Sorption and Desorption of the Industrial Chemical MCHM into Polymer Pipes, Linings and Activated Carbon

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Abstract

Polyethylene pipes and epoxy or polyurethane linings are increasingly used in drinking water infrastructure. As a recent introduction to the water industry, there are still many unknowns about how polymers will behave in the distribution system specifically relating to sorption and desorption of chemical contaminants. This study is in response to a spill of 4-methylcyclohexane methanol (MCHM) that occurred in January 2014 contaminating the drinking water of nine counties in West Virginia. This study investigated sorption and desorption of the odorous chemical MCHM into polymer drinking water infrastructure and granular activated carbon (GAC). Experiments for sorption of non-polar toluene and polar 1-butanol were conducted as a comparison for MCHM sorption. Additionally, a brief odor analysis was done on the ability of activated carbon to remove odor from contaminated water and on leaching of MCHM from pipe material into clean water. The results show that MCHM diffusion and solubility in polyethylene pipe materials is low. Solubility in polyethylene ranged from 0.003-0.008 g/cm^3 and was more similar to the polar contaminant n-butanol than the non-polar contaminant toluene. Desorption experiments indicated that MCHM sorbed to polyethylene diffused back into water at levels that produced odor. MCHM diffused very quickly into epoxy; its solubility was similar to polyethylene pipe. MCHM caused the polyurethane lining to swell and deform. Granular activated carbon effectively sorbed MCHM to below its odor threshold. The sorption properties of MCHM indicate the potential for contamination of infrastructure and the desorption indicates subsequent recontamination of drinking water.

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Lastly, I would like to thank my parents, my sisters and Daniel for all of their constant encouragement throughout my entire education. I would not have been able to accomplish all that I have done without their love and support.

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Preface

This work is presented in the Virginia Tech manuscript format. The first section contains an introduction and literature review covering the use of polymers in water infrastructure. The main chapter has been prepared for ASCE Journal of Environmental Engineering on the topic of a chemical spill of 4-methylcyclohexane methanol in January, 2014. This article covers the sorption and desorption of MCHM into polymer pipe materials as well as an isotherm for GAC and a brief odor analysis. There are two manuscripts included in this document. The first represents the majority of research done for my thesis. I performed all of the experiments and aided with the statistical analysis. Dr. Dietrich and Dr. Gallagher are co-authors because they helped give direction throughout the research and helped to edit the paper. Dr. Gallagher also helped with the R-coding for much of the statistical analysis. The second manuscript included is a combination of many researchers' work from our lab and those from the chemistry department at University of Memphis. My contribution to that paper includes the section for the activated carbon isotherm. The other contributors and a brief description of their involvement is as follows.

Andrea Dietrich of the Virginia Tech civil and environmental engineering department oversaw the research and helped with much of the editing for this paper. Ashly Thomas and Yang Zhao of the Virginia Tech civil and environmental engineering department did work with the partitioning and aqueous solubility of MCHM respectively. Daniel Gallagher of the Virginia Tech civil and environmental engineering department helped with much of the statistical analysis. Elizabeth Smiley of the Virginia Tech chemistry department helped with much of the instrumentation used during research. Narasimhamurthy Shanaiah of the Virginia Tech chemistry department performed and interpreted NMR. Katherine Charbonnet, Nathan DeYonker, and William Alexander from the University of Memphis chemistry department performed theoretical chemical calculations for dipole moment, free energy, enthalpy and interpreted data for the cis and trans isomers of MCHM.

Introduction

Polymer pipes have been used to replace copper pipes in drinking water distribution systems since the 1970's (AWWSC 2002). These polymer pipes have many benefits over the traditional metal pipes; they do not corrode like copper and they are made of affordable material that can last up to 100 years (Davis 2006). Lining pipes with epoxy or polyurethane is done to fix leaks or cracks in existing pipe systems. It is well known that the infrastructure for water systems is quickly becoming outdated and is in need of much attention, however, most of the infrastructure in need of repair is buried underground. Using pipe linings will allow for many issues to be fixed without replacing an entire pipe system. In some cases these linings are used as more that a spot repair and can coat the entire interior of a pipe, creating an essentially new pipe without the expense of digging up the full existing pipe system (Opflow 2014).

With increasing popularity in the use of polymer pipes, it has been important to understand how polymers react with potential contaminants such as organic chemicals. Studies have been done to see how these polymer pipes may leach chemicals into the water running through them (Whelton 2013). The diffusion and solubility of different organic chemicals into polymer pipes has also been of particular interest. (Tang, Gallagher, Dietrich 2013 and Whelton 2010) The diffusivity and solubility can be of importance when assessing fate and transport of a chemical in a water distribution system. Previous research has determined that polarity, molar volume and pipe density all play important roles in the diffusion of chemicals into polymers and can be used to help predict how contaminants will behave when introduced to polymer pipe material. (Tang, Gallagher, Dietrich 2013) Supporting the common idea that 'like dissolves like' it was found that less polar organics adsorb more readily into non-polar polymer material than polar organic chemicals (Whelton 2010).

Diffusion

One common model used to determine the diffusivity and solubility of an organic contaminant into a solid material was developed by Crank and Park (Crank 1968). This model uses the mass gain data of a material to determine the amount of chemical diffusing into that material; for a contaminant study this would be a polymer pipe. The mass gain at a specific time (Mt) is related to the total mass gained after equilibrium. The thickness of a sample is used to determine the distance travelled by the contaminant depending on whether the sample is considered to have one side or two side diffusion. Traditionally two sided diffusion best describes the sorption process because the sample is exposed to chemical on all sides and the most diffusion occurs from the two sides with the largest surface area (Aminabhavi 1999, Whelton 2010). The Crank equation for diffusion is below for two sided diffusion.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{4\ell^2} \right)$$

Equation 1

Where

M_∞ = Mass of contaminant in polymer at equilibrium (M)

M_t = Mass of contaminant in polymer at time t (M)

t = Elapsed time (T)

ℓ = Half sample thickness (L)

D = Diffusion coefficient (M^2/T)

Polymer Linings

An even newer advancement in the water infrastructure field is the use of polymer linings, such as epoxy and polyurethane, to fix leaks or cracks in existing pipe systems. It is well known that the infrastructure for water systems is quickly becoming outdated and is in need of much attention, however, most of the infrastructure in need of repair is buried underground. Using pipe linings will allow for many issues to be fixed without replacing an entire pipe system. In some cases these linings are used as more that a spot repair and can coat the entire interior of a pipe, creating an essentially new pipe without the expense of digging up the full existing pipe system (Opflow 2014). Another advantage to using these materials is the quick cure time. Polyurethane cures in a matter of hours while epoxy will cures in about 10 days (Deb et al. 2010). This assists in the ability to keep water running to consumers without the need to divert flow for a prolonged period of time (Opflow 2014). Epoxy linings have begun to be used widely in the United States while polyurethane is the more popular choice in the UK and Europe (Opflow 2014).

Some research has been done to look at how linings may affect water quality of the water running through the nearby pipes. Many of the findings suggest that the most contamination from lining material occurs in the time shortly after installation. After the material finishes curing, less contamination will occur. Other parameters may contribute to more leaching of chemicals from the lining materials including the temperature of the water and the length of time the material is left to cure (Alben 1989 and Bae 2002). One of the major changes seen in water quality is the increase in pH after exposure to a new lining material (Whelton 2013). Changes due to water quality because of leaching chemicals vary with the material of the lining. One study showed that cement mortar linings leached these organic chemicals for less time than their polyurea counterparts (Whelton 2013)

There are many advantages to using polymer linings in distribution pipes, but not much research has looked into how these linings may react with organics that could be introduced to the water distribution system. It is the hope that no such contamination event would occur, but is important to know what the fate and transport of an organic contaminant would be if it were to enter into a drinking water pipe system.

MCHM Spill

Such a contamination event occurred January 9, 2014. Early in the morning Approximately 10,000 gallons of crude methylcyclohexane methanol (MCHM) spilled into the Elk River in West Virginia (Smith 2014). Approximately 2.4 km downstream, the uptake for West Virginia American Water (a drinking water treatment plant servicing a large portion of West Virginia) began pumping the contaminated water into the treatment plant (Gallagher 2015, Manuel 2014). MCHM was not completely removed by the treatment plant processes and contaminated water was sent throughout the distribution system to consumers. Early in the morning, shortly after the spill occurred, nearby residents began identifying a strange odor that was described as licorice (Smith 2014).

Throughout the day, more complaints came in and people were nervous to use their water. Approximately 300,000 people in 9 counties were affected by the chemical spill and noticed MCHM odor present in their drinking water (Lannom 2014). The odor persisted for many weeks resulting in a large amount of media attention. A state of emergency was declared on January 9 with Governor Earl Ray Tomblin saying 'Do not use' the water (Smith 2014). This order lasted for 51 days and people continued to not use the water for many months due to lack of trust (Lannom 2014). The treatment plant noticed leaching of MCHM from inside the plant many days later, MCHM levels were higher in the effluent than influent (Ward 2014). After this the filters were replaced on April 1, 2014 and MCHM was no longer detected in the effluent of the wastewater treatment plant (Marra 2014). Consumers still complained about a licorice odor for many months after there was no more detection of MCHM from the treatment plant (Gallagher et. al. 2015, Lannom 2014, Whelton et. al. 2015).

Pure MCHM is a polar organic molecule with the molecular formula C8H16O. Crude MCHM, a chemical used to process coal fines, was developed by Eastman Chemical Company and was spilled from a tank farm owned by Freedom Industries in January of 2014 (Smith 2014). There was little known information about this organic material available when the spill occurred. The MSDS sheet was lacking numbers for odor threshold, evaporation rate, flammability, vapor pressure, water solubility and the octanol water partition coefficient among many other properties that would be useful in determining fate and transport of MCHM in the environment and water infrastructure (MCHM MSDS 2011). The scientific community did not know what environmental concerns were caused by the spill but no toxic events such as fish kills occurred following the January spill. However, there were many taste and odor complaints to the water utility in the local community. Pure MCHM has two major isomers that have different odors and different solubilities in water (Kat and solubility paper). The *cis* and *trans* isomer have a different orientation of the methyl and hydroxide groups. The crude compound is made up of 86.5% pure MCHM and a mixture of other cyclobenzene compounds (Dietrich et. al. 2015). The trans and cis isomer exist at an approximately 2:1 ratio respectively in crude MCHM.(Dietrich et. al. 2015) It was found the MCHM had an odor detection limit for MCHM in the air of 0.060 and 120 ppb-v for the trans and cis isomers respectively (Gallagher et. al. 2015).

Activated Carbon

Activated carbon is used as filter media in many drinking water treatment plants. The purpose of activated carbon is to chemically adsorb unwanted materials in the water often to help with taste and odor issues. This process enhances conventional filtration by removing smaller particles. Activated carbon is created from carbonaceous materials that are processed and refined to have a large amount of pore space per volume and a large surface area. This allows for a higher amount of chemical sorption. Different chemical forces draw contaminants out of water and into the pores of the activated carbon (Cabot 2015). To determine the amount of material that can be sorbed per mass of carbon, an isotherm can be used. The Freuindlich isotherm model is accurate at representing the loading in activated carbon (Schwarzenbach 2003). This isotherm model assumes that loading is almost infinite but slows as more mass of material is sorbed.

Research Objective

This study aimed to address the fate and transport of crude MCHM in the water distribution system and the possible concern of MCHM uptake into distribution system polymer pipes. The diffusion and solubility of MCHM into a variety of polymer pipe material was determined used to assess the potential interaction of MCHM with distribution system pipes during the chemical spill. Additionally this study addresses the behavior of desorption (leaching) of crude MCHM from pipes into water, sorption of crude MCHM into activated carbon and the ability of people to detect intensity differences in the odor of MCHM.

Industrial Spills and Water Distribution: Crude MCHM Sorption and Desorption in Polymer Pipes and Linings

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Manuscript in review for ASCE Journal of Environmental Engineering

Abstract

Polyethylene pipes and epoxy or polyurethane linings are increasingly used in drinking water infrastructure. This study investigated sorption and desorption of the odorous industrial chemical crude [(4-methylcyclohexyl)methanol] (MCHM) into polymer drinking water infrastructure. The research was in response to the MCHM spill that contaminated drinking water in Charleston and nine counties in West Virginia. Additionally, the ability of granular activated carbon to remove MCHM to below its odor-threshold level was evaluated. The results show that MCHM diffusion and solubility in polyethylene pipe materials is low. Solubility in polyethylene ranged from 0.003-0.008 g/cm^3 and was more similar to the polar contaminant n-butanol than the non-polar contaminant toluene. Desorption experiments indicated that MCHM sorbed to polyethylene diffused back into water at levels that produced odor. MCHM diffused very quickly into epoxy; its solubility was similar to polyethylene pipe. MCHM caused the polyurethane lining to swell and deform. Granular activated carbon effectively sorbed MCHM to below its odor threshold. The sorption properties of MCHM indicate the potential for contamination of infrastructure and the desorption indicates subsequent recontamination of drinking water.

Key Words: MCHM, polyethylene, lining, pipes, GAC, sorption, desorption, odor

Introduction

Polymer Infrastructure Review

Polymer pipes and linings have been replacing metal pipes in drinking water distribution systems since the 1970's (AWWSC 2002). High density polyethylene pipes began to be used in the 1970s (AWWSC 2002), while cross-linked polyethylene (PEX) pipes were only approved in 2007 for buried water service (AWWA 2007) and are also used for premise plumbing. Polymer materials have many benefits over metals for water distribution: they do not corrode, can be more affordable material, and may last up to 100 years (Davis et al. 2006). They also have a detrimental side in that polymers are more likely to sorb organic contaminants that enter the distribution system and later release them (Clark and Deininger 2000; USEPA 2002).

Lining existing distribution system pipes and tanks with epoxy or polyurethane is an established method to extend the life of buried and above ground water infrastructure such as water tanks (Deb et al. 2010). Epoxy was first used in the USA in 1993 (Conroy et al. 1993), followed by polyurethane a few years later. A major difference between these two materials is cure time: polyurethane cures in a matter of hours while epoxy will take over a day to cure. (Deb et al. 2010). These linings are becoming widely used, and there are many rules and regulations that have been set up to instruct on how to properly use these materials (AWWA 2000, AWWA 2007). These have been approved for both interior and exterior use for drinking water infrastructure including pipes and water towers. Additionally, research has been conducted to determine how the installation of these linings will affect the water quality. It has been discovered that small amounts of organics leach into the water shortly after curing with a decline in water quality changes over time (Deb et al. 2010, Alben 1989).

