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TAP WATER AND INDOOR AIR CONTAMINATION DUE TO AN UNINTENTIONAL CHEMICAL SPILL IN SOURCE WATER

PINAR OMUR-OZBEK[1], DUYGU AKALP[2], and ANDREW WHELTON[3]

[1]*Dept of Civil and Environmental Engineering, Colorado State University, Fort Collins, USA*
[2]*Dept of Construction Management, Colorado State University, Fort Collins, USA*
[3]*Dept of Civil, Environmental and Ecological Engineering, Purdue University, Lafayette, USA*

A chemical storage tank was found leaking into the Elk River, West Virginia, on January 9, 2014. The tank held ~10,000 gallons (38,000 L) of 4-methylcyclohexanemethanol (MCHM). The chemical spilled 2.4 km away from the West Virginia American Water's (WVAW) Kanawha Valley Water Treatment Plant, traveling downstream and entering the treatment plant (50 MGD). West Virginia Poison Center started to get phone calls from the public, concerned about nausea, vomiting, diarrhea, rashes, and other symptoms. Simultaneously, the emergency departments observed an increase in the visit rates to emergency rooms, which were related to the above-mentioned symptoms. It was determined that the chemical spill ended up in the tap water and started affecting the people who used the tap water and inhaled the contaminated indoor air due to tap water use. This study employed available shower, tap water use at the sink, washing machine and dishwasher models and the reported tap water concentrations for the MCHM to determine the indoor air concentrations of MCHM. The results indicated that the exposure to hazardous levels of MCHM is most likely through showering and while during flushing out of the home plumbing. This study also considered natural and forced ventilation to provide guidance while flushing the home plumbing as it plays a critical role in indoor air concentrations of MCHM.

Keywords: 4-methylcyclohexane methanol (MCHM), Drinking water, Air quality modeling, West Virginia USA, Elk River spill

1 INTRODUCTION

In the morning of January 9, the West Virginia Department of Environmental Protection (WVDEP) received complaints of a strong licorice smell near from the Freedom Industries, Inc.'s storage tank farm (Manuel 2014). It was found that, a chemical storage tank was leaking into the Elk River, West Virginia. The tank held ~10,000 gallons (38,000 L) of 4-methylcyclohexanemethanol (MCHM), which is used for coal processing (Manuel 2014, McGuire *et al.* 2014). The chemical spilled 2.4 km away from the West Virginia American Water's (WVAW) Kanawha Valley Water Treatment Plant, traveling downstream and entering into the treatment plant (50 MGD) (Foreman *et al.* 2014). By 4:00 PM, MCHM was detected at the treatment plant. Right after the detection, the do-not-use order was issued at 5:50 PM to inform the residents that the tap water is not safe for drinking, cooking, bathing and washing (Cooper 2014, Manuel 2014). By that time, West Virginia Poison Center started to get phone calls from the public about nausea, vomiting, diarrhea, rashes, and other symptoms. Simultaneously, the emergency departments (EDs) observed an increase in the visit rates, which were related to the above-mentioned symptoms. To investigate the relationship between increased ED visits and MCHM side effects; West Virginia Bureau for Public Health (WVBPH) and the Agency for Toxic Substances Disease Registry (ATSDR) investigated 369 patients' records of whom visited the EDs (WVBPH and ATSDR 2014). The most common exposures were identified through showering/bathing (52%) followed by drinking (44%) as well as inhalation (15%). To determine a safe consumption level of MCHM in the water, the Center for Disease Control and Prevention (CDC) became involved with local and state health authorities in the investigation. Despite limited available data of MCHM on human health, 1 ppm was established as short-term screening level (CDC 2014).

Previous related studies have focused on the dermal and oral contact/consumption of the contaminated water, while inhalation studies were not the topic of research. The purpose of this study was to estimate indoor air concentrations of MCHM associated with contaminated water use in a dishwasher, washing machine, shower, and kitchen faucet. Additionally, the recommended flushing procedure for West Virginia incident was simulated for kitchen, bathroom and half-bathroom faucets (WVAW 2014).

2 METHODOLOGY

In this study, experimentally supported, two-phase mass balance models were utilized to estimate the chemical volatilization from each source based upon the study of Howard-Reed and Corsi (2000). The models were programmed in a computing program, MATLAB R2015a. The aqueous concentrations of 4-MCHM modeled were based on the levels determined in the tap water between January 18 to 26, when the "do not use order" was lifted for the entire area (see Table 2). To evaluate the exposure under "Do not use order", the highest known concentration in the water distribution system, 3.77 mg/L, was also included in the study (Casteloes *et al.* 2015). 4-MCHM aqueous concentrations were also used for the kitchen, bathroom, half-bathroom sink models flushing procedure under various air exchange rates ranging from 0.53 ac/hr to 10.61ac/hr.

