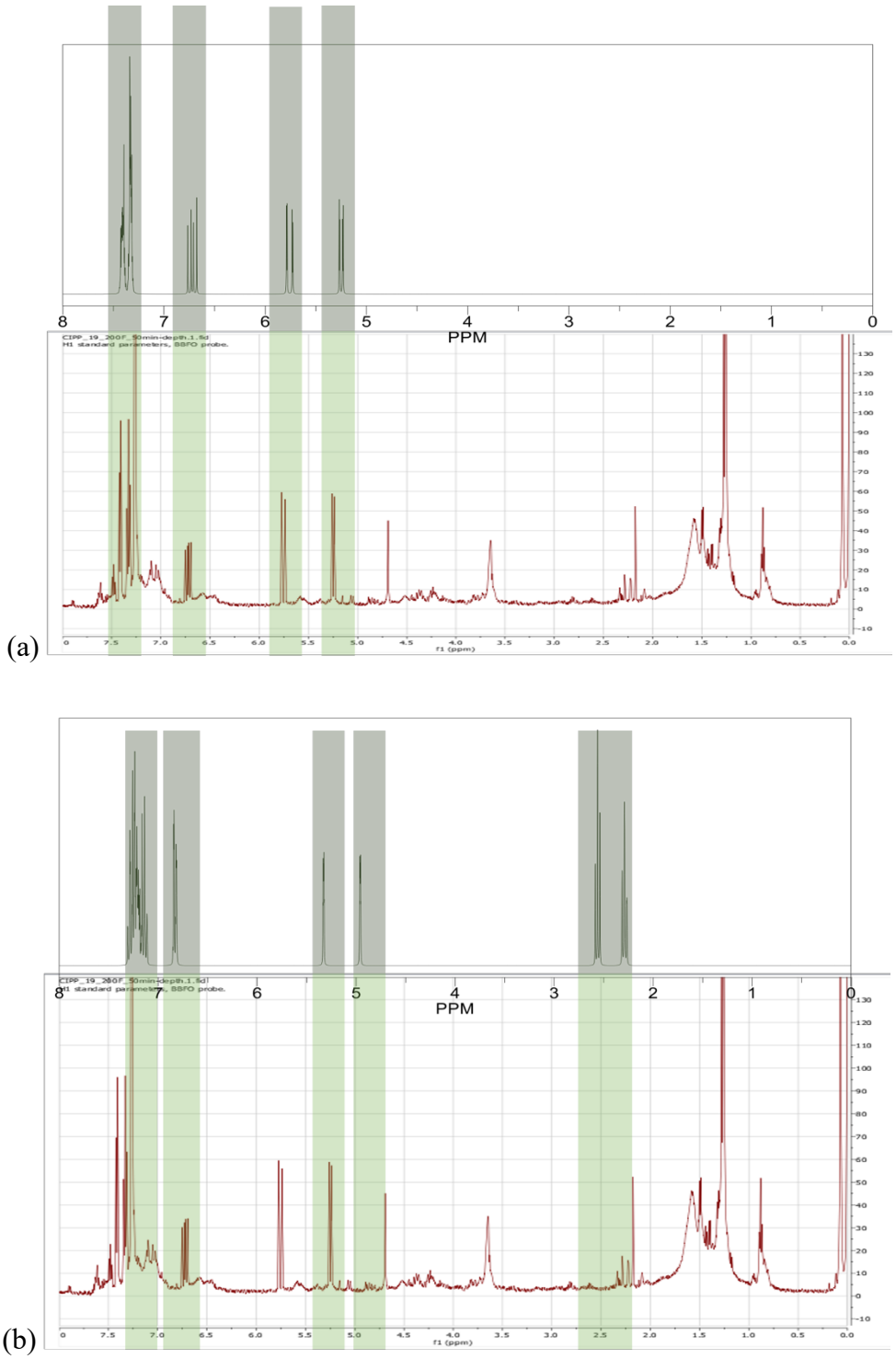
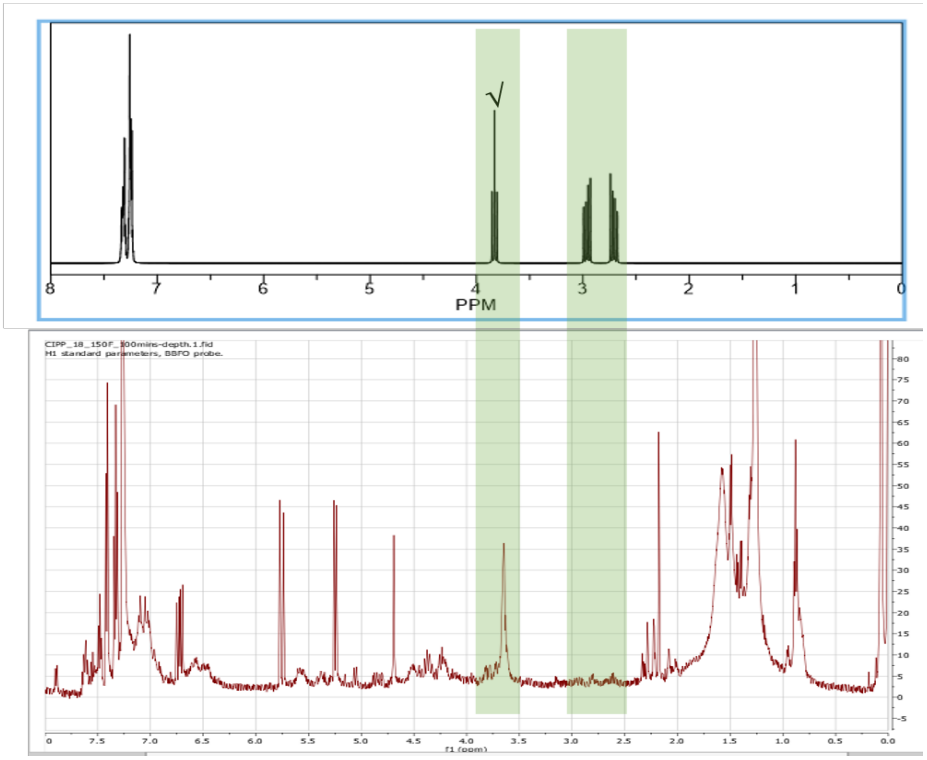


