Array of prediction tools for understanding extent of wall effects on DBP formation in drinking water distribution systems
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ABSTRACT
The Stage 2 Disinfectant and Disinfection By-Product (D/DBP) regulations of the United States force water utilities to be more concerned with their distributed water quality. Improved compliance requires understanding of reaction kinetics and wall effects of different distribution materials used on DBP formation. To validate results in a full-scale system, effect of different materials, wall effects, bulk reactions, and water movement is analyzed using simulated distribution system (SDS) tests, material specific simulated distribution system (MS-SDS) tests, pipe loop, and pipe section reactor (PSR); all built using materials from the city of Columbia, Missouri’s distribution system. On average, the choice of polyvinyl chloride (PVC) and ductile iron can account for as much as 36% difference in trihalomethane (TTHM) formation and 60% difference in chlorine residual decay over time irrespective of the prediction model and operational strategy used. In the case of ductile iron, pipe effect (PE) is $<1$, which shows that in the ductile iron pipe systems there is a net loss of TTHM yield due to non-TTHM forming chlorine demand imposed by the pipe environment, whereas in PVC pipe, PE is $>1$. In PVC systems there is an overall increase in TTHM formation as a result of pipe wall surface reactions.

Key words | chlorine decay, DBPs, prediction models, trihalomethanes, wall effects

INTRODUCTION
Public utilities provide potable water for 90% of the United States (United States Environmental Protection Agency USEPA 1999). Federal regulation of drinking water quality began in 1914 with the U.S. Public Health Service setting standards for the bacteriological quality of drinking water. More than 500 disinfection by-products (DBPs) have been identified in tap water (Clark et al. 1996) and thousands more exist. To date, the identifiable DBPs cumulatively account for no more than 50% of the total organic halogen (TOX) in most chlorinated drinking waters, numerous halogenated DBPs formed from chlorine still remain unknown (Singer et al. 1995). The Stage 1 Disinfection and Disinfection By-Products Rule (D/DBP1) (63 FR 69390-69476, December 16, 1998, Vol. 63, No. 241) and Stage 2 Disinfection and Disinfection By-Products Rule (D/DBP2) (71 FR 388, January 4, 2006, Vol. 71, No. 2) are the current regulations for the control of carcinogens in potable water throughout the United States (USEPA 1998). These regulations aim to reduce exposure to contaminants including total trihalomethanes, five haloacetic acids, bromate, chlorite, chlorine, chloramines, and chlorine dioxide (USEPA 1998).

Pipe surfaces play a large part in the formation of DBPs occurring throughout the water treatment process (Digiano
& Zhang 2005). Even medium-sized water utilities may have hundreds of miles of pipes constructed from various types of materials, ranging from newly lined pipes to unlined pipes that are more than 50 years old. Many opportunities arise for water quality to change as it moves between the treatment plant and the customer (Boccelli et al. 2003; Clark 2011).

Cross-connections, failures at the treatment barriers, and the transformations in bulk phase can all degrade water quality. Corrosion, leaching of the pipe material and biofilm formation and scour can occur at the pipe wall and are subject to change with changes in materials, as well as with the operational strategies used. The distribution system can be considered a reactor where scale, surface reactions, chemical and biological corrosion, detachment, particulates, heterotrophs, and coliforms all play a role in impacting distributed water quality in terms of chlorine residuals and trihalomethanes (Clark 2011). This work addresses surface reactions in different pipe materials under different operational strategies as compared to bulk reactions in simulated distribution systems.

In order to understand the change in water quality during distribution, one needs to understand the effect of different materials in addition to effects of operational strategies (Clark et al. 1996; Sadiq & Rodriguez 2004). The most commonly used pipes today for water mains are ductile iron, pre-stressed concrete, polyvinyl chloride (PVC), reinforced plastic, and steel. For the purpose of this research, pipe sections made of PVC and ductile iron were used. The selection is justified by the fact that most of the treatment plants in Missouri and around the USA are either still using ductile iron or upgraded to PVC in the last decade (Gang 2001).

