OBSCURE CHEMICAL TAINTS WATER SUPPLY

Chemical contamination of West Virginia **DRINKING WATER** system raises scientific, policy shortcomings

ALEXANDER H. TULLO, C&EN NORTHEAST NEWS BUREAU; JYLLIAN KEMSLEY, C&EN WEST COAST NEWS BUREAU; CHERYL HOGUE & SUSAN R. MORRISSEY, C&EN WASHINGTON

WEST VIRGINIA GOV. EARL RAY TOMBLIN gave the 300,000 residents of Charleston unwanted and unexpected news on Jan. 9. Their water was tainted with an obscure chemical used in coal processing. He ordered them to stay away from their taps.

"I learned about the water contamination from watching the announcement on TV at about 6 PM," recalls Juliana Serafin, an assistant professor of chemistry at the University of Charleston. She was worried. She'd taken a shower that afternoon after her regular 4-mile run. Her daughter had drunk a huge cup of hot tea.

But other than a slight black-licorice odor in her laundry room, she says, "neither of us noticed anything unusual." This telltale smell, in fact, was reported by many residents earlier in the day and led to officials discovering the contamination.

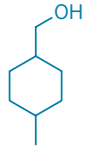
In any case, Serafin headed out to the grocery to buy bottled water.

"There was no regular water left, but I was lucky enough to get three 2-L bottles of club soda," she says. "We started eating off paper plates. And I successfully made coffee with club soda."

Another West Virginia resident, Mark Darcy, a manufacturing process chemist at

DRINKING WATER CRISIS UNFOLDS

Jan. 9 Leak Detected Chemicals leak from a storage tank into the Elk River, tainting the drinking water of 300,000 people in the Charleston, W.Va., area. Initial 4-methylcyclohexanemethanol (MCHM) volume estimate is 2,000 to 5,000 gal.



MCHM

Left, tank 396 is the one that leaked MCHM. Below, people wait in line on Jan. 10 for bottled water.

8:15 AM Residents complain of black licorice odor → **10:30 AM** Freedom Industries employees discover leak → **11:15 AM** State officials find crude MCHM tank leaking at Freedom site → **6 PM** Governor announces water ban

Jan. 10 Sampling Begins Initial water testing shows 1.04 to 3.35 ppm MCHM at the West Virginia American Water intake on the Elk River and 1.02 to 1.56 ppm MCHM in treated drinking water. The Centers for Disease Control & Prevention says 1 ppm in drinking water is unlikely to be associated with adverse health effects.

Jan. 15 More Warnings Issued CDC and the West Virginia Bureau for Public Health say that pregnant women, "out of an abundance of caution," may wish to avoid drinking tap water until MCHM levels are not detectable.

Jan. 18 Most Restrictions of Water Use Lifted West Virginia American Water lifts water use restrictions for last of affected households, but suggestion for pregnant women to avoid drinking the water remains.

Jan. 11 Volume of Spill Revised Upward Spill estimate is revised to 7,500 gal.

Jan. 13 Household Water Restrictions Lifted West Virginia American Water instructs some households to begin flushing pipes and clears use of municipal water without restrictions.

On Jan. 13, water was tested as it was flushed in a restroom at the State Capitol in Charleston.

Jan. 16 Toxicity Data Disclosed Eastman Chemical publicly releases toxicology studies on crude and pure MCHM.

Jan. 17 Bankruptcy Declared Freedom Industries files for Chapter 11 bankruptcy.

a local chemical plant, found out about the water ban on his way home from work.

The first thing Darcy did when he got home was try to find out the name of the chemical, he tells C&EN. It turned out to be crude 4-methylcyclohexanemethanol (MCHM). "That doesn't sound fantastically hazardous," Darcy recalls thinking. But after pulling up the chemical's safety data sheet, "I figured I wouldn't want to drink it," he says.

State officials referred to the same document, but it contains little toxicity information, leaving them in the dark about the threat posed by the water contamination. This situation has since raised many questions with lawmakers and the public about the chemical as well as other substances later disclosed to be blended with it. The questions vary from what these chemicals are used for to why more toxicity information about them isn't available.

