Evaluation of Dibutyltin and Monobutyltin Leaching from PVC pipe: A Bench and Pilot Scale Approach

by

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Abstract

Bench scale pipe-section reactors (PSRs) along with pilot scale pipe-loops were used to examine the leaching of toxic dibutyltin (DBT) and monobutyltin (MBT) heat stabilizers which are commonly used in drinking water distribution systems across North America from C900 and C909 PVC pipe. PSR trials were conducted using artificial freshwater containing up to 4 mg/L free chlorine, as typically employed for drinking water distribution. Pipe-loops located onsite at a water treatment facility continuously received chloraminated water. MBT was observed above the detection limit only during the first 24 hours of the PSR trial, with the presence of chlorine showing a positive impact on leaching. Pipe-loop and PSR results did not show DBT above the detection limits during the trials. These findings suggest that DBT leaching from C909 and C900 PVC pipes within a typical drinking water distribution system should not pose a concern to consumers.

Acknowledgements

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NOMENCLATURE

"	Inch
%	Percent
>	Greater than
<	Less than
≥	Greater than or equal to
±	Plus/minus
A	Area
AFW	Artificial Freshwater
ASTM	American Society for Testing and Materials
AWWA	American Water Works Association
C	Degrees Celsius
˚C/min	Degrees Celsius per min
cm	Centimetre
CPVC	Chlorinated Polyvinyl Chloride
DBT	Dibutyltin
DI	De-ionized
DMT	Dimethyltin
DO	Dissolved Oxygen
DOT	Dioctyltin
EI	Electron Ionization
EPA	Environmental Protection Agency
eV	Electron Volt
g	Gram
GCMS	Gas Chromatography - Mass Spectrometry
h	Hour
HRT	Hydraulic Retention Time
L	Litre
m	Metre
M	Molarity
m(t)	Organotin leaching rate at time t
m/s	Metre per second
m/z	Mass to charge ratio
m^2	Metre squared
m^2/m^3	Metre squared per metre cubed
m^3	Metre cubed

MBT	Monobutyltin
MDL	Method Detection Limit
mg	Milligram
mg/L	Milligram per litre
min	Minute
mL/min	mL per minute
mm	Millimetre
MS	Mass Spectrometer
MΩ	Megaohm
n	Number of instances
$NaBEt_4$	Sodium Tetraethyl Borate
ng	Nanogram
ng/g	Nanogram per gram
NSF	National Sanitation Foundation
pH	-log (hydrogen ion concentration)
PSR	Pipe Section Reactor
PVC	Polyvinyl Chloride
PVCO	Molecularly aligned Polyvinyl Chloride
R^2	Coefficient of Determination
RPM	Revolutions per minute
s	Second
s/m^2	Second per metre squared
SIM	Selected Ion Monitoring
Sn	Tin
$SnC_{10}H_{23}^+$	Ethylated derivative of dibutyltin
$SnC_8H_{19}^+$	Ethylated derivative of monobutyltin
TBT	Tributyltin
TPT	Tripropyltin
V	Volume
WHO	World Health Organization
x	Times
y(t)	Organotin Concentration at time t
µg	Microgram
µg/L	Microgram per litre
µL	Microlitre
µm	Micrometre

1. Introduction

Organotin compounds represent a large class of tetravalent tin organic derivatives which are characterized by at least one carbon-tin bond (Pagliarani et al., 2012). Dimethyltin (DMT), dibutyltin (DBT), and dioctyltin (DOT) are used as heat stabilizers in the manufacturing of polyvinyl chloride (PVC) as well as chlorinated polyvinyl chloride (CPVC) plastic, accounting for more than 65% of the global use of organotin compounds (Sadiki et al., 1996; WHO, 2020). Pipe materials used in drinking water distribution systems commonly contain PVC and CPVC polymers, consequently, concern exists regarding the potential for organotin compounds and other additives to leach into water and reach consumers (Adams et al., 2011; Forsyth & Jay, 1997). The presence of organotin compounds may pose a potential health concern as immunotoxicity associated with tributyltin (TBT), triphenyltin (TPT), DBT, and DOT has been reported (Boyer, 1989; Hennighausen & Lange, 1980; Kishi et al., 2006; Snoiej et al., 1985). A health-based value for daily drinking water organotin ingestion of 1.5 μg/L (0.6 μg/L as Sn) has been derived for the sum of TBT, TPT, DBT, and DOT (WHO, 2020).

Only limited studies have investigated organotin leaching into drinking water despite their known toxicity. Sadiki & Williams (1999) analyzed tap waters from 28 sites across 8 Canadian provinces, reporting the highest organotin concentrations (as ng Sn/L) of 290.6 for monomethyltin, 49.1 for DMT, 28.5 for monobutyltin (MBT) and 52.3 for DBT, of which are all lower than the World Health Organization (WHO) value of 1.5 μg/L. Organotins are not regulated in drinking water, however organotin leaching is monitored as part of PVC pipe certification practices to address this potential issue (NSF/ANSI 61, 2016). The maximum contaminant level for the NSF Drinking

Water System Components – Health Effects standard is 20 µg/L for mono- and di- butyltins; 30 µg/L for mono- and di- methyltins (NSF/ANSI 61, 2016).

As described in the NSF standard (NSF/ANSI 61, 2016) the organotin testing procedure employs bench scale pipe-section reactors (PSRs) to assess organotin levels following a 14-day conditioning period and subsequent 62 h of stagnant exposure time. Conditioning involves filling the PSR with water containing 2 mg/L free chlorine and refreshing the water at least 10 times at a minimum interval of 24 ± 1 h over 14 days. Subsequent stagnation exposure involves filling the conditioned PVC PSR with water at pH 8 which contains no chlorine, refreshing the water following 24 h and 48 h of stagnant exposure time and measuring the target organotin after 62 h of stagnant exposure. This procedure does not represent a typical drinking water distribution system due to the absence of chlorine as well as continuous flow. Similar testing procedures have been employed in the literature. Forsyth & Jay (1997) conducted 20-day static PSR trials using tap water without first conditioning the test pipes whereby water was refreshed daily with samples collected at 1, 2, 5, 10, 15 and 20 days. Organotin concentrations were reported to be highest after the first day at 5.9 ng/g Sn and 2.7 ng/g Sn for DBT and MBT, respectively. Subsequent samples were observed to have decreasing organotin concentrations. Similarly, Jones-Lepp et al. (2001) conducted 96-hour static PSR trials without pipe conditioning. Deionized water (pH 5) was sampled and refreshed every 24 hours. The highest DBT concentration (1 µg/L) was observed following 24 hours, decreasing to 0.8 µg/L after 96 hours. In trials conducted by both Forsyth & Jay (1997) and Jones-Lepp et al. (2001) the water in the PSR remained stagnant, and as such not representative of flow conditions observed within typical distribution systems.

In lieu of PSRs, pilot-scale pipe-loop systems can be employed to simulate distribution system flow under controlled operating conditions. In pipe-loop systems, water is continuously recirculated through sections of virgin (or harvested) PVC pipe to approximate distribution flow conditions. Pipe-loops can be operated as either batch or steady-state (with continuous inflow and outflow). Employing a pipe-loop system operated in batch mode and using water which had first been passed through activated carbon and ion exchange, Wu et al. (1989) reported total tin within the recirculating water to reach equilibrium after 12 h. The same authors also reported that reusing previously tested PVC pipe reduced the equilibrium total tin concentration from approximately 4.5 µg/L Sn (in the first test) to 1.5 µg/L, indicating that the rate of organotin leaching decreases with exposure time. Adams et al. (2011) used a batch pipe-loop system to develop a leaching model for DBT and DMT when employing ultrapure water, 18.2 MΩ. Leached DBT and DMT reached equilibrium within 24 h at concentrations of 0.35 µg/L and 0.12 µg/L, respectively. A Summary of experimental conditions reported in previous pipe-loop and PSR studies is presented in Table 1-1. None of the studies evaluated pipe-loop organotin leaching using steady state conditions. Previous studies have shown flow rate (Wu et al., 1989) and exposure time (Forsyth & Jay, 1997; Jones-Lepp et al., 2001; Wu et al., 2023) to exert the greatest impacts on the rate of organotin leaching; the specific influence of water matrix, pH, and pipe material were not examined.