The objective of this study is to evaluate the magnitude of the effect of different pipe materials on both the chlorine decay rate and the trihalomethane (TTHM) formation rate under commonly used operational strategies such as normal run (NR), high chlorine (HC) and usage of chlorine boosters (BR) runs at constant pH and temperature. For this purpose, the well-documented prediction methods simulated distribution system (SDS), material specific simulated distribution system (MS-SDS), pipe section reactor (PSR), and a physical model of the distribution system (here referred to as pipe loop) were built using PVC and ductile iron pipe sections from an existing water distribution system.

### METHODS

#### Materials

Both a 6-inch (15 cm) diameter and a 4-inch (10 cm) diameter ductile iron pipe with an estimated age of over 40 years was extracted from the distribution system for PSR and MS-SDS processes, respectively. A 4-inch diameter PVC pipe with an age of one year was extracted from the pipe loop experiment for this study. Finished water from the filters with about 40 μg/L TTHMs, 2.5 mg/L chlorine residual, total organic carbon (TOC) 2.5 mg/L, and pH 8.6 was used as the source water for this work. These experiments are designed to show relative differences between systems as a way to understand optimum conditions to maintain water quality in terms of chlorine residual and TTHMs.

#### Design and testing

The physical model of a distribution system (pipe loop) was built in the filtration building of the city of Columbia (Missouri, USA) water treatment facility, as a means to understand changes in DBP formation kinetics under different operational conditions. City of Columbia is a lime softening facility with average ultraviolet absorbance at 254 nm (UV254) value of 0.052 cm⁻¹ within the source water. Surface conditions were close to a real system, thereby increasing the accuracy and feasibility of the conclusions/results presented (Figure 1(a)).

MS-SDS and SDS are most commonly used for determining the formation of biofilm inside pipes over time, but the test is flexible enough to be used for many other analytical purposes. MS-SDS test was conducted parallel to SDS test in accordance with Standard Method 5710C (American Public Health Association et al. 1998; Chan et al. 2002), with an objective to determine the extent of influence of wall reactions in DBP formation (Figure 1(b)). MS-SDS was set up in the laboratory at the university using pipe sections from the city of Columbia’s water distribution system and from the pipe loop. MS-SDS represents different materials in the same experiment with no movement. SDS was conducted using an amber glass jar and both tests used finished water from the Columbia water treatment facility (Figure 1(c)).
The PSR was designed using pipe sections from actual distribution systems. The reactor set up was designed to allow for change in pipe length and material, collection of samples and addition of chemicals (Figure 1(d)). The flowrate in PSR and loop systems is maintained at 40 GPM.

Normal run (NR) was used as the control or baseline for comparing other strategies and is based on typical operation of a drinking water treatment process which models treated water with a measurable disinfectant residual entering the distribution system. Finished water from the city of Columbia water treatment plant (before addition of ammonia) enters the pipe loop via a storage tank attached to it, the PSR via a stand pipe attached to it, and for MS-SDS and SDS purposes water was transported back to the laboratory.

In the case of the HC run, the pipe loop was operated in exactly the same manner as in NR, except the chlorine residual of the water entering the loop, PSR, SDS, and MS-SDS averages 6.4 mg/L (compared to 2.5 mg/L in NR). Many water utilities, in order to maintain residual throughout the distribution system, end up adding a much higher concentration of chlorine which leads to finished water leaving the system with a much higher residual.

To simulate the BR in the pipe loop, PSR, SDS, and MS-SDS finished water from Columbia water treatment plant (before addition of ammonia) was added to them. The average concentration of chlorine residual in the water was 2.4 mg/L. After 2 days of recirculation in the apparatus, additional chlorine was introduced into the system and the water continued to recirculate/stay for 2 more days before the apparatus was drained and the strategy was repeated.