THE BAN ON USING TAP WATER for everything from drinking to washing lasted more than a week for some residents. As of C&EN press time, the federal Centers for Disease Control & Prevention (CDC) continued to say that "out of an abundance of caution," pregnant women living in the affected area might want to avoid drinking the tap water. At a House of Representatives hearing held on Feb. 10 in Charleston, federal lawmakers repeatedly quizzed state and local water and health officials about whether the water was safe to drink. But the state and local officials hesitated to say with certainty that it was. Meanwhile, some residents are sticking to bottled water.

The chemicals entered the water supply when a tank storing crude MCHM leaked into the Elk River. The tank, owned by Freedom Industries, is located about 1.5 miles upstream from the intake pipe for Charleston's water supply system.

It remains unclear when the leak started, but Freedom determined that some 10,000 gal of material had escaped from the storage tank.

On Jan. 17, Freedom filed for Chapter 11 bankruptcy. In its bankruptcy documents, Freedom hypothesizes that a water line break saturated the ground beneath the storage tank, which then froze, leading to the rupture of the tank. The state has ordered Freedom to dismantle all the chemical storage tanks and their associated piping and machinery at the site.

Freedom disclosed to the West Virginia Department of Environmental Protection in the wake of the spill that the tank contained by weight 88.5% crude MCHM, which is a blend containing 68 to 89% MCHM along with other chemicals; 7.3% Dowanol PPh, Dow Chemical's brand of propylene glycol phenol ether; and 4.2% water.

According to CDC, however, the component Freedom cites as Dowanol PPh is a blend of PPh and a high percentage of dipropylene glycol phenyl ether (diPPh). Because there have been more toxicity studies on PPh, CDC is using it as a proxy for the blend. The screening limit calculated for PPh should also work for diPPh, the agency says.

Eastman Chemical, which manufactured the crude MCHM that leaked from the tanks, won't provide many details regarding how it makes MCHM. However, published references suggest that it is a coproduct of the hydrogenation of the polyester raw material dimethyl terephthalate into cyclohexanedimethanol, which Eastman uses to make high-performance polyester copolymers. Eastman notes on the safety data sheet for crude MCHM that the mixture contains between 1 and 2% cyclohexanedimethanol. This small percentage of cyclohexanedimethanol suggests that the two chemicals are manufactured in tandem.

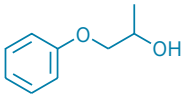
MCHM, A COPRODUCT of a little-known specialty chemical, is about as obscure as a petrochemical can be. Had it not been for the incident in West Virginia, it likely would have remained relatively unheard of, familiar primarily to technicians who operate froth floating lines at coal processing plants.

And that isn't a particularly large group. Only about 10% of coal runs through the froth flotation process, says S. Komar Kawatra, a professor of chemical engineering at Michigan Technological University. The process is mostly used to purify residual material that is left after bituminous coal has been mechanically processed and gravel-sized chunks are separated out.

The leftover coal particles, most less than 1 mm in diameter, are wetted into a slurry, which is fed into a flotation cell. Air

ASSOCIATED PRESS (STORAGE TANK, PEOPLE IN LINE, STATE CAPITAL); COURTESY WEST VIRGINIA UNIVERSITY (WEST VIRGINIA WATER RESEARCH INSTITUTE

Jan. 21 Contents of Tank Clarified Freedom Industries reports that the leaking tank contained a second chemical, a proprietary mixture primarily composed of propylene glycol phenyl ether (PPh). CDC reports this mixture to contain dipropylene glycol phenyl ether (diPPh). The PPh mixture accounted for 7.3% of the tank's content by weight.



PPh

Researchers from West Virginia Water Research Institute collect soil and water samples from the Elk River.

Jan. 23 Testing of Additional Chemicals Begins Water testing begins for PPh and diPPh; testing includes stored water samples going back to Jan. 10. All samples fall below CDC's screening limit of 1.2 ppm.

Jan. 27 Volume of Spill Revised Upward Again Freedom Industries revises spill estimate to 10,000 gal of crude MCHM and PPh blend.

Jan. 30 Federal Grants Issued To Study Spill The National Science Foundation announces Rapid Response Research grants to study the chemical spill.

