

St. John the Baptist Parish Chloroprene Monitoring Demonstration

*Subproject of
“Cancer Reporting in St. John the Baptist Parish (CRISP”) Project*

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SUMMARY

This report is part of a larger project to review cancer cases in St. John the Baptist Parish,

Louisiana “Cancer Risk in St John Parish” (CRISP).¹ This report presents the results of a proof-of-concept demonstration to evaluate the feasibility of applying specific analytical procedures for detecting chloroprene in air and urine. This demonstration was not designed to characterize average chloroprene concentrations at resident homes or to estimate ongoing resident exposures to Denka’s chloroprene emissions. Due to limited financial resources, we could collect and analyze only a small number of air and biomonitoring samples.

Several logistical issues and field conditions impacted the likelihood of detecting chloroprene in the air, or chloroprene metabolites in urine. By the time researchers commenced monitoring, chloroprene and neoprene production at Denka had ceased due to Hurricane Ida, which severely impacted the area on August 29th, 2021. A retrospective review of Denka’s emissions reported to the US Environmental Protection Agency (EPA) for September 2021 revealed that facility operators reported that all chloroprene and neoprene production had ceased throughout the entire month of September.² Thus, the air monitoring and biomonitoring results in this report are more characteristics of months in which there is no chloroprene production.

However, the limited air and biomonitoring that was conducted indicate there is a need for further investigation and precautionary policies. Air monitoring revealed chloroprene in the air offsite in areas downwind of the facility, including one elementary school, at levels exceeding the EPA’s recommended maximum annual average chloroprene concentration of 0.2 µg/m³ (0.78 and 0.85 µg/m³), during a month in which no chloroprene was being produced and emissions were reportedly the lowest on record (Sept 2021). Biomonitoring of residents in the surrounding area also suggested the presence of metabolites of three parent compounds, chloroprene, 1,3-butadiene, and epichlorohydrin, which EPA classifies as likely, known and probable carcinogens, respectively.

¹ For more information about this project see: <https://louisianacancer.org/st-john/>

² In the EPA Emergency Response report from Hurricane Ida, Denka Performance Elastomer, LLC Facility Report, Denka reported on September 1, 2021, no pollution threat. Assessment condition was reported as “damaged- no discharge/release, facility did not flood, facility is operating on generator, no further action”. On September 17, 2021, Denka reported “The damage to the report is extensive, but limited almost entirely to office buildings and we sustained no releases of chemicals. If we have reasonable expectations of tropical storm force winds or stronger impacting the site, we clear out all the units and send everything back to tanks for the duration of the storm, and we maintain a crew onsite to deal with any issues should they arise, which they didn’t in this case, aside for losing power for several days.”

APPROACH

Ten residents within a half mile of the Denka Performance Elastomer facility in LaPlace, LA were recruited by word of mouth for air and urine sampling at locations # 1,3 and 4 on **Figure 1**). Participants were recruited in the month prior to field sampling, but Hurricane Ida hit the area on August 29, 2021, disrupting monitoring plans as many residents had evacuated and could not return due to widespread destruction. Between September 22nd and 23rd, 2021, air monitoring around the Denka Performance Elastomer on River Road, LaPlace, LA commenced. Prior to sample collection we asked study participants to avoid using products or engaging in activities that would ordinarily expose them to VOCs, in an attempt to isolate exposures that may be coming from Denka. Air samplers were situated outside at the residence location. There were no active generators or other potential sources of VOCs in the area of air sample collection. Active sampling was used where air is pumped through a tube with sorbent material to capture volatile organic compounds (VOCs). On the 22nd wind was blowing from the northwest to the southeast and air samples were collected at sites 1,2, 3, 4 and 8 (**Figure 1**). On the 23rd wind was blowing from the northeast to the southwest and air samples were collected at sites 4, 5, 6, 7 and 9 (**Figure 1**). Urine samples (30 mL) were also collected from available participants residing at the locations where air samples were collected. Urine samples were collected on the night of September 22 and/or the morning of September 23 (sites 1,3 and 4, **Figure 1**). All urine samples were coded for de-identification purposes, double-wrapped in zip lock bags, placed in ice chests immediately after collection, transferred to a freezer and frozen for 24 hours before being packed in ice and shipped to the appropriate laboratory overnight. Dr. Adrienne Katner of LSU Health conducted all sample collection. Dr. Chung-Ho Lin conducted all sample analyses at the University of Missouri-Columbia.³ Air samples were evaluated for chloroprene and other VOCs; and urine samples were evaluated for chloroprene metabolites. **Appendix A** presents the laboratory report on the air sample analysis, QA/QC protocols and results. **Appendix B** presents the laboratory report on urine sample analysis, QA/QC protocols and results.⁴ **Appendix C** presents a summary of all air and urine sample results.

³ Sorbent Tube Analysis: INSTAAR Labs (Institute of Arctic and Alpine Research—Dr Dellef Helmig) INSTARR uses FID/MS protocols for VOC analysis in air samples collected in sorbent tubes. Sorbent tubes (SKC Inc. Eighty Four, PA, Cat# MX062131 4-1/2" L packed with 20:35 mesh Tenax-TA/ Carboxen 1000/Carbosieve SIII) are the most widely used collection media for sampling hazardous gases and vapors in air, mostly as it relates to industrial hygiene. They were developed by the US National Institute for Occupational Safety and Health (NIOSH) for air quality testing of workers. Sorbent tubes are typically made of glass and contain various types of solid adsorbent material). Commonly used sorbents include activated charcoal, silica gel, and organic porous polymers. Solid sorbents are selected for sampling specific compounds in air because they: 1. Trap and retain the compound(s) of interest even in the presence of other compounds 2. Do not alter the compound(s) of interest 3. Allow collected compounds to be easily desorbed or extracted for analysis. Sorbent tubes are attached to air sampling pumps for sample collection. A pump with a calibrated flow rate in ml/min is normally placed on a study participant's belt or other clothing, and it draws a known volume of air through the sorbent tube. Chemicals are trapped onto the sorbent material throughout the sampling period. The absorbent tube is then placed in a heated chamber and purged with an inert gas. VOCs are thermally desorbed into a cryogenic trap, cryofocused onto the transfer line, separated by GC and analyzed by a positive ion electron impact Mass Spectrometer (MS).

⁴ Urine Analysis Protocol: Dr Chung-Ho Li (University of Missouri) Analysis of VOCs by SPME followed by GC-MS To quantify the volatile organic compounds (VOCs) in the urine samples, including benzene, toluene, xylene, trimethylbenzene, the toluene-d8 was spiked into the samples as the internal standard, the VOCs were extracted by a headspace solid-phase microextraction (SPME) using a 85mm carboxen/polydimethylsiloxane fiber followed by the analysis with an Agilent 6890N gas chromatography coupled with an Agilent 5973N quadrupole mass spectrometer (GC-MS). Analysis of Hydrophobic Metabolites by Liquid-Liquid Extraction followed by GC-MS The hydrophobic metabolites in the urine samples were extracted by a water:dichloromethane (1:1, v/v) liquid- liquid procedure described

RESULTS

Air Sampling and Analysis

Two out of ten air samples had detectable chloroprene (Sample #4 and 5 in **Figure 1** and **Appendix C**). Both sampling sites were downwind of the Denka plant on the day the sample was collected (9/23/2021). **Chloroprene was not detected in the air samples collected for the remaining samples on September 22 or 23, 2021.** This could occur if there were no chloroprene in the air at the specific sample collection site on that date or if the chloroprene levels were below the analytical limits of detection ($<0.005 \mu\text{g}/\text{m}^3$).

- **One positive air sample ($0.78 \mu\text{g}/\text{m}^3$) was collected on September 23, 2021 by the 5th Ward Elementary School** at the gate of the EPA air monitor (west of Denka) at 158 Panther Dr. Reserve LA 70084 (site #5 in **Figure 1**). No air samples were collected from this site on Sept 22nd. Active air sampling started at 11:33 am on this day and lasted until 5:58 pm. Winds were from the northeast to the southwest that day, thus this area would be in the direction of winds blowing from Denka. On this same day, the school also had relatively higher levels of toluene, benzene and xylene (**Appendix C**); however, air concentrations for these VOCs did not exceed EPA's chronic exposure Reference Concentrations (RfC) for non-cancer health effects. It should be remembered that Denka was not operational during the month of September 2021 due to Hurricane Ida.⁵ EPA had previously requested that Denka undertake air monitoring for 1,3-butadiene, along with chloroprene, toluene, benzene, xylene and ethylbenzene.⁶ Results for 1,3-butadiene are still pending due to delays in the specific reference standards.
- **Another positive chloroprene sample ($0.85 \mu\text{g}/\text{m}^3$) was collected on September 23, 2001,** at residence #4 across the street from the 5th Ward Elementary School (see **Figure 1**). Active air sampling started at 11:37 am and lasted until 5:58 pm. Winds were blowing in this direction from Denka. This residence also had relatively higher concentrations of benzene and toluene on the same day; however, air concentrations for these VOCs did not exceed EPA's RfC. The prior day (Sept 22nd), this residence had relatively higher concentrations of benzene, 1,2,4-trimethylbenzene,⁷ toluene and xylene; however levels were lower than EPA's RfC. The resident at this home also had detectable DHBMA, HOBMA, CHPMA, CI-MA-II

by Lin (2007 and 2008). The identification and quantification of these metabolites were performed using a Varian 3400cx GC with a Hewlett Packard cross-linked methylsiloxane DB-5 capillary column (30 m x 0.25 mm I.D.) coupled with a Varian Saturn 2000 ion-trap mass selective detector (Varian Inc., Walnut Creek, CA).

