

# Public Health Assessment

**Public Comment Release**

Evaluation of Air Contamination

Kalamazoo River Enbridge Oil Spill  
Calhoun and Kalamazoo Counties, Michigan

**Prepared by the  
Michigan Department of Community Health**

**AUGUST 26, 2014**

**COMMENT PERIOD ENDS: OCTOBER 27, 2014**

Prepared under a Cooperative Agreement with the  
U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES  
Agency for Toxic Substances and Disease Registry  
Division of Community Health Investigations  
Atlanta, Georgia 30333

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Prepared by:

Michigan Department of Community Health  
Under A Cooperative Agreement with the  
U.S. Department of Health and Human Services  
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## Foreword

The Michigan Department of Community Health (MDCH) conducted this evaluation under a cooperative agreement with the federal Agency for Toxic Substances and Disease Registry (ATSDR). ATSDR conducts public health activities (assessments/consultations, advisories, education) at sites of environmental contamination. The purpose of this document is to identify potentially harmful exposures and actions to minimize those exposures. This is not a regulatory document and does not evaluate or confirm compliance with laws. This is a publicly available document that is provided to the appropriate regulatory agencies for their consideration.

The following steps are necessary to conduct public health assessments/consultations:

- Evaluating exposure: MDCH toxicologists begin by reviewing available information about environmental conditions at the site: how much contamination is present, where it is found on the site, and how people might be exposed to it. This process requires the measurement of chemicals in air, water, soil, or animals. Usually, MDCH does not collect its own environmental sampling data. We rely on information provided by the Michigan Department of Environmental Quality (MDEQ), U.S. Environmental Protection Agency (EPA), and other government agencies, businesses, and the general public.
- Evaluating health effects: If there is evidence that people have been or are being exposed – or could be exposed – to hazardous substances, MDCH toxicologists then determine whether that exposure could be harmful to human health, using existing scientific information. The report focuses on public health – the health impact on the community as a whole.
- Developing recommendations: In its report, MDCH outlines conclusions regarding any potential health threat posed by a site, and offers recommendations for reducing or eliminating human exposure to contaminants. If there is an immediate health threat, MDCH will issue a public health advisory warning people of the danger, and will work with the appropriate agencies to resolve the problem.
- Soliciting community input: The evaluation process is interactive. MDCH solicits and considers information from various government agencies, parties responsible for the site, and the community. If you have any questions or comments about this report, we encourage you to contact us.

Please write to: Toxicology and Response Section  
Division of Environmental Health  
Michigan Department of Community Health  
PO Box 30195  
Lansing, MI 48909

Or call us at: 1-800-648-6942 (toll free)

For more information, please visit:

[www.michigan.gov/mdch-toxics](http://www.michigan.gov/mdch-toxics)

## Acronyms and Abbreviations

AEGL	Acute Exposure Guideline Levels
ATSDR	Agency for Toxic Substances and Disease Registry
CCPHD	Calhoun County Public Health Department
CNS	central nervous system
CO	carbon monoxide
CREG	Cancer Risk Evaluation Guide
CST	National Guard 51st Civil Support Team
CTEH	Center for Toxicology and Environmental Health, L.L.C.
Enbridge	Enbridge Incorporated
EPA	United States Environmental Protection Agency
ERT	EPA Environmental Response Team
GASTEC	Gas Detector Tube
HAPSITE	Hazardous Air Pollutants on Site
H <sub>2</sub> S	hydrogen sulfide
ICS	Incident Command System
KCHCS	Kalamazoo County Health and Community Services Department
kg	kilograms
LEL	Lower Explosive Limit
MDCH	Michigan Department of Community Health
MDEQ	Michigan Department of Environmental Quality
MDNRE	Michigan Department of Natural Resources and Environment
MRL	Minimal Risk Level
mg	milligrams
ND	not detected
PCC	Michigan Poison Control Center
PHA	Public Health Assessment
ppb	parts per billion
RfC	Reference Concentration
RSL	EPA Regional Screening Level
START	Superfund Technical Assessment and Response Team
US DOT	United States Department of Transportation
VOCs	volatile organic compounds
WESTON	Weston Solutions, Inc.

## Summary

In response to the July 2010 Enbridge oil spill to the Kalamazoo River, government agencies and environmental contractors conducted air monitoring and sampling to evaluate the public health hazards of breathing the air near the spill. Hand-held monitors were used to give real-time information about levels of contaminants in the air, including benzene. Air samples were collected and analyzed for a wide range of oil-related chemicals. The Michigan Department of Community Health (MDCH) evaluated the air data during the emergency response to the spill and continues to evaluate additional data collected during the on-going cleanup of the spilled oil.

This public health assessment summarizes the results of the air monitoring and sampling efforts conducted from July 2010 through 2012. Air monitoring and sampling continues where cleanup work is on-going to ensure that people are protected.

MDCH has reached the following conclusions about chemical levels in air following the July 2010 Enbridge oil spill:

*1. People in the spill area who breathed oil-related chemicals in the air from the time of the spill to August 18, 2010, reported short term (temporary) health effects including: headaches, nausea, respiratory discomfort, and eye irritation. These short term effects diminished or stopped when people were no longer breathing air containing oil-related chemicals. Some individuals may have experienced anxiety related to the event, regardless of their exposure.*

*2. People are not expected to have long term, more serious health effects as a result of breathing the oil-related chemicals. By August 18, 2010, air concentrations of oil-related chemicals fell below human health screening levels that protect everyone from long term health effects including sensitive people such as children, the elderly, and those with pre-existing illnesses. Therefore, people living in the spill area did not breathe oil-related chemicals long enough or at levels high enough to cause long term health effects.*

*3. People are not expected to have health effects as a result of breathing the air near the work areas where oil recovery and cleanup activities were ongoing in 2011 and 2012. Air concentrations of benzene in 2011 and 2012 did not exceed the health-based screening level. No other oil-related chemical was consistently found in 2011 or 2012 at concentrations exceeding the human health screening levels.*

MDCH's conclusions do not apply to workers who took part in the oil recovery and cleanup activities. The data that MDCH reviewed to reach these conclusions was gathered to evaluate the levels of oil-related chemicals that people living in the spill area might have breathed. These data may not represent the air levels of oil-related chemicals inside the work areas.

Next steps: As cleanup of the spill area continues, MDCH will evaluate air monitoring and sampling data to ensure that chemical levels in air do not cause a risk to public health.

## **Purpose and Health Issues**

Beginning on July 26, 2010, federal and state agencies and environmental contractors conducted air monitoring and sampling to evaluate the public health hazards of breathing the air near the Enbridge oil spill to the Kalamazoo River. This Draft Public Health Assessment for Public Comment summarizes the air monitoring and sampling data gathered to evaluate the public health hazards of breathing the chemicals emitted from the spilled oil. This document does not address the risks to workers who took part in oil recovery and cleanup activities.

## **Background**

On the evening of July 25, 2010, a section of a 30-inch-diameter pipeline owned and operated by Enbridge Incorporated (Enbridge) broke in a wetland adjacent to Talmadge Creek in Marshall (Calhoun County), Michigan. The break resulted in the spill of an estimated 843,000 gallons of a crude oil mixture into Talmadge Creek and the Kalamazoo River (NTSB 2012).

The United States Environmental Protection Agency (EPA) assumed the leadership of the response to the spill and a Command Center was established in Calhoun County using guidelines of the Incident Command System (ICS). Members of the ICS Unified Command included Enbridge, the EPA, the Michigan Department of Natural Resources and Environment<sup>1</sup> (MDNRE), the Michigan State Police Emergency Management Division, the Calhoun County Public Health Department (CCPHD), Calhoun County Emergency Management, the Kalamazoo County Sheriff, and the city of Battle Creek. At the request of the EPA Incident Commander and the Calhoun County Health Officer, MDCH staff deployed to the Command Center on July 27, 2010, to provide public health support. Agency for Toxic Substances and Disease Registry (ATSDR) Region 5 staff joined MDCH at the Command Center later that week.

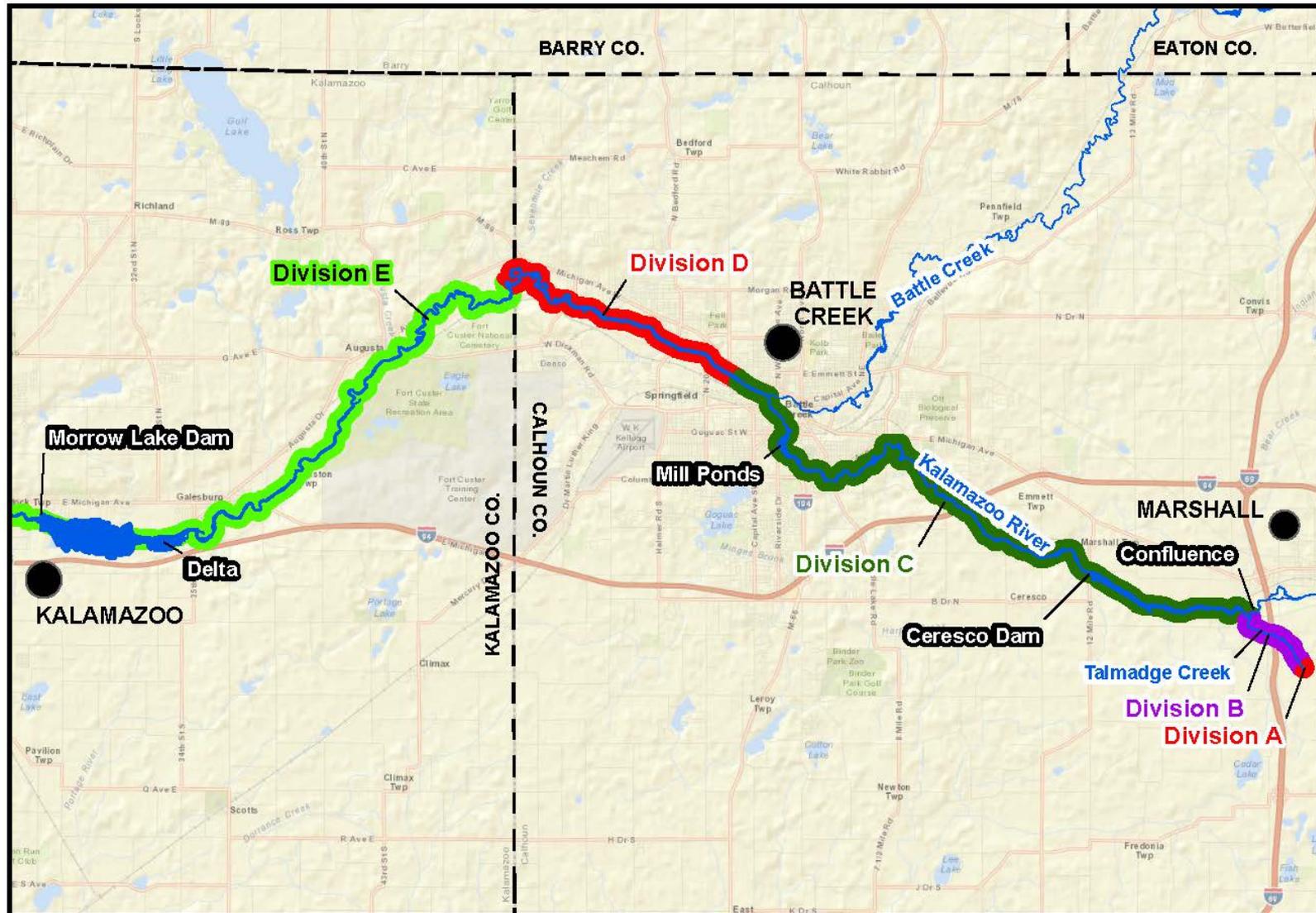
At the time of the spill, Talmadge Creek and the Kalamazoo River were between 25- and 50-year flood levels due to the heavy rain that had fallen in the previous days. Because the river and creek were at high water levels, oil flowed into floodplains, riverbanks (overbank areas), and wetlands. The oil was eventually contained nearly 40 miles downriver from the spill site at Morrow Lake in nearby Kalamazoo County, about 80 miles east from where the Kalamazoo River flows into Lake Michigan. In the emergency response that followed the spill, the affected areas of the creek and river were divided into five segments designated by the letters A through E as shown in Figure 1. As the response changed over time to longer term cleanup activities, quarter-mile markers were used to identify work areas beginning at the spill area and continuing down Talmadge Creek and the Kalamazoo River. Mile markers are used in this document to identify areas under discussion.

The Kalamazoo River is bordered by a variety of land uses including marshland and farmland, as well as residential and commercial properties. The river passes through several residential communities, the city of Battle Creek and many smaller towns before reaching Morrow Lake. Approximately 41,500 people are estimated to live within one mile of the nearly 40-mile affected stretch of the Kalamazoo River.

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<sup>1</sup> Effective March 13, 2011, the MDNRE was split into two state agencies. The Michigan Department of Environmental Quality (MDEQ) assumed responsibility for the continued response to the Kalamazoo River oil spill.

**Figure 1. Overview of the areas of Talmadge Creek and the Kalamazoo River impacted by the July 2010 oil spill, Calhoun and Kalamazoo Counties, Michigan (EPA 2014).**



## Characterization and Composition of the Spilled Oil

The broken pipeline was part of Line 6B of Enbridge's Lakehead System that transports both heavy and medium crude oil from Griffith, Indiana to Sarnia, Ontario (Enbridge 2011). Crude oil is a complex mix of hydrocarbons, which are organic molecules made of hydrogen and carbon atoms. It may also contain small amounts of nitrogen, oxygen, and sulfur compounds and trace amounts of metals.

At the time of the spill, the pipeline was carrying a mixture of 50 to 70 percent heavy crude oil, and 30 to 50 percent hydrocarbon diluent that was estimated to contain up to one percent benzene and less than 0.5 percent hydrogen sulfide (NTSB 2012). The diluent is added to the heavy crude to allow it to flow through the pipeline. The mixture is sometimes called diluted bitumen. Two kinds of oil were in the pipeline when it broke: Western Canadian Select crude and Cold Lake Blend crude (NTSB 2012). Samples of the oil/diluent mixture taken from the pipeline and analyzed at the MDNRE Environmental Laboratory confirmed the chemical composition of the oil and diluent mixture. Only chemicals expected to be in petroleum were found in the samples (MDNRE 2010).

