Research Paper

Water quality profiles during nitrification in a pilot distribution system study

Suibing Liu, J. S. Taylor and David Webb

ABSTRACT

Biochemical nitrification was investigated in a large scale pilot study using aged galvanized steel, unlined cast iron and a hybrid pilot distribution systems consisting of a combination of aged polyvinyl chloride, lined cast iron, unlined cast iron and galvanized steel pipes. Variations of free ammonia, nitrate, nitrite, dissolved oxygen (DO) and chloramine residual in the distribution system water are discussed for each pipe material. Chloramine depletion, DO depletion, free ammonia release, heterotrophic plate count (HPC) growth, NO_2-N and NO_x-N measured as the sum of nitrite and nitrate N were dependent on pipe material. Galvanized steel pipe had the highest chlorine demand and produced conditions without residuals, which corresponded to the higher HPC proliferation and DO consumption and the lowest nitrification. The greatest production of nitrite and nitrate was observed in unlined cast iron pipe. Denitrification was observed in the unlined cast iron pilot distribution system following residual loss and development of anoxic conditions.

Key words | chloramine, distribution system, drinking water, nitrification, pipe material, water quality

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INTRODUCTION

The application of chloramines and associated nitrification in drinking water distribution systems has increased as disinfection by-product (DBPs) regulations have become more stringent. Variations of water quality parameters indicative of nitrification as affected by pipe material, season and time are discussed in this work.

Nitrification was investigated in a large scale drinking water distribution system research facility during a nitrification episode, which lasted six months, and a planned experiment, which lasted another three months. The field facility consisted of seven pilot water treatment processes and eighteen pilot distribution systems (PDS). Three PDSs were made from pipes taken from actual distribution systems and consisted of 100% galvanized steel, 100% unlined cast iron and a hybrid of four different pipe materials, which were polyvinyl chloride (PVC), lined cast iron, unlined cast iron and galvanized steel. Finished waters produced from groundwater by aeration and chloramination, enhanced coagulation of surface water and desalination were blended and distributed to the PDSs to investigate water quality changes during distribution.

APPLIED LITERATURE

Chloramination is used by many utilities in the United States for control of disinfection by-products (DBPs), which are primarily trihalomethanes and haloacetic acids (Brodtmann & Russo 1979; Taylor et al. 1986; Thomas 1987; Leung & Valentine 1994). Chloramine is less reactive than free chlorine and produces less-known and unregulated DBPs (Wolfe et al. 1985).

The Environmental Protection Agency accepted chloramine as a secondary disinfectant in 1978, and as a primary disinfectant in 1983 (White 1999). However, since more contact time is required for equivalent chloramine disinfection relative to free chlorine, chloramine is typically not

used for primary disinfection. Nitrification has been reported in systems using chloramine (Wolfe *et al.* 1990, 1988; Barrios & Stone 1989; Cunliffe 1991; Lieu *et al.* 1993) and was also observed following the blending of different source waters in the Metropolitan Water District, Los Angeles, California, in reservoirs (White 1999). A survey (Wilczak *et al.* 1996; Odell *et al.* 1996) revealed that 63% of the utilities using chloramine had experienced nitrification. Another analytical survey of five chloraminated distribution systems in South Australia showed that 64% of the samples tested positive for nitrifying bacteria (Cunliffe 1991; Regan *et al.* 2002).

Nitrification is a two-step biochemical process in which free ammonia is oxidized to nitrite, and then nitrite is oxidized to nitrate. Two groups of chemoautotrophic bacteria, ammonia-oxidizing-bacteria (AOB) and nitrite-oxidizing bacteria (NOB), utilize free ammonia and nitrite, respectively, as their energy source (Lieu *et al.* 1993). Occurrence and speciation of AOB and NOB has been extensively investigated in chloraminated drinking water distribution systems (Regan 2001; Regan *et al.* 2003, 2002). Though the work conducted to date is preliminary, the major AOB species are considered to be *Nitrosomonas*, *Nitrosolobus*, *Nitrosococcus*, *Nitrosospira* and *Nitrosovibrio*. A survey of the major species occurring during nitrification is due in the near future. Wolfe *et al.* (1988) have reported the major NOB species are *Nitrobacter*; however more recently the major NOB species have been reported as *Nitrospira* (Regan *et al.* 2003).

AOB oxidizes free ammonia to nitrite, while NOB converts nitrite to nitrate. Both species utilize the energy released by the associated reactions. These reactions are complicated, but can be summarized as:
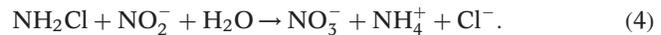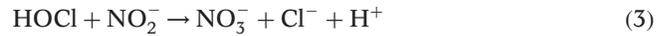
For AOB nitrification:

$$\frac{1}{6}NH_4^+ + \frac{1}{4}O_2 \rightarrow \frac{1}{6}NO_2^- + \frac{1}{3}H^+ + \frac{1}{6}H_2O \qquad (1)$$
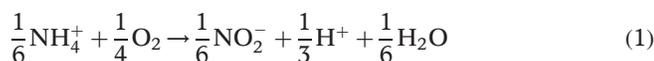
For NOB nitrification:

$$\frac{1}{2}NO_2^- + \frac{1}{4}O_2 \rightarrow \frac{1}{2}NO_3^-. \qquad (2)$$

Furthermore, nitrite in turn rapidly reduces free chlorine (Rittman & Snoeyink 1984) and accelerates the decomposition of chloramine (Valentine 1984). The reactions are

shown as (Chen & Jensen 2001)

$$HOCl + NO_2^- \rightarrow NO_3^- + Cl^- + H^+ \qquad (3)$$

$$NH_2Cl + NO_2^- + H_2O \rightarrow NO_3^- + NH_4^+ + Cl^-. \qquad (4)$$

Nitrification has been observed at high chloramine concentrations (up to 6 mg/L as Cl_2) in distribution systems. Consequently, high chloramine residuals may not stop nitrification (Wilczak *et al.* 1996) and are ineffective to control nitrification once AOB became established. The high chlorine to ammonia–Nitrogen ratio is a prerequisite to nitrification prevention. As shown in Eq. (1), free ammonia is a principal reactant for nitrification. Utilities using chloramine have reported chlorine to ammonia–Nitrogen ratios from 3:1 to 5:1 for the formation of chloramine (Wilczak *et al.* 1996).