Jan. 31 Second MCHM Spill Reported Freedom Industries reports that another crude MCHM release occurred when cleanup crews severed an underground pipe; the spill was contained before it reached the river.

Feb. 3 Toxicity Information for Other Chemicals Released CDC releases a summary report on toxicology studies of PPh and diPPh.

Feb. 5 CDC Gives All Clear CDC says water is safe for everyone, including pregnant women, to drink. MCHM smell persists in water.

bubbles in the flotation cell attach to the hydrophobic coal particles, lifting them to the surface. Hydrophilic impurities such as silica, pyrite, and clay—which would form ash if burned—remain in the liquid phase. The wastewater is either recycled or sent to tailing ponds.

Plant technicians use chemicals called frothers in the process, and crude MCHM and Dowanol PPh belong to this category. Frothers are surfactants that reduce the surface tension of water to stabilize and moderate the size of the air bubbles, according to Timothy C. Eisele, a professor of chemical engineering at Michigan Tech. Most frothers are aliphatic alcohols. A commonly used frother is methyl isobutyl carbinol. MCHM, Eisele says, is "just another alcohol frother."

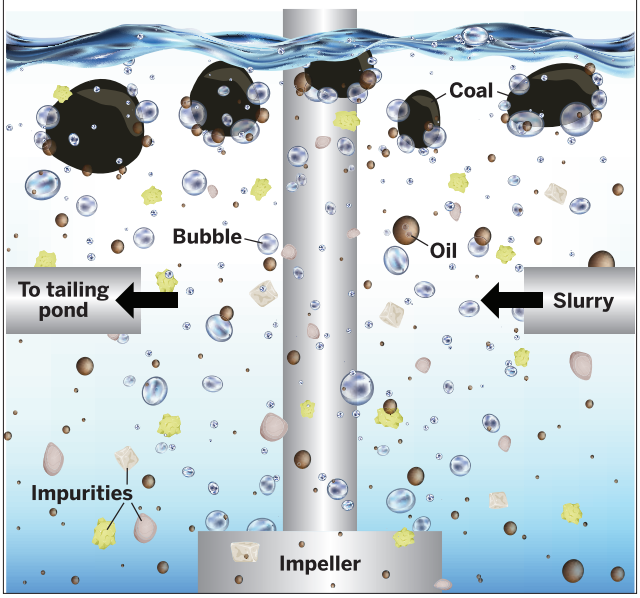
Froth flotation has been around for about 100 years, and methyl isobutyl carbinol has been used for about 70 years. MCHM is a relative newcomer to the process, Eisele says. In fact, water treatment specialist Nalco Chemical was granted a patent on using MCHM in froth flotation in 1990. The patent pitched MCHM as an environmentally friendly alternative to 2-ethyl hexanol.

Unlike MCHM, Dowanol PPh is used by many industries. Dow makes this chemical by reacting propylene oxide and phenol. It is primarily used as a solvent and coalescing agent in applications such as textiles, metal-working fluids, and coatings. It is also found in household and industrial cleaners. DiPPh is a by-product of Dow's process for making Dowanol PPh. Blends incorporating the chemical are used as fuels and in mining.

Despite its relatively recent application in coal processing, MCHM was in commercial production in 1976 when Congress passed the Toxic Substances Control Act (TSCA), the primary federal law governing industrial chemicals. Lawmakers "grandfathered" MCHM and some 62,000 other commercial chemicals then being made in the U.S. This exempted the compounds from the Environmental Protection Agency review required for new substances before they are sold on the market.

MCHM also was not among the 2,200 high-production-volume substances for which the chemical industry generated basic toxicity data under a voluntary program launched in 1998. The High Production Volume (HPV) Challenge Program, founded by EPA, the industry trade group American Chemistry Council, and the activist group Environmental Defense Fund, focused on chemicals produced in amounts of 1 million lb or more per year.

SKIMMING THE TOP Froth flotation tanks are used to purify residual coal material generated during coal processing. Bubbles introduced in the tank attach to hydrophobic coal particles, forcing them to the surface. Hydrophilic impurities such as silica, pyrite, and clay remain in the mixture. Plant operators add chemicals to the slurry to assist in the froth flotation process. One type of chemical is a collector, which coats the hydrophobic material to be separated so the air bubbles attach better. The coal industry largely uses No. 2 oil for this purpose. Another type of chemical is added to the slurry to reduce water surface tension in order to stabilize and moderate the size of the air bubbles. These chemicals include MCHM and PPh.