⁵ The RIC is an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious noncancer effects during a lifetime.

⁶ The EPA request was based on the May 6, 2021, EPA Office of Inspector General's report, "EPA Should Conduct New Residual Risk and Technology Review for Chloroprene and Ethylene Oxide-Emitting Source Categories to Protect Human Health, May 6, 2021: EPA. EPA Should Conduct New Residual Risk and Technology Reviews for Chloroprene- and Ethylene Oxide-Emitting Source Categories to Protect Human Health. Report #21-P-0129. US EPA Office of Inspector General. May 6, 2021. Available at: <https://www.epa.gov/office-inspector-general/report-epa-should-conduct-new-residual-risk-and-technology-reviews>.

⁷ We could not find reports of 1,2,4-trimethylbenzene emissions from Denka. This compound is used to make high performance polymers and resins.

and III metabolites in their urine on Sept 23rd, suggesting exposure to chloroprene, 1,3-butadiene and epichlorohydrin, which are all used in the plastics industry.

- **Other sites had detectable levels of other VOCs.** Relatively higher levels of toluene were detected at Sites 1, 2, 3, 7 and 8; and higher levels of benzene ($>1 \mu\text{g}/\text{m}^3$) were detected at Sites residences 1 and 4, and site 5, the Fifth Ward Elementary School (see **Figure 1** and **Appendix C**).⁸ A resident at site # 1 also had detectable levels of DHBMA, HOBMA, CHPMA, Cl-MA-I, II, and III, suggesting exposure to chloroprene, 1,3-butadiene and epichlorohydrin. EPA monitoring detected other VOCs around Denka on Sept. 16 and 18, 2021, and found acrylonitrile and vinyl chloride at air levels above Response Screening Values.⁹

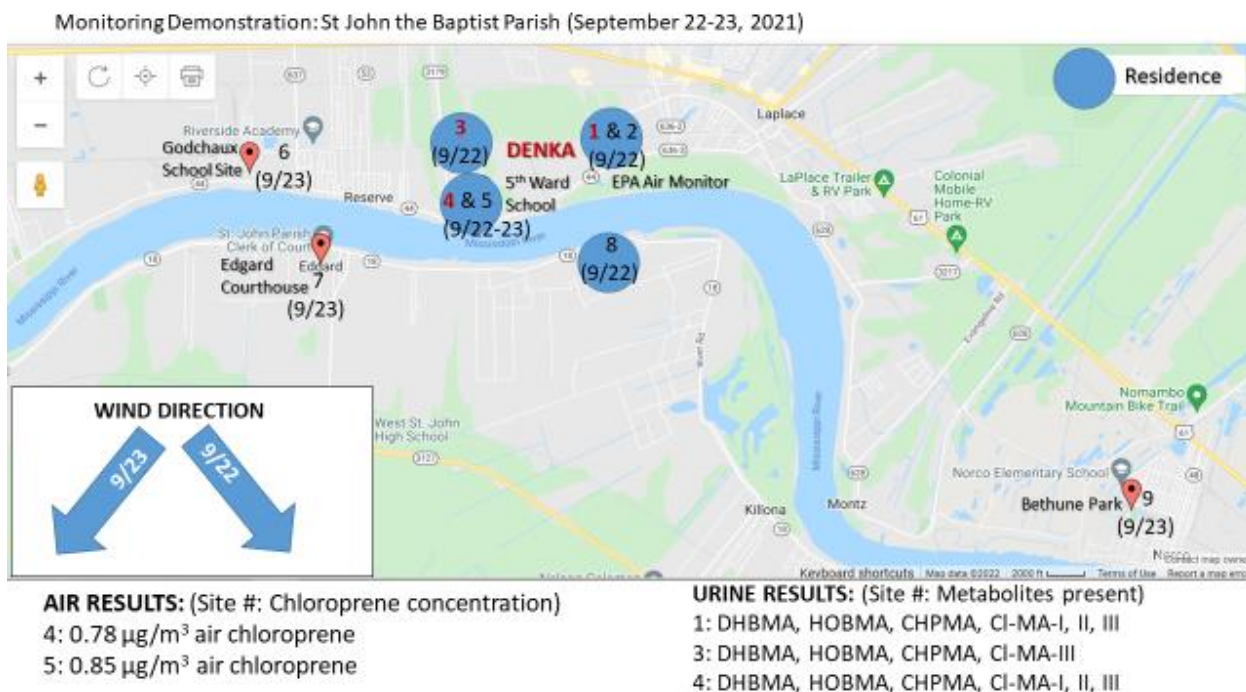


Figure 1. Air sample locations around the Denka facility (2021). In total nine sites were monitored numbered 1 through 9). Dates in which air samples were collected are indicated in parentheses near each site in the map. Sites in bold red are residential areas where urine samples were collected from residents. The locations of residences are shielded with a larger circle to protect residents' privacy.

⁸ For every $1 \mu\text{g}/\text{m}^3$ of benzene there is 2.2 cancers per every one million people exposed, based on EPA's Inhalation Unit Risk value for benzene of $2.2\text{E}-06$ per $\mu\text{g}/\text{m}^3$. Benzene is formed from both natural processes and human activities. Sources include fires, gasoline, cigarette smoke, but it is also emitted by Denka.
⁹ EPA performed 24 hour summa canister collected air samples upwind and downwind of the Denka facility beginning on September 11, 2021. September 16, 2021, the Denka downwind air sample contained Acrylonitrile above the Response Screening Level of $2.09 \mu\text{g}/\text{m}^3$. The value was $3.62 \mu\text{g}/\text{m}^3$. On September 18, 2021, the Denka downwind air sample contained Vinyl Chloride above the Response Screening Level of $2.24 \mu\text{g}/\text{m}^3$. The value was $2.61 \mu\text{g}/\text{m}^3$. **Acrylonitrile** causes severe irritation of the skin and blistering. It can irritate the eyes, nose and throat. Breathing Acrylonitrile can irritate the lungs, causing coughing and/or shortness of breath. Acrylonitrile can cause headaches, dizziness, confusion, nausea, vomiting. **Vinyl Chloride** causes severe irritation and burns the skin and eyes with possible eye damage. Breathing Vinyl Chloride can irritate the nose, throat and lungs, causing coughing wheezing and/or shortness of breath. Vinyl Chloride can cause headaches, nausea, vomiting, dizziness, fatigue, weakness and confusion. Acrylonitrile is used to produce high-impact plastics; while vinyl chloride is used to make polyvinyl chloride (PVC), which is used to make a variety of products, including plastics.

Urine Sampling and Analysis

Metabolites indicating VOC exposures were detected in all of the nine urine samples collected from seven participants residing at the three locations sampled (#4, #3 and #1) (Figure 1). These were the only sites where non-evacuee residents were available to provide urine samples.

Metabolites detected included DHBMA, HOBMA, Cl-MA-I, II, and III, suggesting exposure to chloroprene, 1,3-butadiene and epichlorohydrin.

- **DHBMA, a metabolite of both chloroprene and 1,3-butadiene, was detected in all urine samples collected.** The highest levels of DHBMA were from the participant at site #1, adjacent to EPA's air monitor southeast of Denka (**Figure 1**).¹⁰ DHBMA is the main product in chloroprene metabolism, but it is also a product of 1,3-butadiene metabolism. Denka is the sole source of chloroprene in the area— it does not occur naturally (NTP 2011)¹¹. Chloroprene is classified by EPA as likely to be carcinogenic to humans; and is associated with irritation to eyes, skin, and airways, damage to lungs, liver and kidneys, headaches, fatigue, irritability, dermatitis, hair loss, and cardiovascular and immune systems disorders. While chloroprene is Denka's highest risk emission release (35,718 pounds), the third highest risk emission from Denka based on EPA's analysis is 1,3-butadiene (2,039 pounds), a known carcinogen.¹² Denka's production of chloroprene is dependent on 1,3-butadiene to produce synthetic rubber, but it is also found in smaller amounts in automobile exhaust, tobacco smoke and other sources. EPA requested Denka monitor for 1,3-butadiene, which began in December, 2021, along with monitoring for toluene, chloroprene, xylene, benzene and ethylbenzene. 1,3-Butadiene was detected at the Western edge of Denka property on August 26, 2021 (7.7 µg/m³); at Ochsner Hospital on August 31, 2021 (4.4 µg/m³); and at the Western edge of the Denka property on January 12, 2022 (2.6 µg/m³), and January 26, 2022 (8.1 µg/m³).
- **We suspect the presence of HOBMA, CHPMA, and Cl-MA-I, II, and III metabolites in participant urine;¹³ however, we could not verify the identity of these metabolites due to the lack of specific reference standards.** Cl-MA-I, II and III are unique metabolites of chloroprene; HOBMA is a metabolite of both chloroprene and 1,3-butadiene; and CHPMA is a specific metabolite of the probable carcinogen epichlorohydrin.¹⁴⁻¹⁵ Five of seven residents had CHPMA in urine— the highest levels were at sites 1 and 4 (**Figure 1 and Appendix C**).