A 5:1 ammonia-nitrogen ratio minimizes free ammonia following the formation of chloramine. However, a small amount of free ammonia is still present in the water when a 5:1 ammonia-nitrogen ratio is used to form chloramine (McGuire 1999). Nitrification has been demonstrated in laboratory conditions with as little as 0.05 mg/L of ammonia-nitrogen (Kirmeyer *et al.* 1995; Wilczak *et al.* 1996). Free ammonia-nitrogen can also be generated by nitrification. Chloramine will react with nitrite to produce free ammonia and chlorides, and more chloramine is consumed in an escalating series of biochemical reactions, which has been referred to as a "spiral of nitrification".

Nitrification produces several adverse effects in drinking water distributions systems, which include low chloramine residual (Valentine 1984), decreased alkalinity, decreased pH and associated lessened corrosion protection, low DO, increased nitrites, increased nitrates, increased HPC concentrations and corresponding violations of the Total Coliform Rule (Wilczak *et al.* 1996). Nitrification in drinking water distributions is undesirable but not regulated. Nitrite and nitrate are regulated only at the entry to the distribution system, but nitrification is monitored in distribution systems and is a significant problem for many utilities using chloramine for residual maintenance. The literature review demonstrated several undesirable effects on distribution system water quality associated with nitrification. Gaining knowledge about water quality

variations in different distribution systems during nitrification is essential to proactive nitrification control.

PILOT PLANT DESIGN AND OPERATION

Pilot distribution system

PDSs made of only aged galvanized steel pipe, only aged unlined cast iron pipe and a combination of aged PVC–lined cast iron–unlined cast iron–galvanized steel pipe were used in the study. All pipes were taken from existing distribution systems. Pure galvanized steel PDS were composed of a single material with six pipe reaches totaling 135 feet (41.1 m) of 2-inch (0.05 m) diameter galvanized iron pipe. Pure unlined cast iron PDS were composed of a single material with eight reaches of approximately 12 feet (6.1 m) totaling 96 feet of 6-inch (0.15 m) diameter cast iron. Hybrid PDSs were composed of four materials sequentially as following: 20 feet (6.1 m) of 6-inch (0.15 m) diameter PVC pipe, 20 feet (6.1 m) of 6-inch (0.15 m) diameter lined cast iron pipe, 12 feet (3.7 m) of 6-inch (0.15 m) diameter unlined cast iron pipe and 40 feet (12.2 m) of 2-inch (0.05 m) diameter galvanized steel pipe. All PDSs were provided with a sampling port after each pipe reach to allow an assessment of water quality changes associated with each pipe reach. A picture of the PDS structures is shown in Figure 1. The hydraulic residence time (HRT) of the PDSs was five or two days. The velocities ranged from 20–50 ft/d in the unlined cast iron PDS, from 28–70 ft/d in the galvanized steel PDS and from 19.2–48 ft/d in the hybrid PDS, which simulated near dead end flow conditions in distribution systems. The PDSs were flushed weekly at 1 ft/s (3 m/s) with five pipe volumes. The periodic flush simulated the operation of the actual distribution system (Taylor *et al.* 2001; Liu *et al.* 2003; Liu 2004). Water was passed through the pipe assemblies only once to simulate flow-through conditions.

Pilot water treatment processes

The groundwater simulated the finished water used by the member governments for more than 50 years. The finished groundwater was produced from the Cypress Creek
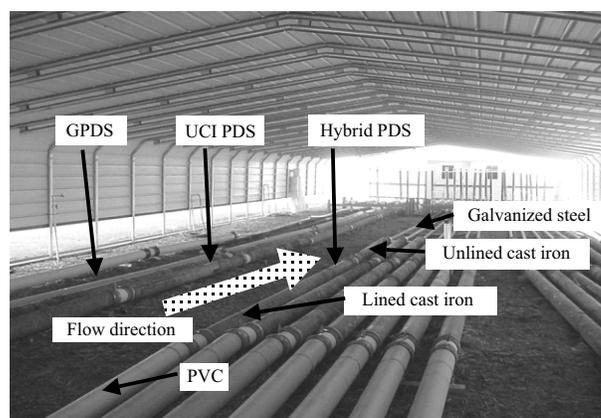
Figure 1 | Polyvinyl chloride (PVC), lined cast iron (LCI), unlined cast iron (LCI) and galvanized steel (G) pilot distribution systems.