With the increasing use of polymer materials in distribution systems, and on-going development and implementation of new polymer materials, it is critical to understand how polymers interact with potential organic contaminants (Ong et al. 2008). Previous research determined that water solubility (e.g., polarity) and molar volume of the chemical contaminant were negatively correlated to sorption into a polymer. Increased density of the polymer was also negatively correlated with contaminant sorption as measured by diffusion and solubility. Supporting the common idea that "like dissolves like" it was found that less water soluble and less polar organic contaminants, such as toluene, sorb more readily into non-polar polymer material than polar organic contaminants such as 1-butanol (Dietrich et al. 2010; Whelton et al. 2010; Tang et al. 2013).

MCHM Contamination

An increasing concern for drinking water providers and consumers is chemical contamination of the water supply and drinking water, which then contaminates the distribution system and premise plumbing (Clark and Deininger 2000; Gullic et al. 2003; Bahadur and Samuels 2014). While the Toxic Substances Control Act inventory lists about 84,000 registered commercial chemicals (Schnoor 2014), very few have been evaluated for their permeation into vulnerable distribution system polymers. Crude (4-methylcyclohexyl)methanol (MCHM), an industrial chemical used in the coal industry, was one of those unevaluated contaminants. This chemical was responsible for the contamination of the entire drinking water distribution system for over 300,000 residents of Charleston, West Virginia and 9 surrounding counties.

Early in the morning of January 9, 2014, approximately 37,800 L (10,000 gallons) of the industrial chemical crude (4-methylcyclohexyl)methanol (MCHM) leaked from the Freedom Industries tank farm into the Elk River in West Virginia (Foreman et al. 2014; Gallagher et al. 2015; Whelton et al. 2015; Dietrich et al. 2015). Approximately 2.4 kilometers (1.5 miles) downstream, the intake for West Virginia American Water (a drinking water treatment plant servicing a large portion of West Virginia) began pumping the contaminated water into their treatment plant (Gallagher 2015, Manuel 2014). By 7:30 AM on the morning of January 9, residents living nearby the Freedom Industries tank farm were calling state officials to complain about a strange licorice odor (Lammon 2014; Smith 2014). Throughout the day, residents across the region complained of licorice-smelling drinking water and were nervous about using their water (Manuel 2014). A state of emergency was declared at 6 PM on January 9 with Governor Earl Ray Tomblin saying "Do not use" the water (Smith, 2014). This order lasted for 4-10 days for different sections of the distribution system. However, residents continued to avoid using the water for many months after the "Do not use" order was lifted; they also continued to episodically smell licorice odors for many months (Lannom 2014; Whelton et al. 2015, Gallagher et. al. 2015). The estimate costs of the spill and financial damage from loss of business/work was $61 million for just the first month after the spill (Manuel 2014).

Concentrations of MCHM in the drinking water were reported to be 0.75 - 2.4 mg/L the day after the spill (WVDHSEM 2014); those in the distribution system were reduced to mostly <0.1 mg/L for six weeks following the spill (Foreman et al. 2014). Monitoring of the influent and effluent to the water treatment plant continued for months after the spill. West Virginia American Water monitoring data indicated that MCHM levels were higher in the effluent from the plant than in the influent in March, two months after the spill (Boucher 2014; Ward 2014). This suggested that sorbed MCHM was desorbing within the water treatment plant, possibly from the granular activated carbon. The carbon in filters beds was replaced beginning in April 1, 2014. Afterwards, MCHM was no longer detected in the effluent of the drinking water treatment plant (Marra 2014).

There was little known information about MCHM's physicochemical properties or toxicology when the spill occurred (MCHM MSDS 2011). Since the spill, research has revealed that crude MCHM is a mixture of at least 10 organic contaminants, many of which are *cis* and *trans* substituted cyclohexane isomers (MSDS; Foreman et al. 2014; Gallagher et al., 2015). According to the MSDS, the major components are *cis* and *trans*-(4-methylcyclohexyl)methanol (4-MCHM) constituting 68-89 % of the crude mixture (MCHM MSDS 2011) in an approximately 1:2 ratio with a combined solubility of 2250 mg/L at 23 °C and the *cis* isomer being 34% more soluble than the *trans* (Dietrich et al. 2015). The more polar and soluble *cis*-4-MCHM had a higher solvated dipole moment of 2.454 D, and 138.9 cm^3/mol molar volume, while the *trans* had a solvated dipole moment of 2.425 D and the same molar volume (Dietrich et al. 2015). The *trans*-4-MCHM has an air odor threshold concentration of 0.060 ppb-v and a sweet licorice odor, while the cis isomer is 2000 fold less odorous (Gallagher et al. 2015).

Summary

This study addresses the fate and transport of crude MCHM in water distribution system materials. Specifically, the diffusivity and solubility of crude MCHM into polyethylene pipe materials and epoxy and polyurethane linings were determined through experimentation and modeling using Crank's diffusion equation and were compared to toluene and 1-butanol, two well-studied chemicals that are representative of non-polar and polar contaminants. Thereafter, the desorption (leaching) of sorbed crude MCHM from polyethylene pipes into water was evaluated. A Freundlich isomer was developed for *cis* and *trans* 4-MCHM in crude MCHM on activated carbon and the odor intensity of MCHM was evaluated in water after sorption onto activated carbon.

Methods

Materials

Toluene (CAS#108-88-3, 99% pure) was purchased from Acros Chemical. 1-butanol (CAS # 71-36-3) was purchased from Acros Chemical. Crude MCHM was courtesy of Eastman Chemical Company. GC analysis (Dietrich et al. 2015) indicated that crude MCHM was a mixture primarily comprised of 86.5% *cis*- and *trans*-4-MCHM. Reagent water was produced from a Nanopure® System. Characteristics for each contaminant are presented in Table 1.

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Table 1. Characteristics of Contaminants

Contaminant	M_m, g/mol	ρ, g/cm^3	S_w, mg/L (23°C)	Log K_{ow}	Hydrogen Bonding Power
1–Butanol[a]	74.12	0.81	91000	0.88	Strong
Toluene[b]	92.13	0.87	515	2.73	Poor
Crude MCHM	-	0.91[c]	~2250[d]	-	Moderate
cis-4-MCHM (31.5% crude)	128	0.907[e]	~2700[d]	2.35[d]	Moderate
trans-4-MCHM (55% crude)	128	0.907[e]	~2400[d]	2.46[d]	Moderate
Other cyclohexanes (5.9% crude)	-	-	-	-	-
Water and methanol (8.1 % crude)	-	-	miscible	-	Strong

[a] USEPA 1994, 1-Butanol, water solubility at 25°C

[b] USEPA 1994, Toluene, water solubility at 20°C

[c] Measured in this research

[d] Dietrich et al. 2015

[e] MCHM MSDS 2011, water solubility at 23°C

Samples of the new polyethylene pipe were purchased from a home supply store and were the same as those previously used for contaminant uptake research: McMaster HDPE resin, monomodal HDPE pipe, PEX-A MDPE pipe, PEX-B1 HDPE pipe and PEX-B2 HDPE pipe (Dietrich et al. 2010; Whelton et al. 2010). These pipe samples were cut into dogbone shapes and the thickness measured (Table 2).

The epoxy and polyurethane lining materials were those approved for use in water distribution systems and previously described and used with drinking water (Deb et al. 2010). Samples were provided from the manufacturers in the form of pre-coated glass coupons. For this sorption research, the polyurethane was peeled from the glass coupon and trimmed to 1 x 1 cm^2 samples in our lab. The epoxy was tightly bound to the glass and could not be separated; 1 x 1 cm^2 coupons of one-sided epoxy coated glass were tested.

Sorption of Contaminants into Polymer Materials

Since previously published experimental procedures for contaminant uptake by polymers were followed (Aminabhavi and Naik, 1999; Whelton et al. 2010; Dietrich et al. 2010), the method is only briefly described herin. Triplicate samples of pre-weighed polymer samples were submerged at 23 °C in crude MCHM, 1-butanol, or toluene in 20 mL amber glass vials with perfluoroethylene faced lids. Periodically, polymer samples were removed, wiped dry with a KimWipe, then immediately weighed on a Mettler H10 analytical scale to the nearest 0.0001 g.

Samples were weighed for 2-4 month periods at appropriate time intervals to monitor weight gain until achieving constant weight. It is important to note that the weight gain for crude MCHM is for a mixture of contaminants for which *cis* and *trans*4-MCHM constituted 86.5% of the mixture, while weight gain for toluene and 1-butanol are for the single pure contaminants.

Desorption of Contaminants from Polyethylene Pipe

Desorption of crude MCHM from polyethylene materials into water was determined. Samples of PEX-B and monomodal HDPE pipe were saturated with crude MCHM by submersion until no further weight gain was observed. The MCHM saturated samples were weighed to the nearest 0.0001 g, then placed in 10 mL reagent water in 20 mL amber glass vials. Decrease in weight was monitored over time when in contact with water. Samples weights were taken multiple times the first day, then daily, and then approximately weekly until weight change was negligible.

Calculation of Diffusivity and Solubility

The weight gain data were fitted to Crank and Park's 'Diffusion in a Plane Sheet' model and evaluated for diffusion and solubility coefficients (1968). R 3.1.3 (R Core Team 2015) was used for the fitting of the diffusion curves. Polyethylene and polyurethane samples were modeled as two sided sorption. The epoxy samples were modeled as one sided sorption because a layer of epoxy was exposed on only one side with glass on the other.

The Crank equation for diffusion is below for two sided diffusion.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{4\ell^2}\right)$$

Equation 1

Where

M_∞ = Mass of contaminant in polymer at equilibrium (M)

M_t = Mass of contaminant in polymer at time t (M)

t = Elapsed time (T)

ℓ = Half sample thickness (L)

D = Diffusion coefficient (M^2/T)

Tukey's HSD multiple comparison test with α-0.05 was used to evaluate differences among diffusivities and among solubilities for each contaminant and polymer pairing.

Activated Carbon Sorption

Adsorption on a commercially available virgin granular activated carbon approved for drinking water was investigated at 23°C. Carbon fines were removed by rinsing with reagent water. The carbon was heated at 110 °C and then placed in a desiccator until completely dry. A solution of ~450 mg/L crude MCHM in reagent water, determined by GC-FID to contain 117 mg/L *cis*- and 233 mg/L *trans*-4-MCHM, was placed in 100 mL amber glass jars with either 0.01g, 0.05g, 0.1g, 0.3g, 0.5g, 0.75g or 1g activated carbon. A control with no carbon was also prepared. The jars were placed on a shaker table at 150 rpm for two days, after which aqueous *cis*- and *trans*-4-MCHM were determined by GC-FID. Data were fitted to a Freundlich isotherm (Freundlich 1906).

The concentration of MCHM in the solution was measured by headspace GC-FID with splitless injection (Thermo Scientific, Finnigan TraceGC Ultra with Thermo HS2000 autosampler). Aqueous sample vials were heated to 80 °C for 30 min. Injections of 0.2 mL headspace were at a rate of 5 mL/min onto a 30 m Restek RXi-5sil MS column of 0.25 mm i.d. and 1.0 µm film thickness. The oven temperature was 50 °C (1 min), then ramped to 150 °C over 10 minutes and held at 150 °C for 3 minutes. The *trans* and *cis* isomers eluted at 10.47 and 10.75 min respectively; individual isomers were quantitatively determined. Standard were prepared using known concentrations of *cis* and *trans*-4-MCHM. The method detection limits for *cis* and *trans* isomers are 0.13 and 0.2 mg/L 4-MCHM, respectively (Sain et. al. 2015).

Odor Intensity Rating

The Total Intensity of Odor (TIO) (proposed Standard Method 2150C) (APHA 2015) in combination with the Attribute Rating Test (Dietrich et al. 2004) was used to assess the odor intensity of water samples after contact with GAC and crude MCHM. Human subjects were required to be at least age 18 and to report having no health problems and not being pregnant (IRB Project No. 14-174). Total Intensity of Odor uses a reagent water control and three soy sauce solutions as odor reference standards for: odor free (0), slight (4), moderate (8) and strong (12). Six researchers experienced with sensory analyses and MCHM odors were the subjects. The attribute was the licorice odor of MCHM. Subjects first smelled the reference standards to calibrate themselves. Next, in a randomized order they smelled the solutions of 0.01 g, 0.05 g, 0.1 g, 0.3 g, 0.5 g, 0.75 g or 1 g activated carbon that had been in contact with the solution of ~450 mg/L crude MCHM in reagent water. All MCHM and odor reference samples were at room temperature. The intensity of odor ratings of individual subjects were recorded for each MCHM/GAC sample, then means and standard deviations calculated.

Additional odor samples were prepared to represent leaching. Three dogbone pipe samples from the adsorption experiment (HDPE resin, monomodal HDPE pipe and PEX A-MDPE pipe) were immersed in nanopure water in 20mL amber glass vials. Subjects were asked to smell and rank the intensity of odor for these samples according to the same method.

Results and Discussion

Sorption into polyethylene pipes

Polyethylene pipes were submerged in reagent water for two weeks and no weight gain was observed; thus, water sorption into polyethylene is negligible as has previously been observed (Dietrich et al. 2010; Whelton et al. 2010). Diffusion data for all three contaminants are presented in Table 2 and also in Figure 1 for monomodal HDPE pipe; sorption curves were similar for the other polyethylene materials (resin, PEX-A, and PEX-B). Very similar diffusivity and solubility values were determined for MCHM in the different polyethylene materials tested (Table 2). Data show that crude MCHM diffuses slowly and has a low solubility in polyethylene materials. Compared to diffusion behavior of non-polar toluene and polar 1-butanol, MCHM diffusion is similar to the 1-butanol. Based on Tukey's HSD multiple comparison, there were no statistically significant differences for either diffusivity or solubility for any of the polyethylene pipes for MCHM and 1-butanol.

Toluene sorbs quickly then reaches full saturation within about one week. MCHM and 1-butanol show a gradual uptake that required months to each saturation level; their levels are typically one-tenth of that for toluene (Table 2). Tukey's HSD multiple comparison found that toluene had statistically higher diffusivities and solubilities than either MCHM or 1-butanol, and the toluene results varied by polyethylene type.

