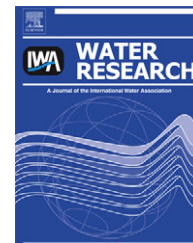


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Investigation of factors affecting the accumulation of vinyl chloride in polyvinyl chloride piping used in drinking water distribution systems

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ABSTRACT

Plastic piping made of polyvinyl chloride (PVC), and chlorinated PVC (CPVC), is being increasingly used for drinking water distribution lines. Given the formulation of the material from vinyl chloride (VC), there has been concern that the VC (a confirmed human carcinogen) can leach from the plastic piping into drinking water. PVC/CPVC pipe reactors in the laboratory and tap samples collected from consumers homes ($n = 15$) revealed vinyl chloride accumulation in the tens of ng/L range after a few days and hundreds of ng/L after two years. While these levels did not exceed the EPA's maximum contaminant level (MCL) of 2 $\mu\text{g/L}$, many readings that simulated stagnation times in homes (overnight) exceeded the MCL-Goal of 0 $\mu\text{g/L}$. Considerable differences in VC levels were seen across different manufacturers, while aging and biofilm effects were generally small. Preliminary evidence suggests that VC may accumulate not only via chemical leaching from the plastic piping, but also as a disinfection byproduct (DBP) via a chlorine-dependent reaction. This is supported from studies with CPVC pipe reactors where chlorinated reactors accumulated more VC than dechlorinated reactors, copper pipe reactors that accumulated VC in chlorinated reactors and not in dechlorinated reactors, and field samples where VC levels were the same before and after flushing the lines where PVC/CPVC fittings were contributing. Free chlorine residual tests suggest that VC may be formed as a secondary, rather than primary, DBP. Further research and additional studies need to be conducted in order to elucidate reaction mechanisms and tease apart relative contributions of VC accumulation from PVC/CPVC piping and chlorine-dependent reactions.

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1. Introduction

1.1. PVC pipe use in drinking water delivery

As drinking water distribution system lines are replaced in the United States at a cost of \$250 billion over the next few decades, research is needed on the strengths and limitations

of the materials that will be installed ((AWWA) 2001). Polyvinyl chloride (PVC) piping is popular due to its relatively low cost, structural strength, ease of installation, and corrosion-resistant properties (Al-Malack and Sheikheldin, 2001). It is currently estimated that 69% of the piping used in the main drinking water distribution system is plastic, and the majority of the plastic pipe is PVC (Burn, 2005). During the

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manufacturing of PVC, chlorine and ethylene are combined to create ethylene dichloride, which is converted into vinyl chloride (VC) monomers through a cracking process before polymerization to PVC (Saeki and Emura, 2002). Additionally, chlorinated PVC (CPVC), which is PVC that has been chlorinated via a free radical chlorination reaction and the application of heat, is commonly found in hot water drinking systems and residential homes ((ATSDR) Sept. 2004).

1.2. Vinyl chloride monomer in PVC pipe

There have been reports that residual VC monomer in the pipe matrix of the PVC/CPVC piping can be released into air or drinking water (Sano et al., 2001). VC is a known human carcinogen and is regulated by the Environmental Protection Agency (EPA) with a maximum contaminant level (MCL) of 2.0 µg/L and an MCL-goal (MCLG) of 0 µg/L in water for potable water (Flournoy and Monroe, 1999). Vinyl chloride concentrations well above the EPA's MCL were reported in stagnant PVC pipe lines in Kansas, Missouri, Texas, and Arkansas ((MDNS), 2006; Flournoy and Monroe, 1999). Additional studies have detected VC levels above the EPA's MCL at 14 µg/L in PVC pipe manufactured before 1977 (Flournoy and Monroe, 1999; The Vinyl Institute and Uni-Bell PVC Pipe Association, 1994). While modifications to the manufacturing process in 1977 drastically reduced the VC monomer residual in US-manufactured pipe, little work exists that examines the leaching of VC into water from modern US PVC/CPVC pipes – particularly as the pipe ages. Recent work in Saudi Arabia has been performed indicating that static unplasticized PVC (uPVC) accumulates 2.3 µg/L of VC over 14 days when exposed to ultraviolet radiation (Al-Malack, 2004), 2.5 µg/L of VC over 30 days when exposed to temperatures of 45 °C (Al-Malack et al., 1999), 2.0–2.1 µg/L of VC in both raw groundwater and chlorinated drinking water (Al-Malack et al., 1999), and 2.5 µg/L of VC over 30 days when exposed to direct solar radiation (Al-Malack and Sheikheldin, 2001); however, all of these analyses used locally manufactured pipes from Saudi Arabia. Another study with Japanese pipe (unknown manufacturer and production date) found that static PVC pipes filled with deionized water or phosphate buffer did not accumulate detectable VC over a three day period (detection limit in mg/L range), but that segments sealed in serum vials did produce detectable VC at more than 50 mg/L (Ando and Sayato, 1984). Finally, an Italian study looking at the migration of VC into drinking water bottled in locally obtained plasticized PVC found that VC accumulated at a rate of 1 ng/L/day (Benfenati et al., 1991).