groundwater by aeration and disinfection. All finished waters were stabilized and chloraminated prior to distribution. Stabilization was achieved by aeration. Primary disinfection was accomplished using sodium hypochlorite to produce free chlorine, which was allow to react for two minutes prior to ammonia addition The target for monochloramine residuals entering the PDSs was 4 mg/L as Cl_2. A 5:1 chlorine to ammonia-N ratio was used to produce chloramines, which were stored in a day tank. Chloramine makeup occurred daily and chloramine boosting in the day tank occurred every four to eight hours. Chloramines were dosed in individual PDS standpipes before entering the PDSs. Standpipes were an essential PDS component and maintained a constant hydraulic head on the PDSs, which never allowed them to become dry but did cause a slight variation in the recorded influent residual concentrations. The standpipe residence time was 5.3–2.1 h, depending on a 5- or 3-day HRT. Influent residual measurements were made in the standpipes randomly and were sometimes less than 4 mg/L as Cl due to the demand associated with the standpipe residence time (Taylor *et al.* 2001). Finished waters were stabilized with respect to $CaCO_3$ by aeration and the addition of $NaHCO_3$ and $CaCl_2$ to achieve a minimum of 50 mg/L carbonate alkalinity. NaOH was added to raise the final pH 0.1–0.3 pH units greater than the initial pH, which varied from 7.6–8, depending on which source and process was used to produce the finished waters. The conceptual schematic design of a groundwater process plant is shown in Figure 2.
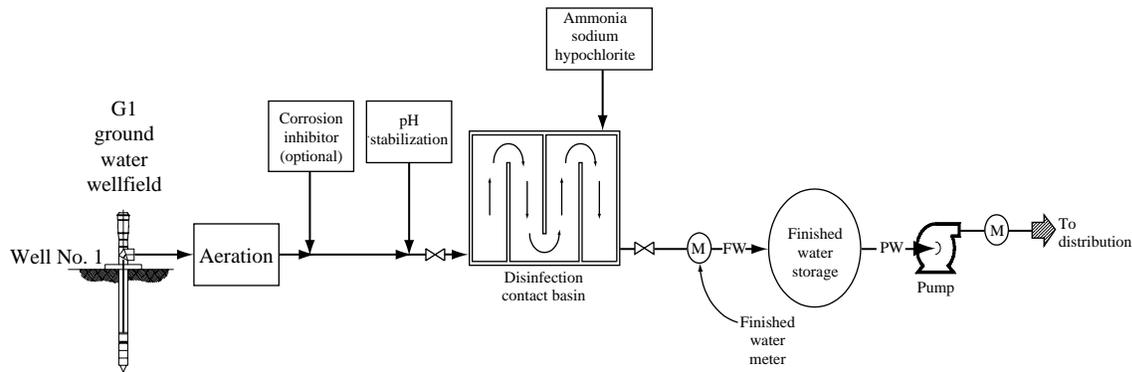
Figure 2 | The conceptual schematic design of groundwater treatment process.

Finished surface water was produced by enhanced coagulation–sedimentation–filtration, ozonation, biologically activated carbon filtration, aeration, chloramination and pH stabilization. The treatment process used to produce the finished surface water mimicked the TBW Regional Surface Water Treatment Facility's treatment process. The raw surface water was taken weekly from the Hillsborough River to the field facility. The raw surface water was coagulated using ferric sulfate to reduce the total organic carbon (TOC) to 3.6 mg/L or less. The coagulated water was settled for 24 h and filtered through a 1 micron bag filter and a 0.35 micron cartridge filter before ozonation. A minimum ozone residual of 0.6 mg/L was used to produce a 1.4 mg/L min CT. The ozonated water passed through activated carbon with a 5 minute empty bed contact time, a 0.35 micron bag filter and aerated to achieve equilibrium with DO. The treated surface water was then chloraminated and NaOH was added to make the finished water slightly supersaturated with respect to $CaCO_3$, which produced an

average final pH of 8. The conceptual schematic design of a surface water process plant is shown in Figure 3.

Desalinated water was produced by passing ground water through a reverse osmosis membrane. The processes consisted of 2.7 mg/L antiscalent addition, 5 micron cartridge filtration, membrane filtration, aeration, sea salt addition to mimic finished water from actual desalination, alkalinity addition, NaOH addition and chloramination. The membrane was operated at 75% recovery and produced 10 gpm of permeate. Sea salt, $CaCl_2$, $NaHCO_3$ and NaOH were added during post-treatment to mimic finished water produced by the TBW Regional Desalination Facility. Chloramination was identical to groundwater chloramination. The conceptual schematic design of a desalination process plant is shown in Figure 4.

All PDSs received identical water, which consisted of 60% groundwater, 30% surface water and 10% desalinated water. The blending ratio reflected the finished water used in the actual distribution systems. Water quality data was
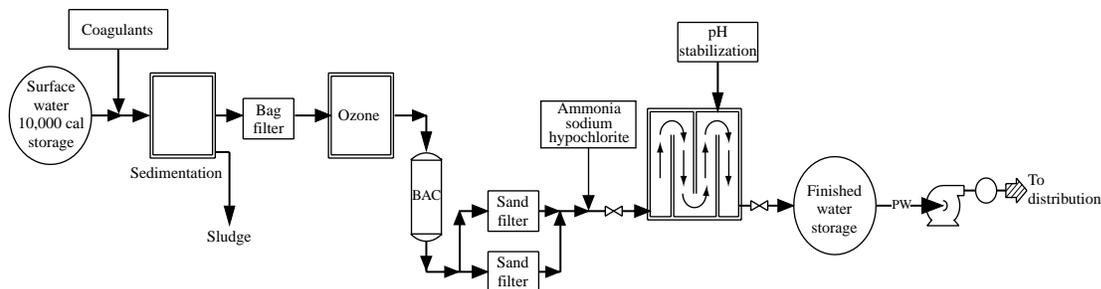