The United Nations' Committee of Experts on the Transport of Dangerous Goods identification number for Western Canadian Select and Cold Lake Blend crude oils is 1267: a generic identification number for petroleum crude oil. The United States Department of Transportation (US DOT) Emergency Response Guidebook recommendations for handling spills of products with this identification number are provided in Guide 128 for Flammable Liquids (Non-Polar/Water-Immiscible) and include isolation of the spill or leak area for at least 50 meters (150 feet) in all directions and elimination of any ignition sources. Following a large spill, Guide 128 suggests that emergency response personnel, "*Consider initial downwind evacuation for at least 300 meters (1000 feet)*" (US DOT 2008). There is no requirement for an immediate mandatory evacuation.

## Air Monitoring and Sampling Methods

At the request of the EPA, the Weston Solutions, Inc. (WESTON) Superfund Technical Assessment and Response Team (START) began air monitoring and sampling activities in the area of the spill on July 26, 2010. Initial efforts were focused in the vicinity of the city of Marshall and the village of Ceresco (approximately six miles downstream from the spill site) and were rapidly expanded to include other populated areas further downstream including the city of Battle Creek.

In emergency situations, air monitoring is conducted with hand-held instruments that give an immediate or "real-time" reading of the level of contaminants in the air. Each of the instruments currently available has its own advantages and limitations. The greatest advantage of all these instruments is that they provide immediate information about the level of hazardous contaminants in air. Monitoring data collected with real-time instruments are only brief snapshots in time and do not represent the levels of contaminants that people could have breathed throughout a day or longer time period.

Initially, START used MultiRAE five-gas meters that measure total volatile organic compounds (VOCs), hydrogen sulfide (H<sub>2</sub>S), carbon monoxide (CO), percent oxygen, and combustible gas

as the percent of the lower explosive limit (Weston 2011). The lower explosive limit (LEL) is the air level below which chemical vapors are not likely to explode. Ten percent (10 %) of the LEL is typically used as a protective screening level. START did not detect combustible gas at air concentrations above or approaching the LEL screening level. All measured oxygen and carbon monoxide concentrations were within normal limits.

EPA also instructed START to specifically monitor the air for the chemical benzene because it is the most toxic of the VOCs that could be released from the oil that was spilled from the Enbridge pipeline. START initially measured benzene in air using colorimetric instruments such as Draeger tubes or the Draeger Chip Measurement System, which can detect benzene beginning at 50 to 500 parts per billion (ppb) depending on which tube or chip is used. GASTEC Color Dosimeter Tubes, which are similar to Draeger tubes and can detect benzene as low as 500 ppb, were used by Enbridge contractors to provide instantaneous measurements of benzene. START also used UltraRAE hand-held monitors to measure levels of benzene in air (as low as 100 ppb) and began collecting Summa and Tedlar bag air samples for laboratory analysis (Weston 2011).

On July 27, 2010, the State of Michigan requested that the National Guard 51st Civil Support Team (CST), located at Fort Custer, Kalamazoo County, be deployed to provide resources and instrumentation to support air monitoring and sampling efforts. The CST used mobile field gas chromatograph monitors called HAPSITEs (Hazardous Air Pollutants on Site) that provide very accurate real-time measurements of benzene levels in air.

On July 27, 2010, the Center for Toxicology and Environmental Health, L.L.C. (CTEH) arrived under contract with Enbridge to conduct air monitoring and sampling activities in response to the spill.

Air samples, collected into Summa canisters, mini-cans or Tedlar bags, provide more accurate measurements of the levels of contaminants in air than can be obtained with real-time hand-held monitors. Air samples collected over several hours in stainless steel Summa canisters are called “time-integrated” samples. The canisters are processed to be chemically inert and the air is evacuated so that the canister is under vacuum. A regulator is attached that allows air to slowly collect in the canister over time, usually a 24- or 8-hour period. The canisters are then sent to a laboratory for chemical analysis<sup>2</sup>, which provides the average air contaminant concentration over the sample time. In emergencies like the Kalamazoo River oil spill, Summa canister results can be available in as little as 24 hours after collection of the sample.

Tedlar bags and mini-cans can be used to collect a representative “grab” sample of air that is then analyzed with laboratory equipment. The EPA Environmental Response Team (ERT) mobile laboratory was mobilized to Marshall following the oil spill to analyze Tedlar bag samples and was functional by August 2, 2010. The laboratory consisted of a gas chromatograph capable of measuring benzene in air samples at levels as low as one ppb.

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<sup>2</sup> Air samples were collected and analyzed following EPA Method TO-15 for volatile organic compounds available at <http://www.epa.gov/ttnamti1/files/ambient/airtox/to-15r.pdf>.

## Human Health Screening Levels

The risk of health effects from chemicals in air depends on who is breathing that chemical and for how long, as well as the toxicity of the chemical. MDCH considered all these factors in choosing health protective screening levels to evaluate the risk of harm to people breathing the chemicals coming from the oil spilled from the Enbridge pipeline.

The spilled oil contained many VOCs, including up to one percent benzene. Because benzene is the most toxic of the VOCs that could have been released to the air, monitoring efforts were focused on this chemical in the emergency response to the spill. MDCH first compared levels of benzene in the air to the Acute Exposure Guideline Levels (AEGLs) developed by the EPA (EPA 2009).

AEGLs are used to evaluate the human health hazards of breathing chemicals for short periods of time ranging from 10 minutes to eight hours. As the exposure time increases from minutes to hours, the chance of harm also increases; therefore the acceptable level in air is lower for longer time periods. AEGLs are developed to be protective for most people including sensitive sub-populations such as children, the elderly, or those with existing health conditions. AEGLs for benzene are available for three categories of health hazards:

- AEGL-1: the benzene level above which most people have discomfort, irritation, or mild central nervous system (CNS) effects such as headaches, dizziness and nausea. These effects are not disabling and cease when a person is no longer breathing benzene.
- AEGL-2: the benzene level at which people could have serious, long-lasting adverse health effects or an impaired ability to escape. The AEGL-2 for benzene is based on serious CNS effects that could make someone unconsciousness and prevent escape.
- AEGL-3: the benzene level at which people could have immediate life-threatening health effects or death.

**Table 1. United States Environmental Protection Agency Acute Exposure Guideline Levels (AEGLs) for benzene in parts per billion (ppb) (EPA 2009).**

	10 minutes	30 minutes	60 minutes	4 hours	8 hours
<b>AEGL 1</b>	130,000	73,000	52,000	18,000	9,000
<b>AEGL 2</b>	2,000,000*	1,100,000	800,000	400,000	200,000
<b>AEGL 3</b>	**	5,600,000*	4,000,000*	2,000,000*	990,000

Available at <http://www.epa.gov/oppt/aegl/pubs/results72.htm>

\*AEGL is greater than 10 percent of the Lower Explosive Limit (LEL) of 14,000,000 ppb.

\*\*AEGL for 3 to 10 minutes is 9,700,000 ppb.

The chance of explosion must be considered when a calculated health-based screening level is higher than the LEL. Benzene was not measured by air monitoring equipment or in any air sample at levels above 10% of its LEL.

Benzene was measured only twice at concentrations exceeding the 8-hour AEGL-1. Since it appeared likely that people could be exposed to benzene in air for more than just 8 hours, MDCH and ATSDR identified health-based screening levels for benzene protective of longer periods of time. MDCH, ATSDR and the CCPHD used these screening levels to develop decision trees to

determine when to recommend that people evacuate residential neighborhoods and when people could safely return to their homes. The Evacuation Decision Tree, shown in Figure 2, is divided into three sections that represent high, medium, and low levels of benzene monitored in air.

- Low levels (6.1 to 60 ppb): These levels require no immediate action beyond continued monitoring for benzene.
- Medium levels (61 to 199 ppb): Areas with results within this range were more closely monitored to determine whether the area should be evacuated.
- High levels (200 ppb and greater): Monitoring results that showed high levels were verified by a second test. If the second result was also high, evacuation was recommended. If the second sample result was lower, more monitoring was done before a decision on whether to evacuate was made.

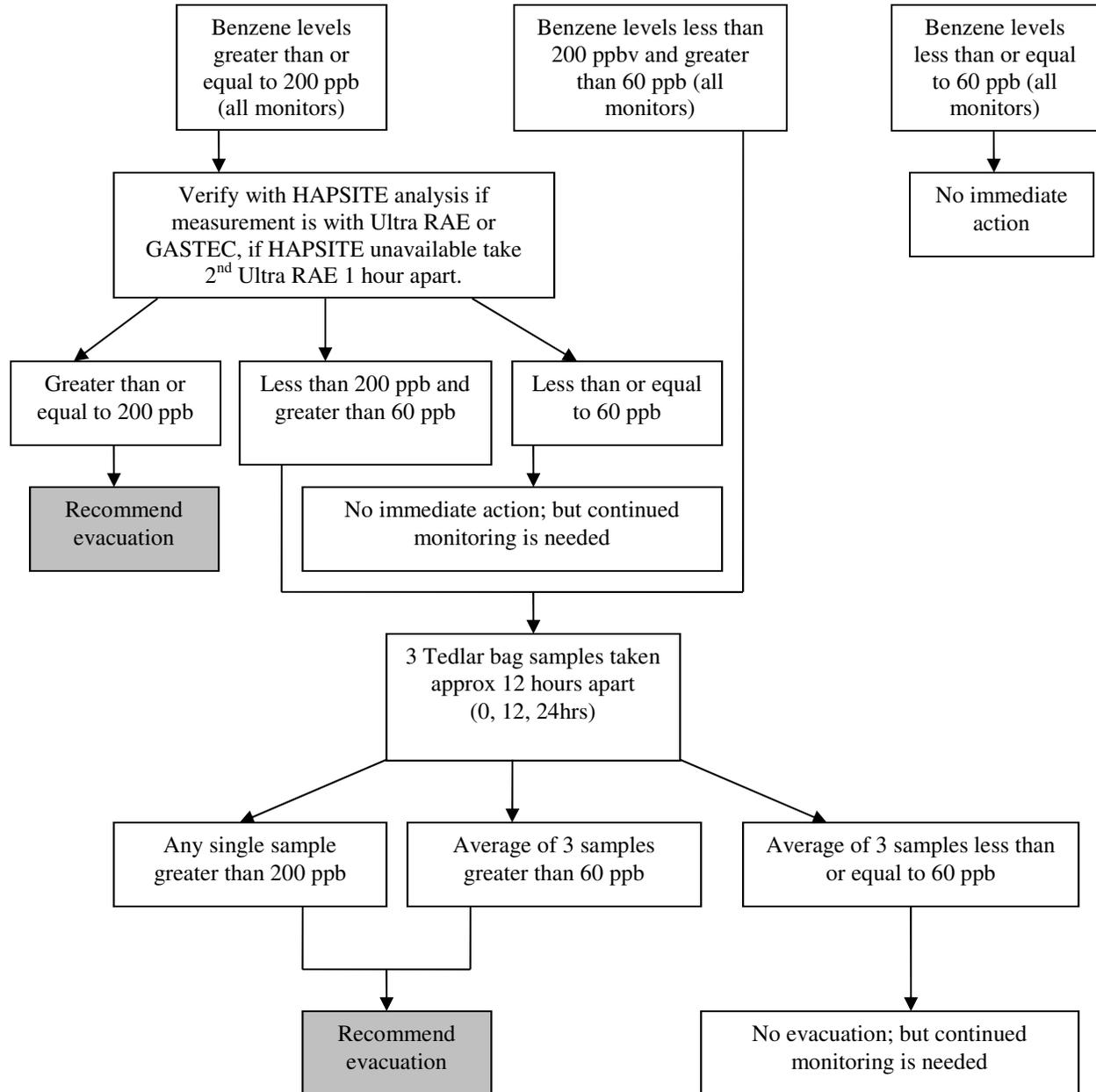
The decision tree also considers the instrument used for air monitoring and recommends additional monitoring if elevated levels are found with less accurate instruments.

MDCH and ATSDR identified 60 ppb as an initial screening level below which most people are not harmed by breathing benzene for a short time. MDCH identified 200 ppb as a benzene level at which evacuation should be recommended. This value was based on the Michigan Occupational Safety and Health Administration level of 500 ppb at which workers are required to wear breathing protection (i.e., respirators) (MDLRA 2003). MDCH adjusted the occupational level to 200 ppb to provide added protection for non-workers, including sensitive groups such as children and people with existing medical conditions.

MDCH and ATSDR also identified human health screening levels for other VOCs in addition to benzene that are protective for people breathing these chemicals for up to one year (i.e., intermediate or sub-chronic exposure). Appendix A, Table A-1, provides the 2010 Human Health Screening Levels used to evaluate levels of VOCs found in “grab” or time-integrated air samples. MDCH and ATSDR identified screening levels from several sources and used the hierarchy below to choose the most appropriate value for each chemical.

- The ATSDR Intermediate MRL is the preferred screening level. The Intermediate MRL is protective of daily human inhalation exposure for up to a year, and is protective for sensitive individuals such as children, the elderly, and those with pre-existing illnesses.
- If no Intermediate MRL was available, the screening level is the ATSDR Chronic MRL or the EPA Reference Concentration (RfC). The chronic MRL and the RfC are protective of daily human inhalation exposure over a lifetime, including sensitive individuals.
- If none of the above were available, the EPA Regional Screening Level (RSL) is the screening level. The RSLs are protective of daily human inhalation exposure over a lifetime, including sensitive individuals.
- If none of the above were available, the MDNRE Air Quality Division, Air Toxics Screening Level is the screening level. The MDNRE screening levels are protective of daily human inhalation exposure over a lifetime, including sensitive individuals.

