Environmental Pollution 214 (2016) 618–626

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Subtleties of human exposure and response to chemical mixtures from spills☆

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ARTICLE INFO

Article history:
Received 11 February 2016
Received in revised form
14 April 2016
Accepted 15 April 2016

Keywords:
Chemical spill
Mixtures
Odors
Water-atmosphere partitioning
Henry's law

ABSTRACT

Worldwide, chemical spills degrade drinking water quality and threaten human health through ingestion and inhalation. Spills are often mixtures of chemicals; thus, understanding the interaction of chemical and biological properties of the major and minor components is critical to assessing human exposure. The crude (4-methylcyclohexyl)methanol (MCHM) spill provides an opportunity to assess such subtleties. This research determined the relative amounts, volatilization, and biological odor properties of minor components *cis*- and *trans*-methyl-4-methylcyclohexanecarboxylate (MMCHC) isomers and major components *cis*- and *trans*-4-MCHM, then compared properties and human exposure differences among them. ^{1}H nuclear magnetic resonance and chromatography revealed that the minor MMCHC isomers were about 1% of the major MCHM isomers. At typical showering temperature of 40 °C, Henry's law constants were 1.50×10^{-2} and 2.23×10^{-2} for *cis*- and *trans*-MMCHC, respectively, which is 20–50 fold higher than for 4-MCHM isomers. The odor thresholds were 1.83 and 0.02 ppb-v air for *cis*- and *trans*-MMCHC, which were both described as predominantly sweet. These data are compared to the higher 120 ppb-v air and 0.06 ppb-v odor thresholds for *cis*- and *trans*-4-MCHM, for which the *trans*-isomer had a dominant licorice descriptor. Application of a shower model demonstrated that while MMCHC isomers are only about 1% of the MCHM isomers, during showering, the MMCHC isomers are 13.8% by volume (16.3% by mass) because of their higher volatility. *Trans*-4-MCHM contributed about 82% of the odor because of higher volatility and lower odor threshold, *trans*-MMCHC, which represents 0.3% of the mass, contributed 18% of the odor. This study, with its unique human sensory component to assess exposure, reaffirmed that hazard assessment must not be based solely on relative concentration, but also consider the chemical fate, transport, and biological properties to determine the actual levels of exposure across different media.

1. Introduction

Worldwide, intentional chemical releases and unintentional chemical spills contaminate water bodies and threaten ecosystems, navigation, human health, drinking water, recreation, and the economy (Jiang et al., 2012). It is common for spills to be mixtures of chemicals; individually and collectively, the chemicals have complex exposure risks due to varying fate and transport properties, monitoring capabilities, and biological effects from ingestion, inhalation or dermal sorption. When a spill directly pollutes drinking water and impacts human health, the concerns are immediate. The Sandoz Chemical spill of over 1300 metric tonnes of pesticides, dyes, and organometallic compounds into the Rhine River captured global attention in 1986. That massive spill closed drinking water treatment plants in Switzerland, Germany, France, and the Netherlands as the plume traveled 1320 km and 14 days before discharging into the North Sea (Capel et al., 1988). In 1991, 68,000 L of the pesticide metam sodium leaked into the Sacramento River, California, USA. Following the spill, residents smelled the chemical-horseradish-rotten-egg odors of metam sodium and also its degradation products methylisothiocyanate and hydrogen sulfide (Bowler et al., 1994). The known toxicity of

☆ This paper has been recommended for acceptance by Eddy Y. Zeng.

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http://dx.doi.org/10.1016/j.envpol.2016.04.056
0269-7491/

volatilized methylisothiocyanate caused evacuation of residents as the plume traveled for days to Lake Shasta, a drinking water and recreational reservoir. In 2005, an estimated 90 metric tonnes of mostly nitrobenzene and some carcinogenic benzene spilled into the Songhua River in Jilin City, Jilin Province, China. The resulting 80 km chemical slick caused undrinkable water for millions of people during its six weeks of travel from Jilin City through Jilin and Heilongjiang Provinces and into Russia before discharging to the Sea of Okhotsk (BBC News 2005; Zhang et al., 2010). In 2014, nearly 38,000 L of sweet licorice smelling crude (4-methylcyclohexyl) methanol (MCHM) spilled into the Elk River, West Virginia, USA. Contaminated river water was processed into drinking water, distributed, and its odor and chemical contamination disrupted lives and livelihoods of about 300,000 people for several months (Manuel, 2014; Schade et al., 2015). Crude MCHM was a mixture of at least ten cyclohexanes (Foreman et al., 2015; Dietrich et al., 2015). Furthermore, the crude MCHM plume traveled nearly 600 km through the Ohio River, causing closure of drinking water intakes in Ohio and Kentucky (Foreman et al., 2015). In 1988, prompted by the lack of fate, transport and toxicity data for chemicals in the Sandoz Chemical spill into the Rhine River, Capel et al. (1988) stated, "A data bank that stores environmentally useful information on anthropogenic chemicals should be made accessible …" Nearly a quarter century later, there was a severe lack of fate, transport, odor, and toxicity data for crude MCHM (Eastman Chemical Company, 2011). Thus, there are still large data gaps that need to be filled and many lessons to learn for managing the effects chemical mixtures from spills.