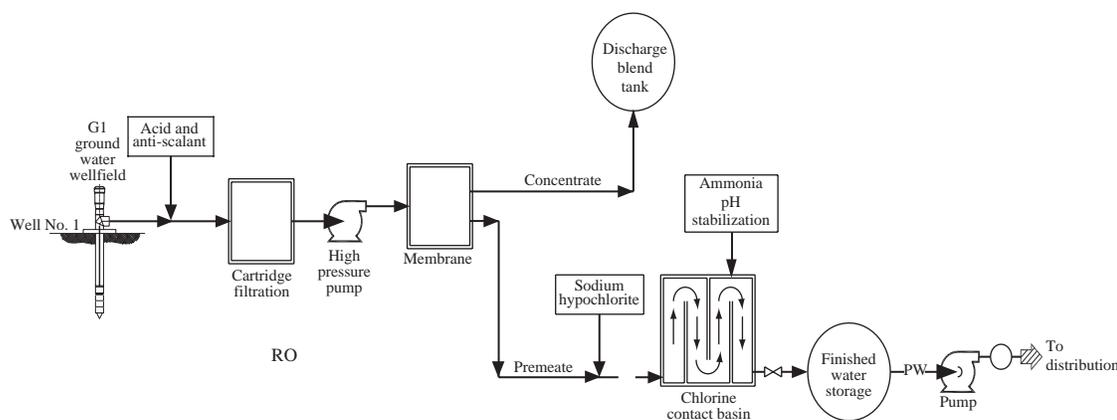**Figure 3** | The conceptual schematic design of surface water treatment process.

Figure 4 | The conceptual schematic design of desalination treatment process.

collected over four 3-month phases during the first year of operation. Phase I was from 12/06/2001 to 3/14/2002, phase II from 3/15/2002 to 6/13/2002, phase III from 6/14/2002 to 9/12/2002, and Phase IV from 9/13/2002 to 12/14/2002. Nitrification occurred in phase III. As a reactive measure to control nitrification in phase III, the PDS HRT was reduced from five to two days at the end of Phase III. The water quality profiles data were collected at Phase IV. The average and standard deviation (SD) of the feed stream water quality of the three PDSs is shown in Table 1, which reflects the consistency of the processes and the slight effect of the standpipes on influent residual.

Analytical methods

The major methodologies used in the field are summarized in Table 2, which are either standard methods (*Standard Methods* 2001) or methods published by Hach for nitrite and nitrate analyses (Hach 8192; Hach 8507). All the parameters listed in Table 2 were measured in the field immediately after sample collection. Actual nitrate (NO_3-N) was reduced to nitrite (NO_2-N) by the cadmium reduction method and both nitrite–N and nitrate–N were measured as NO_x-N. Hence, NO_x-N was reported and nitrate–N was determined by the difference between NO_x-N and NO_2-N. Typically NO_x-N and NO_2-N were reported. Comparison of NO_x-N in the PDS influent and effluent represents the

total nitrogen produced from ammonia due to nitrification and is therefore a direct indication of nitrification.

RESULTS AND DISCUSSION

Occurrence of nitrification

The influent and effluent chloramine residual and temperature in the hybrid, unlined cast iron, and galvanized steel PDSs are shown in Figure 5, 6 and 7, respectively, during the year of operation. The PDS feed stream chloramine concentration varied from 4.0–4.5 mg/L as Cl_2. The temperature range from December 2001 to June 2002 was 10–25°C. The temperature increased above 25°C during the summer, which accelerated residual depletion. The chloramine concentration in the hybrid PDS was greater than 1 mg/L as Cl_2 until May, 2002. The chloramine concentration in galvanized steel PDS was essentially always depleted, which removed the only means of controlling bacterial growth in the galvanized steel distribution system. Chloramine residual in hybrid and unlined cast iron PDSs decreased rapidly when temperature increased in May 2002, as shown in Figure 5 and Figure 6. Effluent residual was lost in all PDSs after May 2002, although influent chloramine concentrations were always above 4.0 mg/L as Cl_2, which illustrates the difficulty of maintaining residual. Beginning on 22 June 2002, all finished water chloramine

Table 1 | Average water quality for hybrid, unlined cast iron, and galvanized steel PDS influent (09/05/02–12/20/02, observations = 10)

Parameters	Unit	Hybrid PDS		Unlined cast iron PDS		Galvanized steel PDS	
		Average	SD[*]	Average	SD[*]	Average	SD[*]
Chloramine	mg/L Cl_2	4.3	0.8	4.3	0.6	3.9	0.8
Free Ammonia	mg/L N	0.3	0.1	0.3	0.1	0.3	0.1
PH	–	8.1	0.2	8.1	0.2	8.1	0.2
Alkalinity	mg/L $CaCO_3$	143	27	147	17	87	19
Ca hardness	mg/L $CaCO_3$	59	10	60	8	38	4
UV_{254}	cm^{-1}	0.049	0.006	0.052	0.004	0.035	0.008
Color	CPU	6	2	6	2	7	3
Turbidity	NTU	0.5	0.1	0.6	0.1	0.6	0.1
DO	mg/L	8.2	0.9	8.3	0.8	8.6	1.2
Conductivity	µS/cm	559	41	541	54	552	53
TOC	Mg/L	2.2	1	2.4	1.2	1.5	0.8
Temperature	°C	23.8	4.7	23.8	4.4	23.9	4.8
Chloride (Cl^-)	mg/L	32	5	35	5	43	6
Sulfate (SO_4^+)	mg/L	65	20	50	4	66	16
Total iron (Fe)	mg/L	0.06	0.01	0.07	0.01	0.06	0.02