**Figure 2. Decision tree for evacuation decisions based on benzene levels, Kalamazoo River oil spill, July 2010, Calhoun County, Michigan.**



ppb = parts per billion

HAPSITE = Hazardous Air Pollutants on Site (field portable gas chromatograph/mass spectrometer)

UltraRAE = a benzene-specific photoionization detector made by RAE Systems

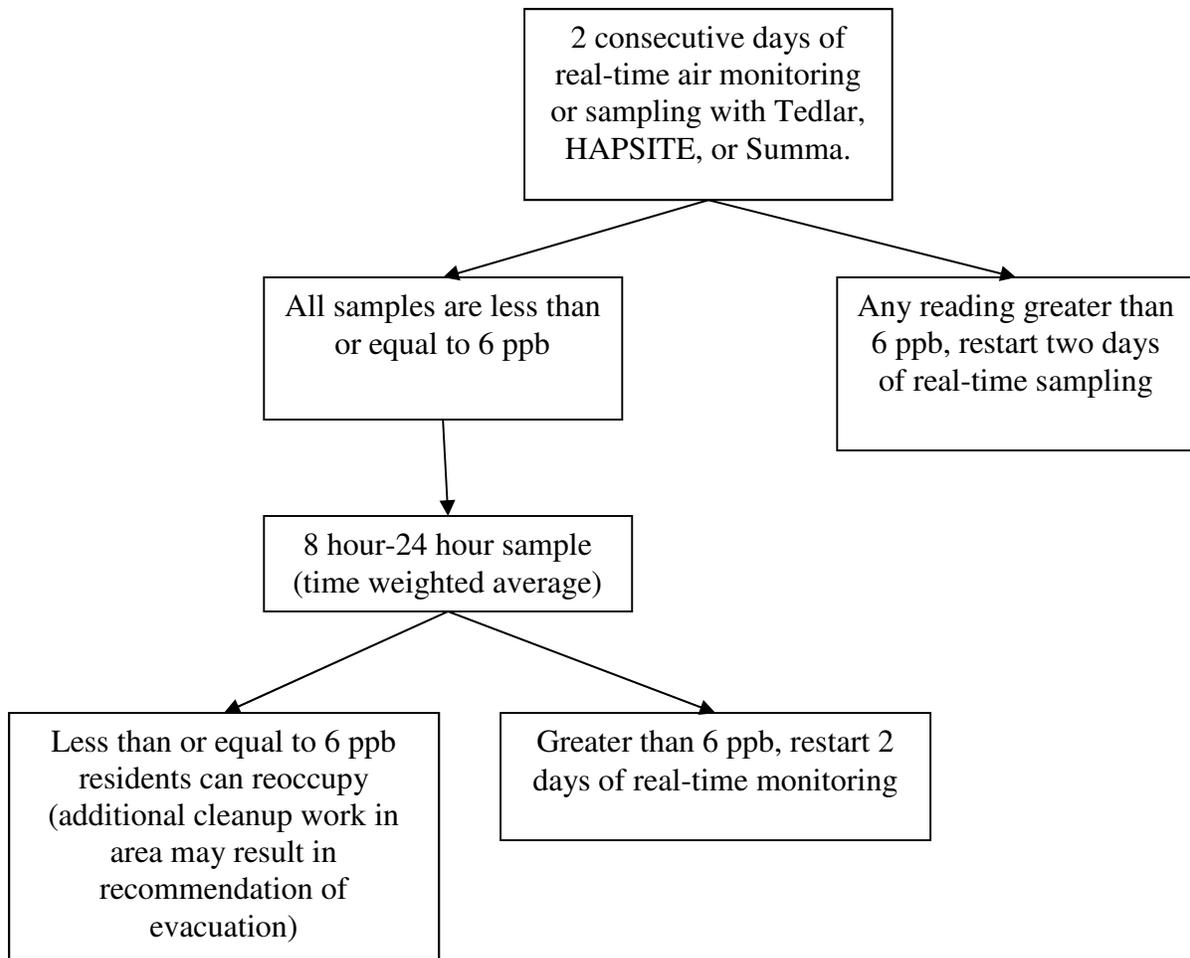
GASTEC = Gas Detector Tubes

Tedlar = Tedlar Gas Sampling Bags

In 2011, MDCH further revised the human health screening levels for VOCs to include air screening levels that are protective of people breathing these chemicals for a lifetime (i.e., chronic exposure). The 2011 Human Health Air Screening Levels, provided in Appendix A, Table A-2, were selected using a hierarchy similar to the one above.

Figure 3 provides the Re-Occupancy Decision Tree used to evaluate concentrations of benzene in air to determine when people could return to their homes after an evacuation. Re-occupancy was acceptable when levels of benzene in air were below the ATSDR intermediate MRL of 6 ppb.

**Figure 3. Decision tree for re-occupancy decisions based on benzene levels, Kalamazoo River oil spill, July 2010, Calhoun County, Michigan.**



ppb = parts per billion

HAPSITE = Hazardous Air Pollutants on Site (field portable gas chromatograph mass spectrometer)

Tedlar = Tedlar Gas Sampling Bags

Summa = Summa Canister Samples

## Community Health Concerns

Beginning at 9:25 pm on July 25, 2010, the Calhoun County 911 dispatch center began receiving numerous calls about strong “natural gas or crude oil” odors. City of Marshall fire department personnel as were sent to investigate, but were not initially able to locate the source of the odors (NTSB 2012). Individuals near Talmadge Creek and the Kalamazoo River also began reporting strong, noxious odors and associated health symptoms in calls to CCPHD and the Michigan Poison Control Center (PCC). Subsequently, citizen calls were routed to a phone hotline provided by Enbridge. Callers reported respiratory, gastrointestinal, and neurological symptoms, predominantly headache and nausea.

In response to community concerns, MDCH, CCPHD, and the Kalamazoo County Health and Community Services Department (KCHCS) implemented a public health surveillance system to collect information about the health effects experienced by people who were exposed to the spilled oil and the air contaminants coming from it. The goal of the system was to describe the magnitude and distribution of health effects, so that decision-makers could make informed decisions about actions needed to protect the public.

The surveillance system included four parts:

- Under the authority of the Michigan Public Health Code, health care providers were asked to provide reports of patients who were seen due to illness or symptoms associated with oil spill exposure.
- A door-to-door health survey was conducted in August 2010 in four communities along the Talmadge Creek and Kalamazoo River and in one small workplace.
- MDCH received daily counts of self-reported illnesses from the PCC.
- MDCH also used its syndromic surveillance system to track the incidence of illnesses in the affected communities

The surveillance system received 147 health care provider reports on 145 patients, identified 320 (58%) of 550 individuals with adverse health effects from four community surveys along the impacted waterways, and tracked 41 calls that were placed to the PCC by the public.

Headache, gastrointestinal complaints (e.g., nausea and vomiting), and respiratory symptoms (e.g., breathing difficulty, cough) were the most often reported health symptoms (MDCH 2010). These symptoms are consistent with the published literature regarding the potential health effects of acute exposure to crude oil (Solomon 2010). Some people also reported effects on their skin and eyes, anxiety, and other symptoms such as dizziness, fatigue, and chest pain. Just over 12 percent of people surveyed had seen their doctor because of these effects (MDCH 2010).

MDCH provided information to area health care providers to help them recognize symptoms of oil exposure and to provide resources to assist them in caring for their patients. Additional materials were developed by state and local health agencies in cooperation with the EPA. These materials were provided to community members through a variety of means including the internet, public meetings, and local media sources. Health officials also visited the homes of people in some affected neighborhoods to ensure that residents there were kept informed.

## Discussion

### Environmental Contamination

The database of information gathered to evaluate the public health hazards of breathing chemicals emitted from the spilled oil includes more than 900,000 individual air contaminant measurements. Real-time monitoring instruments were used to evaluate 19 air parameters, and over 350 different chemicals were measured in the laboratory analysis of air samples.

Air monitoring and sampling began on July 26, 2010 and has continued throughout the on-going response to the spill. To better understand how air contaminant concentrations changed over time, MDCH grouped air monitoring and sampling data into five response time frames;

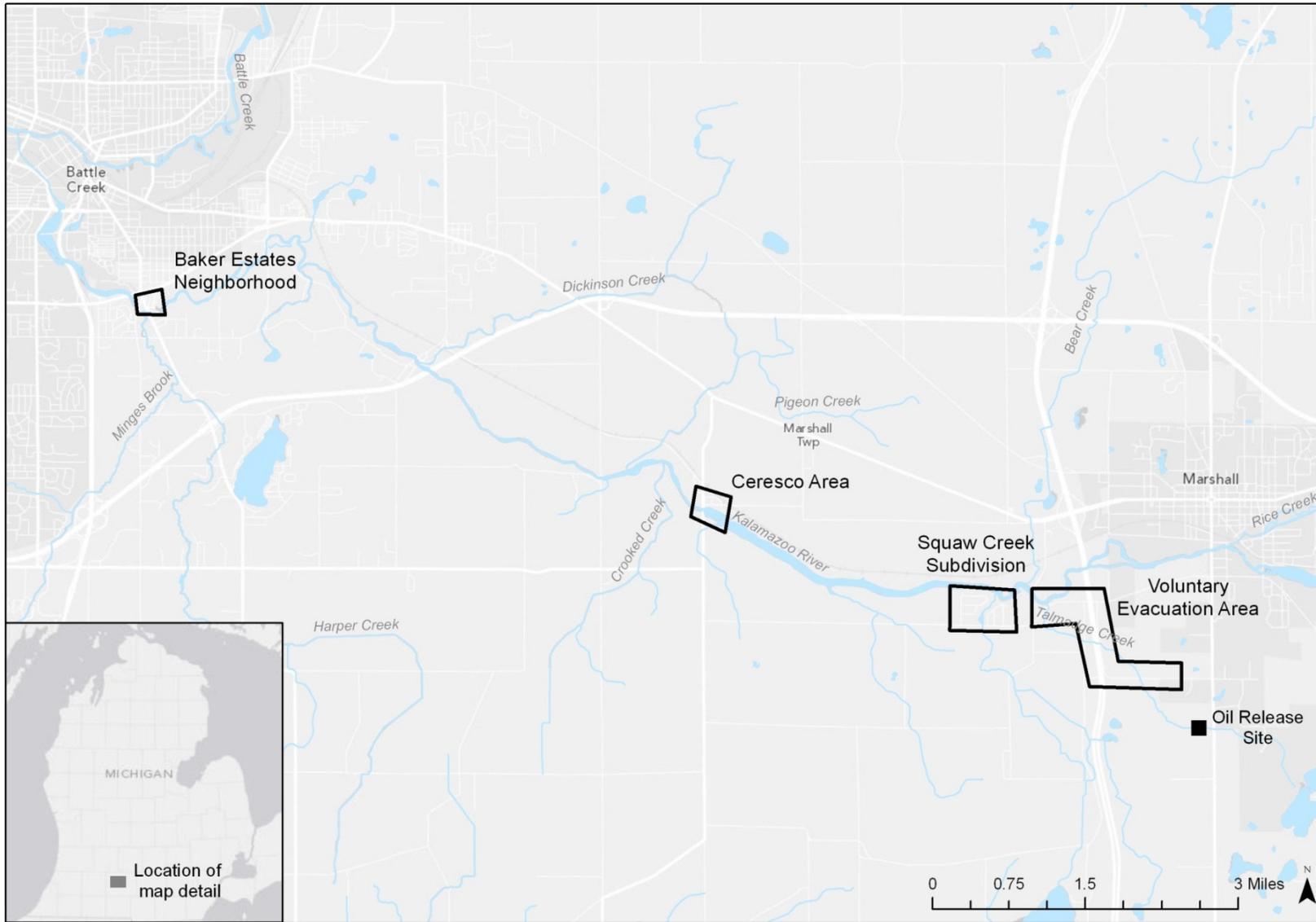
- The Initial Response from July 26 through July 28, 2010
- The Voluntary Evacuation Period from July 29 to August 17, 2010
- The Post Evacuation Period from August 18 to December 31, 2010
- All of 2011
- All of 2012

Some of the monitoring data represent measured concentrations of contaminants in air immediately above pools of spilled oil. No homes were located in Division A (Oil Release Site), where the highest air concentrations were measured. With the exception of the response workers, it is not likely that people breathed these concentrations of air contaminants. Further, many of the air measurements were taken at some distance from the Kalamazoo River to define how far the air contamination had traveled from the spill. These data are also not representative of the levels of contaminants in residential areas closer to the spill.

To better understand the levels of air contaminants that people may have breathed following the oil spill, MDCH identified four residential areas closest to the creek and river (Figure 4). The residential area closest to the Oil Release Site is the Voluntary Evacuation Area. This area roughly follows the course of Talmadge Creek to the bridge at 15 Mile Road, just before mile marker 2.25. It includes approximately 60 homes on Division Drive, 16 Mile Road, 15 ½ Mile Road and A Drive North. The other areas selected include: the Squaw Creek Subdivision, which lies between mile marker 2.5 and 3.25 and includes at least 120 homes; the village of Ceresco Area beginning at about mile marker 5.75, which includes more than 80 homes; and the Baker Estates Neighborhood in the city of Battle Creek that lies between mile markers 13.5 and 13.75, and includes about 75 homes (MDCH 2010).

It is also important to identify and consider the response activities that were on-going when evaluating whether measured air contaminant levels could have affected people's health. Active oil recovery and excavation work continued in both the Voluntary Evacuation Area and the Ceresco Area for much of 2010, and periodically in 2011 and 2012. Elevated air contaminant concentrations were sometimes found by work-site and work area-perimeter sampling and monitoring that was conducted to ensure the safety of both workers and nearby neighborhoods. MDCH further evaluated these data to determine if air concentrations during response activities posed a health hazard to people living or working nearby (other than the cleanup response workers).

**Figure 4. Location of the Voluntary Evacuation Area, the Squaw Creek Subdivision, the Ceresco Area, and the Baker Estates Neighborhood, Calhoun County, Michigan.**



## *Air Monitoring and Sampling Results*

### Total Volatile Organic Compounds (VOCs)

There are no human health screening levels for total VOCs because the mixtures (and resulting health effects) of these chemicals in air vary depending on the source and the nature of the release. However, VOC concentrations above 1,000 ppb are an indication of the need for chemical-specific monitoring (NJDHSS 2003). Tables B-1 and B-2 in Appendix B provide the results of air monitoring for total VOCs in response to the Enbridge oil spill.