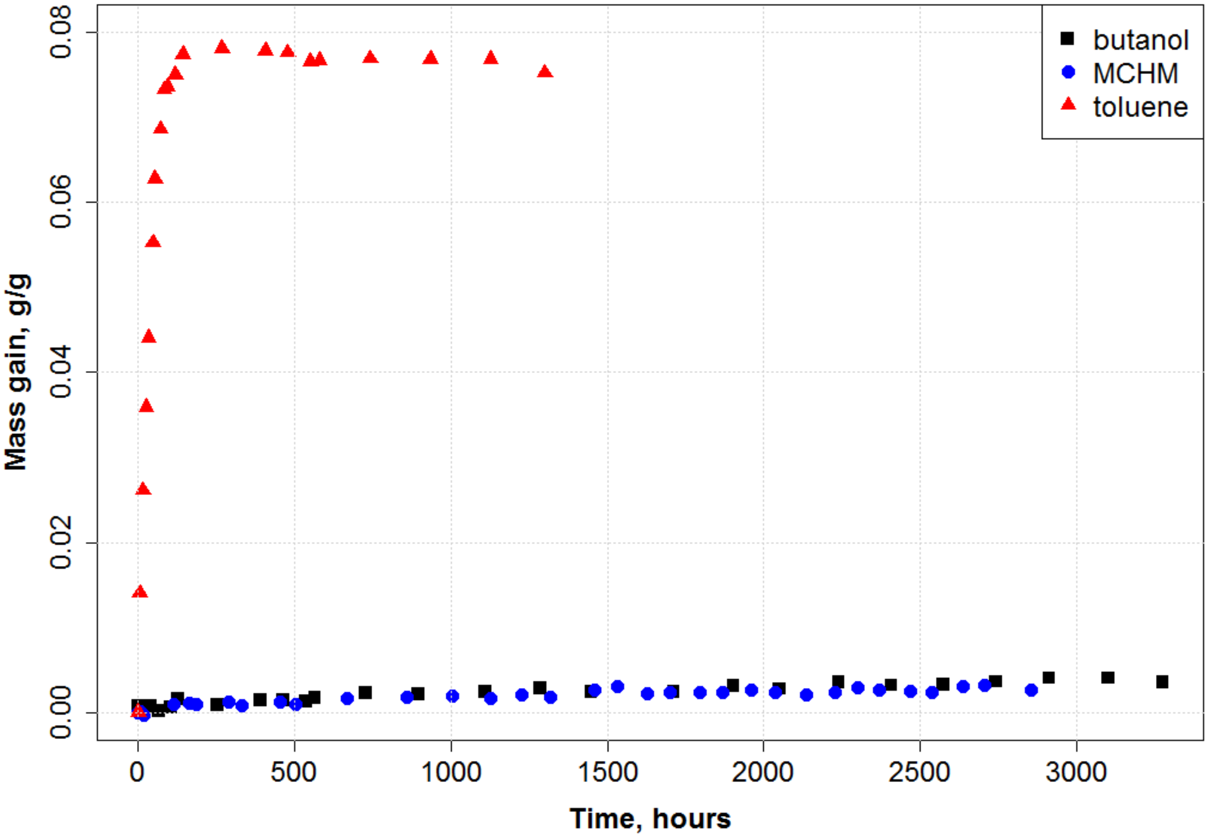

Figure 1. Mass uptake in polyethylene (monomodal HDPE)

The data confirm previous reports that contaminant polarity is acknowledged to be inversely correlated with the rate of diffusion into polyethylene; more polar molecules will diffuse less readily into polymer pipe materials (Tang et. al. 2013). MCHM is a moderately polar molecule with and overall aqueous solubility of 2250 mg/L and solvated dipole moments of 2.454 D and 2.425 D for *cis*- and *trans*-4-MCHM, respectively (Dietrich et al. 2015). The diffusivity of MCHM is low and similar to other polar contaminants such as 1-butanol (Aminabhavi 1999; Whelton et.al. 2010; Dietrich et al. 2010).

Table 2. Characteristics of Polymer Materials

Parameter	HDPE Resin	Monomodal HDPE Pipe OilCreek	PEX–A MDPE Pipe (FLEXPEX)	PEX–B1 HDPE Pipe (ZURN)	PEX–B2 HDPE Pipe (VIEGA)	Epoxy Lining	Polyurethane Lining
Thickness, mm	1.64 ± 0.02	2.59 ± 0.06	2.60 ± 0.02	2.61 ± 0.01	2.63 ± 0.03	1.17 ± 0.21	1.73 ± 0.11
Bulk Density, g/cm^3	0.9572 ± 0.0001 [a]	0.9494 ± 0.0002 [a]	0.9371 ± 0.0005 [a]	0.9524 ± 0.0001 [a]	0.9510 ± 0.0001 [a]	1.3 [b]	1.12 [c]
Diffusivity[d] 10^{-9} cm^2/s							
MCHM	0.94 ± 36% C	1.36 ± 45% C	0.36 ± 76% C	0.52 ± 114% C	1.15 ± 51% C	35.05 ± 123% B	Swelling[e]
1-Butanol	0.80 ± 69% C	0.70 ± 37% C	0.94 ± 69% C	-	-	Dissolved[f]	Swelling[g] 1.53 ± 14% C
Toluene	83.36 ± 9% A	43.35 ± 7% B	66.11 ± 1% AB	-	-	1.03 ± 110% C	2.48 ± 12% C
Water Control	0	0	0	0	0	1.71 ± 74% C	2.39 ± 33% C
Solubility[d], g/cm^3							
MCHM	0.0035 ± 15% D	0.0031 ± 25% D	0.0080 ± 22% D	0.0077 ± 28% D	0.0042 ± 21% D	0.0024 ± 54% D	Swelling[e]
1-Butanol	0.0052 ± 24% D	0.0051 ± 20% D	0.0062 ± 35% D	-	-	Dissolved[f]	Swelling[g] 0.4694 ± 5% A
Toluene	0.0375 ± 4% C	0.0752 ± 4% B	0.0815 ± 1% B	-	-	0.0028 ± 26% D	0.4639 ± 2% A
Water Control	0	0	0	0	0	0.0050 ± 56% D	0.0352 ± 5% C
Desorption Diffusivity, 10^{-9} cm^2/s	-	8.37 ± 3%	-	6.66 ± 21%	-	-	-

[a] Dietrich et al. 2010; Whelton et al. 2010.

[b] MSDS AquataPoxy A-6

[c] MSDS AquataFlex 510

[d] Mean ± relative standard deviation (%) for three replicates

[e] Mass gain continued for the 3000 hours of the experiment.

[f] Butanol dissolved the epoxy lining; mass loss was observed.

[g] The polyurethane samples in 1-butanol expanded up to 11% of the thickness

Sorption into Epoxy

The data for sorption into epoxy lining show different trends compared to polyethylene pipes. Figure 2 presents the sorption patterns for the three contaminants and Table 2 presents the values for water and contaminant diffusivity and solubility. There were no statistically significant differences among the solubilities for the three contaminants and water. The solubility results were similar to those for MCHM and 1-butanol in polyethylene pipe. Similar results were found for diffusivities with the exception of MCHM which sorbed at a much higher rate. MCHM diffused in a similar manner but at least 30-fold faster into epoxy compared to polyethylene pipes materials, although the ultimate solubility was similar (Table 2). Toluene was sorbed less in epoxy than polyethylene, with about a 0.13% mass gain in epoxy compared to a 5.7-8.4% mass gain for polyethylene. Unlike polyethylene materials, the epoxy coupons sorbed water and moderately polar MCHM indicating that contaminant polarity is positively correlated with sorption.

Results for 1-butanol in epoxy indicate that this contaminant dissolved the epoxy. A slight color change on the surface was noticed as the light blue epoxy gained a green tint. In addition, the replicates exposed to butanol lost weight for the first 60 days. Because of the dissolution, the Crank diffusion model was not applied to 1- butanol. Butanol and pentanol are acknowledged to be incompatible with epoxy (Beacon Adhesives 2014). Solvents are also known to be incompatible with epoxy. Select solvents are designed to dissolve and remove epoxy, including petroleum distillates and alkylated cyclohexene (MSDS Dynasolve).

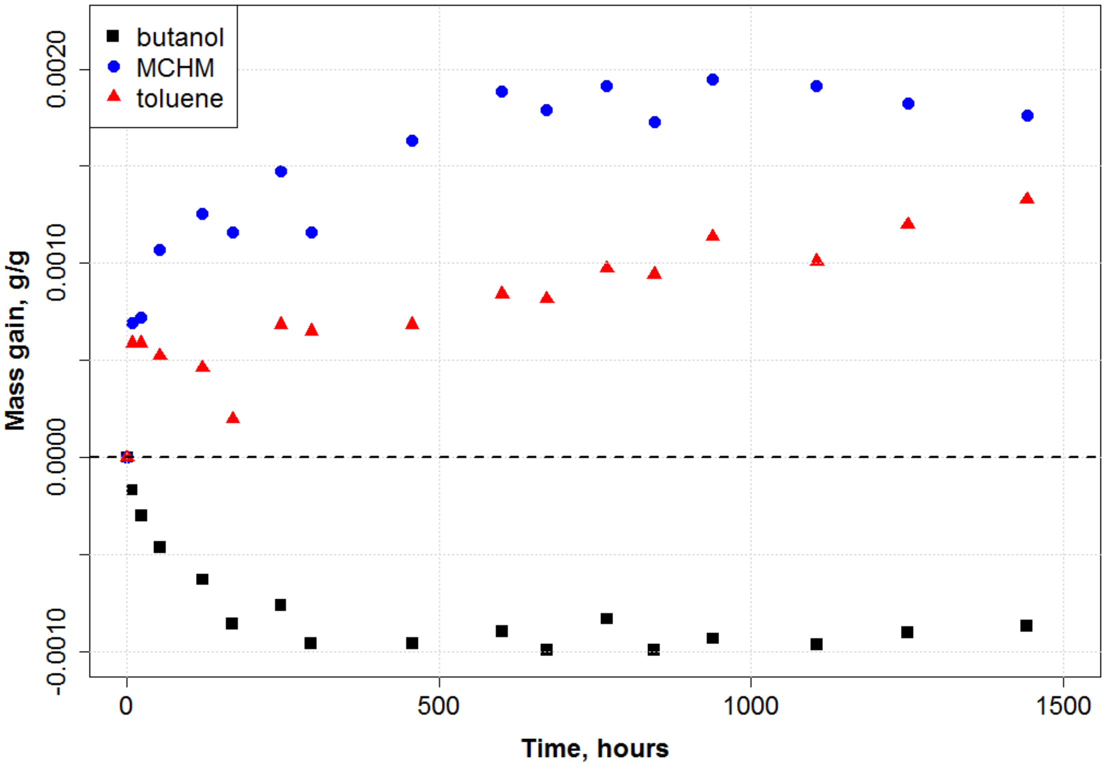

Figure 2. Percent mass uptake for epoxy lining

Sorption into Polyurethane

The polyurethane lining demonstrated a different diffusion pattern than the contaminants had in polyethylene pipes as shown in Figure 3. With the exception of MCHM, the diffusivities were not statistically different than those for 1-butanol and MCHM in polyethylene pipes. The estimated solubilities, however, for 1-butanol and toluene were statistically higher than any other contaminant / polymer pair. Even water had a solubility in polyurethane as high as toluene in HDPE resin which was the largest for any polyethylene contaminant pair.

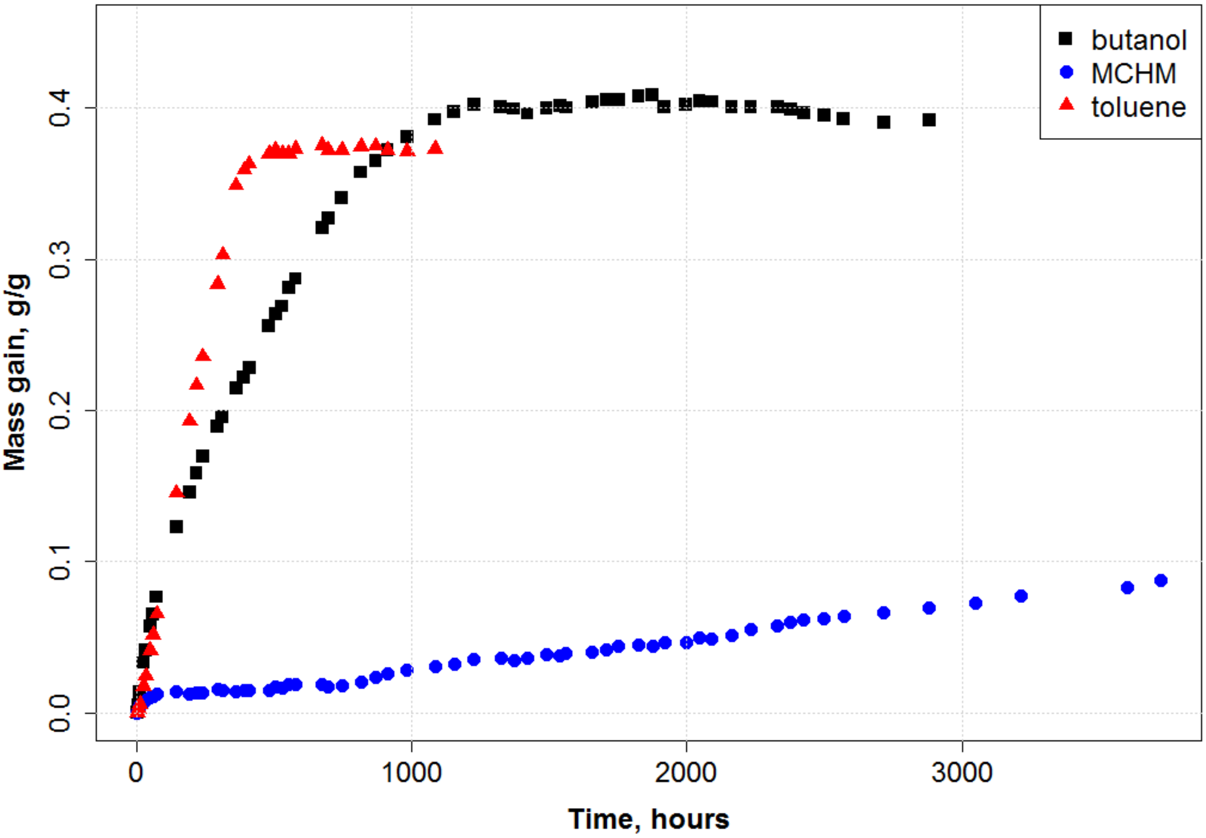

Figure 3. Percent mass uptake for polyurethane.

Some physical changes were noted during polyurethane exposure to the contaminants. Before and after pictures of each sample and property changes of polyurethane in 1-butanol samples are shown in Figure 4.