[*]SD = standard deviation

Table 2 | Major water quality analytical methods

| Parameter	Method	Reference	Approximate range
Free ammonia	Membrane probe method	SM 4500-NH3 C	0.1–3 mg/L as N
Chlorine, free	DPD colorimetric	SM 4500-Cl G or Hach 8021	0.1–2 mg/L as Cl_2
Chlorine, total	DPD colorimetric	SM 4500-Cl-G or Hach 8167	0.1–2 mg/L as Cl_2
NO_x–N	Cadmium reduction	Hach 8192	0.1–0.5 mg/L as N
NO_2–N	Diazotization	Hach 8507	0.1–0.3 mg/L as N
Dissolved oxygen	Membrane probe	SM 4500-O G	0.1–20 mg/L
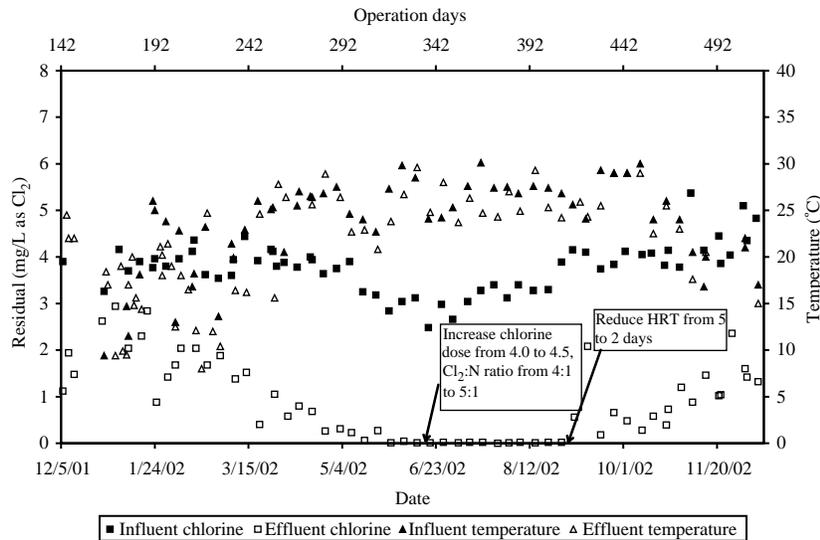
Operation days

Figure 5 │ Hybrid pilot distribution system total residual and temperature during operation.

concentrations were increased to more than 4.5 mg/L as Cl_2. However, no effluent residual was produced in any PDS. On 12 September 2002 the PDS HRT was reduced from five to two days, which produced a high chloramine residual in the hybrid PDS effluent, a low residual in the unlined cast iron PDS effluent and no residual in the galvanized steel PDS effluent (Liu 2004).

The chlorine demand in the unlined cast iron and galvanized steel PDSs was much higher than in the hybrid

PDS. The effluent residual in the galvanized steel PDS was 0.5 mg/L as Cl_2 from December until March and zero after March 2002 through to the end of the year as shown in Figure 4. The influent and effluent residuals in the unlined cast iron PDS were higher than the residuals in galvanized steel PDS. The lower residual in the galvanized steel can be easily attributed to the higher demand of the galvanized steel relative to any other material used in the PDSs. However, the higher demand of the galvanized steel also
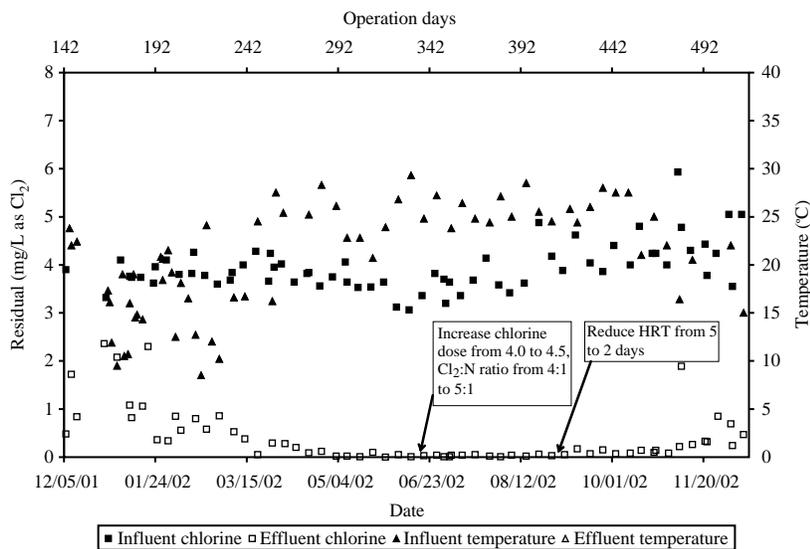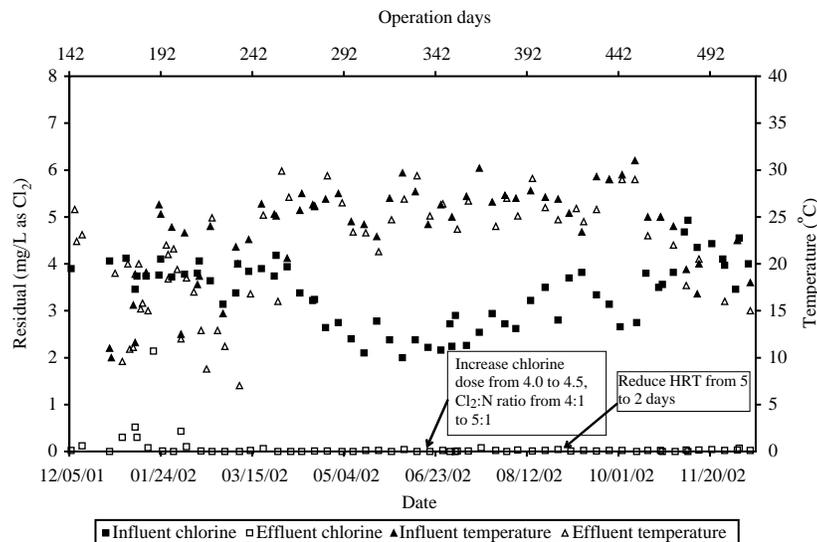
Operation days

Figure 6 │ Unlined cast iron pilot distribution system total residual and temperature during operation.