Other studies examined parameters which may impact the leaching of organotins into water (Chen et al., 2019; Chen et al., 2022; Wu et al., 2023). When investigating additives which drive toxicity in a range of plastic products, Chen et al. (2022) compared organotin concentrations associated with three different PVC pipe materials. The authors reported concentrations of 92.1, 0.15, 0.005, and 0.05 µg/g for DBT, TBT, DPT, and TPT, respectively for a pipe which satisfied the AWWA

Table 1-1. Experimental conditions of prior pipe-loop and pipe-section reactor (PSR) organotin leaching studies

Reference	Apparatus	Pipe Material	Flow	Conditioning	Water Discharge	Water Matrix	pH
Adams et al. (2011)	Pipe-Loop	CPVC	7.6 L/min	6 Milli-Q Fills	None	Ultrapure water	Not Stated
Wu et al. (1989)	Pipe-Loop	PVC	0.34 – 1.39 m^3/h	None	None	Water post activated carbon and ion exchange	Not Stated
Jones-Lepp et al. (2001)	PSR	PVC	No Flow	None	None	Deionized Water	5
Forsyth & Jay (1997)	PSR	CPVC	No Flow	Vacuum source attached to remove debris	Water replaced every 24 h	Tap Water	6.7
NSF Procedure	PSR	Any PVC	No Flow	14-day with 2 mg/L chlorine,	Water replaced every 24 h	Ultrapure water with 100 mg/L hardness 0 mg/L free chlorine	8

C909 standard. Pipes which met the AWWA C900 and ASTM D1785 standards were reported to have no observable DPT and TPT, and lower DBT and TBT concentrations (2.19, and 0.0037 µg/g for C900 pipe, and 44.8, and 0.19 µg/g for D1785 pipe). A subsequent study by Wu et al. (2023)

investigated the leaching of DBT from the same three PVC pipe materials (C909, C900 and D1785) reporting the ratio of DBT concentrations to be 2.9:1.4:1, with the highest observed at pH 8. Their study also showed the presence of free chlorine to increase DBT leaching, whereas chloramine was reported to have a negligible impact. As such, studies to-date suggest that a worst-case scenario for organotin leaching in a distribution system would occur at high pH (≥8) and in the presence of free chlorine. As such, the existing NSF testing procedure does not capture the worst-case scenario since it dictates a pH of 8 and only requires chlorinated water (2 mg/L) during an initial conditioning phase beyond which no chlorine is required during testing.

Previous studies which utilized bench or pilot-scale trials (Table 1-1) to evaluate organotin leaching have not employed representative systems to simulate water distribution. Most pilots were not operated at steady-state; PSR trials did not simulate flow within the reactor. None of these studies considered the presence of chlorine or chloramines on leaching of organotins from PVC pipe. The primary objective of the current study was to examine PVC organotin leaching using PSRs to simulate flow conditions as well as in pipe-loops under steady-state operation, in the presence of chlorine or chloramine (representing secondary disinfectants). Results from this study will further the understanding of organotin leaching within typical distribution systems that include PVC pipe.

2. Materials and Methods

2.1 Test Pipes

Previous studies by Chen et al. (2022) and Wu et al. (2023) investigated organotins associated with AWWA C909, AWWA C900 and ASTM D1785 pipes. To select the appropriate pipe types for the current study, a list of pipe standards used in counties and municipalities located in Southern Ontario, Canada, was compiled (Table 2-1). All employed C900 pipe, followed by C905, and C909 pipe. C905 pipe (>350 mm diameter) was not selected for pipe-loop and PSR trials as its diameter was too large. C909 pipe differs from C900 pipe in that it is molecularly oriented PVC (PVCO), created by stretching PVC pipe stock during the manufacturing process which orients molecules in both hoop and longitudinal directions. C909 (PVCO) pipe is reported to be stronger and more flexible with approximately half the wall thickness of C900 (PVC) pipe (Westlake Pipe & Fittings, 2022).

2.2 Pipe-Loop Design

The pipe-loop design employed in the current study was based on that described by Arbiv et al. (2023) and allowed for the control of hydraulic residence time (HRT) as well as recirculation velocity. An expansion for 12 additional pipe-loops was designed (Appendix E). The pipe-loops were located onsite at a water treatment facility and received finished water as influent. The water was chloraminated whereby primary disinfection with free chlorine was followed by the addition of ammonia to obtain 1.85 ± 0.10 mg/L as total chlorine to provide secondary disinfection. All test

Table 2-1. Polyvinyl chloride (PVC) pipe usage for Town/Region A-F

Town/Region	**AWWA Pipe Standard**
A	C900
	C905
	C909
B	C900
C	C900
D	C900
	C905
E	C900
F	C900
	C909

pipes used in leaching trials were 150 mm (6”) in diameter and 183 cm (72”) long. The hydraulic retention time (HRT) and recirculation velocity of water within the pipe-loops was held constant at 24 h and 0.09 m/s respectively (typical flow velocity reported for the water treatment facility’s distribution network). These conditions were similar to reported recirculation velocities and hydraulic residence times used in previous PSR and pipe-loop studies (Arbiv et al., 2023; Curling et al., 2022).

Flow within the loops was achieved using a variable-speed recirculation pump (Grundfos TP 50-80/2 A-G-A-BUBE-EX2, Chicago, IL) and monitored with an inline magnetic-inductive flow meter (IFM Efector SM9601, Malvern, PA). A recirculation velocity of 0.09 m/s was achieved in the pipe-loops by setting the flow rate to 98.54 LPM (26 GPM) within the loops. A second pump (Intuitech 5130, Salt Lake City, UT) was used to continuously feed influent water. Varying the flow rate of this pump allowed control of the HRT within the pipe-loop. For all trials the influent flow rate was set at 11.3 mL/min to achieve an HRT of 24 h.

Pipe-loop effluent was sampled hourly using solenoid valves. Four online sensors were used to measure pH (Thermo Scientific Aquasensor pH, Beverly, MA), oxidation reduction potential (ORP) (Thermo Scientific Aquasensor ORP, Beverly, MA), conductivity (Thermo Scientific Aquasensor conductivity/resistivity, Beverly, MA), and total chlorine (HACH CL17Sc, Denver, CO). To be consistent with previous PSR and pipe-loop studies (Mutoti et al., 2007; Westbrook and Digiano, 2009) total chlorine concentrations were monitored. Dissolved oxygen (DO) and temperature were measured on site using a YSI 500A DO meter (YSI Inc., Yellow Springs, OH).

To determine background concentrations of DBT and MBT within a single pipe-loop (of four recirculating pipe-loops) a blank trial was conducted using two harvested unlined cast iron pipe sections (Figure 2-1). To quantify the DBT leaching rate from virgin PVC pipe, two sections each of C909 pipe and C900 pipe were installed (Figure 2-2).

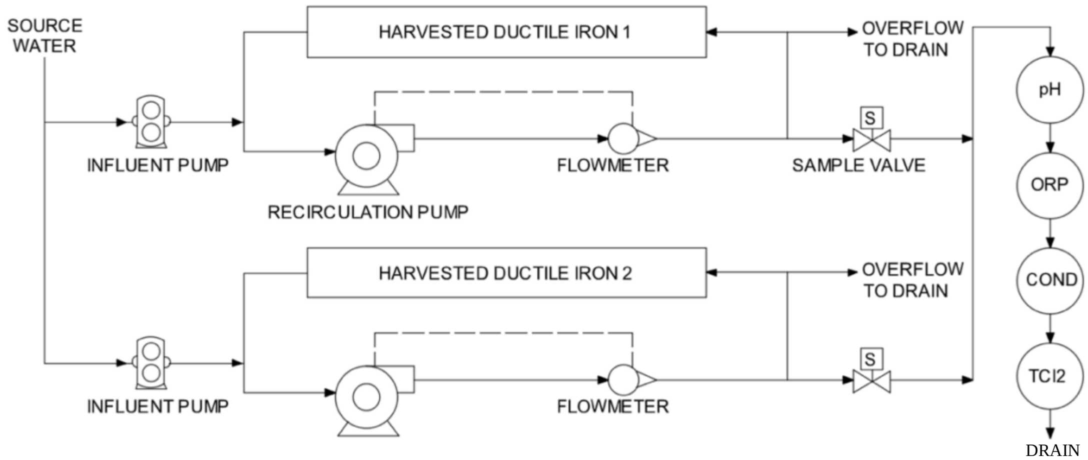

Figure 2-1. Blank MBT and DBT leaching trial pipe-loop schematic.