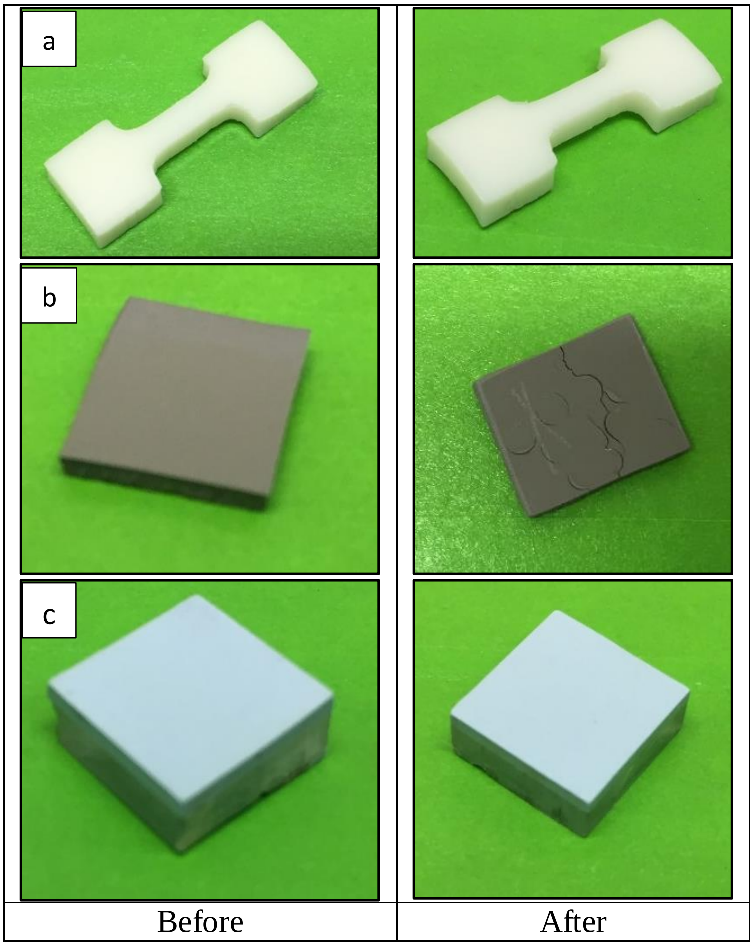

Figure 4. Polymer materials and visual property changes. Images are of material before contact with 1-butanol and after 4 months of contact. The polyethylene pipe materials (a; PEX-B2 HDPE Pipe) were unchanged in appearance, while the polyurethane (b) cracked and swelled and the epoxy was unchanged (c)

Both toluene and 1-butanol reached saturation. The time to saturation for toluene in polyurethane was about 400 hours while saturation happened more quickly in the polymer pipe materials, approximately 50 hours. In addition, a much larger % mass gain of toluene was observed in the polyurethane than polyethylene. Polyethylene samples had a 5.7-8.4% mass gain while polyurethane had a 37% mass gain. Butanol saturation was reached quickly, in about 1200 hours and a large mass gain was seen of about 39%, much more than seen in polyethylene. The physical properties of the polyurethane samples in butanol also changed. The polyurethane began as a rigid material that would not bend easily. After being immersed in butanol, the samples became very flexible and could bend easily, seen in Figure 5. These samples also increased in width up to 11%. This suggests that more than sorption could be occurring to uptake butanol, a sponge-like expansion could be taking place as well. Because of these changes, the diffusion modeled by the Crank model may not be representative for this contaminant lining pair. These property changes have been previously reported with a polyurethane material used for screen printing when exposed to solvents used in the process (Jewell, 2004). In that study the polyurethane material showed expansion and increased ductility in the material.

Figure 5 Polyurethane in 1-butanol, bending

Lastly, for MCHM in polyurethane, there were no similarities in the resulting diffusion curve to those of polyethylene pipes or the other contaminants in polyurethane. Mass gain from MCHM in polyurethane was about 8.7%, more than was seen in polyethylene pipes. A very rapid weight gain was observed for the first 100 hours followed by a saturation like equilibrium until 750 hours. At that point, weight gain linearly increased at an approximate rate of 5×10^{-6} g/hr for the next 125 days when the experiment was finally stopped. Similarly to the butanol samples, MCHM examples experienced an expansion up to 3% of the original thickness of the samples. No other property changes were observed with exposure to MCHM. Due to the nature of the diffusion, this data for the entire could not be fit to Crank's model.

Polyurethane has not had much use in the United States and most of the research dedicated to its reactions with organics study water quality shortly after curing (Whelton et. al. 2013). The results of this study suggest that polyurethane may not be as stable a material as polyethylene pipe because more uptake of organic materials was seen in the lining than in the pipe material. Some of these differences could be attributed to the sample property. When polyurethane cures, it is meant that only one side is exposed to the water flowing in a pipe. However, during this experiment both more than just that edge was exposed to the contaminant. This experiment may better represent the type of adsorption that could be seen if there was a crack or uniformity in the pipe lining. The side of the sample, normally not exposed distribution water, is much more porous than the cured side and could be acting more as sponge that the desired adsorption process being tested. These samples as seen by the expansion in the thickness of the samples and the changes seen in the physical properties. More than diffusion was occurring in the polyurethane material. Previous research has shown that organics may be leached from the lining material during curing and at the beginning of exposure to water.

Implications for MCHM Sorption into Water Distribution Infrastructure

MCHM requires months of exposure to reach full saturation in polyethylene pipe material and the amount of MCHM that will be adsorbed is low. Knowing this, it is unlikely that MCHM was able to diffuse into polyethylene pipe materials or linings in concentrations to approached saturation due to distribution system contamination for the industrial chemical spill. First, MCHM concentrations were dilute, with an estimated high concentration of 2.4 mg/L MCHM (WVDHSEM 2014). Second, MCHM contaminated water was only exposed to the pipe infrastructure for periods of weeks at concentrations that were mostly < 0.1 mg/L (Foreman et al. 2014).

Desorption

The desorption study showed that MCHM readily desorbs from pipes into water. The desorption trend observed is similar to diffusion, but in reverse and over a shorter time scale. Most MCHM diffusion occurred in the first 240 hours but then approached a residual saturation. The mean desorption curve for monomodal HDPE pipe can be seen in Figure 6. While approximately 40% of the sorbed MCHM was released rapidly back into solution in a typical desorption type curve, the remaining 60% of the sorbed MCHM appeared irreversibly bound.

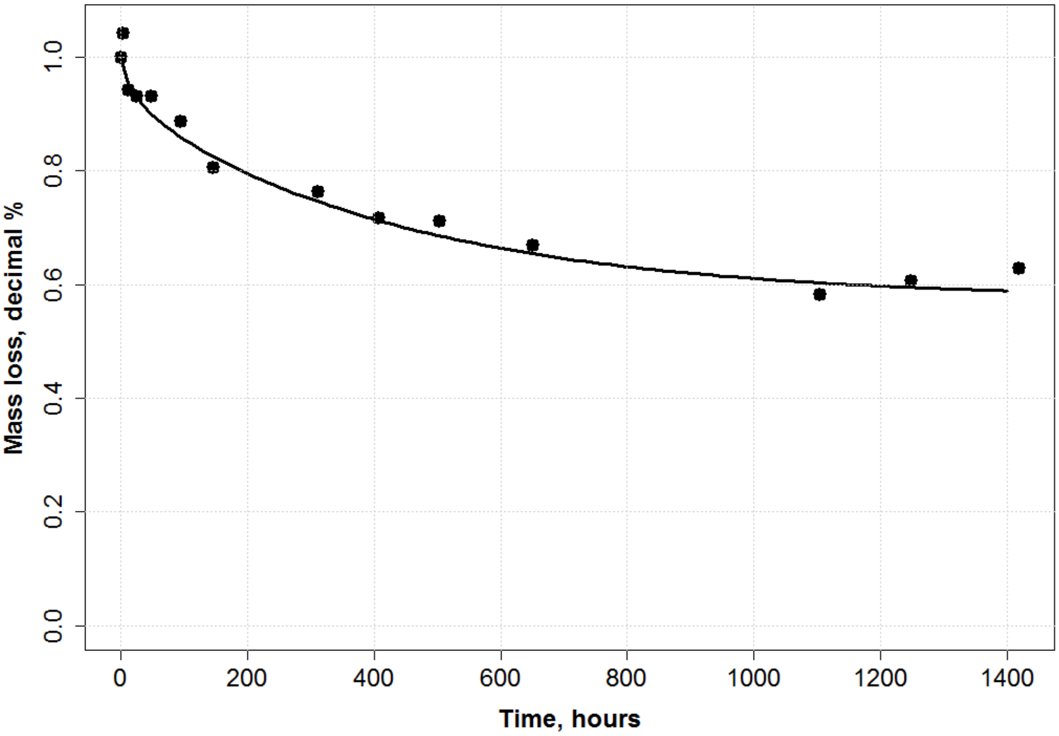

Figure 6. Desorption of MCHM from polyethylene pipe materials.

Activated carbon sorption and odor removal

As a reminder, the crude MCHM mixture was used for the polymer sorption experiments and was comprised of 31.5% *cis*-4-MCHM and 55% *trans*-4-MCHM (). While the GAC sorption was performed with crude MCHM, data were fit to separate Freundlich isotherms (Freundlich 1906) for *cis* and *trans*-4-MCHM. These isomers were measured by headspace GC (see methods). The resulting isotherm equations are:

cis-4-MCHM

$\log_{10} x/m$ (mg cis/g GAC) $= 0.42 \log_{10} C_e$ (mg/L cis) $+ 1.11$; $R^2 = 0.96$

trans-4-MCHM

$\log_{10} x/m$ (mg trans/g GAC) $= 0.48 \log_{10} C_e$ (mg/L trans) $+ 1.42$; $R^2 = 0.92$

These equations are statistically different (α=0.05) in y-intercept but not slope; thus, sorption behavior was different for each isomer. The *trans*-4-MCHM was better sorbed as indicated by the loading capacities at 1 mg/L aqueous equilibrium concentrations, which are 12.8 ± 1.1 mg/g for *cis* and 26.5 ± 1.2 mg/g for *trans*. The higher capacity of GAC for *trans*-4-MCHM is consistent with its lower water solubility (Table 1) compared to *cis* and also its higher octanol-water partitioning coefficient and lower solvated dipole moment (Dietrich et al. 2015).

Odor Intensity Rating

Sensory analysis using the Total Intensity of Odor produced results that parallel the measured concentrations of *trans*-4-MCHM in aqueous solution after contact with GAC (Figure 7). *Trans*-4-MCHM was considered for this comparison as it is the dominant odorant in crude MCHM with an odor threshold concentration in air of 0.060 ppb-v; the *cis* isomer is 2000 fold less odorous (Gallagher et al. 2015). The concentrations of *trans*-4-MCHM in solutions treated with activated carbon all exceeded the odor threshold concentration. Addition of GAC substantially reduced both the contaminant concentration and odor.

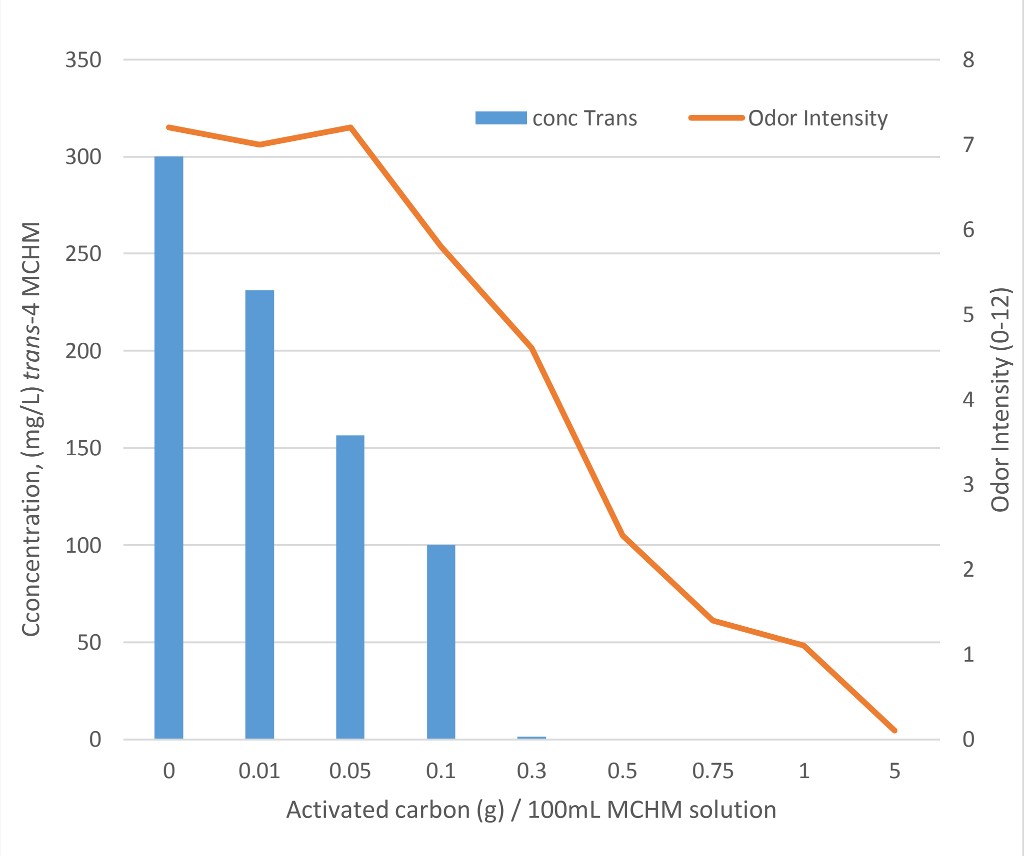

Figure 7. Odor intensity ratings and trans-4-MCHM concentrations for water after contact with granular activated carbon. (Concentrations for 0.5-5 g AC/100mL MCHM Solution were below the GC method detection limit of 0.2 mg/L) (Sain et.al. 2015)

In addition to sniffing activated carbon samples, participants were asked to sniff samples in which MCHM had desorbed from polyethylene pipe. These samples contained leached MCHM from dogbone samples and were ranked to have a slight to moderate odor by participants. This shows that the small amounts of MCHM that had adsorbed into polyethylene over months leached back into the water at detectable odor levels.