Figure 7 │ Galvanized steel pilot distribution system total residual and temperature during operation.

affected the influent residual as measured in the standpipe. The flow through the standpipes and PDSs was very low (0.02 and 0.05 ft^3/d for 5- and 2-day HRTs), which allowed diffusion in any PDS (including galvanized steel) to significantly affect the standpipe residual concentration. The highest bacterial population and growth occurred in the galvanized steel PDS, which was enhanced by high temperatures. Hence, periods of high bacterial growth associated with higher temperatures exerted a higher demand on influent residuals in the galvanized steel PDS relative to the cast iron PDS, as shown in Figures 6 and 7.

Consequently, the demand of the galvanized steel affected both influent and effluent concentrations.

Nitrogen and DO profiles

DO and nitrogen species (NH_2Cl-N, NH_4-N, NO_2-N, NO_x-N and total N) were determined biweekly at different retention times in all PDSs from September to December 2002, as shown in Tables 3, 4 and 5. NH_4-N, NO_2-N, and NO_x-N were measured using the procedures shown in Table 2. Total N was determined by summing of NH_2Cl-N,

Table 3 │ Average DO and nitrogen species water quality for hybrid distribution system during biochemial nitrification (10/10/02–11/22/02, observations = 4)

HRT (h)	PDS** (material)	NH$_2$Cl-N (mg/L as N)	NH$_4$-N (mg/L as N)	NO$_2$-N (mg/L as N)	NO$_x$-N* (mg/L as N)	Total nitrogen* (mg/L as N)	DO (mg/L)
0	PVC	0.85	0.27	0.00	0.03	1.16	8.7
16	LCI	0.78	0.29	0.01	0.05	1.12	8.2
34	UCI	0.65	0.35	0.01	0.03	1.03	8.0
44	G	0.42	0.44	0.02	0.10	0.96	6.7
47	G	0.33	0.48	0.02	0.11	0.91	6.9
49		0.24	0.54	0.02	0.15	0.94	6.8

*NO$_x$–N = NO$_2$–N + NO$_3$–N. Total nitrogen = NH$_4$–N + NH$_2$Cl–N + NO$_x$–N.
**PVC = polyvinyl chloride, LCI = lined cast iron, UCI = unlined cast iron, G = galvanized steel.

Table 4 | Average DO and nitrogen species water quality for unlined cast iron distribution system during biochemical nitrification (10/10/02–11/22/02, observations = 4)

HRT (h)	NH_2Cl-N (mg/L as N)	NH_4-N (mg/L as N)	NO_2-N (mg/L as N)	NO_x-N * (mg/L as N)	Total nitrogen * (mg/L as N)	DO (mg/L)
0	0.80	0.28	0.00	0.01	1.10	8.4
6	0.63	0.40	0.02	0.03	1.06	7.7
19	0.45	0.51	0.03	0.07	1.03	7.1
31	0.21	0.62	0.06	0.17	1.01	6.0
37	0.14	0.61	0.10	0.28	1.03	5.6
48	0.05	0.42	0.24	0.67	1.14	4.4

*$NO_x-N = NO_2-N + NO_3-N$. Total nitrogen = $NH_4-N + NH_2Cl-N + NO_x-N$.

NH_4-N and NO_x-N. NH_2Cl residual was measured and stoichiometrically converted to NH_2Cl-N. The samples were taken nearly simultaneously from a given PDS and represent the average water quality profiles during nitrification in hybrid, galvanized steel and unlined cast iron distribution systems.

As shown in Tables 3, 4 and 5, chloramine residual as shown by NH_2Cl-N loss decreased with time in all PDSs. Note that 4 mg/L NH_2Cl as Cl_2 corresponds to 0.8 mg/L as N. The order of residual (NH_2Cl-N) loss by PDS was galvanized steel > unlined cast iron > hybrid pipe material. Chloramine demand is not only due to nitrification reactions but comes from reactions with organic matter, microorganisms, pipe materials, corrosion products and other materials (Haas 1999). As determined from

Table 3, the NH_2Cl-N loss in the hybrid PDS during the initial 34 h was 0.20 mg/L NH_2Cl-N and increased to 0.41 mg/L NH_2Cl-N in the last 15 h in the hybrid PDS. This represents a five-fold increase in residual depletion when the water in the hybrid PDS contacts the unlined metal pipes relative to the relatively inert PVC and lined cast iron pipes. This observation is even more apparent in the loss of NH_2Cl-N in single material unlined cast iron and galvanized steel PDSs, as shown in Tables 4 and 5. The rate of NH_2Cl-N loss was approximately three times more in the unlined cast iron PDS and eight times more in the galvanized steel PDS as the residual loss in the PVC and lined cast iron reaches of the hybrid PDS. The chloramine demand in the hybrid PDS was lower than in the pure unlined metal PDSs (unlined cast iron and galvanized steel)

Table 5 | Average DO and nitrogen species water quality for galvanized steel distribution system during biochemial nitrification (10/10/02–11/22/02, observations = 4)

| HRT (h)	NH_2Cl-N (mg/L as N)	NH_4-N (mg/L as N)	NO_2-N (mg/L as N)	NO_x-N * (mg/L as N)	Total nitrogen * (mg/L as N)	DO (mg/L)
0	0.76	0.29	0.00	0.01	1.06	8.8
15	0.07	1.01	0.02	0.08	1.16	4.9
31	0.00	1.07	0.01	0.07	1.14	1.4
41	0.00	1.12	0.01	0.07	1.19	0.8
49	0.00	1.11	0.02	0.08	1.19	0.6
52	0.00	0.88	0.10	0.24	1.12	0.8

*$NO_x-N = NO_2-N + NO_3-N$. Total nitrogen = $NH_4-N + NH_2Cl-N + NO_x-N$.

due to the presence of inert material, PVC and lined cast iron, and the rapid loss of residual was delayed.