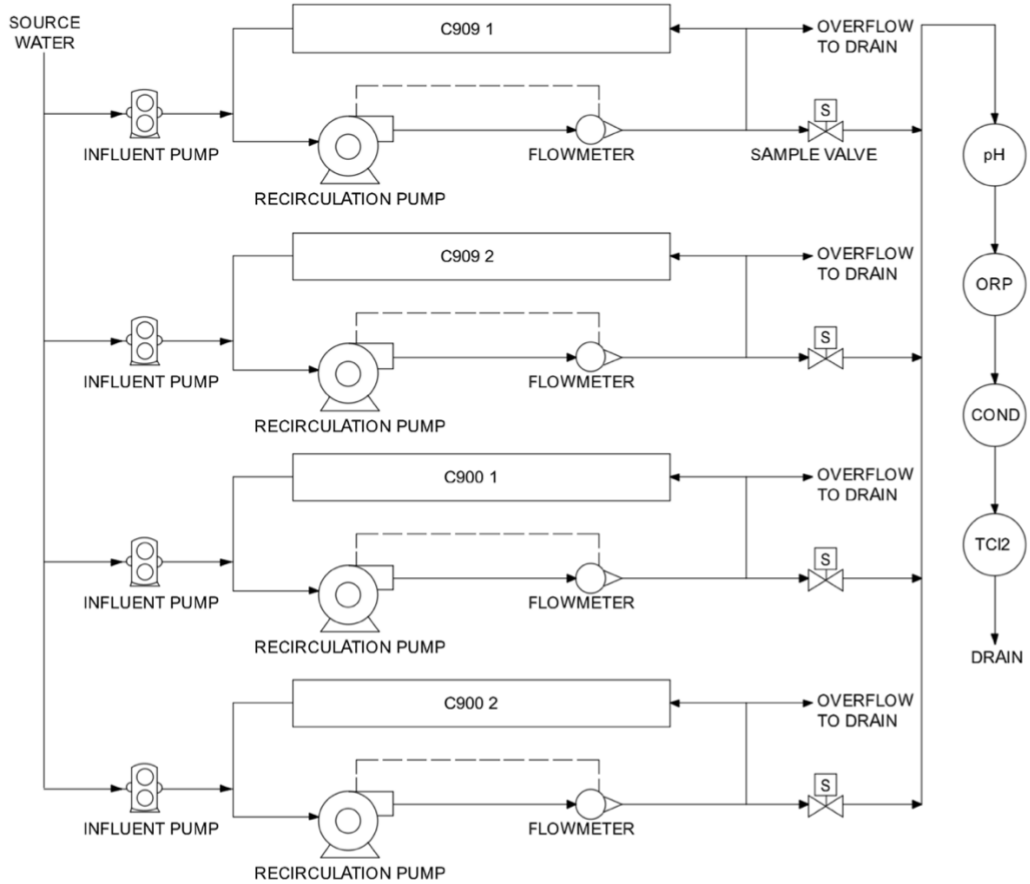

Figure 2-2. MBT and DBT leaching trial pipe-loop schematic.

2.3 PSR Design

A PSR as descried earlier by Curling et al. (2022) was employed (Figure 2-3). Briefly, virgin PVC test pipe sections 61 cm (24”) long, 150 mm (6”) nominal diameter were housed between two stainless steel plates and fastened using Teflon gaskets to create a watertight seal. Water flow was induced by a motor-driven impeller within a 100 mm (4”) nominal diameter stainless steel annular pipe inside located within the test pipe. Rotational speed was adjusted to achieve a desired water velocity of 0.09 m/s within the annular region. Water temperature was monitored using a thermocouple and adjusted by circulating an equal-volume mixture of water and glycol using a 0.5 horsepower chiller (Penguin Chillers, Knoxville, TN). A baffle plate was also placed across the inner pipe to prevent short circuiting and ensure even water distribution throughout the PSR. 0.5 L samples were withdrawn via a sampling tap. Prior to each trial, the PSR internal pipe was scrubbed with a 5% triclosan-based soap solution, an acrylic outer pipe was installed, the PSR was filled headspace-free with an 800 mg/L sodium hypochlorite solution, and left for 24 h before being rinsed in triplicate with deionized water to remove surface chlorine demand, based on procedure adapted from the Environmental Protection Agency (EPA) Office of Water (2019) (Table 6-3).

To quantify the presence of any potential background MBT and DBT a blank PSR trial (artificial freshwater (AFW), pH 8, 4 mg/L chlorine) was conducted using a harvested cast iron pipe. A harvested cast iron pipe was used as no DBT or MBT is used in the manufacturing process, as such any MBT or DBT observed would be associated with components other than the pipe itself. Leaching trials for C909 pipes were conducted at a 0.09 m/s recirculation velocity and using 4.00

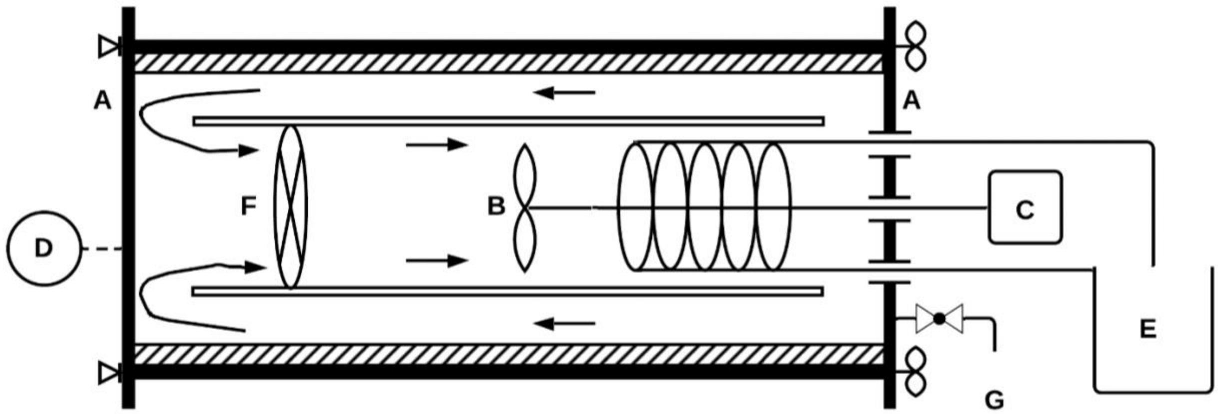

Figure 2-3. Schematic of PSR, cross section of outer PVC pipe represented by diagonal lines. A: stainless steel outer plates; B: impeller; C: motor drive; D: thermocouple for temperature control; E: temperature-controlled glycol bath; F: baffle plate; G: sampling tap.

mg/L and 0 mg/L free chlorine. Leaching trials for C900 were conducted at a 0.09 m/s recirculation velocity for 8.00 mg/L, 4.00 mg/L and 0 mg/L free chlorine concentration. 4.00 mg/L was selected to represent the maximum chlorine concentration allowed in water distribution networks following the EPA (Office of Ground Water and Drinking Water, 2007). A trial without chlorine allowed comparison between PSR trials and chloraminated pipe-loop leaching trials as an earlier study by Wu et al. (2023) reported that chloramine does not increase the leaching rate of organotin, making trials with no chlorine, and trials with chloramine comparable with respect to organotin leaching rates. All PSR trials were conducted using AFW buffered to a pH of 8 using sodium phosphate. A description of AFW, buffer solution, and chlorine is found in Appendix D Table 6-4, Table 6-5, and Table 6-6, respectively.

2.4 Sampling Methods

Previous studies which assessed PVC organotin leaching operated for either a few days (56 – 96 h) (Forsyth & Jay, 1997; Wu et al., 2023) or several weeks (336 – 672 h) (Adams et al., 2011;

Jones-Lepp et al., 2001). To allow comparison to previous studies, PVC related leaching trials were conducted for two weeks. Wu et al. (2023) reported leaching of DBT from PVC in chlorinated AFW to reach equilibrium within 24 h. Initial sampling was conducted at a higher frequency (0, 1, 1.5, 2, 4, and 6 h), followed by daily sampling thereafter for 14 days. For the pipe-loop trials, 0.5 L samples were collected from each loop as well as from the influent feed line. For PSR trials, 0.5 L samples were collected from each PSR and immediately derivatized using sodium tetraethyl borate ($NaBEt_4$) for organotin analysis. Samples were collected using 0.5 L amber glass bottles.

2.5 Analytical Methods

DBT and MBT were analyzed using gas chromatography tandem mass spectrometry (GC/MS), following a method adapted from Babu Rajendran et al. (2001). Samples were derivatized using a 5% $NaBEt_4$ solution (Table 6-7), following pH adjustment to pH 5 using 1 mL of a 1 M acetate buffer solution and the addition of 2.5 mL of tripropyltin (TPrT) internal standard. Subsequently 2 mL of the 5% $NaBEt_4$ was added to the sample and stirred at 500 RPM for 35 minutes; 10 mL of hexane was then added and stirred at 500 RPM for 30 minutes, prior to liquid-liquid extraction after allowing the sample stand for 30 minutes. A glass Pasteur pipette was used to transfer 2 mL of hexane into a 2 mL GC/MS vial.

An Agilent 7890B-5977B GC/MS incorporated a DB-5MS column (30 m x 250 µm x 0.25 µm); temperature program 50 °C for 1 min, followed by an increase to 280 °C at 20 °C/min for 2.5 minutes. Column flow rate 1.7 mL/min, injection volume 2 µL, inlet temperature 275 °C, and high purity helium used as the carrier gas.

The MS conditions included a transmission line temperature of 280 °C, ion source temperature 230 °C, quadrupole temperature 150 °C, an electron ionization (EI) source, ionization energy 70 eV. Selected ion monitoring (SIM) mode was used with a solvent delay of 2.7 min. Target ions for MBT and DBT were $SnC_8H_{19}^+$ and $SnC_{10}H_{23}^+$ respectively, representing the ethylated derivatives of MBT and DBT. Quantitation and qualification m/z values for MBT were 235 and 233. Quantitation and qualification m/z values for DBT were 263 and 261.