The program called for studies to be conducted to determine physical constants, environmental fate, and toxicity data. These studies have been estimated to cost thousands to millions of dollars for each substance, depending on which tests were conducted.

Although Eastman says it has manufactured between 5 million and 10 million lb of crude MCHM per year in the past decade, that wasn't the case when the HPV voluntary program began. EPA filings show that production of the substance didn't exceed 1 million lb per year until 2002, says Richard Denison, a senior scientist and TSCA expert with the Environmental Defense Fund.

Eastman's ramp-up of MCHM output may be the result of a doubling of capacity for cyclohexanedimethanol by the company in 2006. Eastman expanded capacity by another 25% in 2010.

Some information on the safety of MCHM does exist. After the leaked compound was identified, Eastman voluntarily released data it had from a suite of toxicity tests on both pure and crude MCHM. The company had conducted the tests in the late 1980s and '90s to evaluate short-term risks to its workers who might be exposed to the substance.

As the company pursues commercialization of products, it puts them through a regulatory and toxicity review, explains Clark Jordan, Eastman's vice president and assistant general counsel for global trade and compliance. As part of that review, the company evaluates the product's intended use, the geographic location where it will be sold, what regulatory requirements must be met, what is known about physical and toxicological hazards, and possible exposure based on how a substance will be used and in what volume.

The firm then decides what testing it will do. Eastman generally looks to have data from acute oral, dermal, eye, and mutagenicity studies, Jordan says.

From the results, "we determine what recommendations we want to make on employee personal protective equipment, inhalation risk, or other factors that we would want our employees and those of our customers to consider," he says. He was not involved in the MCHM decisions so could not comment on them specifically.

THE STUDIES Eastman conducted on pure and crude MCHM included both environmental and human exposure. The environmental studies involved exposure of two freshwater aquatic species, neonatal fleas and juvenile fathead minnows, as well as biodegradation. The tests followed routine protocols that are still standard today,

comments Ronald Tjeerdema, a professor of environmental toxicology at the University of California, Davis.

The minnow and water flea studies showed that crude MCHM is moderately toxic to those organisms, Tjeerdema says. Crude MCHM proved to be not readily biodegradable in a solution of microbes extracted from wastewater treatment sludge but still showed more than 50% degradation after 28 days, Eastman's study report says.

"That's pretty good," Tjeerdema says. "Most microbial activity is in sediment, not in water, so to get that kind of degradation in water is not bad." He notes, however, that microbial degradation would likely be lower in a cold West Virginia river in January.

A MUTAGENICITY TEST, commonly called the Ames assay, was also done by Eastman to look at the ability of crude MCHM to cause genetic mutations in strains of bacteria engineered to be particularly susceptible to DNA damage. Crude MCHM did not induce mutations in tests the company conducted.

Additionally, Eastman performed a series of acute oral, dermal, and eye toxicology tests on rats, guinea pigs, and rabbits using both pure and crude MCHM. As with the environmental tests, the toxicology protocols are still routinely used, although toxicologists are trying to validate new methods to reduce the use of animals, says Sharon Meyer, a professor of toxicology at the University of Louisiana, Monroe. The longest exposure was a 28-day oral toxicity study of pure MCHM in rats. For an industrial chemical not intended to be a pesticide, Meyer says that the set of tests would be fairly standard, with the addition of a 90-day oral study.

Overall, the mammalian studies showed that pure and crude MCHM are skin and eye irritants. "You don't want to shower in water with substantial concentrations of it," Meyer says, adding that "rashes are a definite possibility."

The irritant effects also may have caused gastrointestinal damage in rats dosed orally. Stumbling and weakness observed in rats after oral or high dermal dosing may have been an effect common to organic liquids. Pure and crude MCHM both showed low systemic toxicity.

The *Charleston Gazette* reported on Jan. 18 that some area residents were experiencing rashes, mild burns, and stomach upset after contamination of their water supply. A Jan. 18 news release from the governor's office suggested that some effects could be from sediment stirred up in pipes and hot-water tanks as water systems were flushed to remove MCHM so people could resume using the water.