Figure B.3. HNMR images of compounds detected in uncured resin and cured composites at different curing conditions: (a) Styrene, (b) 2,4-diphenyl-1-butene (styrene dimer), (c) styrene oxide, (d) 2-ethylhexanoic acid, (e) 1,3,5-trimethylbenzene, (f) phthalate anhydride, (g) propylbenzene

Figure B.3 continued.

(c)



(d)

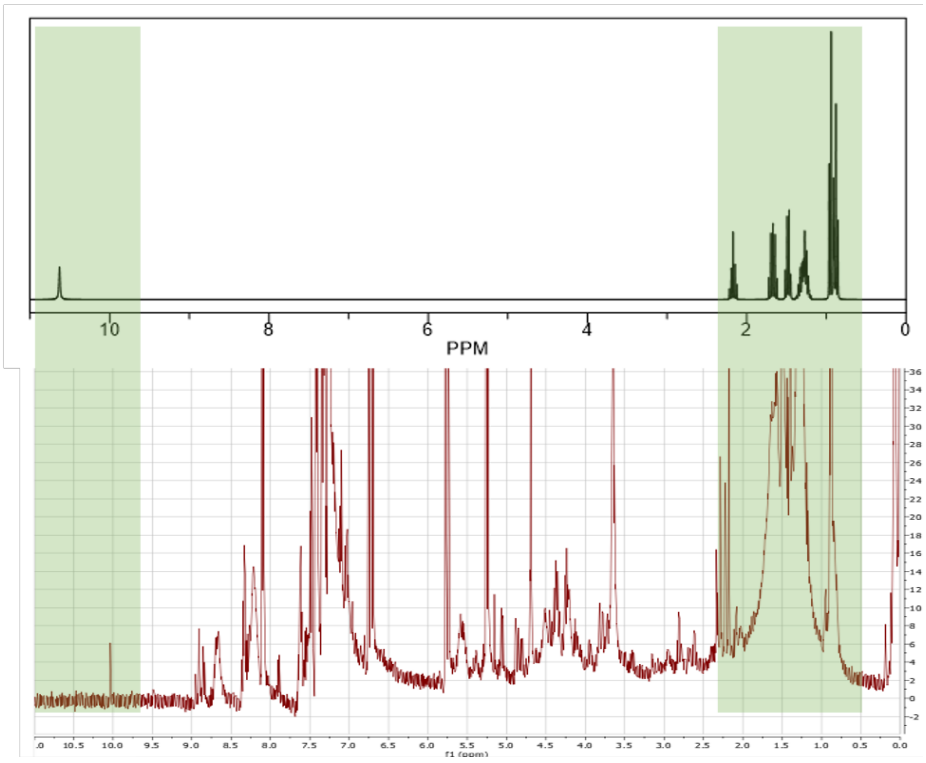
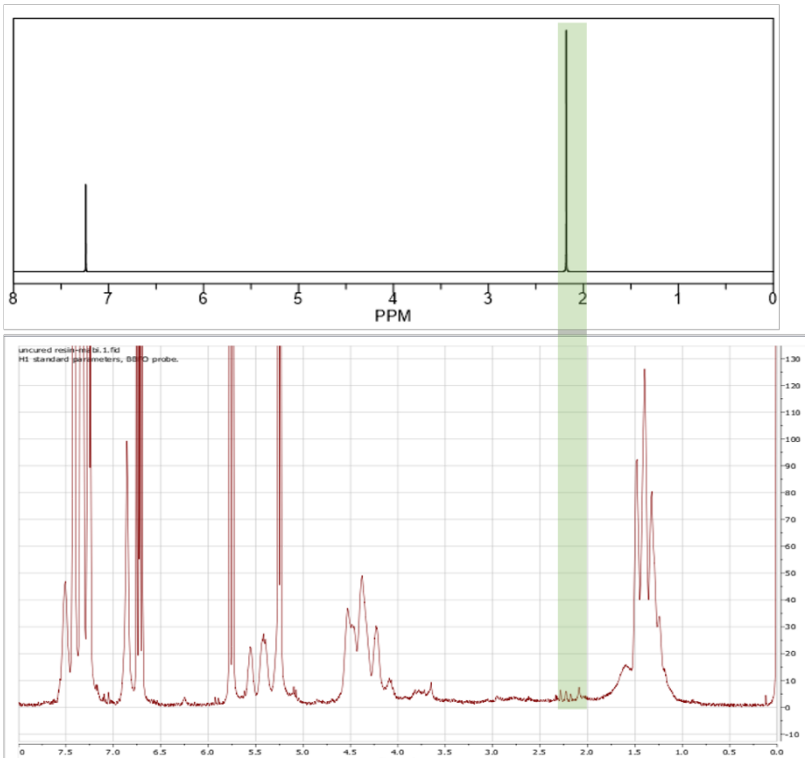


Figure B.3 continued.

(e)



(f)