Implications

With an increasing use of industrial chemicals and large numbers of recorded oil and chemical spills, it is important that protection of drinking water infrastructure become a priority (USCGNRC 2015). It is known that polymer materials can uptake and then leach chemicals that contaminate drinking water distribution systems; however, more work needs to be done on understanding how this infrastructure will react when exposed to a variety of contaminants. This research, like previous research (Tang et al. 2013), shows that prediction of sorption behavior is possible for polyethylene materials based on contaminant polarity. In contrast, the newer polymer linings did not demonstrate predictable behavior and may have reactions beyond sorption/desorption that are possible when exposed to a contaminant in the water.

Looking more closely at polymer infrastructure during the chemical spill of MCHM, a “worst case scenario” of uptake can be estimated from the sorption of 100% crude MCHM into polyethylene materials. Polyethylene pipes after 18.75 hours and 6.75 days of exposure exhibited 0-0.015% and 0.025-0.065% mass gain respectively. The sorption after 6.75 days exposure to 100% crude MCHM averages 9% of the total sorption possible at saturation. The concentrations of MCHM in the distributed drinking water in West Virginia were reported at less than 3 mg/L; therefore sorption would be expected to be much lower for the time during the spill (WVDHSEM 2014).

Conclusions

Polyethylene pipes exhibited the expected properties of diffusion and solubility of an organic into a polymer material. The data showed that MCHM behaved much more like the other polar molecule when diffusing into the pipe. For a future chemical spill of a contaminant with unknown properties, polarity may be a quick way to estimate the potential amount of diffusion into polymer water infrastructure materials. A portion of sorbed MCHM readily desorbs from polyethylene, although more than half appears to be irreversibly bound.

While capacities were quite different, sorption onto activated carbon also illustrates the same polar / nonpolar relationship. The *trans* and *cis* isomers behave differently when adsorbing into activated carbon. The slightly less polar trans-4-MCHM achieved a higher capacity.

Linings often had a contaminant specific physical reaction. Polyurethane swelling was noted for MCHM and 1-butanol. Dissolution was observed for epoxy and 1-butanol. Both linings sorbed water, which was not seen for any of the polyethylene pipe materials. Epoxy diffusivities and solubilities were generally low, similar to polar contaminants in polyethylene. MCHM however, sorbed into epoxy much more rapidly, even though its overall solubility was consistent with other pairings. While polyurethane’s diffusivities were also similar to polar contaminants in polyethylene, the calculated solubilities were much higher. This may be an artifact of the swelling or physical changes that occurred. The different surfaces of the material may have an impact on how it will react with organics. Linings are installed so that only the side open to air is meant to be in contact with the water. If there are cracks in the lining and the porous interior is exposed, this experiment may represent the type of sorption/expansion that could occur with contaminated water.

Sensory analysis by the Total Odor Intensity method proved an efficient method for assessing the effectiveness of GAC for removing MCHM odors. Using sensory analysis, the odor could be quickly confirmed to be present or below the odor threshold level after contact with GAC. The trend for MCHM removal was the same when using sensory analysis as when quantitative gas chromatography was applied (Figure 7). The sensory method was more sensitive; an odor could be detected in samples treated with GAC even when the equilibrium concentration MCHM was below the 0.2 mg/L detection limit of the gas chromatographic method. Likewise, sensory analysis confirmed that MCHM migrated from the polyethylene pipe into water at a level that exceeded the odor threshold. The ability of sensory analysis to provide data within minutes for samples is a major advantage as gas chromatography requires about an hour per sample, and only after scheduling use of gas chromatography instrumentation which may require days.

The desorption data from polyethylene and the corresponding sensory analysis confirmed that desorption can occur and, if the initial sorbed mass is great enough, the resulting water concentrations have a detectable odor. Thus consumers may possibly detect odors even after the pipes were flushed as desorption takes place. This situation would not last, however, because desorption is complete after approximately ten days.

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Partitioning, Aqueous Solubility, and Dipole Moment Data for *cis*- and *trans*-(4-methylcyclohexyl)methanol, Principle Contaminants of the West Virginia Chemical Spill

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ABSTRACT

In 2014, the U.S. National Response Center recorded over 30,000 incidents of oil spills, chemical releases, or maritime security issues, including crude (4-methylcyclohexyl)methanol (MCHM) that contaminated river and drinking water in West Virginia. This research determined physicochemical partitioning data for the two major compounds released in West Virginia, *cis*- and *trans*-(4-methylcyclohexyl)methanol. Octanol-water partition coefficients (K_{OW}) were 225 for *cis*- and 291 for *trans*-4-MCHM. The aqueous solubility for total 4-MCHM was 2250 mg/L at 23 °C; solubilities of individual isomers were dependent on their mole fractions. The *cis*-isomer was more soluble and less well sorbed to activated carbon than the *trans*-isomer, consistent with its lower K_{OW}. The partition behavior is supported by a larger computed solvated dipole moment for the *cis* compared to *trans* at the MP2 aug-cc-pwCVDZ SMD level of theory. Different partition properties would result in differential fate and transport of *cis*- and *trans*-4-MCHM in aqueous environments.

KEY WORDS: (4-methylcyclohexyl)methanol; MCHM; K_{OW}; solubility; dipole moment; *cis*/*trans* isomers

INTRODUCTION

In 2011, almost 10,000 tons of 287 different chemicals spilled into U.S. waters from 1,374 different facilities.[1] In 2014 alone, the U.S. National Response Center recorded over 30,000 incidents of oil spills, chemical releases, or maritime security issues, up slightly from the over 29,000 incidents recorded for 2013.[2] For spills involving technical grade chemicals or mixtures like petroleum, the chemical complexity can make impact assessment difficult. To assess contaminant fate and transport, accurate environmental partitioning coefficients are essential. The lack of partitioning data hinders protecting human and environmental health, such as when 10,000 gallons of the industrial chemical crude (4-methylcyclohexyl)methanol (MCHM) leaked from storage tanks and spilled into West Virginia's Elk River in 2014. Crude MCHM subsequently contaminated the Elk, Kanawha, and Ohio Rivers, plus the drinking water for over 300,000 people in Charleston, WV and nine surrounding counties.[3-7] "Do not use" the drinking water notices were issued by the water utility and West Virginia government. Residents readily detected MCHM's persistent licorice odor.[7] Lack of MCHM partitioning data impeded predicting short- and long-term fate and transport in the environment, and throughout drinking water treatment plants and distribution systems. For MCHM, partitioning and solubility data were not present on the material safety data sheet (MSDS)[8], nor required for this chemical under the Toxic Substances Control Act.[3,9] The lack of data on MSDS is not uncommon. For example, similar data gaps were noted for other industrial chemicals[9]: 1-chloro-3-methylbenzene (3-chlorotoluene)[10], trichloroacetaldehyde (chloral)[11], and the complex mixture coal tar creosote[12], reported to contain 52 chemicals.[12]

Soon after the spill, monitoring data revealed two major components: *cis*- and *trans*-4-MCHM in approximately a 1:2 ratio in crude MCHM.[5,7] The more abundant *trans*-4-MCHM was primarily responsible for the licorice odor. Its air odor threshold concentration was 0.060 ppb-v, which is approximately 2000 times lower than the *cis*-isomer and illustrates the complexity of evaluating chemical mixtures.[7] Approximate partition values for (4-methylcyclohexyl)methanol can be estimated with USEPA's EPI Suite™[13] but this software cannot distinguish geometric isomers. Crude mixtures of substituted cyclohexanes contain many geometric isomers arising from axial/equatorial substitution patterns. The pesticide hexachlorocyclohexane (i.e., lindane) is a mixture of eight isomers; the isomer K_{OW} values vary by two-fold and bioconcentration factors by 25-fold.[14] Likewise, *cis*- and *trans*-dichloroethene have nearly a two-fold difference in aqueous solubility and K_{OW}[15] and different biological degradation rates.[16]

The research objectives were to: 1) confirm the ratios of *cis:trans* in pure and crude 4-MCHM; 2) measure octanol-water partition coefficients (K_{OW}), aqueous solubilities, and carbon sorption for the *cis*- and *trans*-4-MCHM; 3) calculate dipole moments and molar volumes of these isomers; 4) assess consistency of experimental and computational data, then compare to calculated values from EPI Suite™.[13]

MATERIALS AND METHODS

Reagents

Pure (4-methylcyclohexyl)methanol (CAS#34885-03-5; 98% pure) from TCI America (USA) comprised *cis*- and *trans*-(4-methylcyclohexyl)methanol with a 2.08:1 *cis*:*trans* ratio (see NMR results). Crude MCHM was courtesy of Eastman Chemical (Kingsport, Tennessee, USA) and contained 86.5% *cis*- and *trans*-4-MCHM[7] with a 1:1.75 *cis*:*trans* ratio (see NMR results). Other reagents and crude MCHM components are described in Text S1.

NMR Spectroscopy

The ratios of *cis:trans* in pure and crude MCHM were determined by NMR at 25°C using a Bruker Avance-III 600 MHz spectrometer with TBI probe with Z gradient. Samples of 30 µL of pure 4-MCHM, crude MCHM, or individual HPLC fractions representing *cis*- and *trans*-4-MCHM isomers (see below) were mixed with 690 µL of $CDCl_3$ containing 0.05% tetramethylsilane; details are provided in Text S1.

Dipole Moment and Molar Volume Computations

Stochastic conformational searches of *cis*- and *trans*-4-MCHM were performed using the MOE software package.[17] From these guess structures, geometry optimizations and vibrational analyses were carried out using post-Hartree-Fock *ab initio* methods. All dipole moments were computed using Gaussian09[18] at the MP2 (full core) aug-cc-pwCVDZ level of theory in the gas phase and with the SMD implicit solvation model with water parameters.[19] Relative contributions to dipole moments of the *cis*- and *trans*-4-MCHM were determined using Boltzmann averaging (at 298.15 K) of all conformers based on free energy differences. Molar volumes were computed using the geometria polihedro (GePol) algorithm in Gaussian03 (see Text S1).[20,21]

K_{OW} Partitioning and HPLC Method

As described in Text S1, reversed phase HPLC was used to separate the isomers and determine K_{OW} values. To prepare individual isomers for NMR, *cis* and *trans* isomers in 27,000 mg/L pure 4-MCHM in methanol were separated with 60% methanol and 40% water. Prior to NMR, methanol was removed from the two collected fractions under a nitrogen stream, and water was lyophilized. K_{OW} was determined using the OECD HPLC method,[22] reference K_{OW} values,[23] and 5 replicates for each isomer as described in Text S1.

Aqueous Solubility

The slow stir method[24] determined water solubilities at 23°C and 4°C for quadruplicate samples of five different mole-fraction ratios of *cis*- to *trans*-4-MCHM: 1) pure 4-MCHM with 0.67:0.33; 2) crude MCHM with 0.35:0.61; three mixtures of pure and crude: 3) Mix 1, 0.43:0.54; 4) Mix 2, 0.57:0.41; and 5) Mix 3, 0.50:0.47. Replicates were contained in silanized[25] 40 mL vials with 40 mL reagent water and 1 g 4-MCHM mixture. Experimental data at two temperatures allowed calculation of the excess enthalpy of solvation. Mole fraction calculations, solubility, GC-FID, and thermodynamic solvation property calculation methods are described in Text S1.

Carbon Sorption

Adsorption experiments at 23°C used crude MCHM and reagent water to prepare a solution containing 117 mg/L *cis*- and 233 mg/L *trans*-4-MCHM in contact with a commercially available virgin granular activated carbon typically used to treat drinking water. A 100 mL volume of crude MCHM solution was added to amber glass jars containing 0.01 to 1 g carbon. The jars gently shook on a shaker table for two days, after which aqueous *cis*- and *trans*-4-MCHM were determined by GC-FID (See Text S1). Data were fitted to a Freundlich isotherm.[26]

Statistical Analyses

R version 3.1.2.[27] determined trend lines and significance at $\alpha = 0.05$. Unless stated otherwise, reported values are mean ± standard error.

Estimated Parameters from USEPA EPI Suite™

For 4-MCHM, log K_{OW} and aqueous solubility were estimated with KOWWIN™ (v1.68) and WSKOWWIN™ (v1.42), respectively, within EPI Suite™.[13] Inputs were based on CAS#034885-03-5; cyclohexanemethanol, 4-methyl- and Simplified Molecular Information and Line Entry System (SMILES) notation (OCC(CCC(C1)C)C1).

RESULTS and DISCUSSION

NMR Spectroscopy

As demonstrated in Table S1 and Figure S1, ^{1}H NMR of pure 4-MCHM and crude MCHM show two upfield doublets at δ 0.92 and 0.89 ppm (J ~ 7 and 6.6 Hz) and two downfield doublets at δ 3.55 and 3.45 ppm (J ~ 6.6 and 5.3 Hz), assigned to CH_3 protons and CH_2 protons of CH_2-OH, respectively, indicating the presence of two isomers. Signals in the 1.2 to 2.16 ppm region are attributable to cyclohexane ring protons. For cyclohexanes substituted with methyl groups like 4-MCHM, downfield signals are assigned to the *cis*-isomer and upfield signals to *trans*-isomer.[28] The doublets had 2.08:1 *cis*:*trans* ratio for pure 4-MCHM and 1:1.75 *cis*:*trans* ratio for crude MCHM, which are similar to published values.[5]

The proton decoupled ^{13}C NMR for pure and crude MCHM showed 12 singlets spread over 18 to 70 ppm (6 singlets at δ 66.31, 38.09, 30.62, 29.87, 25.16 and 19.99 ppm for *cis* isomer and 6 singlets at 68.70, 40.15, 34.62, 32.8, 29.47 and 22.61 for *trans* isomer) confirming the presence of *cis* and *trans* isomers. The ^{13}C chemical shift values closely agree with the reported values.[28]

^{1}H NMR chemical shift values confirmed that the first eluting HPLC peak was *cis*-4-MCHM and the second *trans*-4-MCHM (Table S1). Purified *cis*- and *trans*-HPLC fractions were used to verify that the first eluting GC peak was *trans*- and the second was *cis*-4-MCHM. Their respective elution times (and temperatures) were 6.20 min (224°C) for *trans* and 6.67 min (233.4°C) for *cis*.

Partitioning and Solubility

Figure 1 presents the plot of log K_{OW} and log k (chromatographic capacity factor; See Text S1) to determine K_{OW} values for *cis*- and *trans*-4-MCHM relative to eight reference compounds.[23] As shown in Table 1, for *cis*-4-MCHM $K_{OW} = 225 \pm 1$ (log $K_{OW} = 2.35 \pm 0.005$), while for later eluting *trans*-4-MCHM the $K_{OW} = 291 \pm 1$ (log $K_{OW} = 2.46 \pm 0.0002$) and was 30% higher than for *cis*. This difference was statistically significant ($p < 0.001$).