DBT (>96% purity) and MBT (>95% purity) standard solutions were obtained from Sigma Aldrich (St. Louis, MO, USA). TPrT obtained from Fisher Scientific (Mississauga, ON, Canada) was added as an internal standard. Calibration standards for DBT, MBT, and TPrT were prepared at concentrations of 0, 0.2, 0.5, 1.0, 1.5, 2.0 µg/L and analyzed every two weeks of GCMS analysis. R^2 values were used to determine linearity of calibration curves. R^2 values for the internal standard remained >0.99 for all calibration curves (Figure 6-1). Check standards prepared at concentrations of 0.15 µg/L, were included following every 10 samples during the first day of analysis and included once per week during daily sampling. Method detection limits were determined for both MBT and DBT by multiplying the standard deviation of eight 0.15 µg/L standards by the student's t value for a 99% confidence level with 7 degrees of freedom. MBT and DBT detection limits were 0.008 µg/L and 0.06 µg/L respectively.

3. Results and Discussion

3.1 PSR Trials

PSR leaching trials were conducted in duplicate over 2-week periods for each set of conditions. As DBT was observed to be <MDL of 0.06 μg/L for the 8 mg/L chlorine leaching trials involving C900 pipes, trials at 4 mg/L and 0 mg/L were not conducted (Figure 3-1A). Similarly, DBT concentrations for C909 leaching trials were all <0.06 μg/L at 0 and 4 mg/L chlorine. This demonstrates that under the worst-case conditions for organotin leaching (virgin pipe, pH 8, 4 mg/L free chlorine, continuous flow) C900 and C909 pipes did not leach DBT above detection limits.

MBT was observed above the detection limit of 0.008 μg/L only during the first 24 hours for both the C900 and C909 leaching trials. MBT results are similar to those reported by Forsyth and Jay (2001), where the highest levels were observed during the first 24 hours of static PSR trials. MBT was observed once above the detection limit of 0.008 μg/L (0.194 μg/L) for the C909 trial in which chlorine was not present (Figure 3-1B). In the presence of 4 mg/L free chlorine MBT exceeded the detection limit within the first 24 hours for the C909 4 mg/L trial, with the highest concentration (0.296 μg/L) observed at 2 hours. This suggests that the presence of free chlorine may enhance leaching, however further investigation at higher and lower free chlorine concentrations is required. MBT has been reported to occur in lakes and oceans due to the degradation of anti-fouling paints which contain TBT and DBT (Gao et al., 2006; Maguire et al., 1983; Pent & Hunn, 1995; Seligman et al., 1986). As such, the concentration of MBT in influent water should always be determined in order to confirm that its presence was due to leaching.

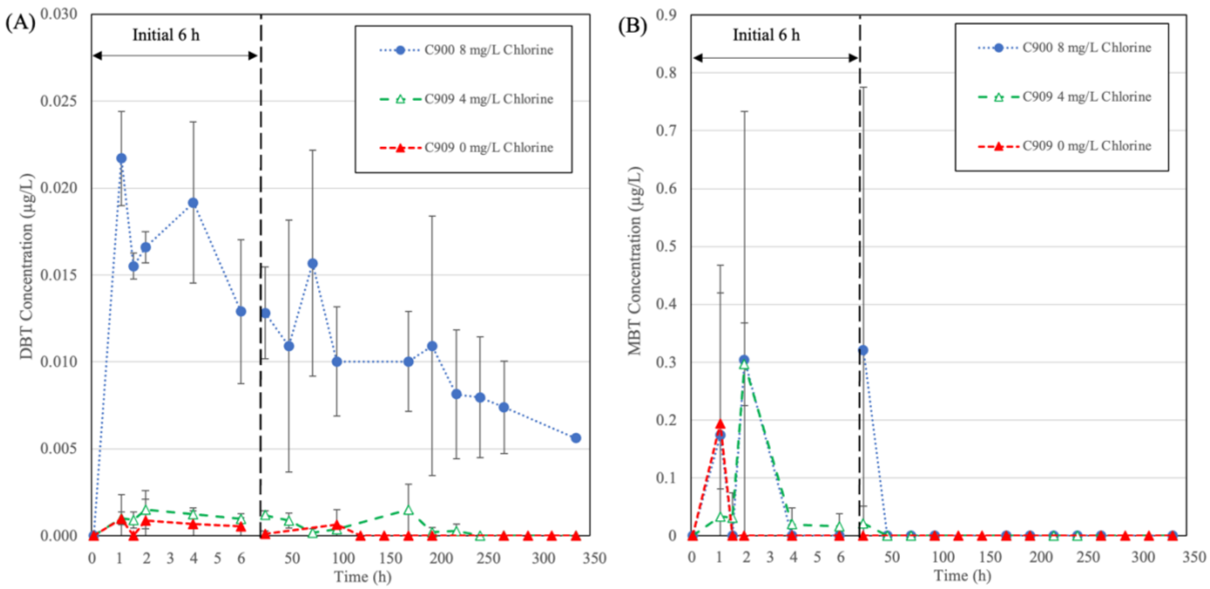

Figure 3-1. DBT (A) and MBT (B) leaching as a function of time using PSRs for C900 and C909 pipes. Trials were run in duplicate. Vertical bars represent ± 1 standard deviation. Detection limits of 0.06 µg/L and 0.008 µg/L for DBT and MBT, respectively.

3.2 Chloramine Decay in Pipe-Loops

Duplicate two week pipe-loop leaching trials employed harvested cement lined ductile iron (blank), as well as virgin PVC C900 and C909, both in duplicate. Both types of PVC pipe displayed similar total chlorine decay during the first 24 hours (Figure 3-2). First order chloramine decay coefficients were determined for both the C900 and C909 pipe. Without a comprehensive understanding of the water profile an empirical first order model can be used to determine chloramine decay coefficients (Roy et al., 2020).

Decay coefficients (0.0166 h^{-1} and 0.0157 h^{-1}) were similar for C900 and C909 pipe (Table 6-2). Previous studies which examined chloramine decay in PVC pipe reported first order decay coefficients <0.01 h^{-1} (Arbiv et al., 2023; Curling et al., 2022). At a recirculation velocity of 0.09 m/s, contact time was 8.25 s/m^2 in the recirculation line compared to 23.58 s/m^2 for the test pipe.

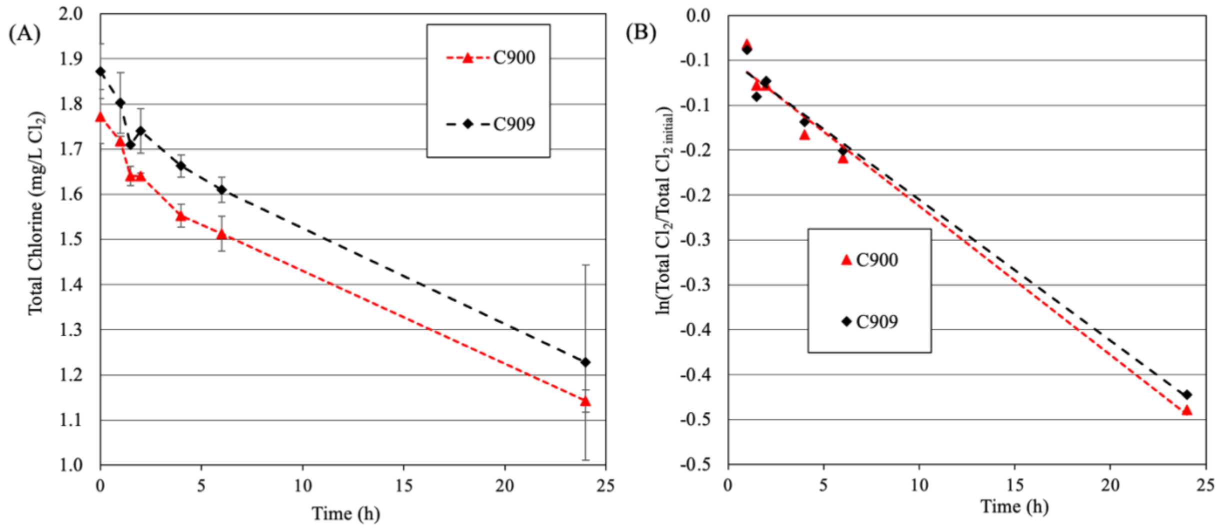

Figure 3-2. Total chlorine concentration (A), and first order chlorine decay (B) as a function of time for duplicate C909 and C900 pipe-loops. Vertical error bars represent ± 1 standard deviation based on pipe-loop duplicates.

