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Water quality variation and tubing metal release due to nitrification

Yongji Zhang[a], Zhengkai Lou[a], Lingling Zhou[b,*]

[a]*Key Laboratory of Yangtze River Water Environment, Ministry of Education, Tongji University, Shanghai 200092, China, Tel./Fax: +86 13701815538; email: yongjizhang@126.com (Y. Zhang), Tel./Fax: +86 18818260951; email: louzhengkai@gmail.com (Z. Lou)*
[b]*State Key Laboratory of Pollution Control and Resources Reuse, Tongji University, Shanghai 200092, China, Tel./Fax: +86 021 65986313; email: Agnelina-Zhou@163.com (L. Zhou)*

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ABSTRACT

Metals are released during nitrification in drinking water distribution systems; therefore, the release of metal due to nitrification and the relationship between pipe material and water quality variation have been investigated in this research by rotating disk reactors (RDRs). As a result, the extent of nitrification depended on the pipe material; nitrifiers grown on metal surfaces would be unfavorable relative to inert surfaces because of metal toxicity. Results implicate that nitrification could affect water quality and metal release. In RDR with Cu coupons, copper release was accompanied by a decrease in pH and an increase in the nitrite concentration resulting from nitrification. Fe and Zn ions from galvanized steel followed a pattern similar to that of Cu coupons. Stainless steel was identified as the material that was the least influenced by nitrification. As for other metal ions, metal coupons generally released more metal ion when nitrification existed, moreover, it released more metal than plastic pipe whether nitrification exists or not. Electrochemical reactions and acidic environments that result from nitrification may induce these differences. Surprisingly, iron and manganese released from steel material were found to be highly correlated ($R = 0.9373$), and iron-to-manganese ratio precisely conform to their composition.

Keywords: Nitrification; Metal release; Water quality; Correlation analysis

1. Introduction

Alternative forms of chlorine, such as chloramines, are widely used as a secondary disinfectant in large- and medium-sized water treatment plants [1]. However, nitrification occurs in water distribution systems after applying chloramines during disinfection. The problems that arise when nitrification occurs have been the focus of many studies. The primary issues include the fast decay rate of the disinfectant, the proliferation of undesirable organisms, and high levels of nitrite and nitrate [2]. These factors deteriorate the water quality in a distribution system. This phenomenon has been increasingly concerned in Chinese drinking water distribution systems and even in the worldwide.

Studies have shown that chloramine dosed during water treatment can decompose into ammonia, and the presence of ammonia stimulates ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB) to grow and convert ammonia to nitrite and nitrate [3,4]. When nitrification occurs in distribution systems, a

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*Corresponding author.

series of effects on the water chemistry and physical characteristics are noted. Among these effects, pipe material corrosion and metal release have not received considerable attention. Bacterial growth potentially increases corrosion [5], and the nitrite generated during nitrification might accelerate corrosion through a change in the redox potential [6]. Increased corrosion can deteriorate the treated water by increasing the concentration of metal ions (e.g. Pb, Cu, Fe, Mn, Ni, and Zn) [7,8].

In the recent years, studies have indicated a possible relationship between nitrification and material corrosion [9–11]. Two hypotheses were suggested for the relationship between nitrification and the unexpected metal release phenomenon: electrochemical corrosion (regenerating ammonium from nitrate via anodic metal oxide corrosion reactions) occurring on the internal surface of pipes [12] and a lower pH resulting from the nitrification process [13]. Other factors could also affect metal release other than a decline in pH. These factors include the disinfectant, alkalinity, dissolved oxygen (DO), and total organic carbon (TOC). During water treatment, a disinfectant was added to maintain a continuous sterilization process to inhibit microorganisms. However, the free ammonia remaining after chloramine decomposition could stimulate nitrobacteria and microbial-induced corrosion. Soluble microbial products from nitrobacteria might increase the level of metals leaching from pipe materials [14]. Otherwise, the soluble metal concentration depends on the system. For instance, Cu release was not affected by a decrease in pH in low-alkalinity water, whereas it was strongly affected by small reductions in pH in high-alkalinity water [15]. However, the opposite trend was found for Pb pipes: Nitrification did not significantly increase Pb contamination at an alkalinity of 100 mg/L as $CaCO_3$ but increased soluble Pb contamination by 65-fold at an alkalinity of 15 mg/L as $CaCO_3$ [16]. The DO consumed by nitrification might control the corrosion rates of specific metals. The TOC also contributes to metal leaching because bacteria can utilize organic carbon, which results in microbial-induced corrosion.