All experiments were run as a function of time in order to maintain consistency in the format of the results from different experimental set-ups and to compare results with one another. All samples collected daily were tested for free and total chlorine residual, TOC, pH, UV254, and TTHM as a function of time over a period of 10 months. This analysis is designed not only to provide the best prediction tool option for each set of operational conditions, but also to give the best set of operational conditions to optimize the system for chlorine residual and DBP formation.
RESULTS AND DISCUSSION

PSR, loop and SDS data analysis

This analysis is intended to demonstrate the effect of each of the pipe materials and operational strategies on the chlorine decay rate and TTHM formation rate. Free chlorine residual change over time is considerably different between strategies as well as pipe materials (Figure 2), although all of them started with similar initial concentrations, except HC run. The difference in residual concentration over time in each run across PSR and loop as compared to SDS indicates the effect that each material and its respective wall effect have and differs between each run. This also differs based on the run, as can be seen in Figure 2 HC run. PSR made out of ductile iron material has the maximum decay rate throughout the runs with the highest in the HC run while SDS has the lowest decay rate. Because of non-reactive material used in the design, SDS accounts for only bulk reactions in the water.

Water treatment plants aim to maintain a minimum free chlorine of 0.5 mg/L in their distribution system and based on the data for the NR, PVC and SDS are able to maintain the required residual whereas ductile iron system becomes non-compliant after day 1. This explains why a large amount of chlorine is needed at treatment plants in order to maintain the minimum required residual throughout a distribution system that it is predominantly ductile iron pipes. The data show that having boosters installed in the distribution system to boost chlorine after day 1 (2 days of run time) would help all the systems (more so in loop and SDS systems) to be in compliance while accounting for loss of chlorine due to bulk and wall reactions.

It is frequently assumed that a majority of the chlorine lost in the distribution system is usually accounted for by the formation of DBPs and other compounds; while this might be true in systems made of PVC and glass where the wall demand of chlorine is minimal, it is far from the truth in ductile iron systems. In ductile iron systems, the wall demand of chlorine dominates to such an extent that the higher rate of chlorine decay is accompanied by lower rate of TTHM formations throughout all the PSR runs (Digiano & Zhang 2005) (Figure 3).

Based on SDS data in the HC run, it can be concluded that high chlorine conditions tend to increase the rate of bulk reactions, which minimizes wall effects on chlorine decay except in the PSR system. This can be partially explained by the concept of collision theory, which states that the presence of a higher concentration of one reactant particle in a solution has a potential to change/influence the reaction path, thereby affecting the concentration and type of products formed (Hill 1997). The high chlorine

![Figure 2](https://iwaponline.com/aqua/article-pdf/68/6/390/600968/jws0680390.pdf)

*Figure 2* Free chlorine residual concentrations in PSR, loop, and SDS under different operational strategies, LOC 95%.
scenario is one situation in which the wall reaction coefficient is less significant during calibration of physical or computer models can justify. However, as with most distribution systems, the operation tends to be more chlorine limited.

Data also show that the booster systems with lower TTHM formation and chlorine decay rates is an optimal solution for both chlorine residual maintenance and TTHM control irrespective of pipe materials. Decay kinetics that dictate rate are favorable in the case of boosters by limiting the rate of reactions due to low concentrations of chlorine available. Boosters allow a balance to be attained between chlorine residual availability and TTHM control.

A considerable difference in TTHM concentration on day 1 is observed in all systems given that day 0 is the same throughout; this can be explained by the difference in chlorine residual remaining and the wall demand for it in each system. It should be noted during the HC run that the required residual is maintained for a longer period while a high concentration (over the maximum limit) of TTHMs formed during day 1 will cause the water systems to become non-compliant. Meanwhile, the PSR systems that require higher concentrations of initial chlorine addition to maintain required residual might also end up non-compliant since initial reactions between the high chlorine concentration and organics will produce TTHMs sufficient to counteract the benefit of higher wall demand of the pipes. In the case of the pipe loop (PVC) system, the addition of a lower chlorine concentration initially and boosting the concentration in the system later can help the systems, in general, achieve compliance for chlorine residual and DBP regulations.