Identifying a subtle spill-like event can also be difficult because the source is not always readily apparent. In addition, the origin may be more biological than chemical. For example, an odorous black water agglomerate infiltrated the main drinking water intake for Wuxi City, China and subjected residents to weeks of odors and health concerns. The agglomerate originated from the accumulation and death of algae, primarily *Microcystis aeruginosa*, and contained high ammonium levels and strong septic/marshy odors from dimethyl trisulfide and related alkyl sulfide compounds, even though minor odors from geosmin and 2-methylisoborneol were initially suspected (Yang et al., 2008; Li et al., 2012; Ma et al., 2015). Likewise, Quintana et al. (2016) described detailed investigations required to identify the source of co-occurring odorous 1,3-dioxanes and 1,3-dioxolanes in a complex and aging urban environment with multiple water sources, multiple treatment plants and processes, and multiple potential dischargers. Low μg/L concentrations of these resin-related contaminants from treated industrial wastewater caused closure of one water source for drinking water.

When chemicals contaminate drinking water, an initial step is to protect public health and attempt a risk assessment that includes these four steps: hazard identification, followed by exposure assessment and dose-response assessment, which then combine to a risk characterization (USEPA, 2000). Investigating chemical effects on biological systems is usually done one chemical at a time, but ultimately chemical mixtures should be treated as a whole because in reality humans are exposed to mixtures (Carpenter et al., 2002). Some chemicals are nonadditive and behave independent of one another, while some are additive and can trigger complex interactions (Mumtaz, 1995; Carpenter et al., 2002). Estimating a dose-response from chemical mixtures is difficult because of potential biological/toxicological interactions between chemicals (Carpenter et al., 2002; Teuschler, 2007). When a chemical is also an odorant, dose-response assessment to measure odor threshold is important to investigate. Risk assessment of chemical mixtures is further complicated when there are multiple routes of exposure. For drinking water, health effects are usually focused on ingestion even though inhalation of volatile and semi-volatile chemicals can be a substantial route of exposure during showering and water use (Villanueva et al., 2014). The relative distribution of chemicals between water, air, and biological organisms also vary among individual chemicals in a mixture depending on the physicochemical partitioning properties such as aqueous solubility, volatility, and octanol-water coefficients (Jahnke et al., 2016). Thus, physicochemical partitioning properties result in varying concentrations, fate, transport, and biological properties of the individual chemicals in a mixture and can ultimately result in substantial differences in exposure for humans via ingestion and inhalation routes.

For select chemical mixtures, decades of science and experience have identified the constituent(s) of concern. For example, gasoline is a mixture of many aliphatic and aromatic hydrocarbons. While the composition of gasoline varies, it typically contains only 2% benzene by weight. However, when an underground gasoline storage tank leaks, benzene can be 15–35% by weight of the total dissolved gasoline-related compounds in the aqueous phase groundwater plume because of its higher solubility compared to other gasoline components (Hathaway and Andrews, 1990). This can lead to greater exposure to benzene in drinking water. Benzene is the primary constituent of concern for gasoline-contaminated drinking water because of its known human carcinogenicity that is acknowledged through regulation in drinking water at 1–5 μg/L benzene (SDWF, 2015). Because of the interplay of fate and transport properties and health risk (i.e., solubility and carcinogenicity), gasoline spills lead to a situation where a minor component of a mixture has the highest risk to human health.

For other mixtures of contaminants in drinking water, the science is not sufficiently developed to identify the constituent(s) causing adverse effects to humans. Chlorinated drinking water contains a mixture of various organic and inorganic components, including disinfection by-products (DBPs). Trihalomethanes (total THMs, which include usually un-equal concentrations of trichloromethane, bromodichloromethane, dibromochloromethane, and tribromomethane with differentiating physicochemical and biological properties) are DBPs from chlorine that since the 1970's have been regulated primarily based on ingestion of drinking water and concerns over possible bladder cancer (SDWF, 2015). However, epidemiological studies do not fully agree with cancer risk estimates from ingesting THMs. The lack of epidemiological support suggests the possibility that some of the other hundreds of known co-occurring chlorinated disinfection by-products (Richardson et al., 2007; Zhang et al., 2012) found at lower concentrations but higher cancer risks may have a role in bladder cancer (Hrudey et al., 2015). Another open question for THMs and DBPs is the extent that the route of exposure plays in exposure risk. Some authors (Miles et al., 2002; Ross and Pegram, 2004) have suggested that dermal or inhalation exposures can bypass liver metabolism and lead to a higher risk than ingestion. Despite decades of study, further research is needed to identify and evaluate the constituents of concern and impact of exposure route for the mixture of chemicals called DBPs (Hrudey et al., 2015).

Establishing which chemicals result in higher human exposure for both ingestion and inhalation is challenging even when the fate, transport, and biological properties of specific chemicals in a mixture are known. Accurate, quantitative physicochemical and biological data are often lacking, especially for the tens of thousands low production volume specialty chemicals, including crude MCHM (Schnoor, 2014). Exposure to multiple chemicals in crude MCHM (Fig. SI-1) occurred during and for months after the spill even when consumers were not drinking contaminated water. Consumers reported smelling and inhaling the licorice and sweet odor of the crude MCHM mixture especially when using heated water for washing and bathing (Gallagher et al., 2015; Schade et al.,