1.3. Study objectives

The objectives of this study were to compare the accumulation of VC from new pipe reactors from different US manufacturers and different PVC formulations (PVC vs. CPVC) over periods from 4 h up to 2 years and to understand the effects of aging, biofilm coverage, and chlorine residual on VC levels. Laboratory studies were performed by creating static pipe reactors using new PVC/CPVC from different manufacturers. Likewise, in-use piping segments aged for 2, 15, and 25 years were procured and tested. Finally, copper piping typically used in water distribution systems was tested, eliminating the

contribution of VC via chemical leaching from plastic piping. Analyses of the tap water of local homes was also conducted to determine which factors led to detectable VC levels at the tap.

2. Materials and methods

2.1. Static pipe reactors

Various $\frac{3}{4}$ " diameter PVC, CPVC, and copper pipe types obtained from different manufacturers, or from in-use drinking water lines, were cut into 6" segments. Before use, all new pipes were rinsed with three changes of water in accordance with NSF 60 standards. All pipes obtained were NSF PW certified. For aged piping, pipe segments were maintained full of water and kept in the dark until the time of the experiment. To remove biofilms, a sterile scraper (Falcon) was used to scrape biofilm from the walls, and tap water was used to rinse the scraped surface. One end of the reactor had a fitted cap, of the same pipe material, glued onto it using Miller Stephenson Epoxy 907 two to three days before the actual experiment. A hole was drilled into the end of the second cap, and a 20 mm blue butyl rubber septum (Bellco Technology) was glued in place several days before the start of the experiment. The static reactors were 90% filled with cold, laboratory tap water (chlorinated or dechlorinated) – leaving 10% headspace to allow gas sampling. After sealing the caps and ensuring that no air bubbles formed in the epoxy, the reactors were allowed to dry for at least 2 h before sampling. All reactors were incubated at room temperature in the dark during the experiment. One milliliter gas samples were removed to monitor VC over time and 1 mL of room air was then injected to avoid the creation of a vacuum in the reactors. VC recovery controls were created by spiking known amounts of VC into subsets of reactors.

2.2. Water characteristics

For all studies performed, cold, laboratory tap water, from Cornell University's Water Filtration Plant (CU-WFP), was employed. The chlorine residual was measured using a Hach Chlorine Test Kit. Total chlorine residual was consistently between 0.55 and 0.7 mg/L, while the free chlorine residual was constantly between 0.5 and 0.6 mg/L. Other characteristics of the source water reported by the CU-WFP were as follows: pH = 6.9; alkalinity = 128 mg/L as CaCO₃; total organic carbon = 2.1 mg/L; turbidity = 0.07 NTU. During all experiments, a 500 mL beaker was filled with water, tested for chlorine, and then used to fill all the reactors in order to ensure the same water in all reactors. For the dechlorinated water, sodium thiosulfate was employed to neutralize the total chlorine in the samples. A 4.03×10^{-4} M stock solution was created and a stoichiometric weight ratio of sodium thiosulfate per mg/L of residual chlorine of 0.556 mg/mg was used based on Metcalf and Eddy's standard for dechlorination (Burton et al., 2002). Residual chlorine testing after dechlorination consistently indicated 0.0 mg/L of both free and total chlorine. Samples of all experimental runs were preserved in glass vials.

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