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1,2,3-Trichloropropane State of the Science

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At a Glance

- TCP is a manmade material that has been detected in drinking water sources.
- It has been classified as "likely to be carcinogenic to humans" (EPA IRIS 2009).
- No federal maximum contaminant level (MCL) has been set for TCP in drinking water.
- Various states have established health-based drinking water guidance values.
- Hawaii has established a state MCL of 0.6 ug/L.
- California has a notification level of 0.005 ug/L.
- Conventional water treatment practices have proven to be relatively ineffective at removing TCP.
- Air stripping is not cost effective for achieving the public health goal.
- Currently, GAC is the only viable technology option for TCP removal.
- For utilities with TCP concentrations above the possible MCL, GAC treatment would likely be required if TCP becomes a regulated contaminant.

Introduction

1,2,3-trichloropropane (TCP) is a manmade pesticide impurity and solvent/degreaser suspected to cause cancer in humans. No federal maximum contaminant level (MCL) has been set for TCP in drinking water. However, various states have established health-based drinking water guidance values. TCP has been detected in hundreds of surface water and drinking water sources at levels of 0.1–100 μg/L. Conventional water treatment practices have proven to be relatively ineffective at removing TCP from water. Despite its high Henry's constant, air stripping is not cost effective for achieving the eventual public health goal. Ultraviolet light (UV), along with hydrogen peroxide, has shown some degradation of TCP, although the degradation rate constant was fairly low. Currently, granular activated carbon (GAC) is the only viable treatment option for TCP removal.

Sources

1,2,3-trichloropropane (TCP) is an anthropogenic industrial chemical and pesticide by-product. It has been used as an industrial solvent and as a cleaning and degreasing agent. It has also been found as an impurity resulting from the production of soil fumigants (EPA 2014). It is used as a chemical intermediate in the production of other chemicals (including polysulfone liquid polymers and dichloropropene), and in the synthesis of hexafluoropropylene (NTP 2014). In addition, it is used as a crosslinking agent in the production of polysulfides. In 1977, estimates for the production of TCP in the United States ranged from 21 million to 110 million pounds. In 2009, TCP was produced by five manufacturers worldwide, including two in the United States, and was available from 22 suppliers, including 15 U.S. suppliers. Reports filed under the U.S. Environmental Protection Agency's (EPA) Toxic Substances Control Act Inventory Update Rule indicated that U.S. production plus imports of TCP ranged from 10 million to 50 million pounds in 1986, 1990, and 1998, and from 1 million to 10 million pounds in 2002 (NTP 2014).

Health Effects and Regulations

Based on the formation of multiple tumors in animals, TCP is classified by the EPA as "likely to be carcinogenic to humans" (EPA 2009). Effects of short-term exposure to high levels of TCP include irritation of the eyes and throat, decreased ability to focus, and decrease in muscular coordination. Long-term exposure can result in kidney and liver malfunction and decreased body weight. The main exposure route for the general public is via ingestion of contaminated drinking water, with minimal exposure contributed by inhalation and dermal contact (Hooker et al. 2012). According to the Unregulated Contaminant Monitoring Rule 3 (UCMR3) Data Summary, cancer development could occur in 1 out of 1,000,000 people exposed to a concentration of 0.0004 µg/L in drinking water over a lifetime (EPA 2016).

No federal maximum contaminant level (MCL) has been set for TCP in drinking water. The EPA has established health advisories for TCP that are drinking water-specific risk level concentrations for cancer (10^{-4} cancer risk), and concentrations of drinking water contaminants at which adverse health effects are not anticipated to occur over specific exposure durations. The EPA established a one-day health advisory of 0.6 milligrams per liter (mg/L) and a 10-day health advisory of 0.6 mg/L for TCP in drinking water for a 10-kilogram (kg) child (EPA 2014). Additionally, various states have established health-based drinking water guidance values. The State of Hawaii has established a state MCL of 0.6 µg/L. Currently, California has a notification level of 0.005 µg/L for drinking water, but the California Department of Public Health (CDPH) is currently developing a state MCL. Finally, TCP is currently included in a group of sixteen carcinogenic volatile organic compounds that are considered as part of carcinogenic volatile organic compounds group regulations.

Occurrence

Various studies, both in North America and Europe, have determined that TCP occurrence is widespread. Within the United States, TCP has been detected in many surface water and drinking water sources, at levels ranging from 0.1–100 µg/L (Samin and Janssen 2012). In the Netherlands,

> *TCP was detected in surface water of the Rhine, Meuse, Westerscheldt, and in the Northern Delta Area. Groundwater samples from the Netherlands were found to contain TCP as well as 1,2-dichloropropane, due to the application of impure nematicides, especially in potato fields. TCP was also detected in the river Nitra (Slovakia) and along with a range of other volatile organohalogens in water at an industrial site in the Osaka area, Japan. These examples illustrate that TCP is a very widespread contaminant* (Samin and Janssen 2012).