¹⁰ For non-smokers, median DHBMA were 100-300 µg/l creatinine. In this demonstration, DHBMA concentrations ranged from 139 µg/m³ to 568 µg/m³.

¹¹ NTP (National Toxicology Program). (1998). Toxicology and Carcinogenesis Studies of Chloroprene (CAS No. 126-99-8). National Toxicology Program Technical Report Series, 9(467), 1–379. Retrieved from <http://www.ncbi.nlm.nih.gov/pubmed/12579206>

¹² EPA classifies 1,3-butadiene as a known human carcinogen. It is also associated with irritation to the eyes, throat, nose, and lungs; damage to the central nervous system, distorted vision, vertigo, fatigue, decreased blood pressure, headache, nausea and fainting. EPA EasyRSEI Dashboard V 2.3.10 for Denka: [LINK](#)

¹³ **Notes:** (1) 3,4-dihydroxybutyl mercapturic acid (DHBMA); (2) 4-hydroxy-3-oxobutyl mercapturic acid (HOBMA); (3) 3-chloro-2-hydroxypropyl mercapturic acid (CHPMA); (4) 4-chloro-3-oxobutyl mercapturic acid (Cl-MA-I); (5) 4-chloro-3-hydroxybutyl mercapturic acid (Cl-MA-II); (6) 3-chloro-2-hydroxy-3-butenyl mercapturic acid (Cl-MA-III). See: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/3527600418.bi12699e2115>

¹⁴ Epichlorohydrin is a highly reactive compound used in the production of glycerol, plastics, epoxy glues and resins, epoxy diluents and elastomers. Exposure to epichlorohydrin may irritate mucous membranes, and cause nausea, cough, labored breathing, lung inflammation, renal lesions, and hematological effects.

¹⁵ The only source of epichlorohydrin in the area appears to be Shell Norco (7-8 miles away). LDEQ EDMS Query for "epichlorohydrin". Available at: <https://edms.deq.louisiana.gov/edmsv2/advanced-search>

DISCUSSION

Several logistical issues and field conditions impacted the likelihood of detecting chloroprene in the air, or chloroprene metabolites in urine. By the time researchers commenced monitoring, chloroprene and neoprene production at Denka had ceased due to Hurricane Ida, which severely impacted the area on August 29th, 2021. A retrospective review of Denka's emissions reported to EPA for September 2021 revealed that facility operators reported no chloroprene production throughout the entire month of September.¹⁶ Denka calculated a monthly average chloroprene emission of 0.04 µg/m³ for September 2021, the lowest on record.

However, chloroprene was detected downwind of Denka on September 23rd, 2021, during a period of no reported chloroprene production. Chloroprene does not occur naturally in the environment—Denka is the sole source of emissions in the area. Chloroprene levels at or across the street from the elementary school were estimated to be 0.78 and 0.85 µg/m³ on Sept. 23rd—approximately four times above the EPA's recommended maximum annual average chloroprene air concentration of 0.2 µg/m³. This recommended chloroprene air concentration was set to limit cancer risk among 1 million persons to 100 cancer cases per year. Denka's air monitors also detected chloroprene in September 2021, with concentrations as high as 4.7 µg/m³ (Sept. 22) at the western edge of Denka's property, and 24 µg/m³ (Sept. 27) at the eastern edge. These levels were between 23 and 2120 times above 0.2 µg/m³.¹⁷ The EPA's chloroprene air limit is a recommendation, not a required regulatory standard. However, it is important to understand that levels below state and national air quality standards cannot always ensure zero health risks,¹⁸ especially when considered in the context of simultaneous exposures to other facility-specific emissions.

The facts presented support concerns about a likelihood of chronic exposure to low doses of chloroprene at levels which may have potential health impacts on vulnerable populations.

Children attending 5th Ward Elementary School and residing in the community may be regularly exposed to levels of chloroprene at or above 0.2 µg/m³, which when considered in conjunction

¹⁶ In the EPA Emergency Response report from Hurricane Ida, Denka Performance Elastomer, LLC Facility Report, Denka reported on September 1, 2021, no pollution threat. Assessment condition was reported as "damaged- no discharge/release, facility did not flood, facility is operating on generator, no further action". On September 17, 2021, Denka reported "The damage to the report is extensive, but limited almost entirely to office buildings and we sustained no releases of chemicals. If we have reasonable expectations of tropical storm force winds or stronger impacting the site, we clear out all the units and send everything back to tanks for the duration of the storm, and we maintain a crew onsite to deal with any issues should they arise, which they didn't in this case, aside for losing power for several days."

¹⁷ LDEQ Electronic Document Management System. AI: 199310 for monthly monitoring and emission estimate reports: [LINK](#)

¹⁸ For example, extensive research suggests that certain pollutants (e.g., PM2.5) have negative health impacts below current air quality standards. See the Oct 22, 2019 Letter to EPA Secretary Andrew Wheeler from the Independent Particulate Matter Review Panel summarizing the scientific evidence that the current PM2.5 standard is inadequate to protect public health. Available at <https://yosemite.epa.gov/sab/sabproduct.nsf/81DF85B5460CC14F8525849B0043144B/%24File/Independent+Particulate+Matter+Review+Panel+Letter+on+Draft+PA.pdf/>.

with exposures to other VOC emissions from Denka, is a concern.¹⁹ Chloroprene has been manufactured at this site since 1969, thus it constitutes a chronic (>5 decades) exposure. Based on air monitoring data from both EPA and Denka, chloroprene continues to occur with some regularity at levels exceeding 0.2 µg/m³, even after emission control technologies were installed in February 2018.²⁰ In 2021, chloroprene air concentrations were as high as 1.8 µg/m³ at a site two miles away from the facility (at Edgard Courthouse, site #7 on **Figure 1**); and as high as 20.2 µg/m³ at a site one mile from the facility (at Ochsner Hospital). When the proximity of 5th Ward Elementary School is considered (0.3 miles or 500 yards from the Denka facility), it is not unexpected that levels were detected at the school in 2021 as high as 20.7 µg/m³ by Denka (103 times higher than 0.2 µg/m³), and as high as 3.34 µg/m³ by EPA (16 times higher than 0.2 µg/m³).

While biomonitoring data did not conclusively link exposures to chloroprene, the presence of metabolites of chloroprene, 1,3-butadiene and/or epichlorohydrin are a concern as these are likely, known and probable carcinogens, respectively, which are associated with plastics production. Furthermore, their presence was unanticipated, given the absence of chloroprene production throughout September (2021). While the source of epichlorohydrin is currently unknown, it was not entirely unexpected to find metabolites of chloroprene and/or 1,3-butadiene in resident urine. On June 15, 2021, the EPA requested Denka to undertake air monitoring for 1,3-butadiene, which commenced in Dec. of 2021, along with monitoring for chloroprene.²¹ 1,3 Butadiene was detected at the Western edge of Denka property on Aug. 26, 2021 (7.7 µg/m³); at Ochsner Hospital on Aug. 31, 2021 (4.4 µg/m³); and again at the Western edge of Denka property on Jan. 12, 2022 (2.6 µg/m³), and Jan. 26, 2022 (8.1 µg/m³).

There is a need for a cumulative risk assessment for all Denka emissions, both carcinogens and non-carcinogens, especially considering the similarities in health outcomes from many of the VOCs found in resident air space and/or urine. The current health assessment approach used by LDH which bases risk decisions on one chemical, chloroprene, is unrealistic and underestimates risks faced by this population from other emissions and emission sources. Currently, LDEQ's process for evaluating whether or not there is an environmental injustice prior to approving a permit application is also limited in scope, such that the real-world exposures to communities are

¹⁹ Even with the decrease in production of Chloroprene and Neoprene from July to August 2021, the August 2021 monthly average Chloroprene ambient air emissions concentration increased 3.4 fold when compared to July 2021 (0.81 ug/m³ to 2.76 ug/m³ monthly average).

²⁰ A review of chloroprene air concentrations based on data collected in 2021, revealed that the highest chloroprene levels occurred in January 2021 at three of the six air monitoring locations: 1) the Intersection of Hwy 44 and IC Railroad (36.9 µg/m³); 2) the southwest corner of Ochsner Hospital (20.2 µg/m³); and 3) the Mississippi River Levee (19.2 µg/m³). During this month (Jan 2021), Denka estimated a monthly average chloroprene emission of 3.49 µg/m³.