3.3 Pipe-Loop Leaching Trials

DBT in the effluent of the C900 pipes was always below the detection limit of 0.06 µg/L. MBT decreased from 0.424 ± 0.130 µg/L (1 hour) to 0.058 ± 0.070 µg/L following 24 hours (Figure 3-3). DBT observed in C909 effluent was below the detection limit; MBT rapidly decreased from 2.034 ± 2.843 µg/L (1 hour) to <MDL by 24 hours (Figure 3-3). Due to the absence of DBT, the highly variable influent MBT, and the high MBT standard deviations the C909 leaching trials were ceased after 1 week. The lack of observable DBT leaching in the current study illustrated the influence of steady state operation when compared to the batch pipe-loop trials reported by Adams et al. (2011) and Wu et al. (1989). Both previous studies operated pipe-loops as a batch system for >200 hours, versus the steady state 24-hour HRT of the present study.

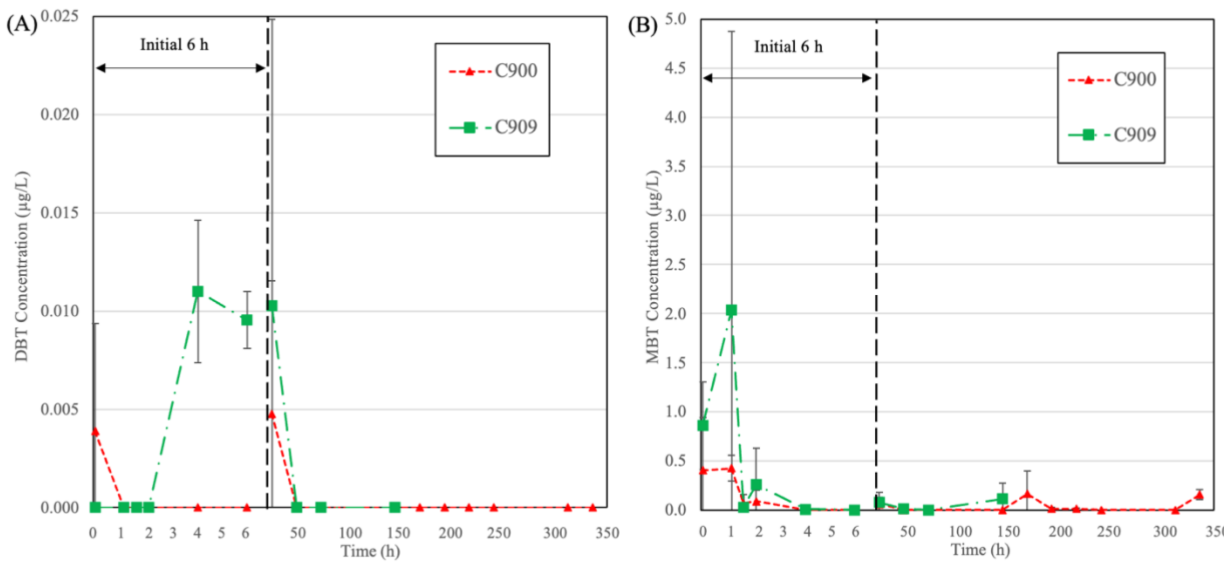

Figure 3-3. DBT (A) and MBT (B) leaching as a function of time for C900 and C909 pipe using pipe-loops. Vertical bars represent ± 1 standard deviation based on pipe-loop duplicates. Average total chlorine concentration, temperature, and pH were 1.11 mg/L, 7.32, 16.3 ˚C. Detection limit of 0.06 µg/L and 0.008 µg/L for DBT and MBT, respectively.

Differences with respect to internal PVC surface area to volume ratios should also be acknowledged when comparing the current study to those by others. The ratio has been shown to be proportional to the rate of DBT leaching using an equation proposed by Adams et al. (2011).

$$\frac{dy(t)}{dt} = \frac{A}{V} \cdot m(t) \tag{1}$$

In the current study, the surface area to volume ratio was 26.2 m^2/m^3 and 20.3 m^2/m^3 for the PSRs and pipe-loops, respectively. Due to the larger diameter pipe employed (150 mm in this current study versus 20 mm and 25 mm reported by Wu et al. (1989) and Adams et al. (2011)) these values are small when compared to 157.5 m^2/m^3 (Wu et al. (1989)) and 212.8 m^2/m^3 (Adams et al. (2011)) (7.7x larger). The DBT concentration observed at 24 h in one of the current C909 pipe-loops (0.021 µg/L) when multiplied by 7.7 is 0.162 µg/L would be closer to the 0.217 µg/L average reported by Adams et al. (2011).

A study of over 800 utilities located in North America reported the average water age in a water distribution network to be 1.3 days (Office of Ground Water and Drinking Water, 2002). With prior batch pipe-loop studies reporting organotin concentrations beyond a 1.3-day retention time, the current (24 h) study provides a more realistic approach to representing an actual distribution network where the water is continuously replaced. Under these conditions, the lack of observable DBT helps confirm that the certification procedure as reported in the NSF Drinking Water System Components – Health Effects standard is appropriate.

4. Summary

This study employed bench scale PSRs and pilot scale pipe-loops to quantify DBT and MBT leaching from C900 and C909 PVC pipe. DBT was below detection limits for both PSR and pipe-loop trials. The surface area to volume ratios used in this study (26.2 m^2/m^3 for PSRs; 20.3 m^2/m^3 for pipe-loops) were small compared to those reported in previous PVC organotin leaching studies. The smaller ratio was associated with the larger diameter (150 mm) pipe used in this study (20 mm and 25 mm in previous studies). In addition, the current pipe-loop system was operated at steady state (constant inflow and outflow), thereby greatly reducing potential DBT accumulation within the system. MBT was only observed within the first 24 hours of PSR trials, and chlorine concentration showed a positive influence on MBT leaching.

5. References

Adams, W. A., Xu, Y., Little, J. C., Fristachi, A. F., Rice, G. E., & Impellitteri, C. A. (2011). Predicting the Migration Rate of Dialkyl Organotins from PVC Pipe into Water. *Environmental Science & Technology*, *45*(16), 6902–6907. https://doi.org/10.1021/es201552x

Arbiv, I., Almuhtaram, H., & Andrews, R. C. (2023). Comparison of pipe loop and pipe section reactor methods for estimating chloramine decay in harvested distribution system pipes. *Science of The Total Environment*, *884*. https://doi.org/10.1016/j.scitotenv.2023.163722

Babu Rajendran, R., Tao, H., Miyazaki, A., Ramesh, R., & Ramachandran, S. (2001). Determination of butyl-, phenyl-, octyl- and tributylmonomethyltin compounds in a marine environment (Bay of Bengal, India) using gas chromatography-inductively coupled plasma mass spectrometry. *Journal of Environmental Monitoring*, *3*(6), 627–634. https://doi.org/10.1039/b106009k

Boyer, I. J. (1989). Toxicity of dibutyltin, tributyltin and other organotin compounds to humans and to experimental animals. *Toxicology*, *55*(3), 253–298. https://doi.org/10.1016/0300-483X(89)90018-8

Chen, C., Chen, L., Yao, Y., Artigas, F., Huang, Q., & Zhang, W. (2019). Organotin Release from Polyvinyl Chloride Microplastics and Concurrent Photodegradation in Water: Impacts from Salinity, Dissolved Organic Matter, and Light Exposure. *Environmental Science & Technology*, *53*(18), 10741–10752. https://doi.org/10.1021/acs.est.9b03428

Chen, W., Gong, Y., McKie, M., Almuhtaram, H., Sun, J., Barrett, H., Yang, D., Wu, M., Andrews, R. C., & Peng, H. (2022). Defining the Chemical Additives Driving *In Vitro* Toxicities of Plastics. *Environmental Science & Technology*, *56*(20), 14627–14639. https://doi.org/10.1021/acs.est.2c03608

Curling, E. A., McKie, M. J., Meteer, L., Saunders, B., Andrews, S. A., & Andrews, R. C. (2022). Estimation of chloramine decay in drinking water distribution systems. *Journal of Water Process Engineering*, *46*. https://doi.org/10.1016/j.jwpe.2022.102558

Filipkowska, A., Kowalewska, G., & Pavoni, B. (2014). Organotin compounds in surface sediments of the Southern Baltic coastal zone: a study on the main factors for their accumulation and degradation. *Environmental Science and Pollution Research*, *21*(3), 2077–2087. https://doi.org/10.1007/s11356-013-2115-x

Forsyth, D. S., & Jay, B. (1997). Organotin Leachates in Drinking Water from Chlorinated Poly(vinyl chloride) (CPVC) Pipe. *Applied Organometallic Chemistry*, *11*(7), 551–558. https://doi.org/10.1002/(SICI)1099-0739(199707)11:7<551::AID-AOC606>3.0.CO;2-0

Gagnon, G. A., Baribeau, H., Rutledge, S. O., Dumancic, R., Oehmen, A., Chauret, C., & Andrews, S. (2008). Disinfectant efficacy in distribution systems: A pilot-scale assessment. *Journal of Water Supply: Research and Technology - AQUA*, *57*(7), 507–518. https://doi.org/10.2166/aqua.2008.103

Gao, J.-M., Hu, J.-Y., Zhen, H., Yang, M., & Li, B.-Z. (2006). Organotin Compounds in the Three Gorges Reservoir Region of the Yangtze River. *Bulletin of Environmental Contamination and Toxicology*, *76*(1), 155–162. https://doi.org/10.1007/s00128-005-0902-x

Guangbao, Y. (2020). Determination of Migration of 11 Organotin Compounds in Food Contact Materials by GCMS. *Materials Science Forum*, *984*, 58–63. https://doi.org/10.4028/www.scientific.net/MSF.984.58

Hennighausen, G., & Lange, P. (1980). Immunotoxic effects of dialkyltins used for stabilization of plastics. *Polish Journal of Pharmacology and Pharmacy*, *32*(1), 119–124.