Free ammonia-N in the PDS influent was typically less than 0.3 mg/L as N. The free ammonia came primarily from chloramine decay during the average 3-day detention time in the storage tanks and was unavoidable due to operational constraints of the field facility. The variation of free ammonia-N for all PDSs is shown by time in Tables 3, 4 and 5. Free ammonia-N increased initially with time in all the PDSs, due to the release of free ammonia from the chloramine decay. However as shown in Table 4, the average free ammonia-N peaked at 31 h in the unlined cast iron PDS and consistently decreased after 31 h. Nitrite and NO_x–N increased steadily with time throughout the unlined cast iron PDS. One explanation for the variation in nitrite and NO_x–N concentrations through the unlined cast iron PDS is that nitrite and NO_x–N concentrations increased due to biological nitrification, and that the release of free ammonia from chloramine was exceeded by ammonia consumption by nitrifiers after the peak free ammonia concentration.

DO should vary stoichiometrically during biochemical nitrification. However, DO can be consumed by chemical oxidation and the growth of other bacteria than nitrifiers. DO decreased from 8.7 to 6.9 mg/L after 48 h through hybrid PDS, from 8.45 mg/L to 4.4 mg/L after 48 h through the unlined cast iron PDS and from 8.8 mg/L to less than 1 mg/L after 35 h galvanized steel PDS. The rate of DO depletion in the galvanized steel PDS was almost an order of magnitude greater than in the unlined cast iron PDS and almost four times greater than in the PVC and lined cast iron reaches of the hybrid PDS. The order of DO depletion by PDS material corresponded to the order of residual depletion by PDS material, which is galvanized steel > unlined cast iron > PVC and lined cast iron.

Aerobic conditions were maintained in both hybrid and unlined cast iron PDS, while anaerobic conditions developed quickly in the galvanized steel PDS. The loss of residual was so rapid in galvanized steel PDS that microorganism proliferation quickly consumed DO and biological nitrification was practically impossible, which is supported by the relative PDS effluent DO concentrations and HPC populations illustrated in Tables 3, 4 and 5 and Figure 8. The average HPCs in the different PDSs varied by
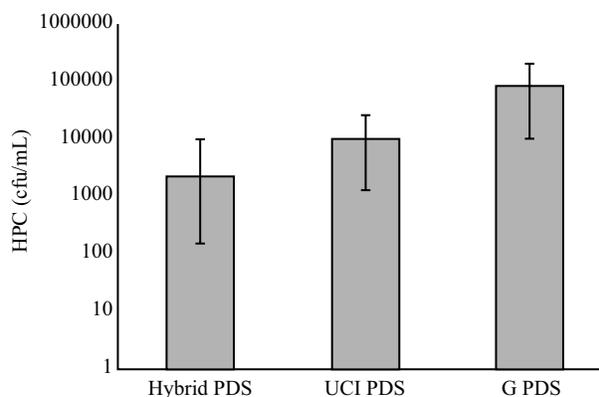
Figure 8 | Effluent HPC concentrations for hybrid, unlined cast iron, and galvanized steel pilot distribution systems (R2A method, 9/09/02–12/20/02, observations = 8).

approximately one log. The approximate average HPC concentrations in the galvanized steel, unlined cast iron and hybrid PDSs were 5 log, 4 log and 3.2 logs. The rate of HPC proliferation by PDS material is of the same order as the rate of DO and residual depletion by PDS material, that is galvanized steel > unlined cast iron > hybrid. Consequently the proliferation of non-nitrifying bacteria severely restricted nitrification in the galvanized steel PDS, whereas the lack of proliferation of non-nitrifying bacteria promoted nitrification in the unlined cast iron PDS. Trace nitrification was observed in the effluent from the galvanized steel PDS because of sample collection from the effluent standpipe, which was open to the atmosphere. As shown by the slight DO increase in the galvanized steel PDS at 52 h, which did not occur in any other PDS, oxygen diffused into the water in the standpipe and induced nitrification. Utilities that maintain low distribution system DO and high residuals can create an undesirable environment for nitrification. However, no utility should risk creating a potential for anaerobic conditions in the distribution system to control nitrification. As can be seen from the previous discussion, HPCs or DO alone cannot be used to proactively monitor nitrification.

The NO_x–N produced in the galvanized steel, unlined cast iron and hybrid PDS was 0.24, 0.67 and 0.15 mg/L, respectively, and the NO_2–N produced in the galvanized steel, unlined cast iron and hybrid PDS was 0.10, 0.24 and 0.02 mg/L, respectively. The order of NO_x–N and NO_2–N production with respect to the material was different than

the order of HPC growth, DO and chloramine depletion with respect to material. More NO_x–N and NO_2–N was produced in the unlined cast iron PDS, whereas more HPC grew and DO and chloramine were depleted in the galvanized steel PDS. This was attributed to the high growth of non-nitrifying bacteria in the galvanized steel PDS. However, the lowest nitrification, HPC growth, DO and chloramine loss occurred in hybrid PDS and was due to a higher disinfectant residual. The hybrid PDS differed significantly from other PDSs because the water in the hybrid PDS spent half of the time in contact with PVC and lined cast iron pipes that had a very low chloramine demand, which restricted bacterial growth. Bacterial processes including biochemical nitrification are sensitive to residuals. High chloramine residual significantly retarded biochemical nitrification, while rapid loss of chloramine residual corresponded to DO loss and produced an undesirable distribution system environment. Results in the hybrid PDS suggest that nitrification could be effectively retarded in any distribution system with pipe materials with a low residual demand such as PVC or lined cast iron.