The overall solubility of 4-MCHM at 23°C is 2250 ± 50 mg/L and at 4°C is 2430 ± 64 mg/L (Table 1). The slightly higher water solubility at 4°C is statistically significant ($p=0.026$). At environmental temperatures, aqueous solubility of organic liquids vary slightly (< factor 2) and can increase or decrease with temperature, or even increase then decrease at certain temperature ranges.[29] The calculated excess enthalpy and entropy of solvation (Table 1) reveal that the solvation thermodynamics for MCHM is consistent with molecules of similar size and polarity.[29]

Interpretation of five mole fraction ratios tested demonstrate that *cis*-4-MCHM is more water soluble than *trans*-4-MCHM (Figures 2 and S2). At 23°C and mole fraction = 0.5 (Table 1), *cis* has 34% higher solubility than *trans*. Like other solvent mixtures, *cis*- and *trans*-4-MCHM solubilities are proportional to their individual mole fractions in the organic phase.[29-32] Although caution is advised for extrapolated data (Figures 2 and S2), extrapolating to mole fraction = 1 for individual isomers yields solubilities of 2700 ± 108 mg/L and 2400 ± 180 mg/L for *cis*- and *trans*-4-MCHM at 23°C, respectively.

Trans-4-MCHM was better sorbed to activated carbon than *cis*-4-MCHM as shown in Table 1 and Figure S3. Statistical analysis revealed that regression equation slopes for the isomers were not different, but the intercepts were different; the loading capacity at 1 mg/L aqueous concentration was 100% higher for *trans* (26.5 ± 1.2 mg/g) compared to *cis* (12.8 ± 1.1 mg/g).

Computed Dipole Moments and Molar Volumes

The Boltzmann-averaged molar volumes of *cis*- and *trans*-4-MCHM were both 139.8 cm^3/mol, with no significant methodological dependence, which does not account for the differential solubility behavior of the *cis* and *trans* isomers.[29] As dipole moments are good predictors of molecular interactions with aqueous environments,[29,33] differences in computed dipole moments were considered. A treatment of electron correlation and conformational averaging is crucial to obtain qualitatively correct dipole moments and relative energies for *cis* and *trans* isomers. Figures S4 and S5 display nine *trans*-4-MCHM and seven *cis*-4-MCHM conformers, and Table S2 lists their computed relative free energies and dipole moments. Boltzmann-averaged MP2 aug-cc-pwCVDZ computations incorporating an implicit aqueous solvation model show *trans/cis* dipole moment values to be 2.425/2.454 D. This 0.029 D difference is sufficient to rationalize the observed trends in solubility and K_{OW}. An accurate level of theory incorporating implicit solvation and conformational averaging produced dipole moments consistent with the observed solubility trend. To further illustrate the complexity in working with conformationally complex molecules, the computed Boltzmann-averaged gas phase *trans/cis* dipole moments, which are not predictors of aqueous phase behaviors, were reversed, with values equal to 1.586/1.530 D for *trans/cis*.

Consistency and Comparison to EPI Suite™

Table 1 shows that EPI Suite™ provided estimates within a factor of two for measured K_{OW} values and solubility at 23°C. A concern is that EPI Suite™ overestimates K_{OW} and underestimates solubility; therefore, multiplicative errors could result when both estimated parameters are utilized. At 23°C, the higher water solubility for *cis*-4-MCHM is consistent with its lower K_{OW}. The measured partition coefficients are consistent with a) larger dipole moment for *cis*-4-MCHM, b) higher boiling point as evidenced by the longer GC t_R for *cis*-4-MCHM, and c) decreased sorption of *cis* on activated carbon. Experimental and theoretical evidence strongly indicate that fate and transport of *cis*- and *trans*-4-MCHM isomers will differ in aquatic environments and may further change over time when variance in their mole fractions occur.

Environmental Implications

Industrial chemical spills commonly involve chemical mixtures. The complexity of a chemical spill can increase when geometric isomers are involved, such as spills containing cyclohexane derivatives. While the tendency may be to treat geometric isomers as one compound, reports in the environmental fate and transport literature indicate that geometric isomers can possess different physicochemical properties which affect fate, transport, and toxicity. EPI Suite™ is currently unable to perform geometric isomer-specific calculations. In fact, to capture subtle isomeric differences when computing fundamental physicochemical properties, thermal ensembles of low-lying conformers of each cyclohexane isomer must be considered. This research illustrates the value of integrating experimental and computational chemistry for determining and explaining physicochemical properties of *cis*/*trans* isomers. For 4-MCHM, the differential octanol-water partitioning (K_{OW} *trans* 30% greater than *cis*), aqueous solubility (*cis* 34% greater than *trans*), sorption onto activated carbon (*trans* 100% greater than *cis*), and odor thresholds (*trans* value 2000-fold more odorous than *cis* value),[7] corroborate that their environmental behavior is isomer specific. Understanding the implications of the 2014 crude MCHM spill and contamination events involving complex mixtures and geometric isomers will require an understanding of the properties of individual components in order to assess environmental fate and transport.

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Notes

The authors declare no competing financial interest.

SUPPORTING INFORMATION

Text S1, Tables S1-S2, and Figs. S1-S5: Additional text, tables, and figures related to the materials and methods, results and discussion, and computations. This information is available free of charge via the Internet at http://pubs.acs.org/.

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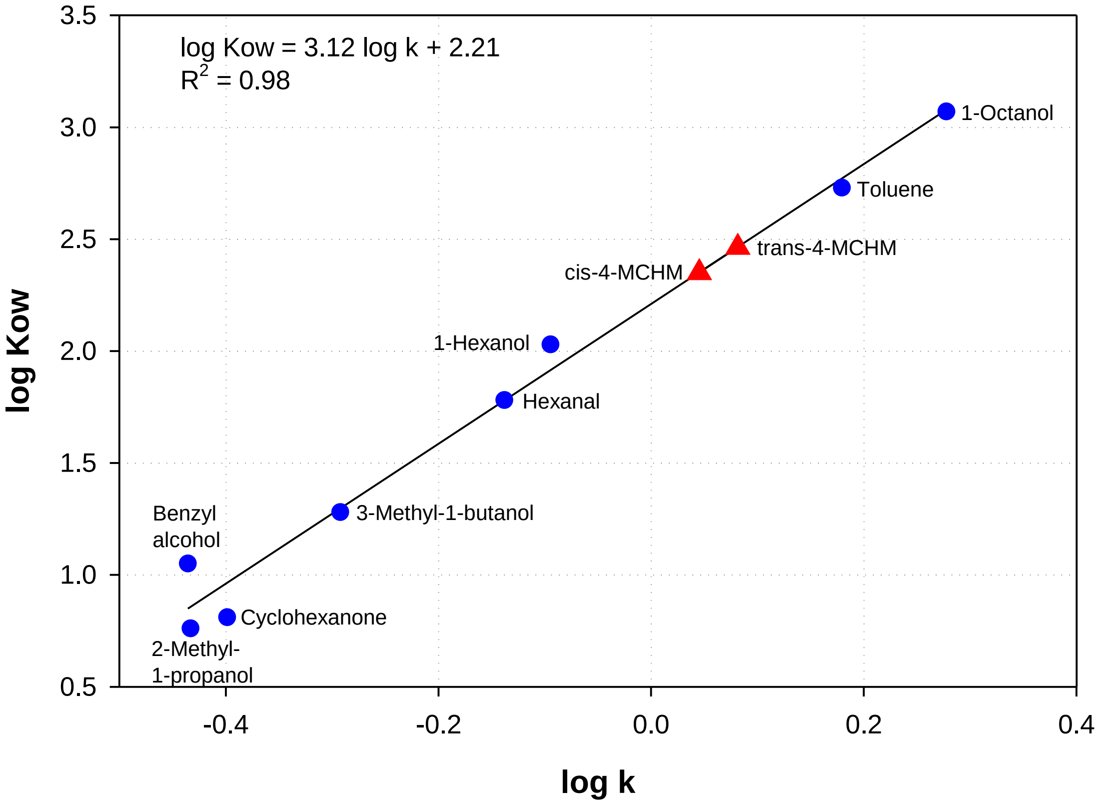

Figure 8 The K_{OW} values of *cis*- and *trans*-4-MCHM (▲) were determined relative to eight compounds (●) with known K_{OW} coefficients and determined capacity factors (k).

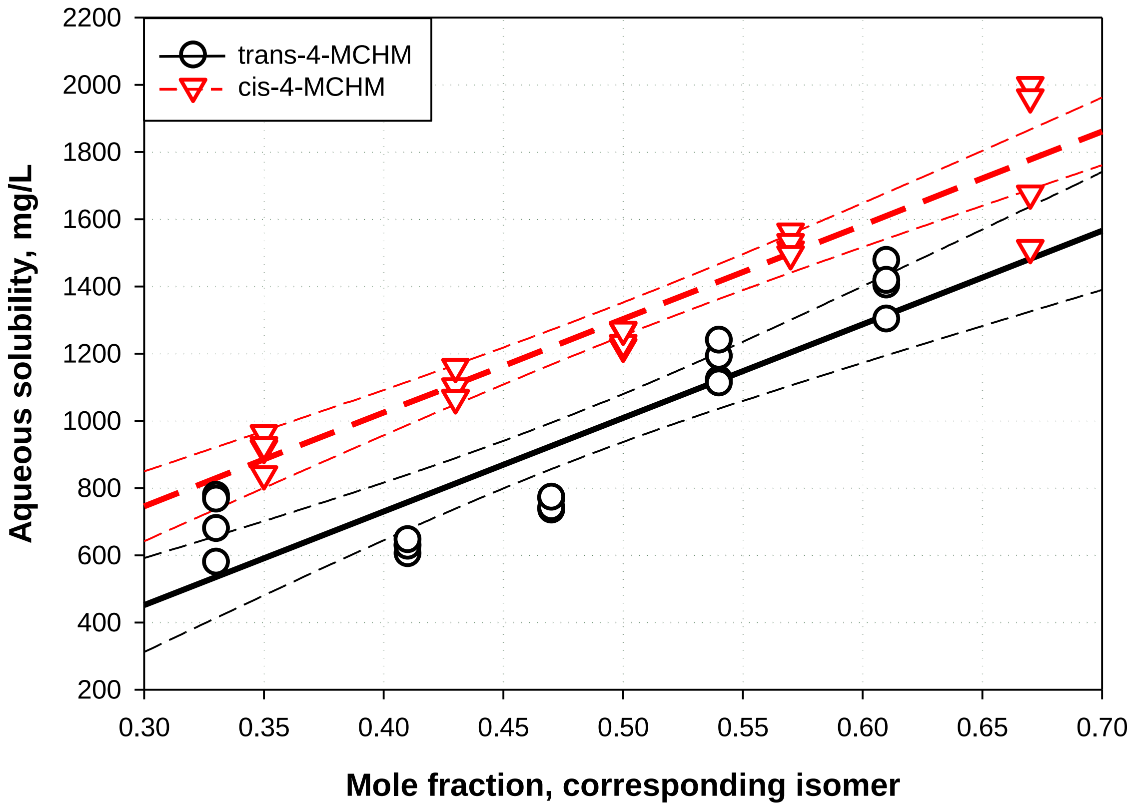

Figure 9 Aqueous solubilities of *cis*- and *trans*-4-MCHM at 23°C are proportional to their individual mole fractions. Thick lines represent regressions. Light dashed lines are corresponding 95% confidence intervals.

Table 3 Physicochemical parameters for (4-methylcyclohexyl)methanol. (Means ± standard error for experimental measurements)

Parameter	MSD Sheet	EPI Suite™ 4-MCHM[1]	*cis*-4-MCHM	*trans*-4-MCHM	Total 4-MCHM
K_{OW}	No data	355	225 ± 1[2a]	291 ± 1[2b]	-
log K_{OW}		2.55	2.35 ± 0.005[2a]	2.46 ± 0.0002[2b]	
Aqueous Solubility					
mg/L, at 23 °C	No data	2024	1300 ± 24[2a,3]	1010 ± 34[2b,3]	2250 ± 50
mg/L, at 4 °C	No data	-	1390 ± 36[2a,3]	1120 ± 32[2b,3]	2430 ± 64
ΔH_w^{ex}, kJ/mol[4]	-	-	-	-	-2.8 ±1.7
ΔS_w^{ex}, J/mol·K[5]	-	-	-	-	76.3 ±5.7
Carbon Loading[6], mg/g	No data	-	12.8 ± 1.1[2a]	26.5 ± 1.2[2b]	-
Dipole Moment					
D, gas phase[7]	No data	-	1.530	1.586	-
D, implicit solvation[8]	No data	-	2.454	2.425	-
Molar Volume, cm^3/mol	No data	-	138.9	138.9	-

[1] EPI Suite™ does not distinguish isomers.[13]

[2] The letters a and b indicate significant statistical difference at α = 0.05.

[3] Values for individual *cis*- and *trans*-isomers presented at mole fraction = 0.5.

[4] $\boldsymbol{\Delta H_w^{ex}}$ = excess enthalpy of aqueous solution calculated from aqueous solubility.[29]

[5] $\boldsymbol{\Delta S_w^{ex}}$ = excess entropy of aqueous solution calculated from aqueous solubility.[29]

[6] Loading on the activated carbon for isomer equilibrium aqueous concentration of 1 mg/L.

[7] MP2 aug-cc-pwCVDZ level of theory.

[8] MP2 aug-cc-pwCVDZ level of theory with SMD.[17,18]

Supporting Information

Partitioning, Aqueous Solubility, and Dipole Moment Data for *cis*- and *trans*-(4-methylcyclohexyl)methanol, Principal Contaminants of the West Virginia Chemical Spill

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Text S1.

METHODS AND MATERIALS

Reagents:
Methanol was OmniSolv methanol (CAS#67-56-1; Spectrum Chemical). Reagent water was produced by Barnstead ultra-purification system. Dichlorodimethylsilane (CAS #75-78-5) and toluene (CAS #108-88-3) were from Sigma-Aldrich. Tetramethylsilane (CAS#75-76-3) and trichlorodeuteromethane (CAS#865-49-6) were from Cambridge Isotope Laboratories.