²¹ The EPA request was based on the May 6, 2021, EPA Office of Inspector General's report, "EPA Should Conduct New Residual Risk and Technology Review for Chloroprene and Ethylene Oxide-Emitting Source Categories to Protect Human Health, May 6, 2021; EPA. EPA Should Conduct New Residual Risk and Technology Reviews for Chloroprene- and Ethylene Oxide-Emitting Source Categories to Protect Human Health. Report #21-P-0129. US EPA Office of Inspector General. May 6, 2021. Available at: <https://www.epa.gov/office-inspector-general/report-epa-should-conduct-new-residual-risk-and-technology-reviews>.

not considered, i.e., the cumulative and synergistic effects of multiple pollutants from all facilities within an area. Cumulative health impacts from population exposures beyond cancer have largely been ignored in studies of this population. The single-minded focus on cancer may have distracted authorities from identifying other health impacts of Denka's emissions. Cancer has a long latency of years to decades, yet, the increasing frequency of disasters like Hurricane Katrina, the Great Flood of 2016, and Hurricane Ida makes it improbable that this population will remain in place long enough to enable a prospective study of cancer rates in this population. It could also be that many in the population aren't living long enough to develop cancer due to earlier deaths from respiratory or cardiovascular diseases, or they may be moving away for access to better healthcare. It is a widespread and oft-repeated misconception that the lack of significantly higher cancer rates for a larger geographic area means there is no problem in a subpopulation within that area. It is hard to achieve statistical significance for any health statistic when the population is small, as is the case in fenceline communities. One also cannot assume that data for a broader geographic area characterizes health effects of a smaller circumscribed community, as rates for the relevant community are often diluted by those of the larger unexposed population. This makes detection of problems difficult to identify in fenceline communities, even if they do exist. Nevertheless, Denka's census tract (708), where Fifth Ward Elementary school is also located, had a statistically significant age-adjusted cancer incidence rate that was 25% higher than the state rate for "all cancers".²²⁻²³

There is a lack of prompt risk communication and transparency from several agencies within the State that is frustrating efforts to establish trust with the surrounding community. Despite years of air monitoring that is now available in the aftermath of the installation of Denka's chloroprene emissions reduction technology, no follow-up to the "Preliminary Assessment of Chloroprene Levels in St. John the Baptist Parish" of 2018 has ever been conducted by the Louisiana Department of Health (LDH).²⁴ However, subsequent review of these data by the author indicate that Fifth Ward Elementary School students may potentially face unacceptably high

²² LDH dismissed the "all cancer" incidence rate on the basis that it "is not very useful for explaining or exploring potential etiologies since there are many known risk factors for cancer such as smoking, occupational exposures, etc. that are not controlled in the cancer incidence rates." While this is true, it should be acknowledged that it is often difficult to link some chemicals to a specific disease especially when the chemical has been associated with different diseases, as is the case with chloroprene. This is particularly important given the fact that chloroprene is a mutagen. One characteristic of mutagenesis is induction of tumors at multiple sites and in different species, and this can be triggered theoretically by a single molecule. In mice, chloroprene caused tumors "in a wide variety of mouse tissues, including lung, kidney, Haderian gland, mammary gland, forestomach, liver, skin, mesentery, and Zymbal's gland." Thus, there is the likelihood that different exposed individuals in a population may manifest cancer in different organs, thereby rendering the investigation of an "all cancer" rate necessary in such cases. Other census tracts in St. John had statistically significant higher cancer rates (vs LA rates) based on LTR data from 2005 and 2016: tracts 702 (prostate cancer and non-Hodgkin lymphoma), 704 (breast cancer), and 710 (all cancers). These tracts lie to the northeast and east of the facility. Of interest is the fact that studies have associated ethylene oxide with increased risk of cancers of the white blood cells (such as non-Hodgkin lymphoma, myeloma and lymphocytic leukemia); and breast cancer in females. See "Reference Document for the Preliminary Assessment of Chloroprene Levels in St. John Parish: Evaluation of Potential Health Risks for Elementary School Students based on Early Sampling Results following Emissions Reduction". Louisiana Department of Health, Office of Public Health, Section of Environmental Epidemiology and Toxicology. New Orleans, LA June 14, 2018. [LINK](#)

²³ ATSDR. 2005. Ch 7: Health Effects Evaluation: Screening Analysis, Public Health Assessment Guidance Manual. [LINK](#); EPA Toxicological Review of Chloroprene [CAS No. 126-99-8]. In Support of Summary Information on the Integrated Risk Information System (IRIS), September 2010, Washington DC: US EPA. [LINK](#)

²⁴ LDH. A Reference Document for the Preliminary Assessment of Chloroprene Levels in St. John the Baptist Parish. June 14, 2018. OPH, SEET. Available at: <https://ldh.la.gov/assets/oph/Center-EH/DENKA/PreliminaryChloropreneReport.pdf>

cancer risks based only on the years of school attendance. This conclusion was based solely on EPA's chloroprene air monitoring data after emissions controls were installed.²⁵ Biomonitoring conducted for this and prior investigations by the lab supporting this demonstration confirms community exposure to chloroprene is occurring.²⁶ In another event from 2015, LDH documented two separate incidents of sudden onset student illnesses that occurred down the street from the Fifth Ward Elementary School, at St. John the Baptist District's Leon Godchaux School, in which it concluded that student illnesses, which included respiratory ailments, headache, vomiting, burning eyes and weakness, were likely due to industry emissions.²⁶ Despite several attempts to get a copy of the health report covering these events, LDH has repeatedly refused to release a redacted report of this very important public health emergency. It is unknown whether school district administrators, parents, residents and other parish officials were ever made aware of these incidents. The school impacted by these releases is on the same block as Air Product/Evonik, which has the dubious distinction of making the EPA's 2018 list of the 25 highest risk facilities releasing the most ethylene oxide in the nation. The specific health symptoms reported by the LDH during the prior 2015 events are similar to those previously associated with ethylene oxide, methyl isobutyl ketone, and other chemicals emitted from the Evonik. EPA alerted Louisiana Department of Environmental Quality (LDEQ) officials about this facility in 2018, and advised LDEQ to educate the community around this facility about potential risks. LDEQ did not communicate these risks to locals. It would not be until August 24th, 2021 when these communications were finally made by the EPA to individuals within this population, six years after the events at the Leon Godchaux school.

These and other facts support the need for further investigation and precautionary practices, considering the five decades of chloroprene use at the site and ongoing release of VOCs during that period, the ongoing detection of chloroprene at levels of potential concern at offsite areas where vulnerable populations congregate and live, the gaps in scientific knowledge about the carcinogenic and noncarcinogenic health effects of chronic exposure to industrially released VOC mixtures, and the plausibility of adverse cumulative health impacts on vulnerable populations from chronic exposures to low levels of chloroprene and VOC mixtures. The presence of children a mere 500 yards from the Denka facility should trigger proactive precautionary measures in the absence of direct evidence of harm, to address gaps in public health protection that may be brought on by weaknesses in LA's regulatory oversight and public

²⁵ Katner A. Independent assessment of the environmental conditions of public school locations within St. John the Baptist Parish, Louisiana. Prepared for the NAACP. September 30, 2020.

²⁶ Action Plan: Denka Performance Elastomer, LLC- Pontchartrain Facility; LaPlace, St. John Parish, Louisiana. US EPA, Washington, DC. June 2016. [LINK](#)

risk communications that were previously reported by other government oversight officials.²⁷ Given LA's history of industrial accidents,²⁸ it is also critical that authorities put in place systems to protect children and residents from adverse outcomes in the event of accidental releases and emergency incidents. Between 2017 and 2021, there were nine emergency incidents reported at Denka alone based on LDEQ records (averaging >1 per year). Louisiana's Administrative code defines an emergency condition as any "which could reasonably be expected to endanger the health and safety of the public, cause significant adverse impact to the land, water or air environment, or cause severe damage to property" (LAC 33:1.3915). Currently, communities are only notified of emergency incidents in their area when there is an order for shelter-in-place or evacuation. Incidents reported to LDEQ, State Police or parish emergency response agencies are often not posted publically, rather they are posted on LDEQ's Electronic Documents Management System (EDMS), a system which the public is unfamiliar with, and which only reports emergency incidents after delays of up to a week.

²⁷ The years-long delayed risk communications by LDEQ to the public regarding ethylene oxide emissions from Evonik and Union Carbide which results in excess risks in every census tract in St. John the Baptist Parish was admonished by the EPA- see EPA Office of Inspector General, 2020. Report #20-N-0128. Management Alert- Prompt Action Needed to Inform Residents Living Near Ethylene Oxide-Emitting Facilities About Health Concerns and Actions to Address Those Concerns. Available at: <https://www.epa.gov/hazardous-air-pollutants-ethylene-oxide/inspector-general-follow-ethylene-oxide-0>.