Regardless of the type of factors, nitrification induces material corrosion in water distribution systems [17,18]. The metals released from nitrified distribution systems are strongly influenced by the material composition of the pipes [19]. To clarify the variety of metals released from different pipe materials because of nitrification and to ultimately control this metal release, studies investigating the effect of nitrification on metal release are urgent to secure potable water supplies and protect public health. The objective of this study focused on the influence of pipe materials and water quality variations on the release of metal ions during nitrification.

2. Materials and methods

2.1. Pipe simulators

Vertical rotating disk reactors (RDRs) were used to simulate an operating drinking water distribution system. Each RDR had eight internal coupons and a rotor that was driven by a magnetic stirring apparatus to maintain water flow. The RDRs had a volume of 900 mL, and each coupon that had an area of 1.5 × 5.0 cm was continuously fed by a peristaltic pump at 1.8 mL/min. The hydraulic retention time was 8.3 h to simulate the frequent water use encountered in buildings. Four types of commonly used plumbing materials were applied in each RDR. These materials were polyvinyl chloride (PVC), Cu, galvanized steel, and stainless steel. PVC was used as a reference material throughout this experiment because PVC is a polymer plastic material and displays relatively little corrosion or metal release. The RDRs were covered with tinfoil throughout the experiment to prevent the possible light inhibition of nitrification and to model the absence of light in drinking water distribution systems.

2.2. Raw water

The raw water used in this study was a mixture of laboratory tap water and AOB culture medium at a ratio of 5:1 to promote nitrification. The characteristics of the raw water are provided in Table 1. Metal was not detected in raw water except aluminum and chloramine content remained stable during the whole experiment process because of continuous operation of the RDRs. The pH of the AOB culture medium was adjusted to 7.5–8 by adding a 50% potassium carbonate solution before the medium was poured into the reactors. This range of pH and nutrients are conducive to the growth of AOB [20].

2.3. Procedure

All RDRs were continuously run for 45 d with tap water and AOB culture medium until the nitrite-nitrogen concentration in the RDR exceeded 0.05 mg/L. This value was considered the critical level of nitrification [21]. The decrease in ammonia nitrogen and

Table 1
Characteristics of the raw water

	pH	TOC (mg L^{-1})	DO (mg L^{-1})	Electric conductivity	Turbidity (NTU)	Chloramine (mg L^{-1})	Al (μg L^{-1})	NH_4^+-N (mg L^{-1})	NO_2-N (mg L^{-1})	NO_3-N (mg L^{-1})	HPC (CFU/mL)	AOB (MPN/L)
Raw water	7.8 ± 0.1	6.51 ± 0.4	7.42 ± 0.3	501 ± 30	1.4 ± 0.1	0.13 ± 0.02	7.44 ± 0.8	0.67 ± 0.04	<0.01	1.65 ± 0.6	71 ± 30	<5

production of nitrite and nitrate can indicate the degree of nitrification.

The AOB, pH, and metal concentration were selected to investigate the relationship among water quality, nitrification, and metal ions. The detected parameters were measured immediately after sampling at room temperature (25℃) to ensure the reliability of the data. The importance of the influencing factors was determined in a correlation analysis.

2.4. Analytical methods

2.4.1. Water characterization

The pH was detected by a pH electrode (METTLER TOLEDO FE20, USA) according to the 4500-H$^+$ method. The DO was quantified using a membrane electrode method (4500-O) with test kits (WTW Multi 3430 Water Test Kits, Germany) [22]. Turbidity was measured by method 2130 with a portable turbidimeter (HACH 2100Q, USA) [22]. The growth of heterotrophic bacteria was monitored by a heterotrophic plate count (HPC) according to pour plate method 9215B [22]. Nitrifiers were quantified by the most probable number (MPN) for the nitrifiers [22]. Ammonium-nitrogen (NH_4^+-N) was measured using the phenate method according to method 4500-NO_3^- [22]. Nitrite-nitrogen (NO_2^--N) and nitrate-nitrogen (NO_3^--N) were measured via colorimetric method 4500-NH_4^+ and the ultraviolet spectrophotometric screening method 4500-NO_3^- (which refers to the standard method), respectively [22].