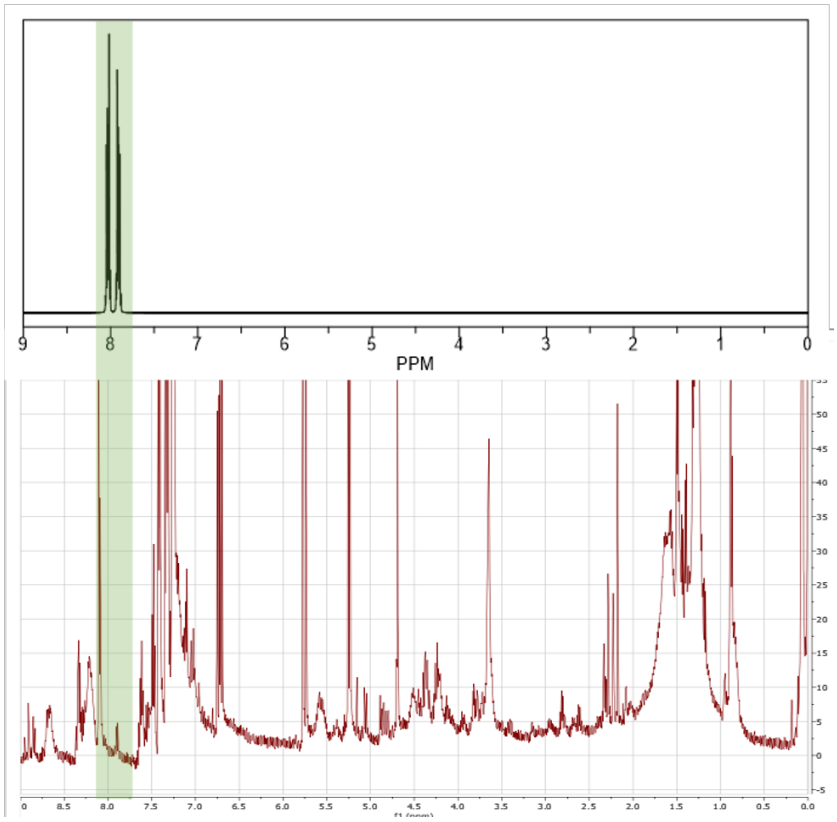
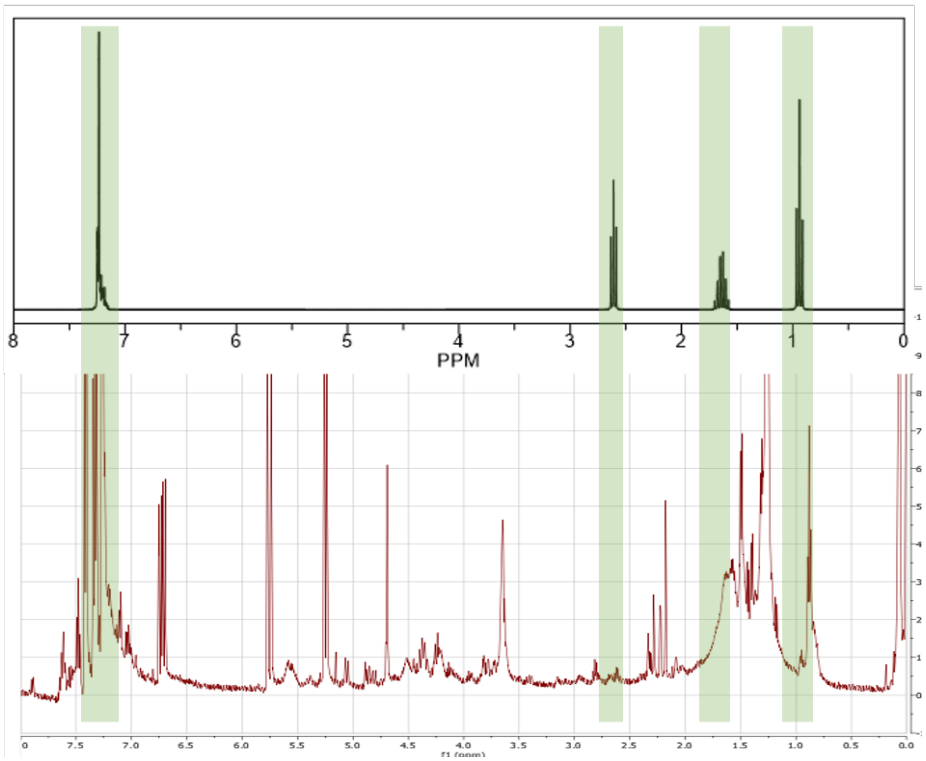