As for longer-term or inhalation studies on MCHM, "we would not normally conduct chronic testing on a chemical of this nature, given the type of environment in which it was expected to be used," Eastman's Jordan says. The company also did not see it as posing a significant inhalation risk, he adds.

But Denison of the Environmental Defense Fund says he is surprised that Eastman did not do toxicity testing using inhalation as a route of exposure. The company conducted tests for a chemical used in workplace settings, and workers would

most likely be exposed to crude MCHM on their skin or by inhaling it, Denison says.

"Conducting an inhalation exposure is more challenging than oral exposures," comments toxicologist Meyer. Material can be inhaled either as a vapor or an aerosol, she says. Inhalation studies require housing test animals in a special apparatus that may deliver airborne material to just the head and nose or to the whole body of individual animals. The atmosphere in the test chambers should be monitored to ensure consistent and known exposure, she adds.

Inhalation aside, Eastman's studies do not touch on a key toxicity end point of concern to officials managing the drinking water contamination: how crude MCHM might affect babies and fetuses, says Jennifer Sass of the Natural Resources Defense Council, an environmental group.

CDC used the results of the 28-day study of pure MCHM in rats to determine that a concentration of 1 ppm or less in drinking water was unlikely to produce adverse health effects. The 28-day study found that a daily dose of 100 mg pure MCHM/kg body weight produced no observed effects in rats.

To get from there to 1 ppm for drinking water, the agency combined 100 mg/kg with the weight of a small child, 10 kg (22 lb), and the estimated water intake of a child (1 L/day). Then it applied three 10-fold reduction factors to account for differences between rats and humans, people who might be more sensitive to MCHM, and the limited amount of data available. This reduction is fairly conservative, Meyer says.

Initial water tests done in West Virginia on Jan. 10 showed 1.04 to 3.35 ppm MCHM at the water system intake on the Elk River, and 1.02 to 1.56 ppm in treated water. West Virginia American Water, the Charleston area utility, lifted the "do not use" order after flushing the distribution system and testing showed MCHM levels below 1 ppm. The utility instructed residents to flush their pipes for 25 minutes before using the water.

Toxicology information evaluated by CDC on another component of the spill, PPh, indicates that the chemical is less toxic than MCHM. The studies on PPh included a maternal toxicity study in rats that yielded a no-observed-adverse-effect limit of 40 mg PPh/kg body weight/day. CDC used that limit combined with the body weight and water consumption of a pregnant woman and the same uncertainty reduction factors to set a screening level of 1.2 ppm for PPh in drinking water.

Testing of stored water samples showed 0.01 ppm PPh in two samples from Jan. 10 and from Jan. 11; PPh was not detected in other water sampling through Feb. 9. The limit of detection was 1.2 ppm or 10 ppb, depending on the lab that did the analysis.

The lack of publicly available toxicology data on MCHM illustrates why TSCA is in dire need of modernization, critics say. Timely access to accurate toxicity information on commercial chemicals is essential to inform and protect the public, Natural Resources Defense Council's Sass says.

Eastman did provide full copies of its MCHM studies to government agencies and emergency responders within 24 hours of their requests, Jordan says. But under TSCA, there is no requirement for chemical makers to submit such data to EPA unless test results indicate that a substance might pose a substantial risk of injury to human health or the environment.

The Freedom site is regulated under the Clean Water Act, the statute that limits the amount of pollution that may enter waterways such as the Elk River. The facility had a permit—issued by West Virginia—that required the company to report on chemicals found in precipitation running off the site. It was also supposed to file a spill prevention plan with the state but apparently never did. The Center for Effective Government, a Washington, D.C., watchdog group, points out that MCHM is not on the list of chemicals that trigger notification to EPA when a substance is spilled into waterways.

Two other key federal environmental laws don't apply to MCHM.

The substance is not among the commercial chemicals covered under the Emergency Planning & Community Right-To-Know Act. This means Freedom wasn't required to inform local emergency responders that it was storing MCHM. Plus, the chemical isn't on the right-to-know law's Toxics Release Inventory. Companies must report environmental releases of chemicals on that list to EPA each year.