Jones-Lepp, T. L., Varner, K. E., & Hilton, B. A. (2001). Speciation and detection of organotins from PVC pipe by micro-liquid chromatography electrospray-ion trap mass spectrometry. *Applied Organometallic Chemistry*, *15*(12), 933–938. https://doi.org/10.1002/aoc.246

Kishi, H., Nemoto, M., Enomoto, M., Shinoda, M., Kawanobe, T., & Matsui, H. (2006). Acute toxic effects of dioctyltin on immune system of rats. *Environmental Toxicology and Pharmacology*, *22*(2), 240–247. https://doi.org/10.1016/j.etap.2006.04.007

Kucharski, D., Stasiuk, R., Drzewicz, P., Skowronek, A., Strzelecka, A., Mianowicz, K., & Giebułtowicz, J. (2022). Fit-for-Purpose Assessment of QuEChERS LC-MS/MS Methods for Environmental Monitoring of Organotin Compounds in the Bottom Sediments of the Odra River Estuary. *Molecules*, *27*(15), 4847. https://doi.org/10.3390/molecules27154847

Kurihara, R., Rajendran, R. B., Tao, H., Yamamoto, I., & Hashimoto, S. (2007). Analysis of organotins in seawater of the Southern Ocean and Suruga Bay, Japan, by gas chromatography/inductively coupled plasma mass spectrometry. *Environmental Toxicology and Chemistry*, *26*(4), 647–654. https://doi.org/10.1897/06-436R.1

Maguire, R. J., Carey, J. H., & Hale, E. J. (1983). Degradation of the tri-n-butyltin species in water. *Journal of Agricultural and Food Chemistry*, *31*(5), 1060–1065. https://doi.org/10.1021/jf00119a035

NSF/ANSI 61. (2016). *Drinking Water System Components-Health Effects*. https://d2evkimvhatqav.cloudfront.net/documents/NSF-ANSI_61_watemarked.pdf?v=1594929800

Office of Ground Water and Drinking Water. (2002). *Effects of Water Age on Distribution System Water Quality*. Environmental Protection Agency. Office of Water. https://www.epa.gov/sites/default/files/2015-09/documents/2007_05_18_disinfection_tcr_whitepaper_tcr_waterdistribution.pdf

Office of Ground Water and Drinking Water. (2007). *The Effectiveness of Disinfectant Residuals in the Distribution System*. (68-C-00-113). Environmental Protection Agency. Office of Water. https://www.epa.gov/sites/default/files/2021-05/documents/effectiveness_of_disinfectant_residuals_final_-_3-7-07.pdf

Office of Water. (2019). *Free Chlorine Distribution System Influent Hold Study Protocol*. (EPA 815-B-19-013). Environmental Protection Agency. https://www.epa.gov/sites/default/files/201908/documents/free_chlorine_distribution_system_influent_hold_study_protocol.pdf

Pagliarani, A., Trombetti, F., & Ventrella, V. (2012). *Biochemical and Biological Effects of Organotins* (A. Pagliarani, F. Trombetti, & V. Ventrella, Eds.). Bentham Science Publishers. https://doi.org/10.2174/97816080526531120101

Pent, K., & Hunn, J. (1995). Organotins in freshwater harbors and rivers: Temporal distribution, annual trends and fate. *Environmental Toxicology and Chemistry*, *14*(7), 1123–1132. https://doi.org/10.1002/etc.5620140702

Roy, R., Sathasivan, A., & Kastl, G. (2020). Simplified chemical chloramine decay model for water distribution systems. *Science of The Total Environment*, *741*. https://doi.org/10.1016/j.scitotenv.2020.140410

Sadiki, A.-I., Williams, D. T., Carrier, R., & Thomas, B. (1996). Pilot study on the contamination of drinking water by organotin compounds from PVC materials. *Chemosphere*, *32*(12), 2389–2398. https://doi.org/10.1016/0045-6535(96)00134-8

Seligman, P. F., Valkirs, A. O., & Lee, R. F. (1986). Degradation of tributyltin in San Diego Bay, California, waters. *Environmental Science & Technology*, *20*(12), 1229–1235. https://doi.org/10.1021/es00154a006

Snoiej, N., van Iersal, A., Penninks, A., & Seinen, W. (1985). Toxicity of triorganotin compounds: Comparative in vivo studies with a series of trialkyltin compounds and triphenyltin chloride in male rats. *Toxicology and Applied Pharmacology*, *81*(2), 274–286. https://doi.org/10.1016/0041-008X(85)90164-4

Westlake Pipe & Fittings. (2022). *PVCO & PVC: WHAT TO KNOW*. https://www.westlakepipe.com/sites/default/files/media/PI-TB-017-US-EN-0522.1_PVCO-vs-PVC.pdf

WHO. (2020). *Organotins in drinking-water*. https://iris.who.int/bitstream/handle/10665/338068/WHO-HEP-ECH-WSH-2020.7-eng.pdf

Wu, M., Chen, W., Peng, H., Almuhtaram, H., & Andrews, R. C. (2023). Leaching of Dibutyltin from Virgin Polyvinyl Chloride Pipe Material. *ACS ES&T Water*, *3*(8), 2161–2167. https://doi.org/10.1021/acsestwater.3c00003

Wu, W., Roberts, R. S., Chung, Y.-C., Ernst, W. R., & Havlicek, S. C. (1989). The extraction of organotin compounds from polyvinyl chloride pipe. *Archives of Environmental Contamination and Toxicology*, *18*(6), 839–843. https://doi.org/10.1007/BF01160298

Zhang, H., & Andrews, S. A. (2013). Effects of pipe materials, orthophosphate, and flow conditions on chloramine decay and NDMA formation in modified pipe loops. *Journal of Water Supply: Research and Technology - AQUA*, *62*(2), 107–119. https://doi.org/10.2166/aqua.2013.077