2.4.2. Metal ions

Cu, Fe, Zn, Pb, Al, and Ni were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrophotometry (ICP-MS) after the sample was filtered through a 0.45 μm membrane.

2.4.3. Statistical analysis

Data collected during the study were analyzed in SPSS version 21 for Windows (IBM, USA) and Microsoft Excel 2013 (Microsoft, USA). Several influencing factors were selected to test hypotheses using Pearson correlations. Bivariate analyses were used to examine the association between factors. Two-tailed p-values ≤0.01 and ≤0.05 indicate statistically significant results.

3. Results and discussion

3.1. Nitrification in RDRs with various pipe materials

Nitrification occurred in different RDR reactors at different times. Nitrification was rapidly and drastically established in the PVC RDR compared with the other three materials. From Fig. 1, the concentration of nitrate in this RDR exceeded 0.05 mg/L after one week of operation (this concentration was considered the critical level of nitrification [21]) and exceeded 1.0 mg/L after two weeks. Nitrification occurred after two weeks in the stainless steel RDR and galvanized steel RDR. Nitrification also occurred in the RDR with Cu coupons after four weeks; the concentration of nitrite was approximately 0.5 mg/L. Similar trends have been observed in other studies; Zhang reported that nitrification was rapidly observed in plastic, Fe, and Pb and then later observed in stainless steel and galvanized steel; new concrete materials displayed the longest time to achieve nitrification [15]. Relative to other materials, AOB and NOB were inactive in the RDR with Cu coupons (nitrification occurred after four weeks). After 35 d, the nitrite level in all RDRs was near zero. The lack of nitrate indicates that the nitrifiers no longer oxidized ammonia and nitrification ceased. Cu(II) is considered a key component of the ammonia monooxygenase enzyme (an essential enzyme for ammonia oxidation). However, excess Cu is toxic to nitrifiers and heterotrophs. Pipe materials can serve as a source of trace nutrients, toxic metals, and disinfectants; these materials are expected to strongly influence nitrification. Many metals released from pipes can stimulate nitrifying bacterial growth at low concentrations and inhibit bacterial growth at high concentrations by blocking enzyme function. Nitrification and nitrifying bacteria tend to deteriorate the water quality in reactors.

3.2. Effect of nitrification on pH and DO

Certain physical factors and chemical substrates are required for nitrifying bacteria to grow. Additionally, the water quality is influenced by the growth of microorganisms. The effects of nitrification on pH are shown in Fig. 2. At the onset of the experiment, the pH in the RDRs increased except for the stainless steel RDR. However, as the experiment progressed, the pH in all RDRs reduced from 7.8 to 6.5–6.8. After nitrification, the pH in the RDRs recovered slightly (6.5–7.2). Nitrifiers tolerate a fairly wide pH range (from 4.6 to 11.2 [23]); therefore, neutral to alkaline pH levels accommodate nitrification in the drinking water distribution systems.

The electrochemical reaction of converting nitrite and nitrate to ammonia via anodic corrosion reactions [24] and alkalinity accumulation before nitrification may increase the pH level. After approximately 10 d, the pH eventually reduces to acidic levels in all apparatuses after the appearance of nitrification. The oxidation of ammonia by nitrifiers reduces the pH and consumes alkalinity. The extent of the pH alteration caused by nitrification depends on the buffering capacity of the water and the activity of the nitrifying bacteria.

Although the results were not significant, a decrease in DO was observed (Fig. 3). DO consumption was maintained between 3.75 and 4.40 mg DO/mg NH_3-N in accordance with the stoichiometric level of 4.33 mg DO/mg NH_3-N in all RDRs except for the Cu coupons (the Cu coupon RDR displayed a DO consumption rate of 10.47 mg DO/mg NH_3-N). This abnormal value signifies a relatively low ammonia conversion in the RDR with Cu coupons because the bacterial activity was inhibited by Cu toxicity. Similar to the pH, the DO also displayed a slight recovery after nitrification ceased.