TCP was recently included in the Unregulated Contaminant Monitoring Rule 3 (UCMR3), which will provide a large database to document the national occurrence of TCP. On January 1, 2013, monitoring of more than 5,000 public drinking water supplies for 28 contaminants began. The monitoring period concluded in December 2015. The data indicate that only 0.4% of the samples have concentrations greater than the method detection level of 0.03 µg/L. For public water supplies, this number jumps to 1.3%. Since the minimum reporting level used for the UCMR3 monitoring is much higher than the 0.0004 μg/L reference concentration associated with a 1×10^{-6} cancer level, occurrence at low concentrations is unknown. Maximum TCP concentration measured was 1.02 μg/L.

Treatment

TCP is very recalcitrant in groundwater systems due to its long hydrolysis half-life and low biodegradability (See Table 1 for its physical and chemical properties) (EPA 2014). Current conventional water treatment practices (e.g., coagulation, sedimentation, and filtration) have proven to be relatively ineffective at removing TCP from water. Despite its high Henry's constant, air stripping is not cost effective for achieving the eventual public health goal. Several studies showed some success removing TCP using reverse osmosis, zero-valent zinc, advanced oxidation, and granular activated carbon.

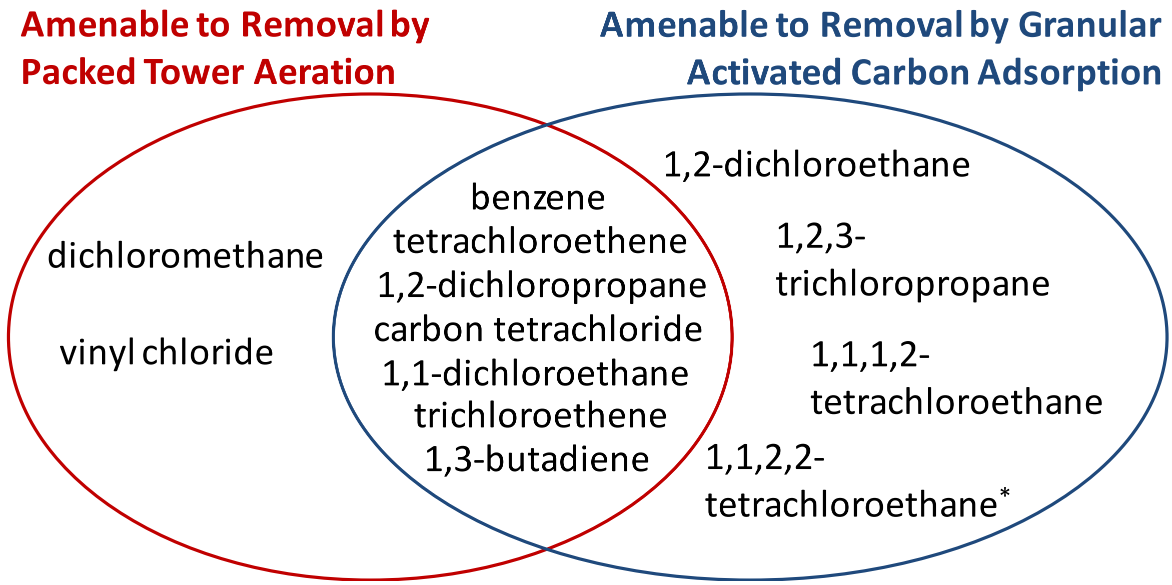
The Water Research Foundation (WRF) has funded projects investigating TCP treatment along with other volatile organic compounds (VOCs). WRF Project #4462 (Detlef et al., forthcoming) has determined Henry's Law constants and Freundlich adsorption constants for the 13 carcinogenic VOCs (cVOCs) most likely to be included in a new cVOC group regulation. Using the two best available technologies for removing VOCs, packed tower aeration (PTA) and granular activated carbon (GAC) adsorption, the research team has categorized treatment options for VOCs based on Henry's Law constants and Freundlich adsorption constants (see Figure 1).

Table 1.
Physical and Chemical Properties of TCP

Property	Value
Chemical Abstracts Service (CAS) Number	96-18-4
Physical Description (at room temperature)	Colorless to straw-colored liquid
Molecular weight (g/mol)	147.43
Water solubility at 25 °C (mg/L)	1,750 (slightly soluble)
Melting point (°C)	-14.7
Boiling point (°C)	156.8
Vapor pressure at 25 °C (mm Hg)	3.1 to 3.69
Specific gravity at 20/4 °C (g/cm^3)	1.3889
Octanol-water partition coefficient (log K_{ow})	1.98 to 2.27 (temperature dependent)
Organic carbon-water partition coefficient (log K_{oc})	1.70 to 1.99 (temperature dependent)
Henry's law constant at 25 °C ($atm\text{-}m^3/mol$)	3.17×10^{-4} - 3.43×10^{-4}

Source: EPA 2014.