²⁸ Surveillance reports are limited due to lack of ongoing funding, but state incidents recorded by the State include: (1) Louisiana Hazardous Substances Emergency Events Surveillance (HSEES) System, 2001-2009: A Cumulative Report. Section of Environmental Epidemiology and Toxicology, LA Department of Health and Hospitals. Available at: https://ldh.la.gov/assets/oph/Center-EH/envepi/LaTSIP/Documents/Annual_Reports/2001-2009_HSEES_Report.pdf; and (2) Louisiana Toxic Substances Incident Program (LATSIP), 2010-2013: A Summation Report. Section of Environmental Epidemiology and Toxicology, LA Department of Health and Hospitals. Available at: Section of Environmental Epidemiology and Toxicology, LA Department of Health and Hospitals. Available https://ldh.la.gov/assets/oph/Center-EH/envepi/LaTSIP/Documents/Annual_Reports/2010-2013_LaTSIP_Report.pdf

RECOMMENDATIONS

It is important to note that the academic reaction to data such as those in this project is to call for more studies. While it is always important to add to the body of knowledge concerning public health, particularly when it is sparse, as is the case with chloroprene, when there are expected risks to a population, the emphasis should be on proactive monitoring, mitigation and exposure prevention.

- **Cumulative risk assessments should be conducted by LDH and LDEQ for health assessments, and permit applications, respectively.** In the case of Denka, both carcinogenic and non-carcinogenic health risks should be estimated, based on the mixtures of chemical releases by source and in association to other sources. These risks can be based on both reported estimated emissions and offsite air monitoring results for chloroprene and other VOCs. Chemicals of potential concern include: chloroprene, 1,3-butadiene, BTEX (benzene, toluene, ethylbenzene, xylene), and 1,4-dichloro-2-butene. Further investigation of the source and levels of epichlorohydrin in the air may also be warranted. Other emissions of potential concern may be released by other facilities in the area, like Union Carbide's and Evonik's release of ethylene oxide. EPA is releasing a revision of its 2003 "Framework for Cumulative Risk Assessment", which enables consideration of chemical mixtures.²⁹ It is recommended that LDH and LDEQ follow this framework to conduct more real-world analyses of risks to fence-line communities.³⁰ Chemicals of potential concern will have to be determined for each site, but they should be based on EPA's Toxic Release Inventory Risk Screening Indicator (RSEI) model.
- **In addition to cancer outcomes, LDH should track non-cancer health outcomes** to evaluate potential impacts to the population from multiple emissions released by Denka and other facilities in the area. Other adverse health outcomes which may be due to cumulative exposures to pollutant mixtures should be evaluated including, but not limited to those which are common for VOC's like irritation to eyes, nose and throat, headaches and nausea, skin reactions, fatigue, damage to lungs, liver, kidneys, and central nervous systems, blurred vision. Other health effects of potential concern include: cardiovascular and respiratory diseases like COPD and asthma, reproductive and immune system disorders, hematological effects and psychosocial impacts. Some of the more serious diseases can be tracked via Louisiana's

²⁹ U.S. EPA. Framework for Cumulative Risk Assessment. Office of Research and Development, Center for Public Health and Environmental Assessment (CPHEA), formerly known as the National Center for Environmental Assessment (NCEA), Washington Office, Washington, DC, EPA/600/P-02/001F, 2003.

³⁰ U.S. EPA. Framework for Cumulative Risk Assessment. US EPA, Office of Research and Development, Center for Public Health and Environmental Assessment (CPHEA), formerly known as the National Center for Environmental Assessment (NCEA), Washington Office, Washington, DC, EPA/600/P-02/001F, 2003.

Hospital Inpatient Discharge Database (LAHIDD), but other sources like Louisiana's Emergency Department dataset will be more useful for documenting less impactful, sudden onset outcomes like asthma outbreaks.

- **LDH should implement a school-based health surveillance system.** High risk schools in fenceline communities should have the infrastructure necessary to implement active health surveillance and support programs. Case counts should be collected daily for asthma, rashes, nausea, vomiting, burning nose and eyes, headache, dizziness, etc. In instances where health risks and/or effects are documented, LDH should be proactive in ensuring access to appropriate health care for affected communities. If a health surveillance system were established in high-risk fenceline schools, this information should be released to the public to enable informed decision-making, especially by parents of sick or immune-suppressed children. School officials should also be taught how to engage with LDH, LDEQ, Parish, and neighboring industry officials to investigate adverse health outcomes and events in relation to suspected industry emissions.
- **If funds allow, biomonitoring should be used by LDH to quantify resident and child exposures to chloroprene.** It is advised to use reference standards specific to chloroprene's unique metabolites, Cl-MA-I, II and III, in conjunction with reference standards specific to DHBMA, chloroprene's predominant metabolite. Simultaneous collection of personal air samples of both chloroprene and 1,3-butadiene will be useful to better characterize exposures and related metabolites by gender, age group, physical activities, and other associated factors. Biomonitoring will establish population exposures to a unique industrially produced compound. It will enable further tracking of these residents over time to establish potential health effects, both carcinogenic and noncarcinogenic. Epidemiologists should be engaged to ensure the study design meets scientific standards needed to characterize dose-response relationships.
- **Denka should be required by LDEQ to conduct online real-time fenceline and offsite continuous air monitoring** to track the spatial dispersion and temporal patterns of chloroprene and other VOC air emissions (i.e., 1,3-butadiene, 1,4-dichloro-2-butene, and BTEX) in areas around the facility used by vulnerable individuals (e.g., 5th Ward Elementary School). This online air monitoring system should allow for real-time text messages or email alerts to residents, authorities and vulnerable groups (e.g., school authorities, day care operators, etc.) when concentrations exceed regulatory standards and health-based guidance.

- **It is critical that the LDH and the LDEQ work together to adopt proactive precautionary practices and policies and establish a trust-based supportive relationship with the community.**

Frequent public communication, timely follow-up of concerns, prompt risk communication during emergencies, and data and report transparency is essential to establishing trust within this and other fenceline communities. Ultimately, there is a need for the LDH and LDEQ to adopt proactive precautionary practices and policies to prevent future siting of industries adjacent to residences, schools, daycares, parks, hospitals, nursing homes, and low-income housing, when these industries put citizens at risk. It is of paramount importance that LDH and LDEQ set higher standards for the safety and well-being of this, and other fenceline communities.

APPENDIX A. Laboratory Analysis of Air Samples for Volatile Organic Compounds

Analysis of Pollutants in the Air Samples by Thermal-Desorption coupled with Gas-Chromatography Mass Spectrometry (TDU-GC/MS)

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Sample collection

The volatile organic compounds (VOCs) were sampled by passing approximately 74 liters of air at flow rate of 0.18 L/min (depending on the sampling duration and individual calibrated pump flow rate) through pre-conditioned sampling tubes (70 mm long and 6 mm in outer diameter) containing layers of sorbent material (CDS 20:35 mesh Tenax-TA/Carboxen1000/Carbosieve). The air pump (SKC Model 222-3, SKC Inc., Pennsylvania, USA) with the sampling tube was carried (or attached) by the individual who worked or lived near by the sources of the pollutants. After completion of the sampling, the tubes were removed from the samplers and sealed in clean glass tubes, and stored at -20°C until analysis.

Thermal desorption and GC-MS analysis

The VOCs were analyzed using a thermal desorption unit (TDU) interfaced to gas chromatography–mass spectrometry. In brief, air sampling tubes were loaded in CDS Model 7500 Thermal Desorption Autosampler (Oxford, PA) which was followed by Dynatherm 9300 TDA (Oxford, PA) interfaced to an Agilent 6890N Gas chromatograph. The VOCs were thermally desorbed by TDU at 300°C for 5 min. Helium was used as carrier gas at a flow rate of 20 mL/min. Following the desorption process, the VOCs were concentrated by a focusing trap packed with 60:80 mesh Tenax-TA/Carboxen 1000/Carbosieve SIII. The focusing trap was initially set at 45°C , and the oven temperature was then raised to 300°C . The analytes were then transferred to an Agilent 6890N gas chromatography system coupled with an Agilent 5973 quadrupole mass spectrometer (GC-MS) through a transfer line set at 225°C . The VOCs were separated by a 5% phenyl 95% dimethylarylene siloxane Agilent DB-5MS capillary column (30 m x 0.25 mm I.D.). The GC temperature program was initially set at 45°C for 3 minutes, then increased to 250°C at $15^{\circ}\text{C}/\text{min}$, and was held for 10 minutes, using split injection with split ratio 5:1 and constant carrier gas flow (He, 1.0 mL/min). Injector temperature was held at 275°C , transfer line between the GC and mass spectrometer was held at 150°C , and the MS source (quadrupole) was held at 230°C . The mass spectra of each peak identified on chromatograms were characterized by comparison with the mass spectra of commercially available reference standards and mass spectral libraries supplied by National Institute for Standard and Technology (NIST/EPA/NIH). Acquisition was started after a 3 minute solvent delay (Lin et al. 2007). The selected ions, retention times, calibration equations, extraction recovery rates, reproducibility and correlation coefficients of the calibration equations, limits of detection (LOD) for the detection and quantification were summarized in **Table 1** as described from our previous air quality studies (Vu et al. 2018).