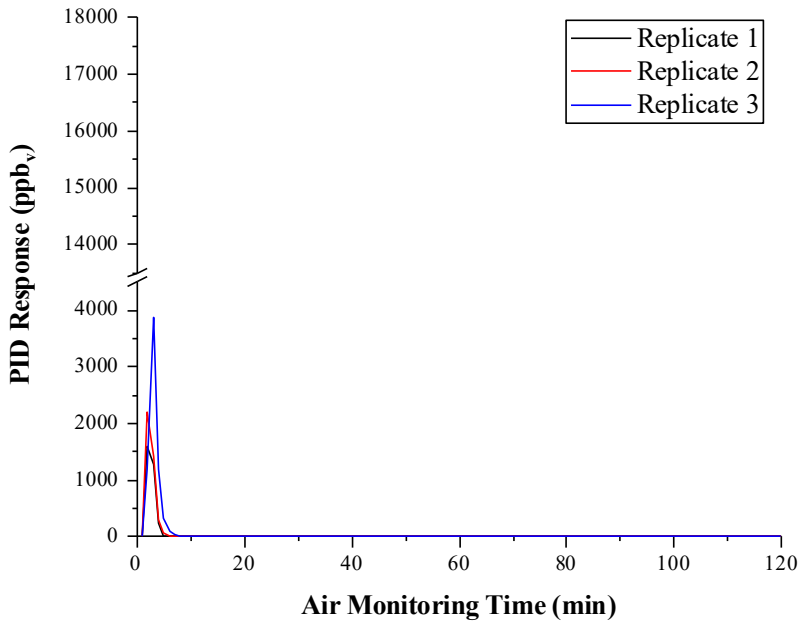