**Normal run vs high chlorine run**

NR and HC are the most commonly used operational strategies by water utilities. In SDS, it is observed that the difference in the chlorine residual decay and TTHM formation is significant yet consistent (Figure 4(c)). This can be attributed to only bulk reactions. The difference in TTHM concentration over time between NR and HC can solely be attributed to the higher reaction rates due to increased availability of free chlorine to the organics in treated water. It should be noted that in both runs, chlorine residual is maintained, but the system is non-compliant for TTHMs after day 1 (Figure 4).

In PSR, a notable difference in chlorine residual can be seen on day 0, which gradually reduces with time and by the end of day 2 they are almost similar in both runs whereas in the case of TTHMs, HC and NR started with the same concentration and the difference on day 1 and day 2 is 18% and 21%, respectively (Figure 4(a)). On day 3, the concentration of residual approaches zero in the difference in TTHM between drops by 14% which can be attributed to limited...
availability of residual for the formation. Another way to explain this is change in kinetics with change in concentrations of chemicals available. The impact of HC run is not as predominant in this system when compared to SDS and loop, yet the system is non-compliant after day 1.

In the loop system made of PVC pipe a considerable difference can be observed in both chlorine decay and TTHM formation rates which is similar to SDS and different from the PSR system. The effect of increased availability of chlorine can be attributed to all the difference in both rates, while the wall effect of PVC pipe explains the difference in rates between SDS and loop systems in both runs. It can be concluded that although HC run in the loop allows for residual maintenance, it hinders TTHM control (Figure 4(b)).

High chlorine run vs booster run

Using boosters to help maintain residual in long distribution systems is well known and documented, yet less frequently used in operational strategy (Poleneni & Inniss 2013). Especially in small-scale water utilities with distribution systems lasting between 1 and 3 days, HC is preferred over boosters for various reasons. HC runs offer increased ease and control and minimal structural and operational changes over boosters. The following analysis shows how these two runs affect chlorine and TTHMs in different systems.

In SDS systems, all is attributed to bulk reactions within the water and not due to wall effects. The bulk reactions in the context for this work are defined as reactions between organic matter and free chlorine. The need for boosters arises when the residual becomes less than 0.5 mg/L before the distribution system end. In SDS systems, the loss of residual due to wall effects is zero and bulk effects is minimal, thus eliminating a need for boosters to maintain the residual (Figure 5).

In PSR systems made of ductile iron pipes, the need for boosters is evident. On day 2, when the residual concentration is near 0.5 mg/L, additional chlorine is added to the system instead of adding an increased amount on day 0.
as seen in HC run (Figure 5). It was observed that when using boosters not only was the residual chlorine maintained, but it also resulted in decreased formation of TTHMs, thus assisting with compliance. A difference of 18% and 24% can be seen in TTHM concentration between HC and BR on day 1 and day 2, respectively (Figure 5).

The merits of BR over HC can be seen clearly in the loop system where both bulk and wall effects result in higher loss of residual and increased formation of TTHMs. On day 2, when the residual in the system is under 0.5 mg/L, additional chlorine is added into the system. It can be noted that both runs maintained the chlorine residual for longer periods, while the TTHM concentration in the HC run is 49%, 39%, and 28% compared to the BR run on day 1, day 2, and day 3 (Figure 5). The difference in residual and TTHM between the loop system and PSR systems for both runs can be attributed to differences in chlorine demand in pipe materials.