Table 2. The sampled initial liquid concentrations of 4-MCHM at the distribution center.

Date	**Highest**	**1/18**	**1/19**	**1/20**	**1/21**	**1/22**	**1/23**	**1/24**	**1/25**	**1/26**
4-MCHM (mg/L)	3.77	0.32	0.17	0.02	0.18	0.12	0.02	0.06	0.04	0.27

2.1 Model Development

The volatilization rates of the chemicals are explained by the two-resistance mass transfer theory with the overall resistance, which is the function of gas, and liquid phase resistances (Ömür-Özbek *et al.* 2011). In accordance with the developed models by Howard-Reed and Corsi (2000), the ratio of gas and liquid phase mass transfer coefficients (K_G / K_L) and overall mass transfer coefficients ($K_L A$) of toluene were used to estimate 4-MCHM overall mass transfer coefficients in this study. Toluene was denoted as a surrogate compound. To estimate dimensionless Henry's law constant

(HLC) values of 4-Methylcyclohexanemethanol, the experimentally estimated HLC values at 7°C, 25°C, 40°C, 80°C were included from the study of Sain *et al.* (2015) and linear regression models were applied. The HLC value at 21°C was regressed from the HLC values at 7°C and 25°C. Similarly, the HLC values at 47.7°C, 60°C, 66°C were estimated from the values at 25°C, 40°C, 80°C. HLC values at 25°C and 40°C were assumed equal to the reported values.

2.1.1 *Dishwasher model*

The liquid phase in the dishwasher model was modeled as a well-mixed batch reactor while the gas phase was considered as a continuous-flow stirred-tank reactor (CFSTR) (Howard-Reed *et al.* 1999, Howard-Reed and Corsi 2000). The sequence of a typical dishwasher operation was simulated as: pre-rinse, wash, rinse and final rinse cycles. Dishwasher operation conditions were set as: system headspace volume (181 L), system ventilation rate (5.7L/min), system liquid volume (7.4 L) values and cycle times were taken from Howard-Reed and Corsi (2000). The operation temperature was selected as 66°C based on the requirement of the NSF/ANSI standard 184.

2.1.2 *Washing machine model*

The mass balance of the liquid phase in fill cycle was modeled as continuous-flow stirred-tank reactor (CFSTR) model, while the rinse and wash cycles were modeled as a well-mixed batch reactor (Howard-Reed and Corsi 2000). Typical residential washing machine operations were modeled as fill, wash, spin, rinse and spin cycles. The liquid flow rate (13.8 L), system ventilation rate (55 L/min, 53 L/min), system liquid volume (46 L), total volume of system (150 L) values and cycle times were taken from the study of Howard-Reed and Corsi (2000), and an operation temperature of 21°C.

2.1.3 *Shower model*

In order to determine the rate of mass transfer coefficients of the liquid droplets; the liquid phase was modeled as plug-flow reactor system (Howard-Reed and Corsi 2000) The gas concentrations were calculated for two different shower durations; 10 and 25 min. The water flow rate (9.1 L/Min), the ventilation rate (379 L/Min) and the volume (1745 L) were obtained from Howard-Reed and Corsi (2000). The initial chemical gas concentration in the stall was assumed to be zero.

2.1.4 *Kitchen sink model*

The kitchen sink model was developed by Corsi (1996) was utilized to determine gaseous contaminant concentrations. The water flow rate (0.0079 m^3/min), the room ventilation rate 2 ac/hr the room volume (64 m^3) and the kitchen sink use time (5 minutes) were obtained from Howard-Reed and Corsi, (2000). The water temperature was set as 25°C.

2.1.5 *Flushing procedure*

In West Virginia incident, the residents were required to flush their systems by a two-step procedure; flushing all hot water taps for 15 minutes and flushing cold water taps for 5 minutes (WVAW 2014). In this study, West Virginia flushing procedure was simulated for a kitchen sink, a bathroom sink and a half-bathroom sink for various aqueous concentrations of 4-MCHM. To estimate the gas concentrations under different scenarios: various natural and mechanical air exchange rates were included into the study: 0.53 ac/hr for all windows and doors closed, 0.92 ac/hr for single window-open, 1.7 ac/hr for multiple windows open (Howard-Reed *et al.* 2002). Additionally, the minimum required ventilation rates for the kitchen and bathroom area were determined from ANSI/ASHRAE Standard 62-2001 requirements (Persily *et al.* 2004). The 15 minutes hot flushing water temperature was assumed to be 47.7°C while the cold flushing water temperature was set to 21°C (Whelton *et al.* 2014). The models were also run for the hot water temperature of 60°C, to see gas concentration behaviors at higher temperatures.