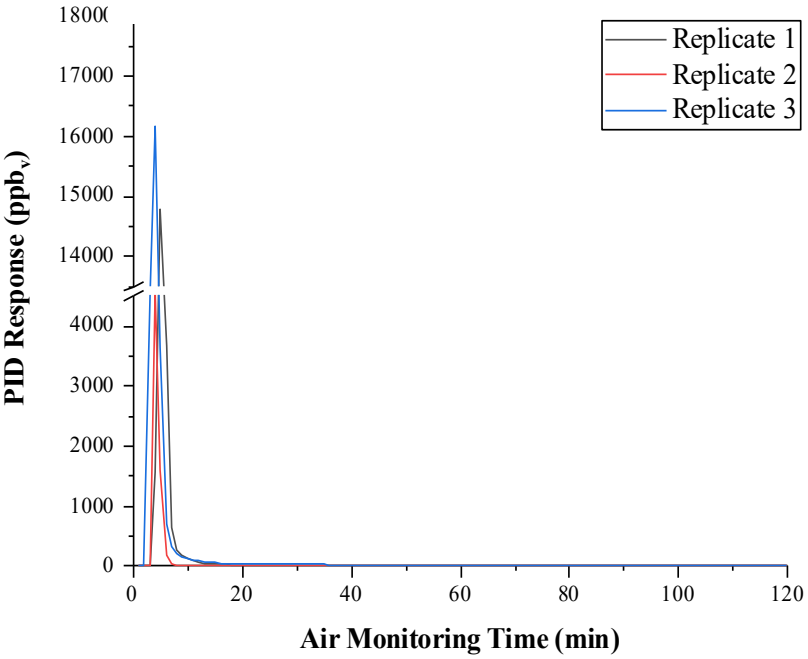
Figure B.3 continued.



(g)