6. Appendices

Appendix A. Calibration Curves

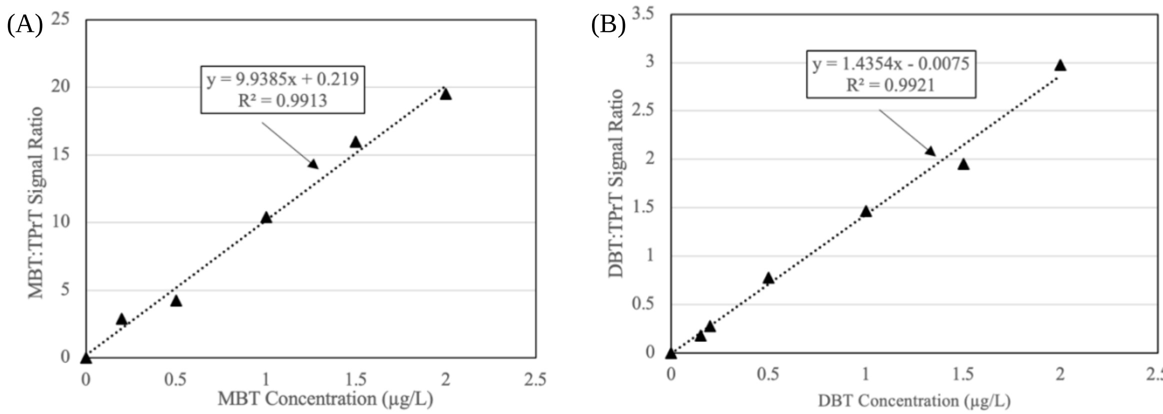

Figure 6-1. First MBT (A) and DBT (B) calibration curves

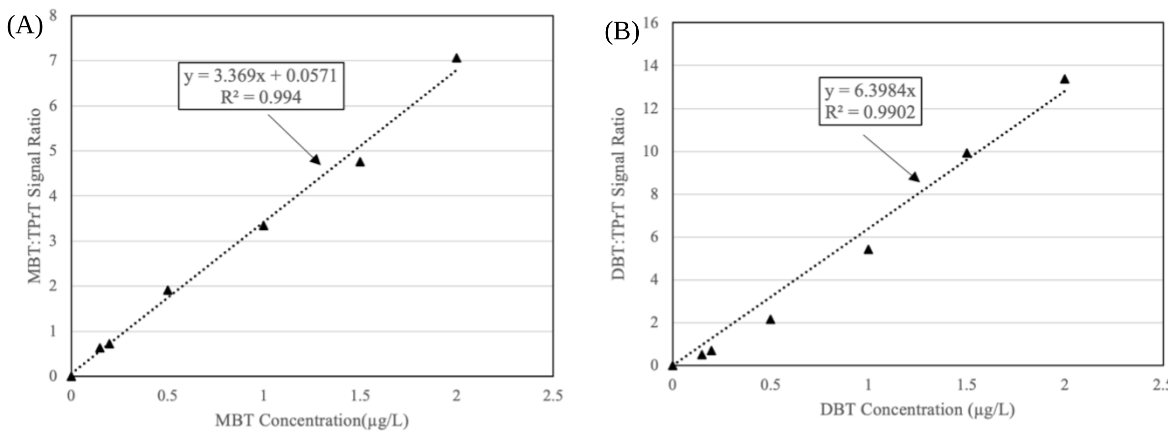

Figure 6-2. Second MBT (A) and DBT (B) calibration curves

Appendix B. Water Quality Data

Table 6-1. Pipe-loop total chlorine, pH and temperature. Averages and standard deviations based on a minimum of n=4 samples obtained after initial 24 hours.

Sampling Point	**Total Chlorine (mg/L)**	**pH**	**Temperature (˚C)**
Influent	1.89 ± 0.07	7.30 ± 0.04	9.39 ± 1.3
C900-1	1.11 ± 0.28	7.32 ± 0.04	16.67 ± 0.51
C900-2	1.10 ± 0.27	7.31 ± 0.05	15.98 ± 0.49
C909-1	1.06 ± 0.11	7.33 ± 0.03	16.86 ± 0.36
C909-2	1.38 ± 0.07	7.32 ± 0.04	16.51 ± 0.80

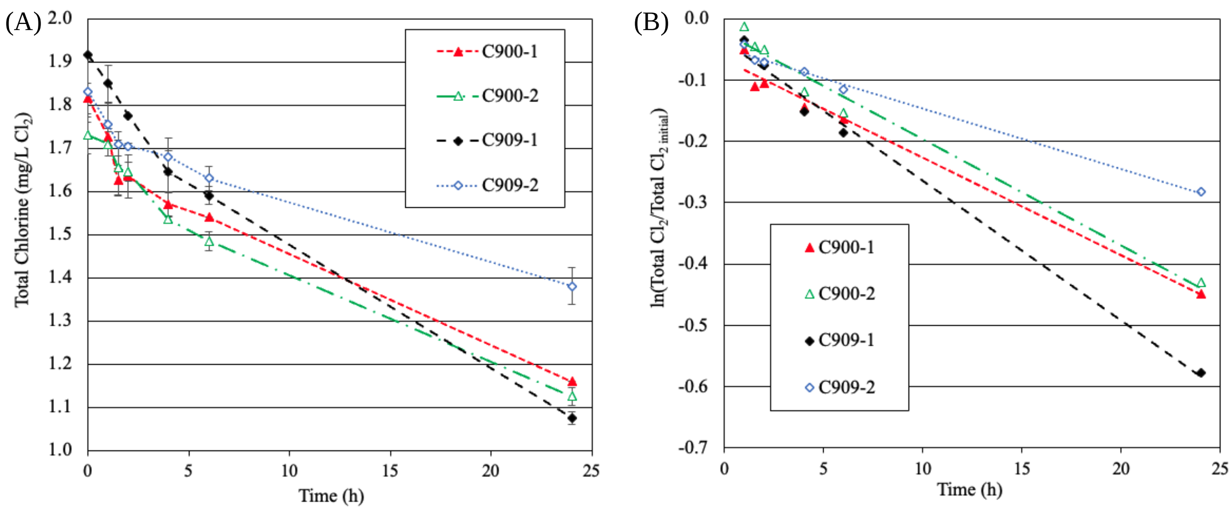

Figure 6-3. Total chlorine concentration (A), and first order chlorine decay (B) as a function of time for individual C909 and C900 pipe-loops. Vertical bars represent ± 1 standard deviation from duplicate total chlorine measurements.

Table 6-2. First order total chlorine decay coefficients for individual C909 and C900 pipe-loops.

Pipe	**First Order Decay Coefficient**	
	h^{-1}	**R^2**
C909-1	0.0228	0.99
C909-2	0.0099	0.99
C900-1	0.0159	0.98
C900-2	0.0173	0.98

Appendix C. Pipe-Loop Blank and Influent Data

A blank trial was conducted in order to determine the presence of any background MBT and DBT in the influent feed water to the pipe-loops. All DBT concentrations observed were below the detection limit (0.06 µg/L); MBT concentrations were greater than the detection limit of 0.008 µg/L ranging from 0.033 µg/L to 0.49 µg/L (Figure 6-4).

Apparent MBT spikes in the influent samples were not observed in any pipe-loops. This suggests that MBT may potentially be volatilizing within the pipe loop system, or may be accumulating in the scale and sediment present in the harvested CLDI pipe as reported in studies by others that have detected MBT in surface water sediments with the MBT originating from the degradation of TBT in water (Filipkowska et al., 2014; Kucharski et al., 2022).

To ensure that MBT was not associated with the piping upstream of the pipe-loops, samples were collected at four locations (Figure 6-5) on three separate days. These included the PVC influent header, effluent of the linear low-density polyethylene tubing which connects the influent header to each pipe-loop, the facility's treated water, as well as untreated source water. With the exception of one influent header sample all had MBT values <0.045 µg/L (Figure 6-6).

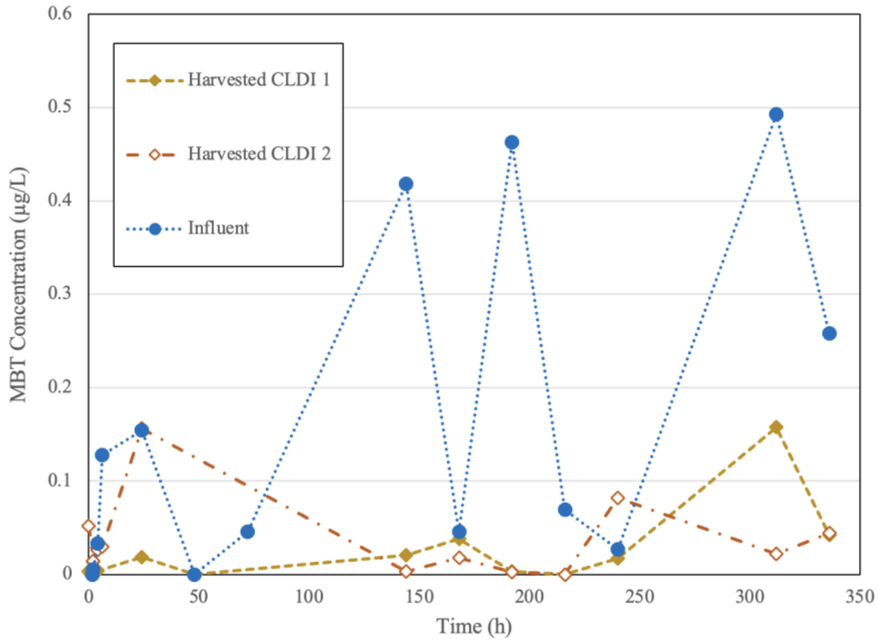

Figure 6-4. MBT concentration as a function of time for harvested CLDI pipes. Influent concentrations were sampled from the pipe-loop system's common influent header. MBT detection limit is 0.008 µg/L.