**MS-SDS data and analysis**

MS-SDS is used to better understand the extent of wall effects of different pipe materials on stagnant treated water over time when all conditions (pH, temperature, etc.) are kept constant (Chan et al. 2002). This method was developed by Brereton (1998) as a modification of standard SDS test that does not account for the biofilm formation on pipe surfaces and, therefore, may not be adequate to evaluate the processes in distribution system. When the two tests are run simultaneously, it is possible to distinguish a change in concentration of certain contaminants or chemicals in the water under the influence of two distinct environments: the bulk water and the pipe environment. For the purpose of this project, MS-SDS was built using glass, iron, and PVC materials and analysis was conducted to understand their effects on chlorine residual and TTHM concentrations over time.

The concentration of TTHMs is the same in MS-SDS and SDS on day 0 while the difference in them on days 1, 2, and 3 can solely be attributed to the pipe material that the water is stored in. These data can be used to evaluate bulk reactions in different pipe materials as compared to glass/SDS. It can be noted that the lowest rate of TTHM formation was observed in ductile iron pipe and the highest in the PVC pipe (Figure 6).

In regards to chlorine residual, the glass pipe maintains residual longer and in higher concentrations over time, as expected, due to zero wall demand for chlorine. Ductile iron pipes have much higher wall demand for chlorine compared to PVC, resulting in a system having chlorine residual 0.5 mg/L on day 2 (Figure 6).

The effect of the pipe material (PE or pipe effect) is defined as TTHM formed during pipe incubation (MS-SDS) divided by TTHM formed during glass incubation (SDS):

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\text{PE value} = \frac{\text{TTHM formed in MS-SDS}}{\text{TTHM formed in SDS}}
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Pipe effect values greater than unity (>1.0) indicate an overall increase in TTHM formation as a result of pipe wall surface interaction with residual chlorine. Pipe effect values less than unity (<1.0) reveal a net loss of TTHM formation. 

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**Figure 5** | TTHM and chlorine residual concentrations HC vs BR in PSR and loop systems.

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[390] S. R. Poleneni & E. C. Inniss | Prediction tools to understand wall effects on DBP formation
Journal of Water Supply: Research and Technology—AQUA | 68.6 | 2019
yield due to non-TTHM forming chlorine demand imposed by the pipe environment (Allen et al. 1980).

Based on the data collected from the SDS and MS-SDS systems daily over 10 months, the above pipe effect (PE) values are calculated (Table 1). The results show that in the case of ductile iron, PE is <1 on all 3 days that the test was conducted, leading us to conclude that in the ductile iron pipe systems there is a net loss of TTHM yield due to non-TTHM forming chlorine demand imposed by the pipe environment, whereas in PVC pipe, PE is >1 on all 3 days. Therefore, in PVC systems, there is an overall increase in TTHM formation as a result of higher pipe wall surface interaction with residual chlorine.

## CONCLUSIONS

The data analysis demonstrates that wall effects due to different pipe materials lead to considerable differences in chlorine residual decay and TTHM formation over time. This difference will dictate whether or not an operational strategy is appropriate for the system at hand. On average, only the choice of pipe materials such as PVC and ductile iron can account for as much as 36% difference in TTHM formation and 60% difference in chlorine residual decay over time, irrespective of the prediction model and operational strategy used. Operators with limited resources can benefit vastly from using MS-SDS with their distribution system pipes and treated water. This will allow them to understand the effect of a particular treatment or operational change that might influence treated water within the distribution system.

Data show that under normal operational conditions, it is easier to maintain residual in PVC pipe distribution systems when compared to ductile iron pipe distribution systems while TTHM formation is much harder to control in PVC systems. Based on the data analysis, it can be concluded that booster systems are optimal solutions for residual maintenance and TTHM control in all systems, more so in PVC. In the case of ductile iron pipe systems, the wall demand for chlorine dominates all other reactions involving chlorine residual leading to increased loss of residual and lower THMs formation over time irrespective of operational strategy in use. The data analysis also shows that assuming that wall effects are negligible while calibrating water quality models will lead to incorrect predictions of water quality parameter concentrations over time. Given that the results are only as good as the prediction model used and the model is only as good as the assumptions made, care needs to be taken while designing and using these model results for decision-making.

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