Likewise, MCHM isn't regulated under the law that requires monitoring of and sets limits on specific contaminants in municipal water, the Safe Drinking Water Act. That means West Virginia American Water isn't legally required to check for MCHM in the municipal water it provides.

FOR THE TIME BEING at least, testing for MCHM in the Charleston area's tap water continues. Traces continue to turn up, such as 0.013 to 0.018 ppm in a sample taken from an elementary school drinking fountain on Feb. 10. News reports say that some residents and employees at other local schools still report being able to smell the characteristic licorice smell of MCHM.

Louisville Water, which serves an area in Kentucky downstream from the leak on the Ohio River, conducted a study of MCHM using a taste and odor panel. The utility knew the crude MCHM was coming and had time to put in place measures that ensured the concentration of the chemical in drinking water was minimized. The utility found that some members of the panel could detect MCHM in concentrations as low as 1 ppb, says spokeswoman Kelley Dearing Smith.

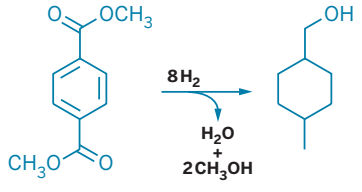
It is unclear how long traces of MCHM will remain in the tap water feeding into Charleston residents' homes. Gov. Tomblin stated on Feb. 5 that, despite the all clear the state issued to residents to use tap water, testing of the water supply for MCHM and PPh will continue.

State and federal officials' ability to give the public clear direction is hampered by a lack of data about how the leaked chemicals absorb onto water piping systems. To help fill in that knowledge gap, the National Science Foundation awarded $150,000

"The experience reminds you just how little data there are about so many of the chemicals that we use."

FORMATION

4-Methylcyclohexanemethanol (MCHM) is made via hydrogenation of the polyester raw material dimethyl terephthalate (DMT).



in Rapid Response Research grants to three groups in late January.

ONE OF THOSE GROUPS, led by Andrea M. Dietrich, a professor of civil and environmental engineering at Virginia Tech, will first determine basic physical-chemical characteristics of MCHM that predict the chemical's fate and transport in the environment. This includes finding the chemical's solubility in water; its Henry's law constant, which determines how much will evaporate into air; and its octanol-water partition coefficient, which describes how well the substance partitions into living tissue or organic materials such as plastic pipes. The team also plans to evaluate sorption and uptake of MCHM by epoxy materials used to line water pipes and storage tanks.

Andrew J. Whelton, an environmental engineering professor at the University of South Alabama, is leading a second team that is studying the absorption of MCHM into different pipe materials and whether flushing can remediate contaminated plastic. He estimates that the contaminated water stagnated in pipes for four to seven days when the community was told not to use it. It's likely that pipes absorbed MCHM, possibly leading to long-term, low-level exposure as it leaches out.

Outside the NSF-funded work, Whelton's group has sampled water in Charleston-area homes and plans to return to do follow-up sampling. Whelton is particularly interested to see how much MCHM turns up in three houses on a dead-end street, all drawing from the same water main but each piped with different materials. His field effort is as yet unfunded, and he is trying to raise money for the work through the crowdfunding website Experiment.com.

The third group funded by NSF will look at short- and long-term fate of MCHM in the water treatment and distribution system and in the river. The team is led by Jennifer Weidhaas, a professor of civil and environmental engineering at West Virginia University. Part of the project involves water sampling to understand how well the flushing protocol worked, as well as examining in detail what happens to crude MCHM and PPh as they go through the drinking water treatment system. The ultimate goal of the work is to help develop better response plans for future disasters, Weidhaas says.

The results of such research can't come fast enough for those affected by the contamination.

"The experience reminds you just how little data there are about so many of the chemicals that we use," process chemist Darcy notes.

Given that dearth of data, it's shocking that Freedom Industries paid so little attention to basic spill containment protocols, says Madan Bhasin, chief scientific adviser at Mid-Atlantic Technology, Research & Innovation Center, a nonprofit research company.

"Everywhere I've worked in the chemical industry safety is the primary concern," Darcy adds. "These guys weren't doing that at all. Fortunately, they've been shut down."

With additional reporting by Amanda Yarnell and Jeff Johnson