During the Initial Response Period (July 26 to 28, 2010), VOCs air concentrations were highest in the Voluntary Evacuation Area ranging from not detectable up to 120,000 ppb, with about half the measured concentrations higher than 1,000 ppb. VOCs in the Squaw Creek Subdivision and the Ceresco Area were also elevated up to 71,600 ppb and 6,000 ppb respectively, with again about half the measured concentrations higher than 1,000 ppb. No VOCs were detected in the Baker Estates Neighborhood during this time period.

During the Evacuation Period (July 29 to August 17, 2010), the highest levels of VOCs increased in the Voluntary Evacuation Area, however only 84 of more than 2,200 measurements were higher than 1,000 ppb. This increase is likely a result of the oil recovery activities that were happening along Talmadge Creek during this time.

The highest level of VOCs dropped in the Squaw Creek Subdivision during the Evacuation Period, with just eight of 658 measurements higher than 1,000 ppb. VOC levels in the Ceresco Area also dropped with only two of 467 measurements higher than 1,000 ppb. Levels of VOCs measured in the Baker Estates Neighborhood ranged from not detected to a high of 266,000 ppb, but only three of 556 measurements were higher than 1,000 ppb.

In the Post-Evacuation Period (August 18 to December 31, 2010), the highest VOC air concentrations fell to 9,000 ppb in the Voluntary Evacuation Area, with only 18 of 4,277 measurements higher than 1,000 ppb. VOCs were slightly over 1,000 ppb only once in the Squaw Creek Subdivision (of 1,059 measurements) and only once in the Baker Estates Neighborhood (of 767 measurements). Air monitoring in the Ceresco Area was intensive because of oil removal activities taking place there during this time period. Just five VOC concentrations out of 5,149 measured in that area were higher than 1,000 ppb.

Total VOCs were not detectable in any of these areas in more than 3,000 measurements taken in 2011. Air monitoring and sampling in 2012 was focused on specific chemicals, rather than monitoring for total VOCs.

### Hydrogen Sulfide (H<sub>2</sub>S)

Hydrogen sulfide (H<sub>2</sub>S) is a natural component of crude oil and natural gas, and can also come from bacterial breakdown of organic matter such as rotting vegetation or animal wastes. The crude oil spilled from the pipeline contained less than 0.5 percent hydrogen sulfide (Cenovus Energy Inc. 2008). Because H<sub>2</sub>S can cause immediate health effects at low levels, both START and CTEH monitored for this gas throughout the response to the spill. Tables B-3 and B-4 in Appendix B presents measured levels of H<sub>2</sub>S in the four target areas.

On August 8, 2010, START accompanied CTEH to a storage barn near Talmadge Creek. The Enbridge supervisor in charge of oil recovery work at 15 ½ Mile Road and the creek had concerns about his workers' safety in regards to the contents of the barn, which included many containers (both open and covered) with liquid contents, old vehicles, a tractor and other machinery. Inside the barn, START and CTEH monitored low concentrations of benzene from not detectable to 50 ppb and moderately elevated concentrations of total VOCs (1,300 to 4,200 ppb). Both START and CTEH measured the concentration of H<sub>2</sub>S inside the pole barn at 5,000 ppb. However, H<sub>2</sub>S was not detected in air outside the building. Elevated H<sub>2</sub>S levels were therefore attributed to the contents of the barn, which have since been removed. Table B-3 does not include these data.

Levels of H<sub>2</sub>S slightly above 100 ppb were measured in work zones located in the Voluntary Evacuation Zone during the Evacuation Period. However, these measurements were fleeting. Air temperatures were elevated at the time, with daily readings consistently exceeding 90 degrees Fahrenheit. The monitored levels of H<sub>2</sub>S may have resulted from disturbed and rotting vegetation along the creek bank.

### Benzene

**Colorimetric Instruments** - Table B-5 in Appendix B presents the benzene levels measured using colorimetric instruments. START measured benzene on July 27, 2010, at 3,000 ppb at the confluence of the Talmadge Creek and the Kalamazoo River. The people living in the homes nearest the confluence had already relocated due to the odors from the spilled oil and the general disruption and noise created by the spill response. Benzene was again measured on July 28, 2010, at 9,750 and 10,000 ppb near where Division Drive crosses the Talmadge Creek. However, lower benzene measurements taken at that location or nearby on the same day and in the days after indicated that these high benzene air concentrations were not sustained over time. No-one was living in the immediate vicinity of this monitoring location.

START, using colorimetric instruments, measured benzene at 500 ppb once in the Squaw Creek Subdivision and at 250 ppb once in the Ceresco Area during the Initial Response Period and again at 100 ppb in the Ceresco Area during the Voluntary Evacuation Period. Benzene was not detected by colorimetric instruments in any area after August 18, 2010.

**Real-Time Monitoring for Benzene** - Several different hand-held monitors were used during the oil spill response to monitor benzene levels in air. For this document, MDCH used only benzene levels measured with HAPSITE and UltraRAE monitors because these provide the most accurate and dependable benzene data. Table B-6 in Appendix B presents the benzene concentrations measured using real-time UltraRAE and HAPSITE monitors. Table B-7 presents the benzene concentrations measured with instruments that were not specifically identified.

On July 28, 2010, benzene was measured with UltraRAE<sup>3</sup> monitors in the Voluntary Evacuation Area at concentrations exceeding the 200 ppb screening level for evacuation. Benzene measurements were highest near containment and collection booms laid across the creek and

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<sup>3</sup> UltraRAEs measure benzene levels by filtering out other chemicals. Other RAE monitors measure multiple chemicals, and should not be compared to UltraRAE measurements.

river as well as near vacuum trucks collecting oil, but were lower away from the river. START, using the Evacuation Decision Tree guidance, collected additional real-time data where initial measurements were high. Most of the benzene concentrations in these additional measurements on July 28, 2010, were between 60 and 200 ppb. Because the capacity to measure benzene in real-time at concentrations less than 60 ppb was not yet available, MDCH advised START to continue UltraRAE monitoring in this area. In addition, START collected a “grab” air sample in a Summa canister placed near where Division Drive crosses the Talmadge Creek. However, the results from this sample were not immediately available because about 24 hours are needed to run the laboratory analysis after the sample is collected.

On July 29, 2010, benzene was again measured with UltraRAE monitors in the Voluntary Evacuation Area at concentrations exceeding the screening level for evacuation of 200 ppb. In addition, 200 ppb of benzene was confirmed in the “grab” air sample taken the previous day. Eight of 13 monitoring measurements taken with an UltraRAE in this area in the first three days following the spill were higher than the 60 ppb initial screening level, with benzene concentrations ranging up to 6,250 ppb. This information prompted local and state health officials to recommend that people living in this area leave their homes until it could be determined that air concentrations of benzene were at safe levels. UltraRAE monitors continued to measure benzene at levels up to 2,200 ppb throughout the Evacuation Period, which ended on August 17, 2010. However, benzene measurements taken with the HAPSITES did not exceed the initial screening level and were far lower than those taken with UltraRAE monitors. All HAPSITE measurements were below the benzene screening level of 60 ppb.

Benzene concentrations measured by real-time monitors in the Squaw Creek Subdivision were not greater than the 60 ppb screening level at any time in 2010. However, many people chose to leave because of the strong petroleum odors coming from the spilled oil.

From July 26 through August 17, 2010, benzene concentrations of 200 to 500 ppb were measured with real-time monitors in the Ceresco Area in three of 278 measurements. However, additional monitoring on the same days suggested that these concentrations were not sustained and all other benzene measurements were below the initial screening level of 60 ppb. Therefore, no evacuation was recommended for the Ceresco Area.

Benzene concentrations were higher than 6 ppb in 10 of the 3,704 real-time measurements taken in the Ceresco Area after August 18, 2010. MDCH evaluated each of these measurements separately to better understand the surrounding circumstances. Each elevated benzene concentration was measured by monitors located either in a work area or at the perimeter of a work area. Benzene concentrations measured by monitors located away from work areas and closer to residential homes were lower than 6 ppb.

Benzene concentrations monitored at the Baker Estates Neighborhood were higher than the initial screening level of 60 ppb in only one of 265 measurements taken before August 18, 2010, and were not detectable in 304 additional measurements that year. Therefore, no evacuation was recommended for the Baker Estates Neighborhood.

**Air Sampling for Benzene** – Air samples, including Summa canister, mini can, and Tedlar bag samples, were collected for laboratory analysis beginning on July 28, 2010. Air samples were collected over varying time periods, ranging from a “grab” sample of just a few minutes up to a time-integrated sample of 24 hours.

Table B-8 in Appendix B presents the benzene levels measured in “grab” air samples. Of the approximately 1,200 “grab” air samples collected, benzene was detected in just 29 and only 11 showed concentrations above the intermediate human health screening level of 6 ppb that is protective of up to one year of exposure. Benzene was measured above the screening level for evacuation of 200 ppb in the Voluntary Evacuation Area once during the Initial Response (July 28, 2010) and once during the Evacuation Period (August 4, 2010).

Benzene concentrations above 6 ppb were measured in four “grab” air samples collected during the Post Evacuation Period as described below:

- The benzene concentration was 190 ppb in one sample collected on October 15, 2010, in a work area near Talmadge Creek adjacent to the Voluntary Evacuation Area. The other 18 air samples collected there on the same day did not detect benzene over the screening level.
- The benzene concentration was 8.4 ppb in one sample collected on October 4, 2010, from the Squaw Creek Subdivision. Benzene was not detected in a second sample collected from the same location on the same day. Additionally, benzene was not detected in the three samples collected from that location on the next day (October 5, 2010).
- The benzene concentration was 20 ppb in two “grab” samples collected from the Baker Estates Neighborhood on two days: August 26, 2010 and October 7, 2010. No benzene was detected in time-integrated samples collected on the same day and location as the “grab” samples. Also, benzene was not detected in samples collected before (August 25 and October 6, 2010) and after (August 27 and October 8, 2010) these days.

Table B-9 in Appendix B presents the benzene concentrations in time-integrated air samples. No time-integrated air samples were collected during the Initial Response from July 26 through July 28, 2010. Of the 181 time-integrated samples collected from July 29 to August 17, 2010, benzene was detected in 14 samples from the Voluntary Evacuation Zone, with three sample concentrations exceeding the screening level of 6 ppb. Benzene concentrations did not exceed the screening level in any other time-integrated sample collected in 2010. Benzene was detected in three of 483 time-integrated samples collected in the Ceresco Area in 2011, but measured concentrations did not exceed 6 ppb. Benzene was not detected in any time-integrated air sample collected in this area in 2012.

#### Individual VOCs Measured in Air Samples

In addition to benzene, many individual VOCs were measured in both “grab” air samples and time-integrated air samples. Tables B-10 through B-17 in Appendix B present the VOC concentrations in air samples collected in the four study areas from July 26, 2010, through the end of 2012. Other than benzene, 12 VOCs were measured at concentrations over their

respective screening levels in air samples collected in 2010 and 2011, and most of these were found in the Voluntary Evacuation Area before August 18, 2010. Chemical concentrations higher than screening levels were found in only 31 out of 120,166 separate laboratory analyses. No measured VOC concentration was greater than its chemical-specific screening level in any air sample collected in 2012.

Exposure Pathways Analysis

There are five parts or *elements* of an *exposure pathway* to consider when deciding if a person may be exposed to a chemical: (1) where is the chemical coming from (the source), (2) what in the environment has been contaminated (environmental medium), (3) is there a place where people might come into contact with the chemical (exposure point), (4) how might people come into contact with the chemical (exposure route), and (5) who might be exposed (exposed population). An exposure pathway is complete if it is expected or there is proof that all five of these elements are present. Table 2 describes the exposure pathway for human exposure to chemicals in air as a result of the Enbridge oil spill.

**Table 2. Exposure pathway for oil-related air contaminants for people visiting, living in, or working in the Enbridge Oil Spill Area, Calhoun and Kalamazoo Counties, Michigan.**

Source	Environmental Medium	Exposure Point	Exposure Route	Exposed Population	Time Frame	Exposure Pathway
Enbridge crude oil spill.	Air	Talmadge Creek and the Kalamazoo River Vicinity	Inhalation	People visiting, living in and working in the target areas.	Past	Complete
					Present	Incomplete
					Future	Incomplete

Toxicological Evaluation

Chemical contaminants in the air can cause harm directly to respiratory tissues or the chemicals may be absorbed through the lungs and cause harm in other body tissues. Direct harm to respiratory tissues, such as irritation and burning of the nose and lungs, is mostly dependent on the characteristics of the chemical and how much of it is in the air. For chemicals that are absorbed through the lungs and cause harm in other parts of the body, the degree of harm is also determined by how the chemical interacts with the respiratory tissues. Animal studies are useful to identify levels of air contaminants that may cause health effects, but how a chemical interacts with respiratory tissues is often different in people compared to test animals. Air concentrations identified as being without health effects in animal studies must therefore be adjusted to a human equivalent concentration that is unlikely to cause health effects in people. The human equivalent concentration is then divided by uncertainty factors to lower it to a level that is protective of all people, including sensitive groups such as children, the elderly, and people with existing medical conditions.

## VOCs

Air monitoring conducted after the Enbridge oil spill found elevated concentrations of total VOCs. There are no health-based air screening levels for total VOCs or for many of the individual VOCs that could be emitted from the complex mixture of hydrocarbons in crude oil. Air monitoring for total VOCs following the Enbridge oil spill indicated that concentrations were elevated and, therefore, chemical-specific monitoring and sampling was conducted.

People who breathe air that contains VOCs for a short time may have eye and respiratory tract irritation, headaches, dizziness, visual disorders, fatigue, loss of coordination, allergic skin reactions, nausea, and memory impairment. These effects stop when a person is no longer breathing the contaminated air. People who have existing health problems like asthma, children and the elderly may be more sensitive to the effects of breathing VOCs (EPA 2013).

Between July 26 and September 4, 2010, people who breathed the VOCs in the air following the Enbridge oil spill reported headache, gastrointestinal complaints, respiratory symptoms, effects on their skin and eyes, anxiety, and other symptoms such as dizziness, fatigue, and chest pain (MDCH 2010). No clear relationship has been defined for total VOCs air concentrations and health effects. Most people's perception of odors, and the related discomfort, increases as the concentration of total VOCs increase. From July 26th to the end of 2010, concentrations of VOCs fluctuated from undetectable to 568,000 ppb, with the highest levels in the Initial Response and the Evacuation Period that ended on August 17, 2010. VOC concentrations in the air likely increased during and in the vicinity of oil recovery activities such as vacuuming oil from the surface of the river or excavation of oil-contaminated soil and sediment. However, after August 18, 2010, VOC concentrations fell dramatically (Tables B-1 and B-2 in Appendix B) and no individual VOC was consistently found at concentrations exceeding the human health-based screening levels (Tables B-10 through B-17 in Appendix B).