WRF Project #4492 (Cotton, forthcoming) was funded to evaluate the effectiveness and reliability of aeration, GAC, and advanced oxidation processes to remove cVOCs, including TCP. Full-scale samples collected from participating utilities using GAC as a treatment technology indicated that TCP was one of the most strongly adsorbed VOCs, with approximately 20% breakthrough at 37,500 bed volume. In another WRF study (Chowdhury et al., forthcoming), TCP breakthrough was observed in approximately 40,000 bed volumes. Bench-scale experiments done using UV have shown no degradation of TCP. However, using hydrogen peroxide along with UV has shown some degradation of TCP, although degradation rate constant was fairly low.



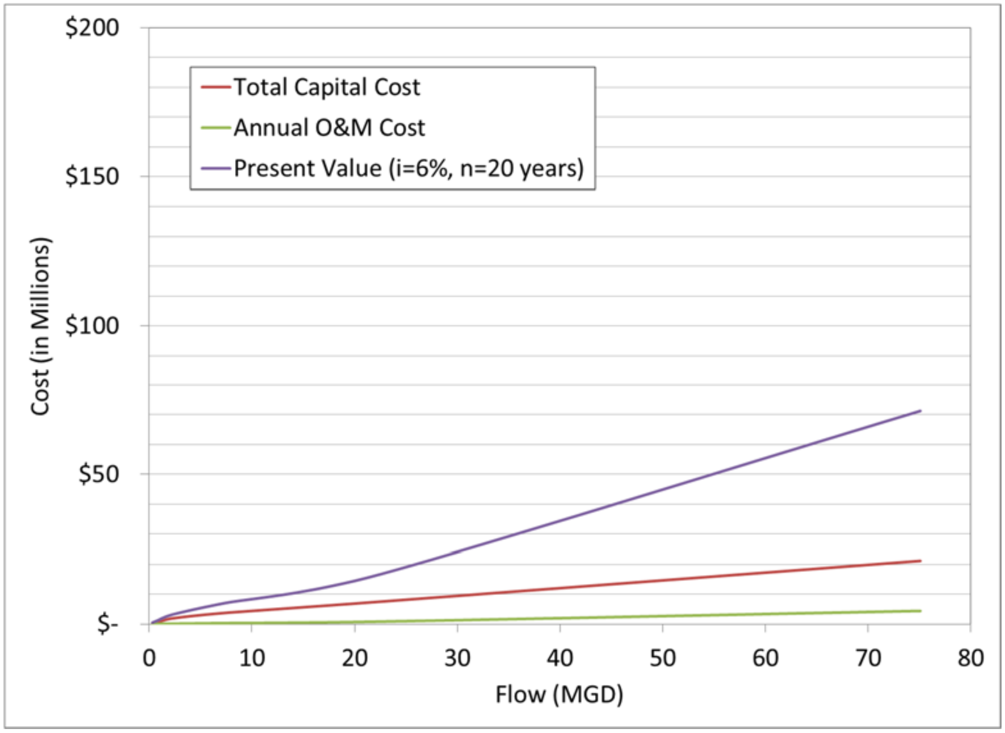
*removal occurs at least partially via hydrolysis to TCE

Source: Detlef et al., forthcoming.

Figure 1. Categorization of cVOCs in terms of treatment options based on HLCs and Freundlich adsorption constants. PTA was considered a viable treatment option for cVOCs with $H_{cc,10°C}$ > 0.05 and GAC was considered a viable treatment option for cVOCs with *K* > 0.02 (mg/g)(L/µg)$^{1/n}$.

Impact of Future TCP/cVOC Regulation on Utilities

Utilities will be affected by a TCP regulation due to the constraints of the initial design specifications. WRF Project #4453 (Chowdhury et al., forthcoming) has evaluated seven regulatory constructs to cover a range of possible regulatory scenarios to evaluate what additional measures (if any) utilities would need to take if required to comply with a cVOC regulation. As an adsorption technology, GAC has the ability to meet of all of the evaluated regulatory scenarios, as long as the system provides adequate empty bed contact time to achieve the necessary removal and account for the mass transfer zone of the target contaminants. However, GAC media has a finite capacity to remove TCP and other VOCs, and will require periodic replacement in order to meet the treatment goals. The frequency of the media replacement will be a function of the target contaminants and raw water concentrations. Among the cVOCs studied in WRF Project #4453, 1,1-DCA concentration in the GAC influent was the driver for GAC replacement frequency in multiple scenarios, followed by TCP. For the evaluated cVOCs, compliance with the evaluated regulatory scenarios will likely be achieved through more frequent media change outs. Packed tower aeration is an effective treatment technology for a range of VOC contaminants. However, due to its chemical properties, TCP is not readily removed through aeration. Therefore, for utilities with TCP concentrations above the possible MCL, GAC treatment would likely be required if TCP becomes a regulated contaminant. WRF Project #4453 has also developed conceptual capital and annual O&M costs for a new GAC facility (Figure 2).



Source: Chowdhury et al., forthcoming.

Figure 2. Conceptual Capital and Annual O&M Costs for New GAC Facility Targeting 1,2,3-TCP (Replacement = 55,600 BV)

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