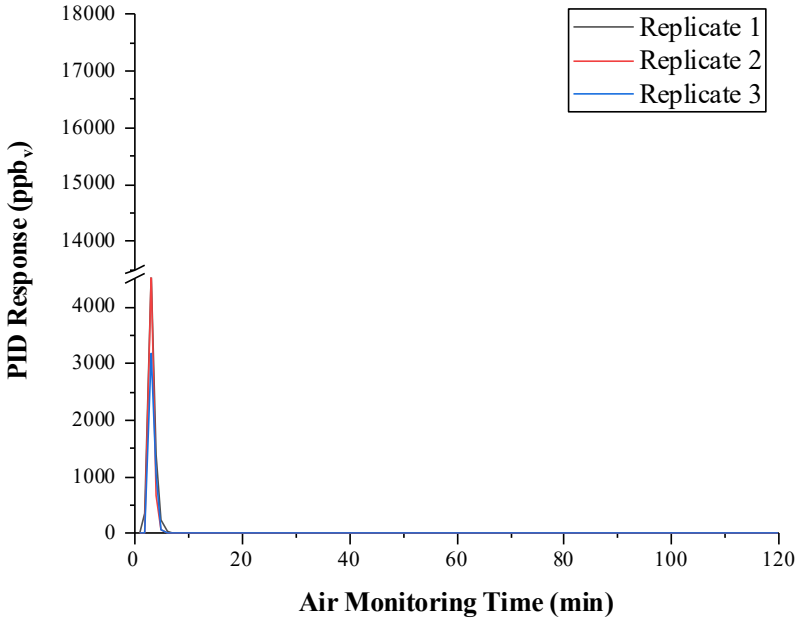
(a)



(b)

Figure B.4. PID air monitoring results from cured composites (a) 65.5 °C/50 min, (b) 65.5 °C/10 min and (c) 93.3 °C/50 min during 2 hr ventilation.

Figure B.4 continued



(c)

Table B.6. Styrene normalized weight and concentration captured during 2hr dynamic air monitoring

	Time (min)	***Normalized styrene weight (ng/cm^2), Concentration (ppm$_v$) Average ± STD***		
		65.5 C/50 min	***65.5 C/ 100 min***	***93.3 C/ 50 min***
Dynamic	0	1.25 ± 1.20, 2.19 ± 1.47	4.81 ± 3.87, 6.11 ± 4.90	1.05 ± 1.63, 1.30 ± 2.04
	5	$5.34\times10^{-2} \pm 5.30\times10^{-2}$, $6.92\times10^{-2} \pm 6.93\times10^{-2}$	$3.26\times10^{-2} \pm 1.40\times10^{-2}$, $4.13\times10^{-2} \pm 1.77\times10^{-2}$	$1.64\times10^{-2} \pm 3.75\times10^{-3}$, $2.05\times10^{-2} \pm 4.53\times10^{-3}$
	10	$9.42\times10^{-3} \pm 4.52\times10^{-3}$, $1.21\times10^{-2} \pm 6.01\times10^{-3}$	$1.49\times10^{-2} \pm 1.58\times10^{-2}$, $1.89\times10^{-2} \pm 1.98\times10^{-2}$	$1.11\times10^{-3} \pm 1.92\times10^{-3}$, $1.38\times10^{-3} \pm 2.38\times10^{-3}$
	20	$6.05\times10^{-3} \pm 2.98\times10^{-3}$, $7.79\times10^{-3} \pm 3.95\times10^{-3}$	$9.30\times10^{-3} \pm 9.17\times10^{-3}$, $1.18\times10^{-2} \pm 1.15\times10^{-2}$	$7.61\times10^{-4} \pm 8.90\times10^{-4}$, $9.46\times10^{-4} \pm 1.10\times10^{-3}$
	40	$3.54\times10^{-3} \pm 2.86\times10^{-3}$, $4.60\times10^{-3} \pm 3.72\times10^{-3}$	$7.49\times10^{-3} \pm 8.42\times10^{-3}$, $9.45\times10^{-3} \pm 1.05\times10^{-2}$	$1.14\times10^{-4} \pm 1.97\times10^{-4}$, $1.42\times10^{-4} \pm 2.45\times10^{-4}$
	60	$3.79\times10^{-3} \pm 1.02\times10^{-3}$, $4.87\times10^{-3} \pm 1.39\times10^{-3}$	$8.46\times10^{-3} \pm 8.45\times10^{-3}$, $1.07\times10^{-2} \pm 1.06\times10^{-2}$	$1.14\times10^{-4} \pm 1.97\times10^{-4}$, $1.42\times10^{-4} \pm 2.45\times10^{-4}$
	80	$2.62\times10^{-3} \pm 2.44\times10^{-3}$, $3.39\times10^{-3} \pm 3.17\times10^{-3}$	$6.81\times10^{-3} \pm 7.66\times10^{-3}$, $8.59\times10^{-3} \pm 9.58\times10^{-3}$	$1.14\times10^{-4} \pm 1.97\times10^{-4}$, $1.42\times10^{-4} \pm 2.45\times10^{-4}$
	100	$3.49\times10^{-3} \pm 1.27\times10^{-3}$, $4.48\times10^{-3} \pm 1.70\times10^{-3}$	$6.62\times10^{-3} \pm 7.79\times10^{-3}$, $8.38\times10^{-3} \pm 9.78\times10^{-3}$	$1.14\times10^{-4} \pm 1.97\times10^{-4}$, $1.42\times10^{-4} \pm 2.45\times10^{-4}$
	120	$2.35\times10^{-3} \pm 1.75\times10^{-3}$, $3.05\times10^{-3} \pm 2.29\times10^{-3}$	$8.15\times10^{-3} \pm 7.82\times10^{-3}$, $1.03\times10^{-2} \pm 9.83\times10^{-3}$	$1.14\times10^{-4} \pm 1.97\times10^{-4}$, $1.42\times10^{-4} \pm 2.45\times10^{-4}$