## *Hydrogen Sulfide*

Hydrogen sulfide has the characteristic odor of rotten eggs and most people can smell it at very low levels in air. Hydrogen sulfide in air is irritating to the membranes of the eye and respiratory tract and can cause pulmonary edema and nasal lesions if people breathe in high levels over time. At very high air levels, hydrogen sulfide causes "olfactory fatigue," meaning people stop smelling it and do not realize they are breathing levels that can cause asphyxiation. Hydrogen sulfide does not build up in the body (ATSDR 2006).

Hydrogen sulfide concentrations slightly above the detection limit of 100 ppb were measured in work zones located in the Voluntary Evacuation Area during the Voluntary Evacuation Period (Tables B-3 and B-4 in Appendix B). However, these were fleeting and there were no reported effects to workers. People living or working in the vicinity of the oil spill, other than response workers, were not likely to have health effects from breathing H<sub>2</sub>S in air as a result of the oil spill.

## *Benzene*

Benzene is emitted to the air from burning coal and oil, gasoline vapors at gasoline service stations, motor vehicle exhaust, cigarette smoke, wood-burning fires, and spills of gasoline or

other petroleum-based products. Pure benzene is a clear, colorless, flammable liquid with a gasoline-like odor. Most people cannot smell benzene until it reaches concentrations of 60,000 ppb or more. Benzene evaporates very quickly into air, where it can react with other chemicals and break down within a few days (ATSDR 2007).

People breathe small amounts of benzene every day, mostly in areas with heavy traffic and around gas stations. Urban and industrial areas generally have higher levels of benzene in the outdoor air than rural areas. In 2010, the MDEQ reported average outdoor air levels of benzene in the Michigan cities of Dearborn and Detroit of 0.29 to 0.36 ppb respectively, with maximum values of 0.80 to 1.44 ppb (MDEQ 2010). People can be exposed to higher than background levels of benzene if they live near manufacturing or waste sites, or near leaking gasoline storage tanks (ATSDR 2007).

Benzene is also a common indoor air pollutant and levels indoors can be higher than in outdoor air (ATSDR 2007). Sources include cigarette smoke; exhaust from motor vehicles or products stored in attached garages; smoke from wood burning fires; and some household products that contain petroleum-based chemicals such as glues, paints, furniture wax, and lubricants. Levels of benzene measured in the air of homes where no one smoked have been reported to average from 1 to 2 ppb. Benzene levels in the air of homes with smokers averaged 1.7 to 3.3 ppb with a maximum level measured at 8.4 ppb (ATSDR 2007).

When people breathe benzene, it passes through the lining of the lungs into the bloodstream. Benzene is metabolized in the liver and bone marrow, and may be temporarily stored in bone marrow or fat. Benzene is mostly excreted in urine within 48 hours of exposure, therefore it is not likely to accumulate (build up) in the body (ATSDR 2007).

People who breathe high levels of benzene for a short time can have effects such as sleepiness, dizziness, headaches, vertigo (a feeling of movement when one is actually still), tremor, nausea, delirium and loss of consciousness. These effects disappear when the exposure to benzene stops (ATSDR 2007).

The air concentrations of benzene measured with Draeger and GASTEC instruments on July 28, 2010, in the Voluntary Evacuation Zone were higher than the EPA (8-hour) AEGL-1 of 9,000 ppb. The AEGL-1 is a benzene level above which most people have discomfort, irritation, or mild central nervous system (CNS) effects such as headaches, dizziness and nausea. These effects stop when a person is no longer breathing benzene. Benzene concentrations in air did not exceed the EPA AEGL-2 and AEGL-3 levels protective of more serious health effects.

People who breathe lower concentrations of benzene for a longer time can have harmful effects to their ability to fight infection and make blood cells, which may cause excessive bleeding and anemia. Depending on the concentration and how long a person breathes the benzene, these effects are likely reversible when the exposure stops. People who work at jobs that make or use benzene or products that contain benzene may consistently breathe elevated levels of benzene for many months or years. Workplace exposure has been shown to reduce the numbers of blood cells (red, white and platelets) made in the blood-forming (hematopoietic) cells in red bone marrow in the vertebrae, sternum, ribs and pelvis. Aplastic anemia is a more severe effect of breathing high

levels of benzene and happens when the red bone marrow stops making any blood cells. People exposed to benzene at their jobs have also had adverse effects to their immune system that harmed their ability to fight disease (ATSDR 2007).

The ATSDR used a well-conducted study of workers to identify an MRL for chronic (lifetime) exposure to benzene in air. In this study, benzene was measured using personal vapor monitors. The workers had been employed at their jobs for an average of more than six years. The workers were grouped as controls (<40 ppb), low level exposure (570 ppb plus or minus 240 ppb), mid-level exposure (2,850 ppb plus or minus 2,110 ppb) and high level exposure (28,730 ppb plus or minus 20,740 ppb). Levels of blood cells in the low level exposure group were eight to 15 percent lower than those measured in the control group (Lan et al. 2004a, 2004b). After adjusting from a workplace 8-hour exposure to continuous exposure and adding an uncertainty factor to protect sensitive people (such as children and the elderly), ATSDR selected a chronic MRL of 3 ppb (ATSDR 2007).

There are no well-conducted studies in people of the effects of breathing benzene for shorter times; therefore ATSDR used animal studies to evaluate these exposures. Mice used in these studies breathed benzene for a few hours per day for 6 to 20 days. ATSDR adjusted benzene levels to continuous exposure and considered the differences between the human respiratory system and that of mice to calculate a human equivalent concentration in air, which was further reduced by dividing by a 300-fold uncertainty factor that protects sensitive people such as children, the elderly and those with pre-existing medical conditions. Using this approach, ATSDR selected 9 ppb as the benzene acute MRL for one to 14 days of exposure, and 6 ppb as the intermediate MRL for greater than 14 days to one year of exposure (ATSDR 2007).

The U.S. EPA classifies benzene as a known human carcinogen based on studies in people that breathed high levels of benzene for a long time (months to years) at their jobs. Workers who breathed benzene in air at 100,000 ppb and above developed leukemia, a type of cancer of the blood or bone marrow. This evidence in people is supported by studies in which both breathing and eating benzene caused cancer at multiple sites in animals (EPA 1998). No association between breathing benzene and cancer was found in studies of workers exposed to up to 9,600 ppb of benzene in air for more than four years (ATSDR 2007).

ATSDR has developed a Cancer Risk Evaluation Guide (CREG) for benzene in air of 0.04 ppb (ATSDR 2013) for lifetime exposure. Breathing levels of benzene higher than the CREG does not mean that a person will develop cancer and does not predict an individual's likelihood of developing cancer. The CREG assumes a theoretical risk of one more cancer in one million exposed people. As a comparison, the American Cancer Society estimates that men in the United States have slightly less than a 1 in 2 lifetime risk of developing cancer; for women, the risk is a little more than 1 in 3 (American Cancer Society 2012).

On July 29, 2010, elevated air concentrations of benzene prompted the CCPHD Health Officer, in consultation with MDCH and ATSDR, to recommend that people living in the Voluntary Evacuation Area leave their homes. About half the families chose to leave, while others remained, citing concerns over the safety of their property. The evacuation recommendation was

lifted on August 18, 2010, when additional air sampling demonstrated that benzene concentrations in air were consistently less than the intermediate MRL of 6 ppb.

Benzene concentrations were higher than the intermediate MRL in only seven “grab” and three time-integrated air samples collected from July 26 to December 31, 2010. While people likely breathed benzene in the air, concentrations above the intermediate MRL were not sustained over this entire time and were mostly found in work areas where oil-recovery activity was taking place. Measured benzene concentrations were not higher than the chronic MRL of 3 ppb for lifetime exposure in any air sample collected in 2011 or 2012.

Many people living and working in the area of the Enbridge oil spill reported the short term health effects of breathing benzene including; headache, gastrointestinal complaints, respiratory symptoms, effects on their skin and eyes, anxiety, and other symptoms such as dizziness, fatigue, and chest pain. However, high benzene concentrations in the air were not sustained and it is unlikely that anyone will experience the more serious long term effects seen in studies of workers who breathed high levels of benzene on their jobs for many years.

### *Odors*

People can smell most chemicals in petroleum products at air concentrations far below levels that may cause respiratory irritation or chemical-specific health effects. A person’s ability to detect an odor, and whether or not it makes them feel sick, may be influenced by age, gender, pre-existing illness or other underlying chemical sensitivity (Shusterman 1999).

In the days following the spill, air concentrations of total VOCs ranged up to several hundred parts per billion and were highest near the creek and river, particularly near cleanup work sites. Many people with homes or businesses in the area of the spill reported the short term health effects caused by breathing these chemicals including; headaches, nausea, respiratory discomfort, and eye irritation (MDCH 2010). These health effects are consistent with those expected from breathing the total VOCs measured in the air following the oil spill.

Some people may have experienced health effects from smelling the odors coming from the spilled oil, even where measured VOC concentrations were below those expected to cause respiratory irritation or other short-term health effects. People who have asthma may be particularly sensitive to odors and respiratory irritants. Others without underlying medical conditions may just be more inherently sensitive and respond to odors with respiratory symptoms like eye irritation, nasal congestion, coughing and headache (Shusterman 1999). Some people, such as pregnant women, are also more likely to experience nausea from smelling unpleasant odors even at low chemical concentrations. Some people may have experienced anxiety related to the event, regardless of their exposure.

People who have experienced health effects from breathing high levels of odor-causing chemicals in the air may subsequently feel sick when they breathe even very low concentrations. This is especially true for people who are very sensitive to chemical odors and their effects (Greenberg et al. 2013; Shusterman 1999; van Thriel et al. 2008, Zibrowski and Robertson 2006). The personal and community stress and disruption that followed the spill may have contributed to people’s aversion to the oil odors and the illness they felt.

### Children's Health Considerations

Children may be at greater risk than adults when exposed to certain hazardous substances. Children play outdoors and are more likely to put their hands in their mouths or touch their faces, which increases their chance of exposure. Young children are also shorter than adults; they breathe dust, soil, and vapors close to the ground. A child's lower body weight and higher intake rate result in a greater dose of hazardous chemicals compared to their weight. If toxic exposure levels are high enough during critical growth stages, the developing body systems of children may be damaged.

ATSDR considered children's health when developing the screening levels used by MDCH to identify when air contaminants coming from the spilled oil posed a human health risk. Children may have a more heightened sense of smell than adults and may be more likely to experience short term health effects as a result. In addition, children with pre-existing health problems such as asthma could have more respiratory symptoms while they breathed the air that contained the oil-related chemicals.

### **Limitations**

MDCH identified some limitations in the air monitoring and sampling data collected to evaluate the chemicals coming from the spilled oil.

- The real-time UltraRAE and other RAE system monitors used in the Initial Response from July 26 through July 28, 2010 are not capable of measuring benzene below 60 ppb. The ability to measure levels of benzene below the initial screening level of 60 ppb was not available until the National Guard 51st CST deployed to the spill on July 28, 2010, and the ERT mobile laboratory was fully functional on August 2, 2010.
- The UltraRAE and HAPSITE monitors sometimes provided very different measurements of benzene concentrations: HAPSITE monitors consistently measured benzene at far lower air concentrations than UltraRAE monitors. The public health agencies considered these differences in deciding where to recommend voluntary evacuations and used the most health protective information to recommend that people living in the Voluntary Evacuation Area leave their homes until laboratory analysis of air samples could demonstrate that benzene concentrations were below the intermediate MRL of 6 ppb.
- Human Health Screening Levels are not available for many of the individual VOCs in the crude oil mixture. In addition, no air screening levels are available for the mixture of total VOCs in the spilled oil.

## Conclusions

MDCH has reached the following conclusions about chemical levels in air following the July 2010 Enbridge oil spill:

*1. People in the spill area who breathed oil-related chemicals in the air from the time of the spill to August 18, 2010, reported short term (temporary) health effects including: headaches, nausea, respiratory discomfort, and eye irritation. These short term effects diminish and stop when people are no longer breathing air containing oil-related chemicals. Some individuals may have experienced anxiety related to the event, regardless of their exposure.*

*2. People are not expected to have long term, more serious health effects as a result of breathing the oil-related chemicals. By August 18, 2010, air concentrations of oil-related chemicals fell below human health screening levels that protect everyone from long term health effects including sensitive people such as children, the elderly, and those with pre-existing illnesses. Therefore, people living in the spill area did not breathe oil-related chemicals long enough or at levels high enough to cause long term health effects.*

*3. People are not expected to have health effects as a result of breathing the air near the work areas where oil recovery and cleanup activities were ongoing in 2011 and 2012. Air concentrations of benzene in 2011 and 2012 did not exceed the health-based screening level. No other oil-related chemical was consistently found in 2011 or 2012 at concentrations exceeding the human health screening levels.*

MDCH's conclusions do not apply to workers who took part in the oil recovery and cleanup activities. The data that MDCH reviewed to reach these conclusions was gathered to evaluate the concentrations of oil-related chemicals that people living in the spill area might have breathed. These data may not represent air concentrations of oil-related chemicals in the work areas.

## Recommendations

MDCH recommends air monitoring and sampling during all on-going oil recovery activities in the areas affected by the Enbridge oil spill.

### Public Health Action Plan

- MDCH will evaluate work plans and make recommendations to the EPA, the MDEQ and Enbridge to ensure that adequate air monitoring and sampling are conducted.
- MDCH will evaluate all sampling and monitoring data to ensure that air concentrations of oil-spill related chemicals do not pose a public health hazard.
- MDCH will work with local health departments and community members to provide health protective information and continue to evaluate human exposure to the chemicals in the remaining crude oil.