Chloroprene

The instrument LOD is $0.25\text{ppm (ng/}\mu\text{L)} \times 2 \mu\text{L} = 0.5 \text{ ng}$

$\text{LOD} = 0.5 \text{ ng}/100\text{L} = 0.005 \text{ ng/L} = 0.005 \mu\text{g}/\text{m}^3$

The signals responses were determined by the signal height and signal peak areas. The R^2 of the correlation for the calibration equation is 0.992.

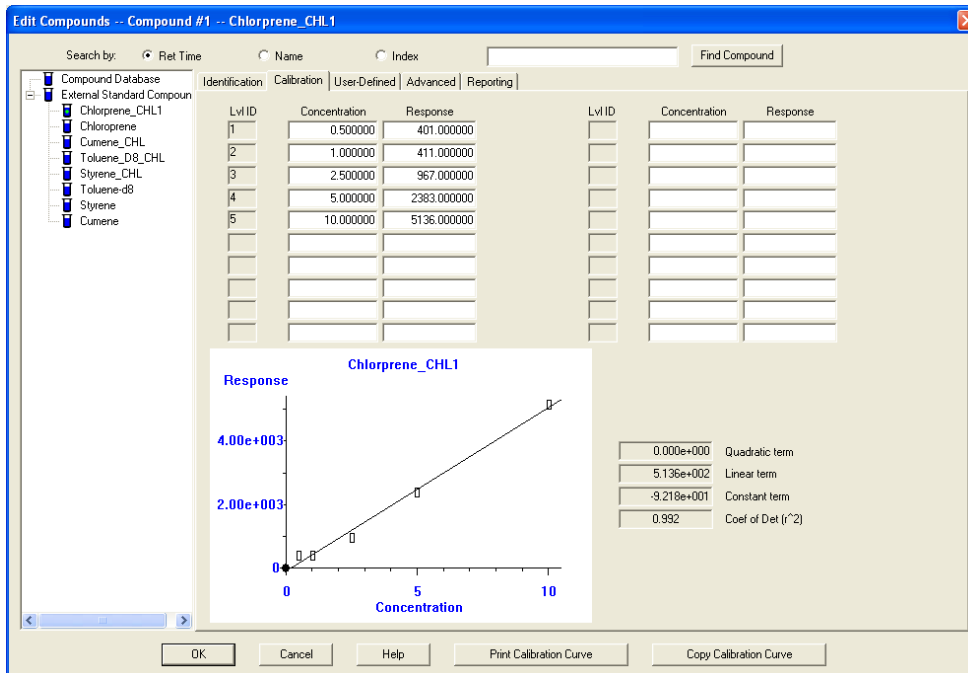
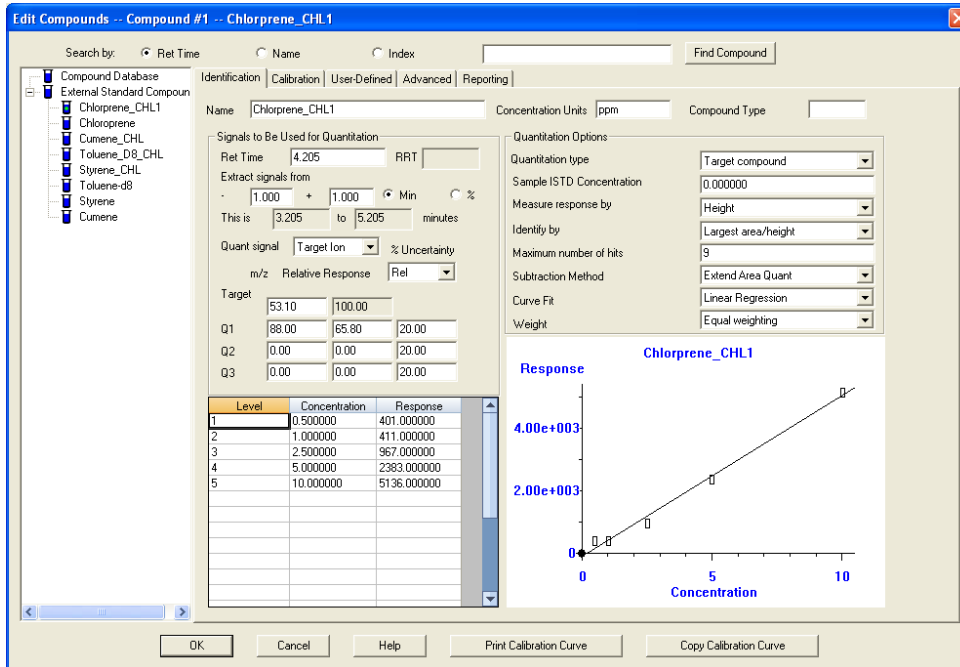


Table 1. Summary of retention times, monitored ions, calibration curves, and recoveries, precisions and detection limits of the other targeted VOCs

No.	Compounds	Retention time (min)	Monitored primary* and secondary ions	Equation	Coefficient of determination R ²	LOD, µg/m ³	LOQ, µg/m ³
1	1,2,3-Trimethylbenzene	10.73	105, 120	1	y = 10650x	0.0026	0.0087
2	1,2,4,5-Tetramethylbenzene	11.81	119, 134, 91	1	y = 13000x	0.0014	0.0047
3	1,2,4-Trimethylbenzene	10.33	105, 120	1	y = 10350x	0.0009	0.0030
4	1,3,5-Trimethylbenzene	9.98	105, 120	1	y = 9590x	0.0007	0.0023
5	1-Dodecanol	15.15	55, 69, 83, 97	0.992	y = 1693x	0.0163	0.0543
6	1-Methylnaphthalene	14.07	142, 141, 115	1	y = 13640x	0.0013	0.0043
7	2 ethyl 1 hexanol	10.58	57, 70, 83, 112	0.998	y = 4391x	0.0121	0.0402
8	2-Heptanone	8.79	58, 71, 114, 59	1	y = 3471x	0.0017	0.0058
9	2-Methylnaphthalene	13.88	142, 141, 115	1	y = 13010x	0.0012	0.0040
10	4-Heptanone	8.55	71, 58, 114, 91	1	y = 4924x	0.0016	0.0055
11	alpha-pinene	9.62	93, 92, 91, 77	0.999	y = 4864x	0.0034	0.0114
12	Benzaldehyde	9.89	77, 106, 105, 78	1	y = 4359x	0.0042	0.0140
13	Benzene	5.34	78, 77	0.999	y = 11790x	0.0021	0.0070
14	Butylcyclohexane	10.81	83, 82, 55, 140	1	y = 5596x	0.0016	0.0054
15	Cumene	9.40	105, 120	1	y = 11090x	0.0011	0.0035
16	Decanal	12.60	57, 70, 82, 112	0.999	y = 1399x	0.0074	0.0247
17	Decane	10.25	57, 71, 85, 142	0.998	y = 3651x	0.0016	0.0053
18	D-Limonene	10.77	68, 93, 67, 79	0.999	y = 3536x	0.0039	0.0131
19	Dodecane	12.51	57, 71, 85, 170	1	y = 4964x	0.0026	0.0084
20	Ethylbenzene	8.52	91, 106	1	y = 11430x	0.0012	0.0039
21	Ethylcyclohexane	8.13	83, 82, 55, 112	1	y = 1723x	0.0062	0.0206
22	Heptanal	8.95	70, 55, 57, 81	1	y = 1602x	0.0071	0.0236
23	Hexanal	7.46	56, 57, 72, 82	1	y = 1643x	0.0047	0.0159
24	m/p-Diethylbenzene	10.98	105, 119, 134	0.998	y = 3193x	0.0061	0.0201
25	m/p-Ethyltoluene	9.89	105, 120	0.998	y = 12780x	0.0006	0.0018
26	m/p-Xylene	8.63	91, 106	1	y = 17860x	0.0004	0.0014
27	Methyl salicylate	12.70	120, 92, 152, 121	0.998	y = 6674x	0.0033	0.0110
28	Naphthalene	12.73	128	1	y = 19720x	0.0011	0.0033
29	n-Nonane	8.94	57, 71, 85, 128	0.998	y = 3049x	0.0034	0.0114
30	n-Octanal	10.28	56, 57, 84, 69	0.999	y = 1081x	0.0048	0.0160
31	n-propylbenzene	9.80	91, 120	1	y = 13520x	0.0004	0.0013
32	Octane	7.48	57, 71, 85, 114	0.995	y = 851.6x	0.0047	0.0156
33	o-Diethylbenzene	11.07	119, 105, 134	0.997	y = 4038x	0.0032	0.0106
34	o-Xylene	8.97	91, 106	1	y = 9568x	0.0007	0.0025
35	Pentadecane	15.36	57, 71, 85, 212	1	y = 5415x	0.0039	0.0132
36	Styrene	8.94	104, 103, 78	1	y = 7932x	0.0015	0.0051
37	Tetradecane	14.47	57, 71, 85, 198	1	y = 5415x	0.0021	0.0069
38	Toluene	7.05	91, 92	0.998	y = 7523x	0.0013	0.0046
39	Tridecane	13.52	57, 71, 85, 184	1	y = 4913x	0.0012	0.0038
40	Undecane	11.43	57, 71, 85, 156	0.999	y = 4510x	0.0011	0.0036