The eight reference substances for K_{OW} measurement were $\geq$98% purity and included these chemicals from Sigma-Aldrich: benzyl alcohol (CAS#100-51-6); cyclohexanone (CAS#108-94-1); 1-hexanol (CAS#111-27-3); 3-methyl-1-butanol (CAS#123-51-3); 2-methyl-1-propanol (CAS#78-83-1); and toluene (CAS#108-88-3). Hexanal (CAS#66-25-18) was from Alfa Aesar Chemical; 1-octanol (CAS#111-87-5) was from Acros Organics.

NMR:
Samples were transferred into 5 mm OD, 7" NMR tubes (Wilmad Glass). Quantitative ^{1}H NMR data were acquired using the standard 1D pulse sequence with spectral width of 7862 Hz, relaxation delay of 5s, and a total of 64 transients for pure and crude MCHM and 8992 transients for HPLC fractions were averaged. Data were Fourier transformed after multiplying by an exponential window function corresponding to a line broadening of 0.3 Hz. 1D quantitative ^{13}C NMR spectra were recorded with inverse gated proton decoupling using the WALTZ-16 sequence. A total of 1024 transients were averaged, and 65536 data points were acquired for each sample. Line broadening of 1.0 Hz was applied before Fourier transformation.

Reversed Phase HPLC and K_{OW}:
The HPLC instrument was a Shimadzu LCMS-2020 HPLC (Columbia, MD) with Refractive Index Detector (RID), Restek C18 column (250 mm x 2.1 mm id) with 5µm particles (Bellefonte, PA), 10 µL injection volume, and an isocratic methanol/water eluant at 1 mL/min. For K_{OW} determination, the isocratic mobile phase was 75% methanol and 25% water at room temperature. Reference compounds were 10,000 mg/L in methanol; pure 4-MCHM was 7,500 mg/L in methanol. Dead time (t_o) was determined by injecting five 10 µL charges of water and noting the time of sudden change in refractive index. Eight reference substances with reliable K_{OW} values[1] were selected: benzyl alcohol, log K_{OW} 1.05; cyclohexanone; log K_{OW} 0.81; hexanal, log K_{OW} 1.78; hexanol, log K_{OW} 2.3; 3-methyl-1-butanol, log K_{OW} 1.28; 2-methyl-1-propanol, log K_{OW} 0.76; 1-octanol, log K_{OW} 3.07; and toluene, log K_{OW} 2.73. The retention times (t_R) were averaged from 3 replicates for reference compounds and 5 replicates for 4-MCHM. Capacity factors (k) were calculated as $k = [(t_R - t_o)/ t_o]$. The log k and log K_{OW} were plotted for eight reference compounds. From these capacity factors and K_{OW} values of the reference compounds, a regression equation was produced and used to calculate log K_{OW} for *cis*- and *trans*-4-MCHM isomers.

Mole Fractions of *cis*- and *trans*-4-MCHM:
Different mole-fraction ratios of *cis*- and *trans*-4-MCHM were prepared by mixing known masses of pure 4-MCHM and crude MCHM. The mass of *cis*- and *trans*-isomers in the pure 4-MCHM was adjusted for 98% purity and a ratio of 2.08:1 *cis*:*trans*. The mass of *cis*- and *trans*-isomers in the crude MCHM was adjusted for 86.5% of the crude being the *cis*- and *trans*-4-MCHM isomers with a ratio of *cis*:*trans* of 1:1.75. The remaining portion of crude MCHM was water, methanol, and a series of cyclohexane compounds that constituted 5.9% of the mass relative to the mass of *cis*- and *trans*-4-MCHM isomers. A small amount of methanol in commercial crude MCHM would have little co-solvent effect.[2] Other cyclohexane compounds were tentatively identified by GC/MS analysis of a 1000 mg/L solution of crude MCHM;[3] they were also mentioned on the MSD sheet but exact percentages were not provided. The relative percent composition of individual cyclohexanes was determined by comparing areas under the individual peaks to the total area for all cyclohexane compounds including *cis*- and *trans*-4-MCHM. Assuming identical response factors, this yields: 0.65% cyclohexanemethanol; 1.0% *cis*- and *trans*-methyl-4-methylcyclohexanecarboxylate; 0.22% *cis*- and *trans*-4-(methoxymethyl)cyclohexanemethanol; 3.22% *cis*- and *trans*-1,4-cyclohexanedimethanol; and 0.13% dimethyl 1,4-cyclohexanedicarboxylate.

Aqueous Solubility:

Solubility was first determined at 23°C, then 4°C. Vials were inverted, excluded from light, and stirred at 40 rpm. The organic layer was constantly visible at the glass-water interface within the inverted vials. After 72 hours, 250 µL of the aqueous solution were removed using a 500 µL airtight syringe and diluted 100-fold with methanol. Determination of solubility at 4°C consisted of placing the vials from 23°C experiments in a 4°C refrigerator for 7 days. After 7 days, 250 µL of aqueous solution was diluted 100-fold with methanol.

GC-FID Method:

The concentrations of *cis*- and *trans*-4-MCHM were measured by 1 µL splitless injection into gas chromatograph with flame ionization detector (GC-FID; Hewlett Packard 5890 with 7673 autosampler) equipped with a 30 m, 0.53 mm ID Restek RTX 502.2 column and 10 mL/min nitrogen carrier gas. Injector temperature was 250°C. Initial oven temperature was 100°C; ramp rate was 20°C/min. Calibration standards were 0, 1, 5, 10, 15, 25, and 50 mg/L of pure 4-MCHM.

Thermodynamic Quantity Calculations[4]:

The activity coefficient, γ_w^{sat}, is calculated from measured solubility values, C_w^{sat}, at each temperature, following:

$$\gamma_w^{sat} = \frac{1}{\bar{V}_{\mathrm{H_2O}}\, C_w^{sat}}$$

where $\bar{V}_{\mathrm{H_2O}}$ is the molar volume of water (0.0180 L mol^{-1}). γ_w^{ex} values for total 4-MCHM of 3.2 (± 0.07) ×10^3 and 2.9 (± 0.08) ×10^3 were obtained for 23 and 4°C, respectively.

From the activity coefficients, the excess free energy of aqueous solvation, ΔG_w^{ex}, can be determined using:

$$\Delta G_w^{ex} = RT\, \ln(\gamma_w^{sat})$$

ΔG_w^{ex} values for total 4-MCHM of 19.8 ± 0.06 and 18.4 ± 0.06 kJ/mol were obtained for 23 and 4°C, respectively.

The excess enthalpy of aqueous solution, ΔH_w^{ex}, can be obtained from solubility data at multiple temperatures using:

$$\ln(C_w^{sat}) = -\frac{\Delta H_w^{ex}}{RT} + \text{ constant}$$

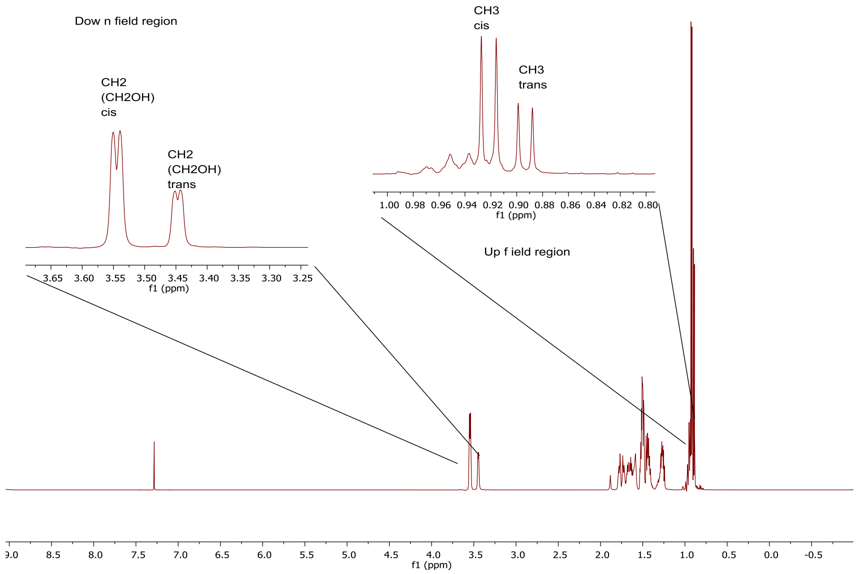
ΔH_w^{ex} is obtained from the slope of a graph of $\ln(C_w^{sat})$ vs. $\frac{1}{T}$. Using this approach, the ΔH_w^{ex} value for total 4-MCHM is -2.8 ± 1.7 kJ/mol. An intentionally conservative error estimate is given here in part because only two data points are available for this linear data fit.

The excess entropy of aqueous solution, ΔS_w^{ex}, is then calculated from ΔG_w^{ex} and ΔH_w^{ex}: $\Delta G_w^{ex} = \Delta H_w^{ex} - T\Delta S_w^{ex}$. Our estimate of ΔS_w^{ex} for total 4-MCHM is -76.3 ± 5.7 J/mol·K.

Table S 1. ^{1}H NMR (600 MHz) chemical shifts and coupling constants of samples in $CDCl_3$ at 25°C.

Samples	Up field doublet				Down field doublet			
	cis		*trans*		*cis*		*trans*	
	δ (ppm)	$^3J_{H-H}$ (Hz)	δ (ppm)	$^3J_{H-H}$ (Hz)	δ (ppm)	$^3J_{H-H}$ (Hz)	δ (ppm)	$^3J_{H-H}$ (Hz)
Pure 4-MCHM	0.92	7.0	0.89	6.6	3.55	6.6	3.45	5.3
Crude MCHM	0.92	6.9	0.89	6.6	3.54	6.8	3.45	6.4
HPLC peak 1	0.90	6.9	-	-	3.55	6.9	-	-
HPLC peak 2	-	-	0.89	6.5	-	-	3.47	6.4

a. Pure 4-MCHM



b. Crude 4-MCHM

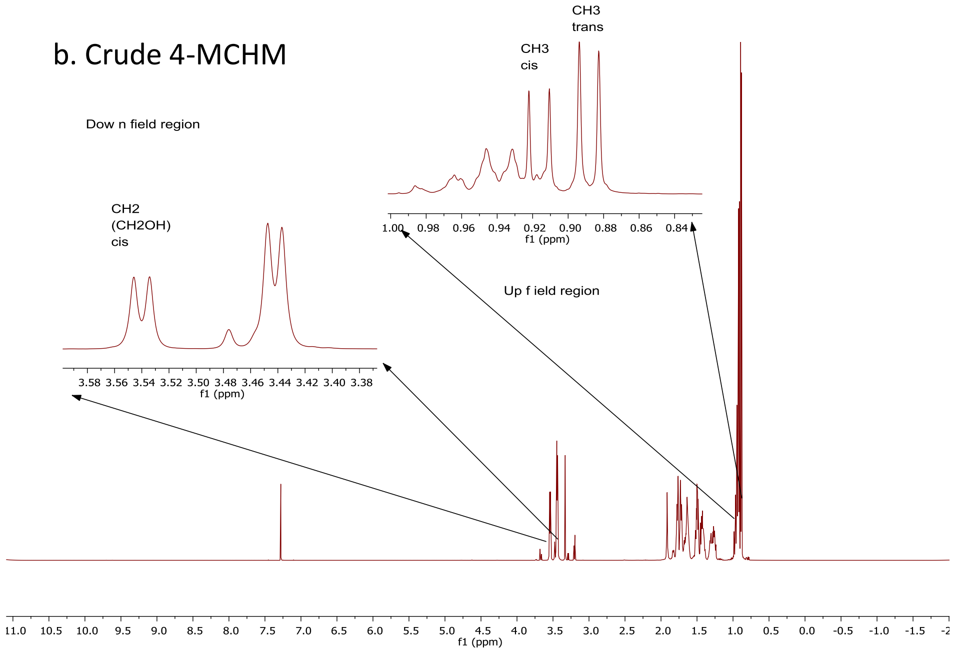


Figure S 1. 1-Dimensional ^{1}H NMR (600 MHz) of (a) pure 4-MCHM and (b) crude MCHM in $CDCl_3$.

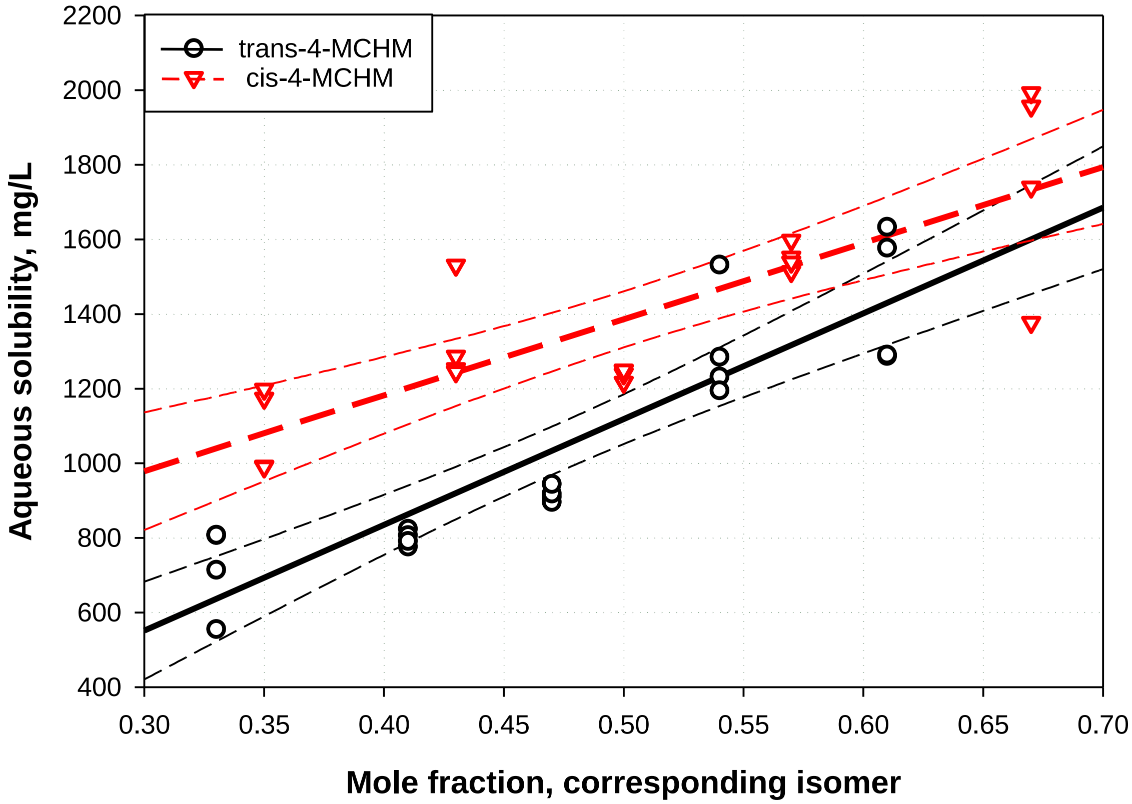


Figure S 2. Aqueous solubilities of *cis*- and *trans*-4-MCHM at 4°C are proportional to their individual mole fractions.