3 RESULTS AND DISCUSSION

3.1 Dishwasher Model

The kitchen volume was modeled as $64\ \mathrm{m}^3$ based on the information given for a typical residential kitchen (Corsi 1996). To estimate the gaseous 4-MCHM concentrations in the air, it was assumed that there is no gas contaminant exchange with the other areas or loses in the pollutant level. Once the total mass of MCHM emitted over the cycles within the kitchen was determined, it was divided by the volume of the area to get the concentration. Based on our results, none of the predicted gas concentrations for different aqueous concentrations exceeded the EPA's extrapolated short-term inhalation screening Level (0.01 ppm) (U.S. Environmental Protection Agency 2014). However, when the kitchen volume is equal or less than $46\ \mathrm{m}^3$, the aqueous concentration of 3.77 mg/L led to higher gas concentration than EPA's extrapolated short-term inhalation screening level.

3.2 Washing Machine Model

Based on the model, none of the predicted gas concentrations for the given aqueous concentrations exceeded the EPA's extrapolated short-term inhalation screening level (0.01 ppm). However, when the initial aqueous concentration was 3.77 mg/L, the screening level was approximately 1.09 times more than the estimated gas concentration in the laundry room (3.4 m^3), which is very close to the predicted level.

3.3 Shower Model

Disregarding any loses in the shower stall, to estimate an average 4-MCHM concentration in the shower stall air, the total mass of emitted 4-MCHM was divided by the volume of the shower stall (1.7 m^3). For a 10 min shower model, the results showed that all of the estimated gas concentrations exceeded EPA's extrapolated short-term inhalation screening level, except 0.02 mg/L, which is the lowest liquid concentration sampled in the distribution system and the estimated gas concentrations ranged between 7.6E-03 ppm to 1.7E+00 ppm. For a 25 min shower event, all of the estimated gas concentrations exceeded 0.01-ppm screening level and ranged between 1.60E-02 ppm to 3.5E+00 ppm.

3.4 Kitchen Sink

The gas phase concentrations of 4-MCHM after a 5 min kitchen sink use were predicted. From the calculations, no gas concentrations exceeded the screening level.

3.5 Flushing Simulation

3.5.1 *Kitchen sink*

When the aqueous concentration was 3.77 mg/L, the gas concentrations at 47.7°C and 60°C exceeded EPA's extrapolated short-term inhalation screening level. On the contrary, none of estimated gas concentrations of cold flushing procedure exceed 0.01 ppm for other aqueous concentrations modeled. The gas concentrations at 47.7°C were ~ 27 times higher than the gas concentrations at 21°C. The gas concentrations were ~ 37 times more for 60°C versus 21°C water temperature for the kitchen sink model.

3.5.2 *Bathroom sink*

The results showed that when the aqueous concentration was 3.77 mg/L, the predicted gas concentrations at 47.7°C and 60°C exceeded the EPA's extrapolated short-term inhalation screening level. When the air exchange rate was 0.53 ac/hr, predicted gas concentrations of 0.32 mg/L and 0.27 mg/L were still greater than the guideline. However, when the air exchange rate was modeled as 0.92 ac/hr, the gas concentrations at 47.7°C didn't exceed 0.01 ppm screening limit.

3.5.3 *Half bathroom sink*

For the aqueous concentration of 3.77 mg/L and the air exchange rate of 0.53 ac/hr, all of the gas concentrations exceeded the screening level of 0.01 ppm including the gas concentrations estimated after cold flushing procedure. Similarly when the aqueous concentrations were 0.32 mg/L, 0.18 mg/L and 0.27 mg/L, the gas concentrations after the hot flushing procedure also exceeded the screening level. The cold flushing procedure did not show the same pattern for these initial aqueous concentrations.

4 CONCLUSIONS

Considering the researchers had started to screen the water samples on January 13th, the exact aqueous concentrations of 4-MCHM remained unknown for four days after the chemical spill, hence, the extent of this incident is still unknown. To prevent similar consequences, the lessons learned from this incident should be put into action. For example, the water resource departments and water treatment facilities across the country and around the world should come up with a comprehensive immediate action plan which includes "do not use" news releases and warnings on social media and other outlets. Moreover, consumer complaint tracking should be investigated with hospital emergency data, so that the officials may make more informed decisions and protect public health. Also a backup plan should be developed to obtain water from other resources or cities. The chemical companies and storage tanks should be inspected more frequently and the construction permits should be given when the risks are minimized, and when it is proven that there are barriers to prevent transport of such chemicals in case of an unintended spill. Also, locations for such storage facilities should be significantly away from surface waters to minimize contamination risks.

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