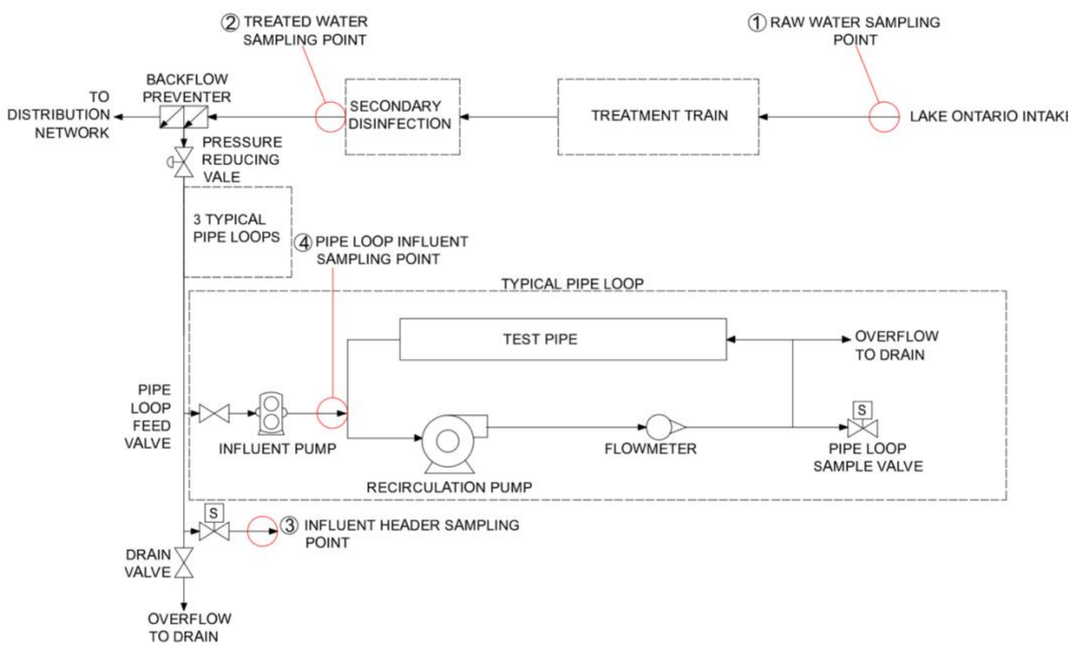

Figure 6-5. Influent sampling point locations; 1 – source water, 2 – treated water, 3 – influent header, 4 – pipe-loop influent tubing effluent.

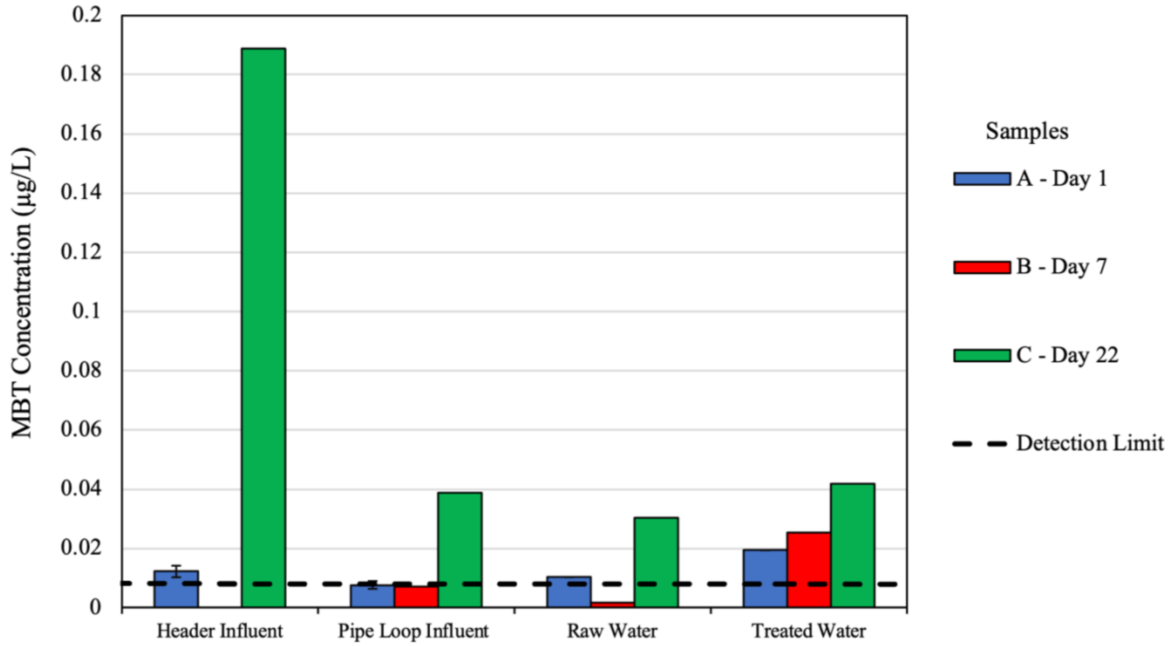

Figure 6-6. Influent MBT concentrations. 0.008 µg/L detection limit displayed as dashed line. Vertical bars represent ± one standard deviation from duplicate samples, (n = 2).

Appendix D. Standard Operating Procedures

Table 6-3. Reduction of chlorine demand within pipe section reactor (PSR) prior to use.

Reducing Chlorine Demand in the Pipe Section Reactors Prior to Experiments
1. Clean the acrylic outer cylinder by scrubbing with a solution of 300 uL dish soap and 600 uL of bleach per 100 mL of de-ionized (DI) water.
2. Rinse the outer cylinder 2x with DI and 1x with Elix® water.
3. Reassemble the reactor.
4. Add 1.5 mL bleach, stored in cabinet next to sink in dishwashing room, per 250 mL of reactor volume.
5. Fill the Pipe Section Reactor headspace-free with DI water.
6. After 24 h, rinse the Pipe Section Reactor 2x with DI water and 1x with Elix® water.

Table 6-4. Preparation of artificial freshwater (AFW) for PSR trials

Preparation of Artificial Freshwater (AFW)

1. Measure 1 L of Elix® water using a 1 L graduated cylinder.
2. Prepare 1200 mg/L KCl, 58000 mg/L $CaCl_2 \cdot 2H_2O$, 13000 mg/L $NaHCO_3$, and 24700 mg/L $MgSO_4 \cdot 7H_2O$ solutions in 250 mL amber bottles with Elix® Water.
3. Add the prepared KCl, $CaCl_2 \cdot 2H_2O$, $NaHCO_3$, and $MgSO_4 \cdot 7H_2O$ solutions to a 1 L volumetric flask containing 800 mL of Elix® water. Stirring continuously for 5 minutes using a stir bar.
4. Use 1 mL of each solution to achieve 1.2 mg/L KCl, 58 mg/L $CaCl_2 \cdot 2H_2O$, 13 mg/L $NaHCO_3$, and 24.7 mg/L $MgSO_4 \cdot 7H_2O$
5. Add Elix® water to the 1 L volumetric flask so that the meniscus reaches the 1 L marking.

Table 6-5. Preparation of pH 8 sodium phosphate buffer (0.1 M)

Preparation of pH 8 Sodium Phosphate Buffer (0.1 M)

1. Weigh out 138 g of monosodium phosphate (NaH_2PO_4) and 142 g of disodium phosphate (Na_2HPO_4) into separate weigh boats.
2. To prepare 1 M NaH_2PO_4, dissolve 138 g of NaH_2PO_4 in a 1 L volumetric flask into a sufficient volume of Milli-Q to make a final volume of 1 L.
3. To prepare 1 M Na_2HPO_4, dissolve 138 g of Na_2HPO_4 in a 1 L volumetric flask into a sufficient volume Milli-Q to make a final volume of 1 L.
4. To prepare pH 8 0.1 M sodium phosphate buffer, add 6.8 mL of the 1 M NaH_2PO_4 solution and 93.2 mL of the Na_2HPO_4 solution into a 1 L volumetric flask using a 100 mL graduated cylinder and an automatic pipette (as needed) into a 1 L volumetric flask. Dilute to 1 L using Milli-Q.

Table 6-6. Preparation of chlorine solution

Preparation of ~2000 mg/L Chlorine Solution
1. Determine the free chlorine concentration of 10-15% NaOCl stock solution, from Sigma-Aldrich.
2. Add about 300 mL of Milli-Q water to a 500 mL volumetric flask.
3. Add 50 mL of 10-15% NaOCl stock to the 500 mL volumetric flask. Mix the contents of the flask, and then raise the volume of the flask to 500 mL with Milli-Q water.
4. Next, aliquot 5 mL of the diluted stock to a new 100 mL volumetric flask and again raise the volume of the flask to 100 mL with Milli-Q water.
5. Next, aliquot 2 mL of the new dilution to a new 100 mL volumetric flask and raise the volume to 100 mL with Milli-Q.
6. Aliquot 25 mL of this stock to the spectrophotometer sample vial. Add a free chlorine powder pillow, shake the sample for 5 seconds, then measure and record the concentration of the sample after an additional 20 seconds.
7. Calculate the concentration of the stock solution based on the dilution and measured free chlorine concentration.

Table 6-7. Preparation of 5% $NaBEt_4$ solution

$NaBEt_4$ Preparation
1. Weigh out 5 g of $NaBEt_4$ into a 200 mL glass bottle in a nitrogen gas filled glove box.
2. Cap the bottle using a cap with a syringe opening and transfer to a fume hood.
3. Inject 100 mL of water into the bottle through the syringe opening using the 2 mL syringe.
4. Let out the flammable gas which builds up in the bottle's headspace into the fume hood.
5. Close the cap and store the solution in a fume hood.

Appendix E. Pipe Loop Expansion Drawings

Expansion drawings are found in supplementary files.