## **Report Preparation**

This Public Health Assessment for the Kalamazoo River Enbridge Oil Spill Site was prepared by the Michigan Department of Community Health (MDCH) under a cooperative agreement with the federal Agency for Toxic Substances and Disease Registry (ATSDR). It is in accordance with the approved agency methods, policies, procedures existing at the date of publication. Editorial review was completed by the cooperative agreement partner. ATSDR has reviewed this document and concurs with its findings based on the information presented. ATSDR's approval of this document has been captured in an electronic database, and the approving agency reviewers are listed below.

### **Authors – MDCH Division of Environmental Health**

Linda D Dykema, Ph.D.  
Toxicologist, Principal Investigator

Jennifer Gray, Ph.D.  
Toxicologist

### **ATSDR Reviewers**

Trent LeCoultre, MSEH, REHS  
Technical Project Officer, Central Branch  
Division of Community Health Investigations

Michelle Watters, MD, PhD, MPH  
Medical Officer  
Division of Community Health Investigations

Tina Forester, PhD, Acting Director  
Division of Community Health Investigations

Rick Gillig, MCP, Central Branch Chief  
Division of Community Health Investigations

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Appendix A: Human Health Screening Levels

**Table A-1. 2010 Enbridge Oil Spill Human Health Air Screening Levels August 13, 2010**

<b>Chemical Name</b>	<b>Chemical Abstract Service Number</b>	<b>Screening Level in parts per billion (ppb)</b>	<b>Source of Screening Level</b>
1,1,1-Trichloroethane	71-55-6	700	ATSDR Int. MRL
1,1,2,2-Tetrachloroethane	79-34-5	0.006	EPA RSL
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	4,000	EPA RSL
1,1,2-Trichloroethane	79-00-5	100	Chronic MRL or RfC
1,1-Dichloroethane	75-34-3	100	Chronic MRL or RfC
1,1-Dichloroethene	75-35-4	20	ATSDR Int. MRL
1,2,4-Trichlorobenzene	120-82-1	30	Chronic MRL or RfC
1,2,4-Trimethylbenzene	95-63-6	1.5	EPA RSL
1,2-Dibromoethane	106-93-4	1	Chronic MRL or RfC
1,2-Dichloro-1,1,2,2-Tetrafluoroethane	76-14-2	9,900	EPA RSL
1,2-Dichlorobenzene	95-50-1	30	Chronic MRL or RfC
1,2-Dichloroethane	107-06-2	1,000	Chronic MRL or RfC
1,2-Dichloropropane	78-87-5	7	ATSDR Int. MRL
1,3-Butadiene	106-99-0	1	Chronic MRL or RfC
1,3,5-Trimethylbenzene	108-67-8	45	MDNRE
1,3-Dichlorobenzene	541-73-1	0.5	MDNRE
1,4-Dichlorobenzene	106-46-7	200	ATSDR Int. MRL
1,4-Dioxane	123-91-1	1,000	ATSDR Int. MRL
2,2,4-Trimethylpentane	540-84-1	750	MDNRE
2-Chloro-1,3-butadiene	126-99-8	2.1	EPA RSL
2-Propanol	67-63-0	3,000	EPA RSL
3-Chloropropene	107-05-1	0.3	Chronic MRL or RfC
Acetone	67-64-1	13,000	ATSDR Int. MRL
Acetonitrile	75-05-8	38	EPA RSL
Acrylonitrile	107-13-1	1	Chronic MRL or RfC
Benzene	71-43-2	6	ATSDR Int. MRL
Benzyl chloride	100-44-7	0.01	EPA RSL
Bromodichloromethane	75-27-4	0.01	EPA RSL
Bromoform	75-25-2	0.21	EPA RSL
Bromomethane	74-83-9	50	ATSDR Int. MRL
Butane	106-97-8	10,000	MDNRE
Carbon disulfide	75-15-0	200	Chronic MRL or RfC
Carbon tetrachloride	56-23-5	30	ATSDR Int. MRL
Chlorobenzene	108-90-7	200	Chronic MRL or RfC
Chloroethane	75-00-3	4,000	Chronic MRL or RfC
Chloroform	67-66-3	50	ATSDR Int. MRL
Chloromethane	74-87-3	200	ATSDR Int. MRL

<b>Table A.1 continued</b>			
cis-1,2-Dichloroethene	156-59-2	8.6	MDNRE
cis-1,3-Dichloropropene*	10061-02-6	4.4	MDNRE
Cumene	98-82-8	100	Chronic MRL or RfC
Cyclohexane	110-82-7	2,000	Chronic MRL or RfC
Cyclohexane,methyl	108-87-2	4,000	MDNRE
Cyclopentane	287-92-3	6,000	MDNRE
Dibromochloromethane	124-48-1	0.01	EPA RSL
Dichlorodifluoromethane	75-71-8	42	EPA RSL
Ethyl acetate	141-78-6	890	MDNRE
Ethyl benzene	100-41-4	700	ATSDR Int. MRL
Heptane	142-82-5	850	MDNRE
Hexachlorobutadiene	87-68-3	10	Chronic MRL or RfC
Hexane	110-54-3	200	Chronic MRL or RfC
Isobutane	75-28-5	10,000	MDNRE
Methyl butyl ketone	591-78-6	10	Chronic MRL or RfC
Methyl ethyl ketone	78-93-3	2,000	Chronic MRL or RfC
Methyl isobutyl ketone	108-10-1	700	Chronic MRL or RfC
Methyl tert-butyl ether	1634-04-4	700	ATSDR Int. MRL
Methylene chloride	75-09-2	300	ATSDR Int. MRL
Napthalene	91-20-3	1	Chronic MRL or RfC
Nonane	111-84-2	100	MDNRE
Pentane	109-66-0	6,000	MDNRE
Propene	115-07-1	2,000	Chronic MRL or RfC
Styrene	100-42-5	200	Chronic MRL or RfC
Tetrachloroethene	127-18-4	40	Chronic MRL or RfC
Tetrahydrofuran	109-99-9	6.1	MDNRE
Toluene	108-88-3	1,000	Chronic MRL or RfC
trans-1,2-Dichloroethene	156-60-5	200	ATSDR Int. MRL
trans-1,3-Dichloropropene*	10061-01-5	0.5	MDNRE
Trichloroethene	79-01-6	100	ATSDR Int. MRL
Trichlorofluoromethane	75-69-4	130	EPA RSL
Vinyl acetate	108-05-4	10	ATSDR Int. MRL
Vinyl bromide	593-60-2	1	Chronic MRL or RfC
Vinyl chloride	75-01-4	30	ATSDR Int. MRL
Xylenes	1330-20-7	2,000	ATSDR Int. MRL

\* MDEQ provisional screening value for Dichloropropene based on a 1 in 100,000 cancer risk

ATSDR = Agency for Toxic Substances and Disease Registry

EPA = United States Environmental Protection Agency

MDNRE = Michigan Department of Natural Resources and Environment

Int. MRL = Intermediate Minimal Risk Level

MRL = Chronic Minimal Risk Level

RfC = Reference Concentration for Chronic Exposure

RSL = Regional Screening Level

**Table A-2. 2011 Enbridge Oil Spill Human Health Air Screening Levels August 31, 2011**

<b>Chemical Name</b>	<b>Chemical Abstract Service Number</b>	<b>Screening Level in parts per billion (ppb)</b>	<b>Source of Screening Level</b>
1,1,1-Trichloroethane	71-55-6	1,000	EPA RfC
1,1,2,2-Tetrachloroethane	79-34-5	0.006	EPA RSL
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	4,000	EPA RSL
1,1,2-Trichloroethane	79-00-5	0.04	EPA RfC
1,1-Dichloroethane	75-34-3	0.4	EPA RSL
1,1-Dichloroethene	75-35-4	50	EPA RfC
1,2,4-Trichlorobenzene	120-82-1	0.3	EPA RfC
1,2,4-Trimethylbenzene	95-63-6	1.5	EPA RfC
1,2-Dibromoethane	106-93-4	1	EPA RfC
1,2-Dichloro-1,1,2,2-Tetrafluoroethane	76-14-2	9,900	MDEQ
1,2-Dichlorobenzene	95-50-1	30	EPA RfC
1,2-Dichloroethane	107-06-2	600	ATSDR Chr. MRL
1,2-Dichloropropane	78-87-5	1	EPA RfC
1,3-Butadiene	106-99-0	1	EPA RfC
1,3,5-Trimethylbenzene	108-67-8	45	MDEQ
1,3-Dichlorobenzene	541-73-1	0.5	MDEQ
1,4-Dichlorobenzene	106-46-7	10	ATSDR Chr. MRL
1,4-Dioxane	123-91-1	1,000	ATSDR Chr. MRL
2,2,4-Trimethylpentane	540-84-1	750	MDEQ
2-Chloro-1,3-butadiene	126-99-8	6	EPA RfC
2-Propanol	67-63-0	3,000	EPA RfC
3-Chloropropene	107-05-1	32	EPA RfC
Acetaldehyde	75-07-0	5	EPA RfC
Acetone	67-64-1	13,000	ATSDR Chr. MRL
Acetonitrile	75-05-8	36	EPA RfC
Acrylonitrile	107-13-1	1	EPA RfC
Benzene	71-43-2	3	ATSDR Chr. MRL
Benzyl chloride	100-44-7	0.2	EPA RfC
Bromodichloromethane	75-27-4	0.01	EPA RSL
Bromoform	75-25-2	0.2	EPA RSL
Bromomethane	74-83-9	5	ATSDR Chr. MRL
Butane	106-97-8	10,000	MDEQ
Carbon disulfide	75-15-0	200	EPA RfC
Carbon tetrachloride	56-23-5	30	ATSDR Chr. MRL
Chlorobenzene	108-90-7	10	EPA RfC
Chloroethane	75-00-3	4,000	EPA RfC
Chloroform	67-66-3	20	ATSDR Chr. MRL
Chloromethane	74-87-3	50	ATSDR Chr. MRL
cis-1,2-Dichloroethene	156-59-2	9	MDEQ

cis-1,3-Dichloropropene*	10061-02-6	4	MDEQ
Cumene	98-82-8	80	EPA RfC
Cyclohexane	110-82-7	2,000	EPA RfC
Cyclohexane,methyl	108-87-2	4,000	MDEQ
Cyclopentane	287-92-3	6,000	MDEQ
Dibromochloromethane	124-48-1	0.01	EPA RSL
Dichlorodifluoromethane	75-71-8	20	EPA RfC
Ethyl acetate	141-78-6	890	MDEQ
Ethyl benzene	100-41-4	60	ATSDR Chr. MRL
Heptane	142-82-5	850	MDEQ
Hexachlorobutadiene	87-68-3	0.01	EPA RSL
Hexane	110-54-3	200	EPA RfC
Isobutane	75-28-5	10,000	MDEQ
Methyl butyl ketone	591-78-6	10	EPA RfC
Methyl ethyl ketone	78-93-3	2,000	EPA RfC
Methyl isobutyl ketone	108-10-1	700	EPA RfC
Methyl tert-butyl ether	1634-04-4	700	ATSDR Chr. MRL
Methylene chloride	75-09-2	300	ATSDR Chr. MRL
Napthalene	91-20-3	1	ATSDR Chr. MRL
Nonane	111-84-2	40	EPA RfC
Pentane	109-66-0	300	EPA RfC
Propene	115-07-1	2,000	EPA RfC
Styrene	100-42-5	200	ATSDR Chr. MRL
Tetrachloroethene	127-18-4	40	ATSDR Chr. MRL
Tetrahydrofuran	109-99-9	6	MDEQ
Toluene	108-88-3	80	ATSDR Chr. MRL
trans-1,2-Dichloroethene	156-60-5	15	EPA RfC
trans-1,3-Dichloropropene*	10061-01-5	0.5	MDEQ
Trichloroethene	79-01-6	2	EPA RfC
Trichlorofluoromethane	75-69-4	130	EPA RfC
Vinyl acetate	108-05-4	10	ATSDR Int. MRL
Vinyl bromide	593-60-2	1	EPA RfC
Vinyl chloride	75-01-4	30	ATSDR Int. MRL
Xylenes	1330-20-7	50	EPA RfC

\* MDEQ provisional screening value for Dichloropropene based on a 1 in 100,000 cancer risk

ATSDR = Agency for Toxic Substances and Disease Registry

EPA = United States Environmental Protection Agency

MDNRE = Michigan Department of Natural Resources and Environment

Int. MRL = Intermediate Minimal Risk Level

MRL = Chronic Minimal Risk Level

RfC = Reference Concentration for Chronic Exposure

RSL = Regional Screening Level

Appendix B: Air Monitoring and Sampling Data

**Table B-1. Total volatile organic compound (VOC) concentrations in parts per billion (ppb) measured in 2010 and 2011 with real-time monitors (Calhoun County, Michigan).**

Time Frame	Area	Number of Measurements	Range of Detections (ppb)
Initial Response (July 26-28, 2010)	Voluntary Evacuation Area	92	ND to 120,000
	Squaw Creek Subdivision	30	ND to 71,600
	Ceresco Area	8	ND to 6,000
	Baker Estates Neighborhood	2	ND
Evacuation Period (July 29 to August 17, 2010)	Voluntary Evacuation Area	2,164	ND to 568,000
	Squaw Creek Subdivision	623	ND to 2,600
	Ceresco Area	431	ND to 3,000
	Baker Estates Neighborhood	511	ND to 266,000
Post Evacuation Period (August 18 to December 31, 2010)	Voluntary Evacuation Area	4,278	ND to 9,000
	Squaw Creek Subdivision	1,058	ND to 1,200
	Ceresco Area	5,148	ND to 2,800
	Baker Estates Neighborhood	767	ND to 1,200
2011	Voluntary Evacuation Area	1,377	ND
	Squaw Creek Subdivision	508	ND
	Ceresco Area	785	ND
	Baker Estates Neighborhood	465	ND

ND = Not detected at the level of detection for the monitor.