STD = standard deviation

Table B.7. Estimated mass of resin lost into atmosphere during CIPP manufacture

Year	*Reported CIPP Information*					*Estimated mass of resin lost if heating was applied for each CIPP application described the reference (kg)*
	Resin Type	*Resin Weight (kg)*	*Application*	*Monomer*	*Curing Method*	
2019 [25]	-	2.72×10^{5}	Storm sewer	-	-	2.41×10^{4}
2018 [26]	Isophthalic polyester	6.12×10^{4}	Sanitary sewer	Styrene	-	5.43×10^{3}
2014 [27]	Vinyl ester	7.94×10^{4}	Sewer	Styrene	-	7.04×10^{3}
2013 [28]	Unsaturated polyester	1.22×10^{8}	Sanitary and Storm	-	-	1.09×10^{7}
2012 [29]	Isophthalic polyester	4.54×10^{5}	-	-	Thermal	4.02×10^{4}
2012 [30]	Styrene-free vinyl ester	6.80×10^{4}	Storm sewer	-	-	6.04×10^{3}
2009 [31]	Vinyl ester	3.47×10^{5}	Sanitary sewer	Styrene	Hot water	3.08×10^{4}

Estimated mass of resin lost is equal to resin weight for each CIPP incidents reported in this Table times the average resin lost obtained in the present study when no vacuum was applied (8.87%).

The most abundant chemical in cured composites

As expected, styrene with the highest loading magnitude (9.74E03 - 2.07 x 10^4 mg/Kg) constituted a significant portion of cured composites. This compound also showed higher vapor pressure (i.e. 6.40 mmHg at 25 ^{o}C) and subsequently, higher volatility compared with other chemicals confirmed in the cured composite extraction. The order of these chemicals with higher vapor pressure (i.e. higher volatility) to lower vapor pressure (i.e. lower volatility) includes: styrene > *N*-propylbenzene > 3-ethyl-1-methylbenzene > 1,3,5-TMB > 1,2,4-TMB > 2-propenylbenzene > benzaldehyde > styrene oxide > 2-ethylhexanoic acid > BHT > benzoic Acid > 1-tetradecanol > hydroquinone. Therefore, it could be assumed that considerable amount of chemicals discharged into air during composite manufacturing contains styrene.