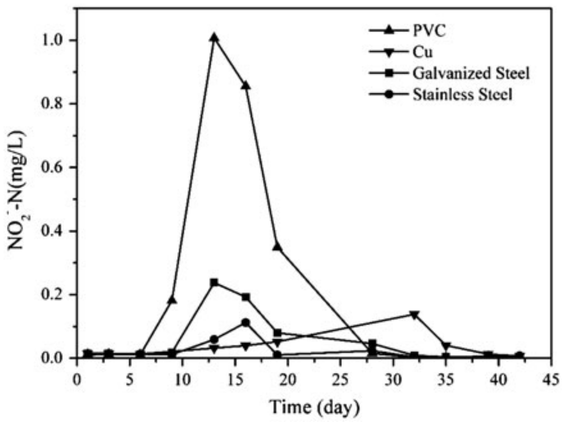

Fig. 1. Nitrite levels in different RDRs.

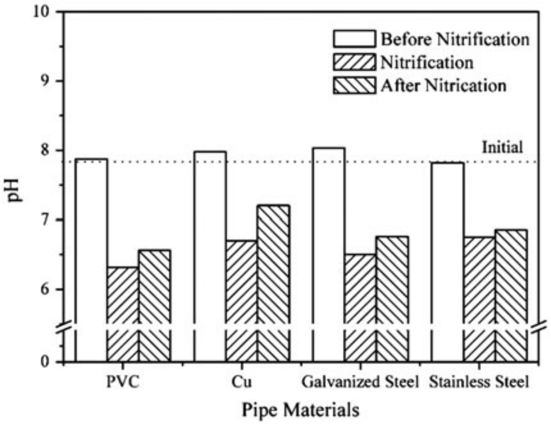

Fig. 2. Effect of nitrification on pH.

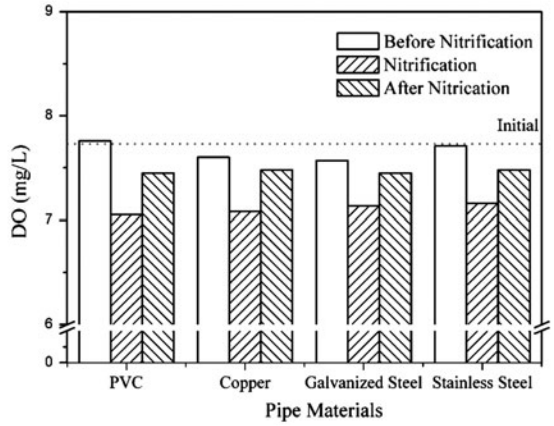

Fig. 3. Effect of nitrification on DO.

3.3. *Effect of the pipe material on metal release*

3.3.1. *Copper*

Trace amount of copper (II) was essential for ammonia oxidation since copper is a key component of the ammonia monooxygenase enzyme. But excess copper is proved to be toxic to nitrifiers and heterotrophs. The amount of Cu released from coupons was highly influenced by variations in the pH conducted by nitrifiers (Fig. 4). The concentration of Cu in this RDR displayed a small increase over the first 15 d. This gradual increase in the Cu concentration was accompanied by an increase in the ammonia concentration and a decrease in the nitrate concentration. The Cu level then gradually rose until it exceeded China's Drinking Water Sanitary Standard (GB 5749–2006). Additionally, the pH decreased from 8.11 to 6.15. The concentration of Cu reached 3 mg/L after 40 d. This Cu release was accompanied by a decrease in pH resulting from nitrification. Compared with Fig. 1, nitrite increased from 0 to 0.14 mg/L in the first 20 d, whereas the concentration of NH_4^+-N was 0.02 mg/L after 35 d. This finding indicates that the overall nitrification process might be lower in the presence of Cu. However, the pH in the RDR continuously decreased; therefore, pH did not recover after nitrification ceased. This decreasing pH influences the release of Cu.