Denitrification

Biochemical nitrification was induced in a controlled nitrification experiment by partially quenching the chloramine residual and adding 0.5 mg/L ammonia-N in the unlined cast iron PDS influent from April to July 2003.

The average associated nitrogen species and DO for varying unlined cast iron residence times are shown in Table 6. Noting 4 mg/L as NH_2Cl–Cl_2 corresponds to 0.8 mg/L as NH_2Cl–N, 0.56 mg/L NH_2Cl–N (2.8 mg/L NH_2Cl–Cl_2) was consumed in approximately 20 h. Given 0.55 mg/L of free ammonia-N was available at time 0 and 0.56 mg/L of free ammonia-N was released from chloramine degradation, 1.11 mg/L of free ammonia-N was available for nitrification between 0–20 h.

Biochemical nitrification occurred almost immediately and appears to be maximized at 31 h based on NO_x–N production. Anoxic conditions developed after 31 h, which created an environment conducive to biochemical denitrification. Nitrite and nitrate concentrations decreased after 31 h due to biochemical denitrification, which is also illustrated by decreased total nitrogen after 31 h and decreased because of the loss of nitrogen gas. As shown in Tables 3–5, the total nitrogen concentration changed very little while passing through any of the three PDSs. However, as shown in Table 6, the average total nitrogen in the water passing through the unlined cast iron PDS from April to June 2003 decreased from 1.13 mg/L to 0.42 mg/L as N. DO and total N depletion were clearly correlated and indicative of biochemical nitrification–denitrification. Chloramine residual is also clearly absent during denitrification, and decreased to nothing during nitrification. As expected, nitrite and NO_x–N concentrations increased during nitrification and decreased during denitrification.

Table 6 | Average DO and nitrogen species water quality for unlined cast iron PDS with denitrification during specially designed nitrification experiment (5/16/03–6/26/03, observations = 3)

HRT (h)	NH_2Cl–N (mg/L as N)	NH_4–N (mg/L as N)	NO_2–N (mg/L as N)	NO_x–N* (mg/L as N)	Total nitrogen* (mg/L as N)	DO (mg/L)
0	0.56	0.55	0.01	0.03	1.13	6.74
6	0.15	0.54	0.03	0.16	0.85	5.03
19	0.03	0.28	0.25	0.45	0.75	2.65
31	0.00	0.07	0.12	0.51	0.58	0.46
37	0.00	0.04	0.10	0.40	0.44	0.23
48	0.00	0.02	0.11	0.40	0.42	0.16

*NO_x–N = NO_2–N + NO_3–N. Total nitrogen = NH_4–N + NH_2Cl–N + NO_x–N.

Nitrification was practically insignificant until the chloramine residual was lost, but was very significant after residual was lost. Utility maintenance of residual at all points in a distribution system is exceedingly important in maintaining distribution water quality. Ammonia and DO consumption can be monitored for proactive control of nitrification, whereas nitrite and nitrate are reactive indicators of nitrification but should also be monitored. HPC population and growth did not always increase simultaneously with biological nitrification but can be monitored for maintaining biological water quality. Monitoring and control of nitrification could be increased at points in the distribution system that are influenced by galvanized steel or unlined cast iron pipes and during periods of high temperatures (>25°C).

SUMMARY AND CONCLUSIONS

- Biochemical nitrification was investigated for one year in a field study using three different pilot distribution systems made of aged galvanized steel, aged unlined cast iron and a hybrid consisting of aged PVC, lined cast iron, unlined cast iron and galvanized steel, which had been used in actual distribution systems. Water temperature and these materials significantly influenced the chloramine demand, and hence biochemical nitrification, in the pilot drinking water distribution systems.

- The rate of chloramine consumption in the unlined galvanized steel and cast iron was, respectively, eight times and three times the rate of chloramine consumption in the PVC and lined cast iron for identical waters and temperatures. Hence, chloramine residuals were better maintained in the hybrid pilot distribution system because of the presence of less reactive PVC and lined cast iron pipe. Corresponding to chloramine consumption, free ammonia initially increased in all PDS in the same material order of chloramine consumption, which was galvanized steel > unlined cast iron > hybrid. The order of free ammonia loss by material was unlined cast iron > hybrid > galvanized steel.

- The order of DO depletion by PDS material corresponded to the order of residual depletion by PDS material, which is galvanized steel > unlined cast iron > PVC and lined cast iron. The rate of DO depletion in the galvanized steel PDS was almost an order of magnitude greater than in the unlined cast iron PDS and was almost four times greater than in the PVC and lined cast iron reaches of the hybrid PDS.

- The approximate average HPC concentrations in the galvanized steel, unlined cast iron and hybrid PDSs were 5 log, 4 log and 3.2 logs. Hence, the rate of HPC proliferation by PDS material is in the same order as the rate of DO and residual depletion by PDS material, that is galvanized steel > unlined cast iron > hybrid.

- More NO_x-N and NO_2-N was produced in the unlined cast iron PDS, indicating biochemical nitrification was greatest in the unlined cast iron PDS, whereas more HPC production, DO depletion and chloramine depletion occurred in the galvanized steel PDS. This was attributed to the high growth of non-nitrifying bacteria in the galvanized steel PDS. However, the lowest nitrification, HPC production, DO depletion and chloramine depletion occurred in hybrid PDS and was due to a higher residual.

- Biological denitrification was observed in the unlined cast iron pilot distribution system during a controlled nitrification experiment. Denitrification was preceded by loss of residual, loss of DO, HPC growth and nitrification. Such phenomena could occur in reaches of distribution systems in the prolonged absence of a residual.

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