Table B.8. Physical and chemical properties of confirmed organic compounds in the uncured resin tube and cured composite

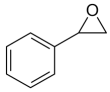
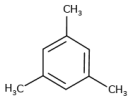
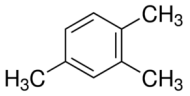
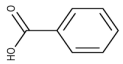
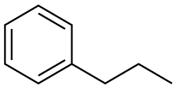
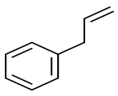
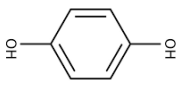
Compound	Chemical Formula	MW, g/mol	Chemical Structure	Vapor Pressure (mmHg 25°C)
Styrene	C_8H_8	104.15		6.40
Styrene oxide	C_8H_8O	120.15		0.30
Benzaldehyde	C_7H_6O	106.13		1.27
1,3,5-TMB	C_9H_{12}	120.20		2.48
1,2,4-TMB	C_9H_{12}	120.20		2.10
Benzoic Acid	$C_7H_6O_2$	122.12		7E-04
1-Tetradecanol	$C_{14}H_{30}O$	214.39		1.1E-04
***N*-Propylbenzene**	C_9H_{12}	120.20		3.42
2-Propenylbenzene	C_9H_{10}	118.18		1.69
Hydroquinone	$C_6H_6O_2$	110.11		1.9E-05

Table B.8 continued

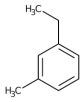
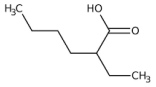
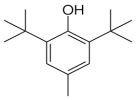
3-Ethyl-1-methylbenzene	C_9H_{11}	120.19		3.04
2-Ethylhexanoic acid	$C_8H_{16}O_2$	144.214		< 7.50E-03
BHT	$C_{15}H_{24}O$	220.36		5.2E-03

Table B.9. The weight of volatile material found in new cured composites based on curing conditions

Parameter	Curing condition and endothermic/exothermic temperature, °C			
	Condition A **50 min, 65.5˚C**	**Condition B** **100 min, 65.5˚C**	**Condition C** **50 min, 93.3˚C**	**Condition D** **25 min, 65.5˚C**
	Endothermic/Exothermic Temperature	**Endothermic/** **Exothermic Temperature**	**Endothermic/** **Exothermic Temperature**	**Endothermic/** **Exothermic Temperature**
After Manufacture, No vacuum				
Surface	£ 62°C, 64°C, 65°C / -	-	-	-
Depth	££ 60°C, 63°C, 64°C, 68°C / 153.5°C 154.5°C	-	-	-
After Manufacture, Vacuum applied				
Surface	€ 58°C, 59°C, 60°C, 64°C, 65°C / 154°C, 154.5°C, 156.5°C, 159°C	§ 57°C, 58°C, 58.5°C, 64°C / 151.3°C, 153.5°C, 155°C, 155.5°C, 159.5°C	¥ 60°C, 61.8°C, 64°C / 154°C, 159.5°C, 164°C, 168°C	†
Depth	€€ 56°C, 59°C, 60°C / 158°C, 160°C, 160.6°C, 161.5°C, 167°C, 168°C	§§ 58°C, 59°C, 62°C, 64°C / 158.5°C, 159.5°C, 163°C, 164°C, 165°C	¥¥ 56.5°C, 58°C, 60°C, 62°C, 64°C / 152°C, 163.5°C, 164°C, 167.5°C, 168.5°C, 172°C	‡ 64.5°C, 66°C, 67°C, 68°C / 161°C, 164.5°C

Initial volatile content of the resin was 39 ± 1.74 %; -: Not measured. The following symbols indicate the number of replicates that showed endothermic peak at approximately 65°C and exothermic peak at 140-160°C per the total number of replicates: £ endothermic peak: 8/8, exothermic peak: 0/9; ££ endothermic peak: 6/9, exothermic peak: 2/9; † endothermic peak:, exothermic peak:; ‡ endothermic peak: 8/9, exothermic peak: 3/9; € endothermic peak: 8/9, exothermic peak: 5/9; €€ endothermic peak: 4/9, exothermic peak: 7/9; § endothermic peak: 4/9, exothermic peak: 5/9; §§ endothermic peak: 3/8, exothermic peak: 7/8; ¥ endothermic peak: 5/9, exothermic peak: 4/9; ¥¥ endothermic peak: 6/9, exothermic peak: 6/9

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