Table 3. Toxicity values

Compounds	RfC, mg/m ³	IUR ×10 ⁻⁶ , (μg/m ³) ⁻¹	References
1,2,3-Trimethylbenzene	0.06		EPA
1,2,4-Trimethylbenzene	0.06		EPA
1,3,5-Trimethylbenzene	0.06		EPA
Benzene	0.03	29	EPA, OEHHA
Cumene	0.4		EPA
Ethylbenzene	1	2.5	EPA, OEHHA
Xylenes	0.1		EPA
Naphthalene	0.003	34	EPA, OEHHA
Styrene	1		EPA
Toluene	5		EPA
2-Butoxyethanol	1.6		EPA
1,4-Dichlorobenzene	0.8	11	EPA, OEHHA
Tetrachloroethylene (PERC)	0.04	6.1	EPA, OEHHA
Trichloroethylene (TCE)	0.002	2	EPA, OEHHA

EPA. 2009. Risk Assessment Guidance for Superfund (RAGS): Part F. 2009. https://www.epa.gov/sites/production/files/2015-09/documents/partf_200901_final.pdf

Integrated Risk Information System (IRIS) Assessments. 2018. <https://cfpub.epa.gov/ncea/iris/search/index.cfm>. Assessed July 4th 2018 The Office of Environmental Health Hazard Assessment (OEHHA). Toxicity criteria on chemicals evaluated by OEHHA.

Results

1. #6 A-1B-23-LF and #9 A-4B-23-FW have the highest concentrations of chloroprene, with 0.85 and 0.78 $\mu\text{g}/\text{m}^3$, respectively. The LOD is 0.005 $\mu\text{g}/\text{m}^3$
2. Significantly higher concentration of benzene ($>1 \mu\text{g}/\text{m}^3$) were detected at A-1A-22-LF (#1), A-2A-22-GH (#2), A-1B-23-LF (#6), A-4B-23-FW (#9), the inhalation unit risks [IURs] and EPA Reference Concentration (RfC) were listed in the Table 3.
3. A-1A-22-LF (#1) and A-2A-22-GH (#2) have the highest concentrations of the naphthalene
4. A-1A-22-LF (#1) and A-4B-23-FW (#9) have significantly higher concentrations of the 1,2,4-trimethylbenzene.
5. A-1A-22-LF (#1), A-4A-22-AM (#4), A-5A-22-LS (#5) and A-4B-23-FW (#9) have significantly higher concentrations of toluene.
6. A-1A-22-LF (#1) and A-4B-23-FW (#9) have significantly higher concentrations of xylene
7. A-1A-22-LF (#1) has the highest concentration of M-methyltoluene.

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https://www.epa.gov/sites/production/files/2015-09/documents/partf_200901_final.pdf
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- The Office of Environmental Health Hazard Assessment (OEHHA).** Toxicity criteria on chemicals
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APPENDIX B. Laboratory Analysis of Chloroprene Metabolites in Urine Samples

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Research Associate Professor

Bioremediation and Phytochemistry

School of Natural Resources

University of Missouri-Columbia

Metabolites of the Chloroprene

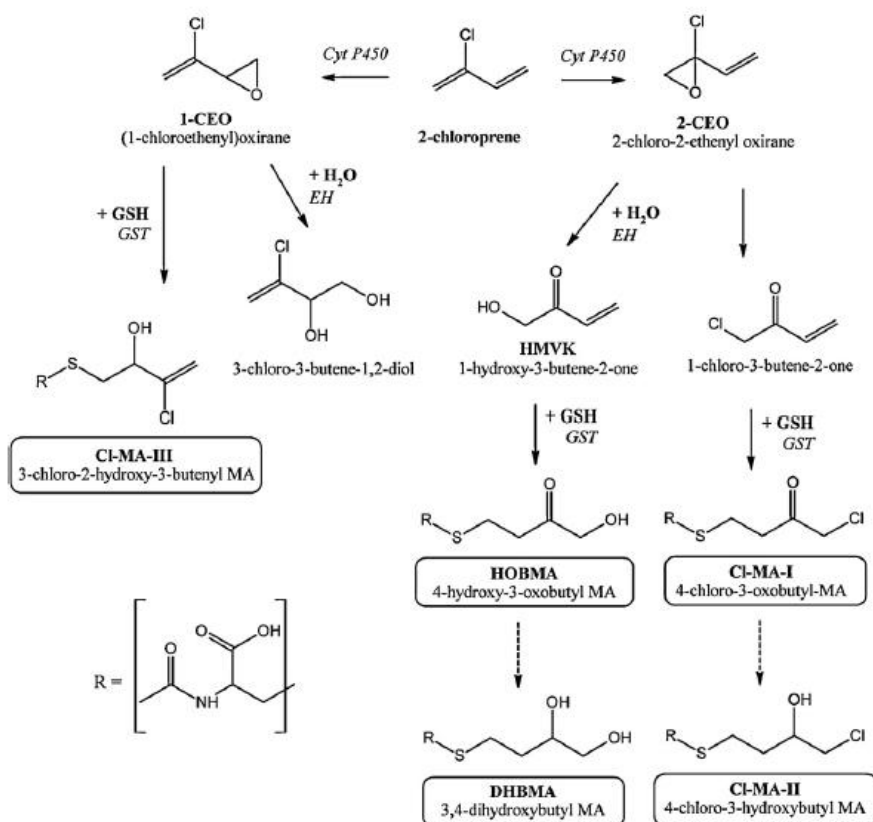


Fig. 1. Proposed biotransformation of 2-chloroprene according to Munter et al. [5,6], modified (Cyt P450 – cytochrome P450; GSH – glutathione; GST – glutathione-S-transferase; EH – epoxide hydrolase; MA – mercapturic acid).

Analysis of the Chloroprene Metabolites in the Urine Samples by UPLC-MS/MS

Sample Preparation

Take 0.5 ml of urine + 9.5 ml (10 mM ammonium acetate with formic acid). Fifty microliter of 40 ppm (mg/L) internal standard enrofloxin-D5** (stable isotope) was added into each sample to achieve concentration of 200 ppb ($\mu\text{g/L}$) for quality control and quality assurance.

The concentrations of the chloroprene metabolites DHBMA**, HOBMA, CHPMA, CI-MA-I, CI-MA-II, CI-MA-III, creatinine (for dilution factor adjustment) and internal standard creatinine-D3 were determined by a Waters Ultra-Performance Liquid Chromatography connected to a Xevo triple-quadrupole mass spectrometer (UPLC-MS/MS). All the samples were injected with triplicates (n =3).

Analytical Standards <https://www.trc-canada.com/checkout/>

3,4-dihydroxybutyl mercapturic acid (DHBMA)** (A173710) (D-Isotope A173712)

4-hydroxy-3-oxobutyl mercapturic acid (HOBMA) (H949823)

3-chloro-2-hydroxypropyl mercapturic acid (CHPMA) (A187838)

4-chloro-3-oxobutyl mercapturic acid (CI-MA-I) (A187828)

4-chloro-3-hydroxybutyl mercapturic acid (CI-MA-II)

3-chloro-2-hydroxy-3-butenyl mercapturic acid (CI-MA-III)

The compounds and the internal standards were separated by a Synergi Max RP C12 150 \times 3.0 mm, 4 μm reverse-phase Phenomenex column (Torrance, CA). A guard column (C12 4 \times 3 mm from Phenomenex) was used. The elution gradient consists of: 1. mobile phase A (mixture of 88% water, 12% methanol and 0.02% formic acid), 2. mobile phase B (mixture of 10% water, 90% methanol and 0.02% formic acid) and 3. mobile phase C (0.5% aqueous formic acid) with a constant flow rate of 0.3 mL/min as shown in Table 1.

Time (min)	Mobile Phase A (%)	Mobile Phase B (%)	Mobile Phase C (%)	Flow Rate (ml/min)
0.0	100	0	0	0.3
2.0	100	0	0	0.3
5.0	75	25	0	0.3
6.5	50	38	12	0.3
11.5	0	88	12	0.3
13.0	0	88	12	0.3
14.5	12	88	0	0.3
19.0	100	0	0	0.3
30.0	100	0	0	0.3

The MS/MS system operated in the multi-reaction monitoring (MRM) mode with the electrospray ionization sources (ES- or ES+). The ionization energy, MRM transition ions (precursor and product ions; Table 1), capillary and cone voltage, desolvation gas flow and collision energy were optimized by Waters optimization software package. The Table 1 summarizes the ionization mode, retention time, precursor and product ions selected for the analysis of chloroprene metabolites, creatinine and internal standard. **Table 1.** The ionization mode, retention time, precursor and product ions selected for the analysis of chloroprene metabolites, creatinine and internal standard. To optimize the method, the gradient was shortened to 15min as follows: Initial conditions 0%B, 1min 0%B; 2.5min 25%B; 3.25min 38%B, 12%C; 5.625min 88%B, 12%C; 6.5min 88%/12%C; 7.25min 88%B, 0%C; 9.5min 100%A; 15min 100%A.