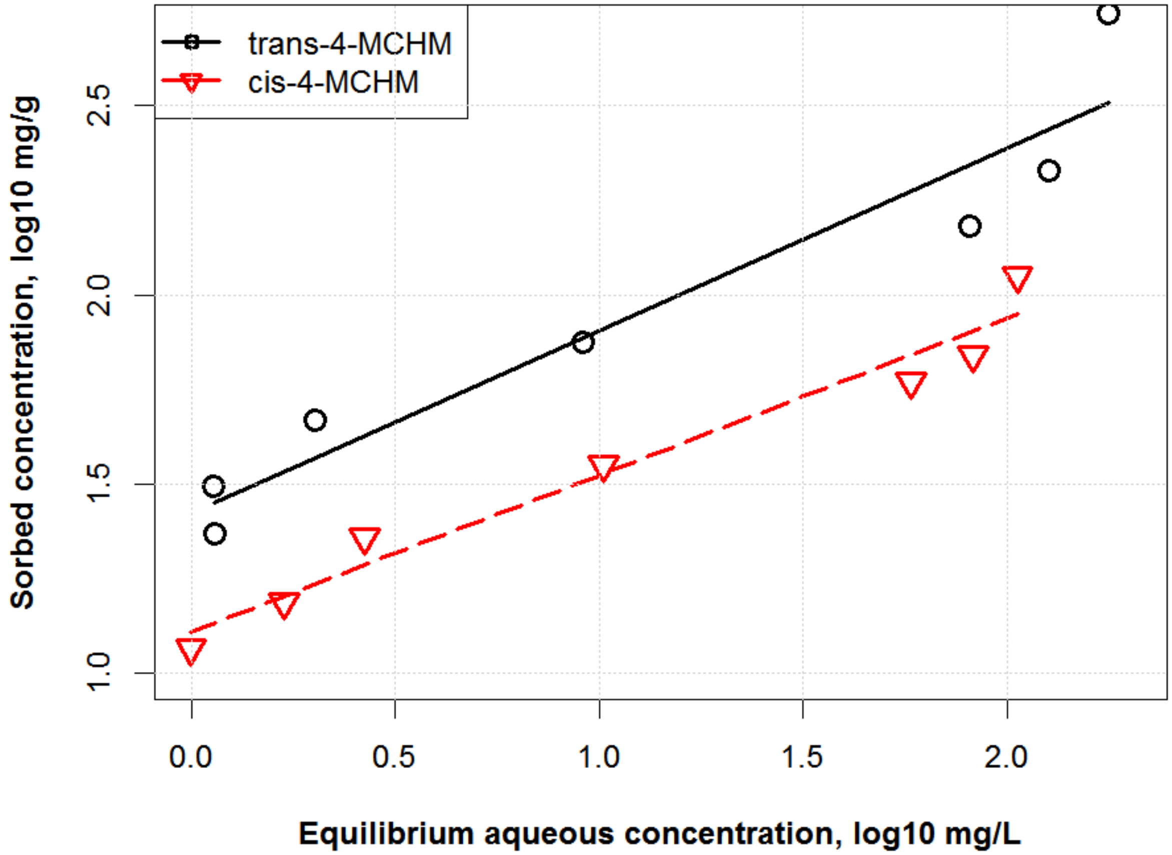


Figure S 3. Freundlich isotherm demonstrating that the *trans*-4-MCHM was better sorbed to a commercial granular activated carbon. The regression equations are: *cis*-4-MCHM: y = 0.42 x + 1.11; R^2 = 0.96; *trans*-4-MCHM: y = 0.48 x + 1.42; R^2 = 0.92. The regression equations are statistically different in y-intercept but not slope.

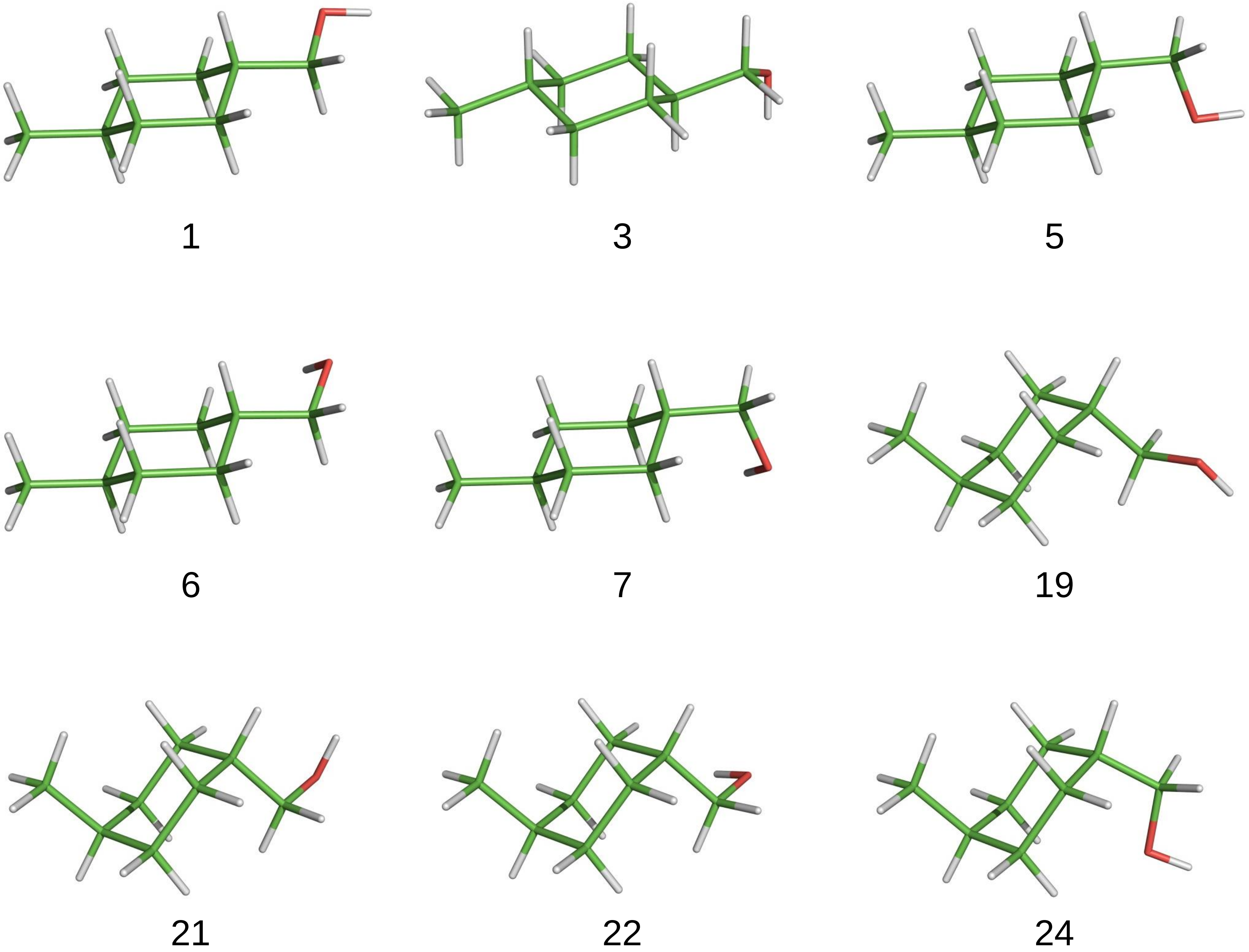
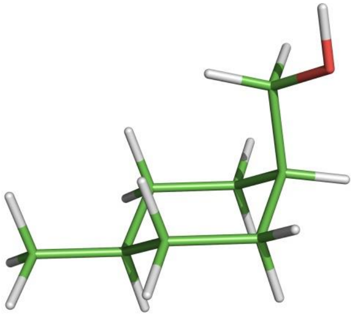


Figure S 4. 3D structures of *trans*-4-MCHM conformers and their conformer ID #



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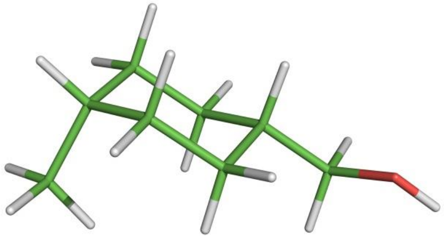

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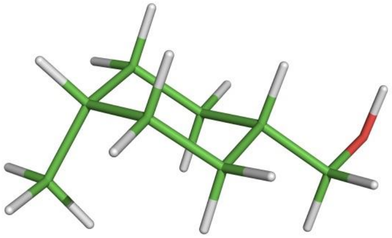

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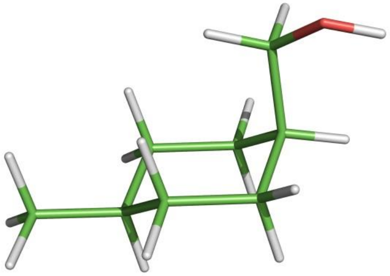

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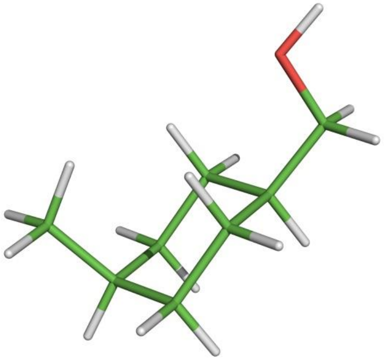

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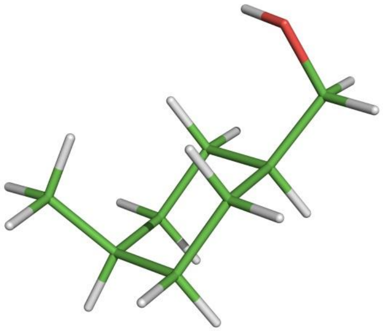

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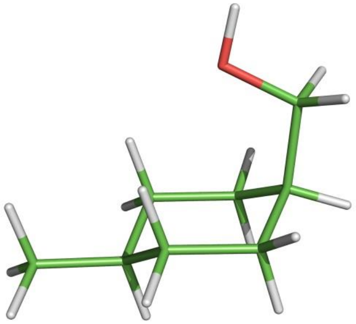

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Figure S 5. 3D structures of *cis*-4-MCHM conformers and their conformer ID #

Table S 2. Molecular properties of *trans*-4-MCHM and *cis*-4-MCHM conformers. Free energies are given in Hartree, relative free energies in kcal mol^{-1}, dipole moments in Debye, computed molecular volumes in cubic Angstroms, and empiricized molar volumes in cm^{-3} mol^{-1}.

Conformer #[a]		Degeneracy	G(gas)	ΔG(gas)	Dipole moment (gas)[b]	G(soln)	ΔG(soln)	Dipole moment (soln)[b]	Molecular volume (soln)	Molar volume (soln)[c]
1	*trans*	2	-388.664779	0.00	1.4727	-388.671797	0.10	2.3336	135.15	139.85
6	*trans*	1	-388.664463	0.20	1.8821	-388.671956	0.00	2.5671	135.02	139.71
3	*trans*	2	-388.664483	0.19	1.6459	-388.671853	0.06	2.4609	135.15	139.85
5	*trans*	1	-388.664292	0.31	1.4451	-388.670699	0.79	2.2348	135.08	139.78
7	*trans*	1	-388.663903	0.55	1.6195	-388.671294	0.42	2.4232	135.06	139.75
15	*cis*	2	-388.662000	1.74	1.7292	-388.669379	1.62	2.5951	135.17	139.86
9	*cis*	2	-388.662126	1.66	1.3469	-388.668862	1.94	2.2155	135.02	139.71
11	*cis*	2	-388.661776	1.88	1.3398	-388.668850	1.95	2.1940	135.00	139.70
16	*cis*	1	-388.661545	2.03	1.4478	-388.667614	2.72	2.2745	135.08	139.78
13	*cis*	2	-388.661491	2.06	1.7748	-388.669137	1.77	2.6121	135.06	139.75
17	*cis*	1	-388.661073	2.33	1.7295	-388.668787	1.99	2.5908	134.96	139.65
23	*cis*	1	-388.659424	3.36	1.7237	-388.665329	4.16	2.4266	135.53	140.23
21	*trans*	2	-388.658715	3.81	1.6064	-388.665867	3.82	2.4537	135.08	139.78
19	*trans*	2	-388.658808	3.75	1.4333	-388.665668	3.95	2.3652	135.12	139.82
22	*trans*	1	-388.658214	4.12	1.7024	-388.665988	3.74	2.5740	135.06	139.76
24	*trans*	1	-388.656036	5.49	1.6452	-388.661528	6.54	2.3064	135.08	139.77

[a] Conformer number is based on the energetic ordering provided by the MOE conformational search, using the MMFF94 force field.

[b] Dipole moments reported in Table 2 of the main text refer to a Boltzmann-average over the individual conformer-specific dipole moment values listed here. For conformationally Boltzmann-averaged properties**:** For each isomer having m conformers, the fractional abundance of individual conformer F_j is based on the free energy difference between conformer, j, and the most stable conformer, ΔG_j , and is expressed as

$$F_j = \frac{\omega_j \exp(-\frac{\Delta G_j}{kT})}{\sum_{i=1}^{m} \omega_i \exp\left(-\frac{\Delta G_i}{kT}\right)}$$

where we have set T = 298.15 K, k is the Boltzmann constant, and ω_i is the degeneracy of conformer i. The final conformationally Boltzmann-averaged dipole moment, μ, is then calculated by taking the sum of the dipole moments of the individual conformers, μ_i, weighted by their fractional abundance.

$$\mu = \sum_{i=1}^{m} F_i \mu_i$$

An analogous treatment is applied for all of the Boltzmann-averaged properties mentioned in this work.

[c]The molecular volume from the second set of data of “GePol: Cavity volume” within the Gaussian output file was used to calculate the molar volume. This second set of data uses a smaller number of vertices to generate the tesserae which defines the molecular surface. All other default parameters were used along with Pauling atomic radii. The molecular volume is converted to molar volume after multiplying by 1.718 * (1.0 x 10^{-8} cm)^3 Å^{-3} * 6.023 x 10^{23} molecules/mol.[5-7]

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