**Table B-2. Total volatile organic compounds (VOCs) concentrations measured with unidentified instruments from July 26, 2010 to December 31, 2011 (Calhoun County, Michigan).**

<b>Time Frame</b>	<b>Area</b>	<b>Number of Measurements</b>	<b>Range of Detections (ppb)</b>
<b>Initial Response (July 26-28, 2010)</b>	Voluntary Evacuation Area	6	242 to 57,300
	Squaw Creek Subdivision	0	NA
	Ceresco Area	0	NA
	Baker Estates Neighborhood	0	NA
<b>Evacuation Period (July 29 to August 17, 2010)</b>	Voluntary Evacuation Area	80	ND to 4,300
	Squaw Creek Subdivision	35	ND to 1,011
	Ceresco Area	36	ND to 20
	Baker Estates Neighborhood	45	ND to 100
<b>Post Evacuation Period (August 18 to December 31, 2010)</b>	Voluntary Evacuation Area	3	ND
	Squaw Creek Subdivision	1	ND
	Ceresco Area	1	ND
	Baker Estates Neighborhood	0	NA
<b>2011</b>	Voluntary Evacuation Area	9	ND
	Squaw Creek Subdivision	2	ND
	Ceresco Area	0	NA
	Baker Estates Neighborhood	0	NA

NA = Not Available

ND = Not detected

**Table B-3. Hydrogen sulfide (H<sub>2</sub>S) concentrations in parts per billion (ppb) measured in 2010 and 2011 with real-time monitors (Calhoun County, Michigan).**

<b>Time Frame and Area</b>	<b>Screening Level (ppb)</b>	<b>Number of Measurements</b>	<b>Number of Measurements Above the Screening Level</b>	<b>Range of Detections (ppb)</b>
<b>Initial Response (July 26-28, 2010)</b>				
Voluntary Evacuation Area	70	4	1	ND
Squaw Creek Subdivision		14	0	ND
Ceresco Area		0	0	NA
Baker Estates Neighborhood		0	0	NA
<b>Evacuation Period (July 29 to August 17, 2010)</b>				
Voluntary Evacuation Area	70	1,666	7	ND to 112
Squaw Creek Subdivision		476	0	ND
Ceresco Area		376	0	ND
Baker Estates Neighborhood		464	0	ND
<b>Post Evacuation Period (August 18 to December 31, 2010)</b>				
Voluntary Evacuation Area	70	3,267	0	ND
Squaw Creek Subdivision		920	0	ND
Ceresco Area		5,070	0	ND
Baker Estates Neighborhood		715	0	ND
<b>2011</b>				
Voluntary Evacuation Area	70	1,317	0	ND
Squaw Creek Subdivision		465	0	ND
Ceresco Area		743	0	ND
Baker Estates Neighborhood		442	0	ND

Shaded values are above the chemical-specific 2010 human health screening levels.  
 ND = Not detected.

**Table B-4. Hydrogen sulfide (H<sub>2</sub>S) concentrations measured with unidentified instruments from July 26, 2010 to December 31, 2011, (Calhoun County, Michigan).**

<b>Time Frame and Area</b>	<b>Screening Value (ppb)</b>	<b>Number of Measurements*</b>	<b>Number of Measurements Above the Screening Value</b>	<b>Range of Detections (ppb)</b>
<b>Initial Response</b>				
Voluntary Evacuation Area	70	0	0	ND
Squaw Creek Subdivision		0	0	ND
Ceresco Area		0	0	ND
Baker Estates Neighborhood		0	0	ND
<b>Evacuation Period</b>				
Voluntary Evacuation Area	70	81	0	ND
Squaw Creek Subdivision		31	0	ND
Ceresco Area		36	0	ND
Baker Estates Neighborhood		45	0	ND
<b>Post Evacuation Period</b>				
Voluntary Evacuation Area	70	3	0	ND
Squaw Creek Subdivision		1	0	ND
Ceresco Area		1	0	ND
Baker Estates Neighborhood		0	0	ND
<b>2011</b>				
Voluntary Evacuation Area	70	9	0	ND
Squaw Creek Subdivision		2	0	ND
Ceresco Area		0	0	ND
Baker Estates Neighborhood		0	0	ND

ND = Not Detected

No H<sub>2</sub>S was found in five measurements taken with GASTEC colorimetric instruments.

**Table B-5. Benzene air concentrations in parts per billion (ppb) measured in 2010 with Draeger and GASTEC instruments (Calhoun County, Michigan).**

<b>Time Frame</b>	<b>Area</b>	<b>Number of Measurements</b>	<b>Range of Detections (ppb)</b>
<b>Initial Response</b>	Voluntary Evacuation Area	16	ND to 10,000
	Squaw Creek Subdivision	6	ND to 500
	Ceresco Area	3	ND to 250
	Baker Estates Neighborhood	2	ND
<b>Evacuation Period</b>	Voluntary Evacuation Area	57	ND to 500
	Squaw Creek Subdivision	10	ND
	Ceresco Area	26	ND to 100
	Baker Estates Neighborhood	15	ND
<b>Post Evacuation Period</b>	Voluntary Evacuation Area	28	ND
	Squaw Creek Subdivision	10	ND
	Ceresco Area	30	ND
	Baker Estates Neighborhood	21	ND
<b>2011</b>	Voluntary Evacuation Area	40	ND
	Squaw Creek Subdivision	5	ND
	Ceresco Area	7	ND
	Baker Estates Neighborhood	1	ND

Shaded values are above the chemical-specific 2010 human health screening levels.

ND = Not detected.

**Table B-6. Benzene concentrations in parts per billion (ppb) measured in 2010 with UltraRAE and Hazardous Air Pollutants on Site (HAPSITE) monitors (Calhoun County, Michigan).**

Time Frame and Area	Screening Level (ppb)	Number of UltraRAE Monitor Readings	Number of UltraRAE Readings Above the Screening Level	Range of Detections with UltraRAE Monitors (ppb)	Number of HAPSITE Monitor Readings	Number of HAPSITE Readings Above the Screening Level	Range of Detections with HAPSITE Monitors (ppb)
<b>Initial Response (July 26-28, 2010)</b>							
Voluntary Evacuation Area	60	13	8	ND to 6,250	4	0	1.2 to 27.3
Squaw Creek Subdivision		4	0	ND	0	NA	NA
Ceresco Area		4	2	ND to 500	0	NA	NA
Baker Estates Neighborhood		1	0	ND	0	NA	NA
<b>Evacuation Period (July 29 to August 17, 2010)</b>							
Voluntary Evacuation Area	60	1,619	62	ND to 2,200	24	0	ND to 17.6
Squaw Creek Subdivision		437	0	ND to 50	7	0	ND to 2.2
Ceresco Area		271	1	ND to 200	2	0	ND to 0.2
Baker Estates Neighborhood		264	1	ND to 250	3	0	ND
<b>Post Evacuation Period (August 18 to December 31, 2010)</b>							
Voluntary Evacuation Area	6	3,095	17	ND to 9,450	NA	NA	NA
Squaw Creek Subdivision		274	0	ND	NA	NA	NA
Ceresco Area		3,704	10	ND to 4,500	NA	NA	NA
Baker Estates Neighborhood		304	0	ND	NA	NA	NA
<b>2011</b>							
Voluntary Evacuation Area	3	1,010	0	ND	NA	NA	NA
Squaw Creek Subdivision		465	0	ND	NA	NA	NA
Ceresco Area		704	0	ND	NA	NA	NA
Baker Estates Neighborhood		414	0	ND	NA	NA	NA

Shaded values are above the chemical-specific 2010 human health screening levels.

NA = No data are available

ND = Not detected.

**Table B-7. Benzene concentrations in parts per billion (ppb) measured with unidentified instruments from July 26, 2010 to December 31, 2011 (Calhoun County, Michigan).**

<b>Time Frame and Area</b>	<b>Screening Value (ppb)</b>	<b>Number of Readings*</b>	<b>Number of Readings Above the Screening Value</b>	<b>Range of Detections (ppb)</b>
<b>Initial Response</b>				
Voluntary Evacuation Area	60	11	7	ND to 9,750
Squaw Creek Subdivision		1	0	50
Ceresco Area		0	0	NA
Baker Estates Neighborhood		0	0	NA
<b>Evacuation Period</b>				
Voluntary Evacuation Area	60	49	6	ND to 1,000
Squaw Creek Subdivision		30	0	ND
Ceresco Area		35	0	ND
Baker Estates Neighborhood		41	0	ND
<b>Post Evacuation Period</b>				
Voluntary Evacuation Area	6	4	0	ND
Squaw Creek Subdivision		1	0	ND
Ceresco Area		1	0	ND
Baker Estates Neighborhood		0	0	ND
<b>2011</b>				
Voluntary Evacuation Area	6	9	0	ND
Squaw Creek Subdivision		2	0	ND
Ceresco Area		0	0	ND
Baker Estates Neighborhood		0	0	ND

NA = No data are available  
 ND = not detected

**Table B-8. Benzene concentrations in parts per billion (ppb) in “grab” air samples (Calhoun County, Michigan).**

Time Frame and Area	Screening Level (ppb)	No. of Samples	Number of Detections	No. Detections Above the Screening Level	Range of Detections
<b>Initial Response (July 26-28, 2010)</b>					
Voluntary Evacuation Area	6	3	1	1	200
Squaw Creek Subdivision		NA	NA	NA	NA
Ceresco Area		NA	NA	NA	NA
Baker Estates Neighborhood		NA	NA	NA	NA
<b>Evacuation Period (July 29 to August 17, 2010)</b>					
Voluntary Evacuation Area	6	19	6	6	7.6 to 290
Squaw Creek Subdivision		4	0	0	ND
Ceresco Area		5	0	0	ND
Baker Estates Neighborhood		33	0	0	ND
<b>Post Evacuation Period (August 18 to December 31, 2010)</b>					
Voluntary Evacuation Area	6	680	9	1	1.1 to 190
Squaw Creek Subdivision		97	1	1	8.4
Ceresco Area		98	7	0	1.0 to 2.2
Baker Estates Neighborhood		249	5	2	1.0 to 20
<b>2011</b>					
Voluntary Evacuation Area	6	NA	NA	NA	NA
Squaw Creek Subdivision		NA	NA	NA	NA
Ceresco Area		3	0	0	ND
Baker Estates Neighborhood		2	0	0	ND
<b>2012</b>					
Voluntary Evacuation Area	3	NA	NA	NA	NA
Squaw Creek Subdivision		NA	NA	NA	NA
Ceresco Area		NA	NA	NA	NA
Baker Estates Neighborhood		NA	NA	NA	NA

Shaded values are above the chemical-specific 2010 human health screening levels.

ND = Not detected.

NA = Data are not available

**Table B-9. Benzene concentrations in parts per billion (ppb) in time-integrated air samples (Calhoun County, Michigan).**

<b>Time Frame and Area</b>	<b>2010 Screening Level (ppb)</b>	<b>No. of Samples</b>	<b>Number of Detections</b>	<b>No. Detections Above the Screening level</b>	<b>Range or Concentration of Detection(s)</b>
<b>Initial Response (July 26-28, 2010)</b>					
Voluntary Evacuation Area	60	NA	NA	NA	NA
Squaw Creek Subdivision		NA	NA	NA	NA
Ceresco Area		NA	NA	NA	NA
Baker Estates Neighborhood		NA	NA	NA	NA
<b>Evacuation Period (July 29 to August 17, 2010)</b>					
Voluntary Evacuation Area	6	124	14	3	0.26 to 122
Squaw Creek Subdivision		4	1	0	0.6
Ceresco Area		14	1	0	0.9
Baker Estates Neighborhood		39	1	0	0.3
<b>Post Evacuation Period (August 18 to December 31, 2010)</b>					
Voluntary Evacuation Area	6	394	0	0	ND
Squaw Creek Subdivision		34	0	0	ND
Ceresco Area		217	0	0	ND
Baker Estates Neighborhood		194	0	0	ND
<b>2011</b>					
Voluntary Evacuation Area	6	98	0	0	ND
Squaw Creek Subdivision		6	0	0	ND
Ceresco Area		483	3	0	1 to 3
Baker Estates Neighborhood		214	1	0	4
<b>2012</b>					
Voluntary Evacuation Area	3	0	0	0	NA
Squaw Creek Subdivision		0	0	0	NA
Ceresco Area		48	0	0	ND
Baker Estates Neighborhood		0	0	0	NA

Shaded values are above the 2010 human health screening levels. ND = Not detected. NA = Data are not available NA = Data are not available

**Table B-10. Volatile organic compound (VOC) concentrations in parts per billion (ppb) in “grab” air samples collected from July 26 through July 28, 2010, in the Voluntary Evacuation Area (Calhoun County, Michigan).**

Chemical	2010 Screening level (ppb)	Voluntary Evacuation Area	
		Number of Detections/Total Number of Samples	Range of Detections (ppb)
acetone	13,000	2/3	17 to 20
cyclohexane	2,000	2/3	6.2 to 480
cyclohexane,methyl	4,000	1/1	12
heptane	850	2/3	8.4 to 540
hexane	200	3/3	6.3 to 760
pentane	6,000	2/2	17 to 24
toluene	1,000	1/3	300
xylenes	2,000	1/3	110

Shaded values are above the chemical-specific 2010 Human Health Screening Levels.

**Table B-11. Volatile organic compound (VOC) concentrations in parts per billion (ppb) in “grab” air samples in the Voluntary Evacuation Period (July 29 through August 17, 2010), Calhoun County, Michigan.**

Chemical	Human Health Screening Level (2010)	Voluntary Evacuation Area		Squaw Creek Subdivision		Ceresco Area		Baker Estates Neighborhood	
		Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)
1,1,2,2-tetrachloroethane	0.006	1/19	6.9	0/4	ND	0/5	ND	0/33	ND
1,2,4-trimethylbenzene	1.5	3/19	7.1 to 120	0/4	ND	0/5	ND	0/33	ND
1,3,5-trimethylbenzene	45	2/19	11 to 55	0/4	ND	0/5	ND	0/33	ND
2,2,4-trimethylpentane	750	2/19	11 to 16	0/4	ND	0/5	ND	0/33	ND
2-propanol	3,000	8/19	6.6 to 17	1/4	16	1/5	5.7	15/33	5.1 to 44
acetone	13,000	9/19	5.1 to 76	2/4	11 to 17	4/5	7.6 to 17	23/33	5.1 to 22
butane	10,000	2/2	15 to 30	NA	NA	NA	NA	NA	NA
carbon disulfide	200	0/19	ND	0/4	ND	0/5	ND	1/33	33
chlorobenzene	200	1/19	10	0/4	ND	0/5	ND	0/33	ND
cyclohexane	2,000	4/19	16 to 730	0/4	ND	0/5	ND	1/33	7.4
cyclohexane,methyl	4,000	4/4	19 to 980	NA	NA	NA	NA	NA	NA
cyclopentane	6,000	2/2	12 to 15	NA	NA	NA	NA	NA	NA
ethyl benzene	700	3/19	5 to 100	0/4	ND	0/5	ND	0/33	ND
heptane	850	5/19	6.1 to 840	0/4	ND	0/5	ND	1/33	21
hexane	200	6/19	22 to 1300	1/4	14	0/5	ND	1/33	29
isobutane	10,000	1/1	7.5	NA	NA	NA	NA	NA	NA
nonane	100	4/4	9.6 to 170	NA	NA	NA	NA	NA	NA
pentane	6,000	5/5	27 to 86	NA	NA	NA	NA	2/2	5.2 to 150
toluene	1,000	6/19	16 to 580	1/4	21	0/5	ND	2/33	57 to 76
trichloroethene	100	1/19	8.4	0/4	ND	0/5	ND	0/33	ND
xylenes	2,000	5/18	12 to 420	0/4	ND	0/5	ND	0/22	ND

Shaded values are above the chemical-specific 2010 human health screening levels.