Chloroprene Metabolites (UPLC-MSMS)	ES	Retention time	Precursor ion	Product ion	qualifer ions
DHBMA** (STD)	ES-	4.96	250.0	121.0	75
HOBMA	ES-	4.95 (confirmed)	248.0	162.0	84
CHPMA	ES-	4.96 (confirmed)	254.0	218.0	89
CI-MA-I	ES-	4.95/7.2	266.0	162.0	84
CI-MA-II	ES-	4.97 (confirmed)	268.0	232.0	75
CI-MA-III	ES-	*4.97/5.97/6.94/7.2	266.0	137.0	128

Results

I. The concentrations of DHBMA in urine samples (absolutely confirmed and quantified using analytical standards)

No.	Samples	DHBMA (ppb; ug/L)	Creatinine (ppb; ug/L)	Creatinine (g/L)	DHBMA ug per g of Creatinine
1	U1B23LF	65	348116	0.35	186
2	U1A22LF	485	1826755	1.83	265
3	U2B23LHW	458	3308768	3.31	139
4	U2B23BLW	652	1147677	1.15	568
5	U2B23LEH	299	653870	0.65	457
6	U2B23GAHSR	1032	1926979	1.93	535
7	U2B23GAH2	535	1880189	1.88	285
8	U3B23BT	331	1035490	1.04	319
9	U3A22BT	360	1096646	1.10	329

The chloroprene metabolite DHBMA was detected in all the urine samples. The highest concentrations of DHBMA (ug/g of creatinine) were found in the samples U2B23BLW, U2B23LEH, and U2B23GA

II. Relative concentrations (signal intensity- number of the ions) of other metabolites HOBMA, CHPMA, CI-MA-I, CI-MA-II, CI-MA-III (no analytical standards available)

No.	Samples	HOBMA*** RT = 7.4 min		CHPMA RT = 7.38 min		CI-MA-I RT = 7.5 min		CI-MA-I RT = 8.2 min		CI-MA-II** RT = 7.98 min		CI-MA-III RT = 6.84 min		CI-MA-III RT = 7.64 min		CI-MA-III RT = 8.34 min	
		248>162	248>84 (q)	254>218	254>89 (q)	266>162	266>84(q)	266>162	266>84(q)	268>232	268>75 (q)	266>137	266>128 (q)	266>137	266>128 (q)	266>137	266>128 (q)
1	U1B23LF	4864.81	930.42	4607.34	0.00	27.08	244.73	0.00	0.00	339.42	1.27	98.97	216.06	100.74	2931.40	33.89	435.54
2	U1A22LF	24048.26	4670.74	51.42	1.61	0.00	1277.68	0.00	0.00	0.79	186.30	666.38	992.11	731.91	6973.20	259.64	3042.21
3	U2B23LHW	49677.89	9577.78	1.41	1.18	0.00	0.00	1017.04	1627.04	0.00	3.12	231.19	390.11	375.28	4459.15	46523.66	23064.76
4	U2B23BLW	70541.73	14684.31	50.37	0.00	0.00	859.02	0.00	0.00	0.00	11.40	963.81	1860.41	525.81	704.47	125.17	1116.11
5	U2B23LEH	111718.53	23060.38	1.07	5.07	0.01	564.29	0.00	0.00	0.33	0.85	802.15	1497.76	420.55	4416.46	19692.81	10414.69
6	U2B23GAHSR	92727.61	19181.89	0.00	0.15	0.00	1531.14	0.00	0.00	0.00	4.91	423.03	1111.24	1041.74	3289.71	464.16	1224.19
7	U2B23GAH2	62944.75	12538.85	0.03	3.02	0.00	0.00	3525.09	6234.25	0.00	0.62	149.39	513.94	141.54	2968.98	161115.79	81873.15
8	U3B23BT	31637.88	6137.57	3132.29	0.25	0.00	36.42	0.00	0.00	75.00	0.01	351.74	738.04	40.06	3092.81	8.16	264.68
9	U3A22BT	43426.81	9065.61	0.25	0.92	0.00	144.77	0.00	0.00	0.02	0.00	567.36	1002.85	129.66	3221.70	8.12	643.51

Similar to the findings from DHBMA analysis, HOBMA was detected in all the samples, and the relative concentrations of HOBMA were highest in the samples U2B23BLW, U2B23LEH, and U2B23GAHSR.

For the analysis of CHPMA, CI-MA-I and CI-MA-II, due to lack of reference analytical standards, we have to rely on the molecular ions and fragmented product ions and qualifier for the confirmation and quantification purpose. The inconsistency between qualifier ion and pair of molecular/product ions made it impossible to draw any conclusion.

For the analysis of CI-MA-III, 3 possible signals could be the CI-MA-III. It could be the signals with retention time 6.84 min, 7.64 min, or 8.34 min. By comparing the results of DHBMA and HOBMA, it is most likely the signal at the retention time of 6.84 min. If that is the case, CI-MA-III were detected in all the urine samples, and the samples U2B23BLW, U2B23LEH and U2B23GAHSR have the highest concentrations of the metabolite CI-MA-III.

APPENDIX C. Summary of Urine Metabolites and Volatile Organic Compounds in Air (St. John Parish, Sept. 2021)

SITE NO.	Name	Urine Metabolites									Volatile Organic Compounds (RFC ug/m3)								
		Urine Sample Date	DHBMA ug/g creatinine (metabolite of chloroprene and 1,3-butadiene)	HOBMA Signal Intensity/g creatinine (metabolite of chloroprene and 1,3-butadiene)	CHPMA Signal Intensity/g creatinine (metabolite of epichlorohydrin)	CL-MA-I Signal Intensity/g creatinine (metabolite of chloroprene)	CL-MA-II Signal Intensity/g creatinine (metabolite of chloroprene)	CL-MA-III Signal Intensity/g of creatinine (metabolite of chloroprene)			Air Sample Date (Duration hr:min)	Chloroprene (ug/m3) (20)	Benzene (ug/m3) (30)	Napthalene (ug/m3) (3)	1,2,4-trimethylbenzene (ug/m3) (60)	Toluene (ug/m3) (5000)	Xylene (ug/m3) (100)	Ethylbenzene (ug/m3) (1000)	
1	Residence 1-Resident 1	9/23 (am)	139	300280	304	0	0	0	1397	2268	281214	9/22 (8:00)	below LOD	1.36	0.17	0.26	1.69	0.63	0.18
1	Residence 1-Resident 2	9/23 (am)	568	1229295	19	0	0	6	16796	9163	2181								
1	Residence 1-Resident 3	9/23 (am)	457	3417148	0	0	0	0	24536	12863	602346								
1	Residence 1-Resident 4	9/23 (am)	535	962414	0	0	36587	0	4391	10812	4818								
1	Residence 1-Resident 5	9/23 (am)	285	669558	33319	0	0	798	1589	1506	1713826								
2	River Road EPA Air Monitor SE of Denka, La Place, LA											9/22 (7:56)	below LOD	0.78	0.07	0.34	7.58	1.14	0.31
3	Residence 3	9/22 (pm)	329	791993	0	0	0	0	10347	2365	148	9/22 (8:00)	below LOD	0.59	0.05	0.11	2.71	0.47	0.12
3	Residence 3	9/23 (am)	319	611071	5	0	0	0	6794	774	158								
4	Residence 2	9/22 (pm)	265	263289	15	0	11135	0	7296	8013	2843	9/22 (8:00)	below LOD	1.87	0.16	1.37	3.03	2.54	0.63
4	Residence 2	9/23 (am)	186	279493	2954	0	0	45	5686	5788	1947	9/23 (6:58)	0.85	1.08	0.07	0.19	2.16	0.42	0.12
5	5th Ward School (by EPA monitor)											9/23 (6:58)	0.78	2.11	0.18	0.95	10.82	2.49	0.66
6	Godchaux School Site, Reserve LA											9/23 (7:33)	below LOD	0.59	0.02	0.06	1.14	0.24	0.06
7	Edgard Courthouse (westbank)											9/23 (9:45)	below LOD	0.86	0.04	0.23	2.86	0.89	0.21
8	Residence 4											9/22 (7:21)	below LOD	0.72	0.04	0.15	5.09	0.73	0.23
9	Bethune Park (between Norco Manufacturing Complex and Shell Refinery, Destrehan LA, St Charles Parish											9/23 (7:08)	below LOD	0.55	0.04	0.09	0.28	0.32	0.07

The RFC is an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious noncancer effects during a lifetime.