NA = Data are not available

ND = Not detected

**Table B-12. Volatile organic compound (VOC) concentrations in parts per billion (ppb) in time-integrated air samples in the Voluntary Evacuation Period (July 29 through August 17, 2010), Calhoun County, Michigan.**

Chemical	Human Health Screening Level (2010)	Voluntary Evacuation Area		Squaw Creek Subdivision		Ceresco Area		Baker Estates Neighborhood	
		Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)
1,2,4-trimethylbenzene	1.5	5/124	0.41 to 52.9	1/4	1	1/14	0.4	1/39	0.5
1,3,5-trimethylbenzene	45	3/124	0.24 to 28.4	0/4	ND	0/14	ND	0/39	ND
2,2,4-trimethylpentane	750	0/94	ND	1/4	0.5	0/13	ND	0/39	ND
2-propanol	3,000	79/118	5.1 to 110	3/4	1.1 to 9.9	9/11	6 to 81	32/36	6.1 to 140
acetaldehyde	NA	4/4	14 to 72	NA	NA	0/1	130	2/2	5 to 5.2
acetone	13,000	97/120	0.98 to 55	2/4	2.3 to 7.9	12/12	1.5 to 52	35/38	0.8 to 31
acetonitrile	38	2/8	57 to 64	1/1	12	2/3	1.4 to 1.7	3/3	2.6 to 7.7
butane	10,000	12/12	1.3 to 120	1/1	1.4	1/1	2.2	1/1	57
chloromethane	200	2/124	0.34 to 0.48	0/4	ND	0/14	ND	0/39	ND
cyclohexane	2,000	23/123	0.49 to 120	0/3	ND	1/12	1.3	0/36	ND
cyclohexane,methyl	4,000	22/22	0.77 to 290	0/4	ND	1/1	2.5	NA	NA
cyclopentane	6,000	3/3	5.8 to 14	NA	NA	NA	NA	NA	NA
dichlorodifluoromethane	42	7/124	0.26 to 0.56	1/4	0.36	3/14	0.3 to 0.4	2/39	0.28 to 0.32
ethyl acetate	890	2/118	5.9 to 31	0/3	ND	0/11	ND	0/36	ND
ethyl benzene	700	5/124	0.3 to 76	1/4	0.35	1/14	0.3	0/39	ND
heptane	850	26/123	0.39 to 170	0/3	ND	1/12	2	0/36	ND
hexane	200	46/124	0.62 to 482	1/4	20	2/14	1.5 to 5.4	0/39	ND
isobutane	10,000	8/8	1.8 to 69	NA	NA	NA	NA	NA	NA
methyl butyl ketone	10	1/118	3.2	0/3	ND	0/11	ND	0/36	ND
methyl ethyl ketone	2,000	10/121	0.37 to 220	0/4	ND	2/14	3.5 to 120	0/39	ND
methyl isobutyl ketone	700	3/124	0.39 to 30	0/4	ND	0/14	ND	0/39	ND

methyl tert-butyl ether	700	0/124	ND	1/4	0.56	0/14	ND	0/39	ND
methylene chloride	300	3/124	2.3 to 9	1/4	18	2/14	0.8 to 1.7	3/39	1.5 to 10.7
nonane	100	10/10	1.2 to 200	NA	NA	1/1	1	NA	NA
pentane	6,000	32/32	1.7 to 460	1/1	3.9	1/1	7.9	6/6	0.8 to 78
propene	2,000	5/118	0.37 to 7.2	0/3	ND	0/11	ND	0/36	ND
tetrachloroethene	40	1/124	1.9	0/4	ND	0/14	ND	0/39	ND
tetrahydrofuran	6.1	1/118	5	0/3	ND	0/11	ND	0/36	ND
toluene	1,000	26/124	0.48 to 345.2	1/4	2.6	1/14	1.9	4/39	0.4 to 60
trichlorofluoromethane	130	2/124	0.27	0/4	ND	0/14	ND	0/39	ND
xylenes	2,000	5/74	3.8 to 41	NA	NA	0/5	ND	0/17	ND

Shaded values are above the chemical-specific 2010 human health screening levels.

NA = Data are not available

ND = Not detected

**Table B-13. Volatile organic compound (VOC) concentrations in parts per billion (ppb) in “grab” air samples collected in the Post Evacuation period (Aug 18 to Dec 31, 2010), Calhoun County, Michigan.**

Chemical	Human Health Screening Level (2010)	Voluntary Evacuation Area		Squaw Creek Subdivision		Ceresco Area		Baker Estates Neighborhood	
		Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)
1,1-dichloroethane	100	0/1	ND	NA	NA	0/2	ND	2/161	14 to 34
1,2-dichloroethane	1,000	0/1	ND	NA	NA	0/2	ND	2/161	6.4 to 17
2,2,4-trimethylpentane	750	0/1	ND	NA	NA	0/2	ND	1/161	11
2-propanol	3,000	0/1	ND	NA	NA	0/2	ND	32/161	5.1 to 98
3-chloropropene	0.3	0/1	ND	NA	NA	0/2	ND	1/161	5
acetone	13,000	0/1	ND	NA	NA	0/2	ND	88/161	5.2 to 110
bromoform	0.21	0/1	ND	NA	NA	0/2	ND	1/161	6.3
carbon disulfide	200	0/1	ND	NA	NA	0/2	ND	1/161	16
chloroform	50	0/1	ND	NA	NA	0/2	ND	1/161	7
cyclohexane	2,000	0/1	ND	NA	NA	0/2	ND	2/161	8.2 to 11
cyclohexane,methyl	4,000	1/1	1,600	NA	NA	2/2	10 to 32	NA	NA
ethyl acetate	890	0/1	ND	NA	NA	0/2	ND	1/161	5
heptane	850	0/1	ND	NA	NA	0/2	ND	1/161	19
hexane	200	0/1	ND	NA	NA	0/2	ND	2/161	17 to 59
methylene chloride	300	0/1	ND	NA	NA	0/2	ND	1/161	5.3
nonane	100	0/1	ND	NA	NA	2/2	6.2 to 16	NA	NA
pentane	6,000	1/1	2,100	NA	NA	NA	NA	2/2	7.2 to 8.3
styrene	200	0/1	ND	NA	NA	0/2	ND	3/161	7.5 to 19
toluene	1,000	1/1	580	NA	NA	0/2	ND	16/161	5.1 to 48
trichloroethene	100	0/1	ND	NA	NA	0/2	ND	0/161	ND to 5.3

Shaded values are above the chemical-specific 2010 human health screening levels. NA = Data are not available. ND = Not detected

**Table B-14. Volatile organic compound (VOC) concentrations in parts per billion (ppb) in time-integrated air samples in the Post Evacuation period (Aug 18 to Dec 31, 2010), Calhoun County, Michigan.**

Chemical	Human Health Screening Level (2010)	Voluntary Evacuation Area		Squaw Creek Subdivision		Ceresco Area		Baker Estates Neighborhood	
		Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)
1,1,1-trichloroethane	700	0/394	ND	0/34	ND	1/217	9.2	0/194	ND
2-propanol	3,000	216/394	5 to 180	22/34	5.3 to 80	55/317	5 to 68	96/194	5 to 2700
acetaldehyde	NA	4/4	6.9 to 56	NA	NA	1/1	54	1/1	16
acetone	13,000	243/394	5 to 240	24/34	5 to 40	73/217	5 to 110	100/194	5.1 to 83
acetonitrile	38	3/3	10 to 16	NA	NA	1/1	16	NA	NA
bromomethane	50	1/394	5.9	0/34	ND	0/217	ND	0/194	ND
butane	10,000	5/5	5.6 to 21	NA	NA	NA	NA	NA	NA
ethyl acetate	890	0/394	ND	0/34	ND	0/217	ND	2/194	11 to 77
methyl ethyl ketone	2,000	1/394	34	0/34	ND	0/217	ND	3/194	5.2 to 9.6
methylene chloride	300	2/394	7.2 to 11	0/34	ND	1/217	52	0/194	ND
pentane	6,000	1/1	8.8	1/1	6.5	1/1	7.9	1/1	8.4
tetrahydrofuran	6.1	3/394	8.3 to 170	0/34	ND	0/217	ND	0/194	ND
toluene	1,000	7/394	5 to 13	1/34	7.7	4/217	5.6 to 14	8/194	5.9 to 110
trichloroethene	100	0/394	ND	0/34	ND	1/217	7.1	0/194	ND

Shaded values are above the chemical-specific 2010 human health screening levels.

NA = Data are not available

ND = Not detected

**Table B-15. Volatile organic compound (VOC) concentrations in parts per billion (ppb) in “grab” air samples collected in 2011, Calhoun County, Michigan.**

Chemical	2011 Human Health Screening Level	Ceresco Area		Baker Estates Neighborhood	
		Number of detections/Total number of samples	Range of detections (ppb)	Number of detections/Total number of samples	Range of detections (ppb)
2-propanol	3,000	1/3	9.1	2	ND
acetone	13,000	2/3	13 to 16	2	ND

ND = Not detected

**Table B-16. Volatile organic compound (VOC) concentrations in parts per billion (ppb) in time-integrated air samples in 2011, Calhoun County, Michigan.**

chemical	2011 Human Health Screening Level	Voluntary Evacuation Area		Squaw Creek Subdivision		Ceresco Area		Baker Estates Neighborhood	
		Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)	Number of detections/ Total number of samples	Range of detections (ppb)
1,2,4-trimethylbenzene	2	0/98	ND	0/6	ND	3/483	2 to 3	4/214	1 to 2
1,2-dichloroethane	600	0/98	ND	0/6	ND	1/483	1	1/214	3
1,3,5-trimethylbenzene	45	0/98	ND	0/6	ND	1/483	1	0/214	ND
2,2,4-trimethylpentane	750	0/98	ND	0/6	ND	1/483	1	0/214	ND
2-propanol	3,000	84/98	5.1 to 71	6/6	7.1 to 26	371/483	1 to 120	175/214	1 to 530
acetaldehyde	5	2/2	7.4 to 12	1/1	6.3	15/48	1 to 15	2/2	1.9 to 9.2
acetone	13,000	90/98	5 to 120	6/6	7.4 to 15	412/483	1 to 57	176/214	1 to 110
acetonitrile	36	NA	NA	NA	NA	12/12	1.2 to 30	8/8	1.5 to 13
bromoform	0.2	0/98	ND	0/6	ND	1/483	1	0/214	ND
bromomethane	5	1/98	15	0/6	ND	1/483	1	0/214	ND
butane	10,000	NA	NA	NA	NA	2/2	2.7 to 7.9	2/2	1.3 to 9.8
carbon disulfide	200	0/98	ND	0/6	ND	27/483	2 to 120	11/214	2 to 11
cyclohexane	2,000	0/98	ND	0/6	ND	6/483	1 to 15	2/214	1
cyclohexane,methyl	4,000	NA	NA	NA	NA	1/1	4.6	NA	NA
cyclopentane	6,000	NA	NA	NA	NA	1/1	4.6	NA	NA
ethyl acetate	890	0/98	ND	0/6	ND	20/483	1 to 33	9/214	1 to 29
ethyl benzene	60	0/98	ND	0/6	ND	2/483	2 to 6	1/214	1
heptane	850	0/98	ND	0/6	ND	4/483	1 to 9	1/214	1
hexane	200	0/98	ND	0/6	ND	6/483	1 to 3	3/214	1
isobutane	10,000	3/3	6.6 to 8.4	NA	NA	15/15	1.1 to 36	8/8	1.3 to 28
methyl ethyl ketone	2,000	0/98	ND	0/6	ND	14/483	1 to 78	6/214	1 to 20
methylene chloride	300	0/98	ND	0/6	ND	483/483	1 to 24	5/214	1 to 7

nonane	40	NA	NA	NA	NA	1/1	5	NA	NA
pentane	300	3/3	6.7 to 7.6	NA	NA	16/16	3.4 to 180	9/9	1.6 to 91
propene	2,000	0/98	ND	0/6	ND	8/483	1 to 2	5/214	1
styrene	200	0/98	ND	0/6	ND	1/483	4	0/214	ND
tetrachloroethene	40	0/98	ND	0/6	ND	0/483	ND	1/214	2
tetrahydrofuran	6	0/98	ND	0/6	ND	2/483	2 to 3	0/214	ND
toluene	80	0/98	ND	0/6	ND	94/483	1 to 140	72/214	1 to 85
vinyl acetate	10	0/98	ND	0/6	ND	0/483	ND	1/214	1

Shaded values are above the chemical-specific 2010 human health screening levels.

NA = Data are not available

ND = Not detected

**Table B-17. Volatile organic compound (VOC) concentrations in parts per billion (ppb) in time-integrated air samples in 2012, Calhoun County, Michigan.**

Chemical	2011 Human Health Screening Level	Ceresco Area	
		Number of detections/Total number of samples	Range of detections (ppb)
2-propanol	3,000	11/48	1 to 14
acetaldehyde	5	1/48	3
acetone	13,000	42/48	1 to 6
butane	10,000	1/1	3.7