3.3.2. *Galvanized and stainless steel*

Fe is a major component of galvanized and stainless steel coupons; additionally, galvanized steel coupons contain Zn as a coating generated during the manufacturing process. The pH in the RDR with galvanized steel coupons reduced from the initial 8 to 6.5 during nitrification. This trend was similar to that described for Cu. The trend lines of Fe and Zn suggested that the content of these metals followed the degree of nitration; the Zn and Fe levels increased gradually and then reduced after nitrification ceased (Fig. 5). Compared with Cu, the release of Fe and Zn from the pipe was fast, and both metals exceeded their standard after 10 d. As a nitrification indicator, nitrite climbed to 0.24 mg/L (the initial value was less than 0.01 mg/L). Fe had a higher concentration than Zn in the RDR with galvanized steel. Fe content far exceeds maximum concentration levels (7.9360 mg/L comparing to MCLs of 0.3 mg/L); additionally, the experiments noted a concentration of Zn that was 3.5 times the MCLs of Zn.

In addition, the release of Fe in the stainless steel RDR followed a pattern similar to that of the galvanized steel RDR (Fig. 6). However, the concentration of Fe in the RDR with galvanized steel was more evident than that in the stainless steel RDR. In terms of the water quality standard, the Fe level in the RDR

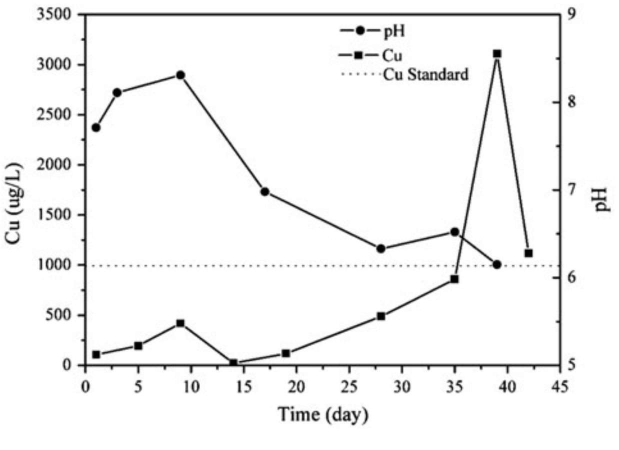

Fig. 4. Cu release in the RDR with Cu coupons.

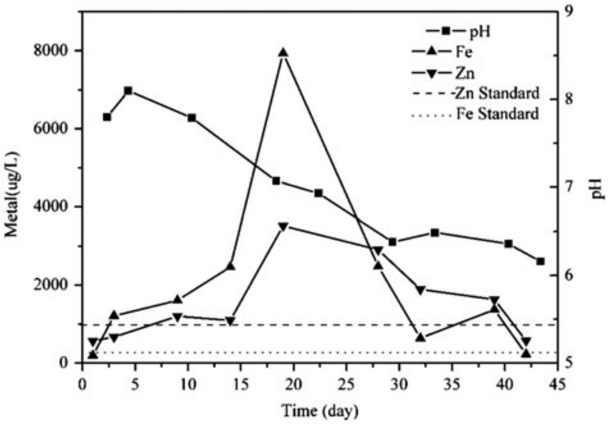

Fig. 5. Metals released in the RDR with galvanized steel coupons.

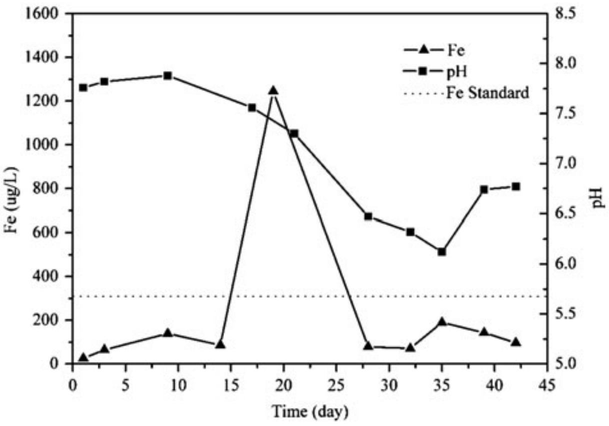

Fig. 6. Fe released in the RDR with stainless steel coupons.

with galvanized steel remained below the standard during the first few days, whereas the stainless steel RDR released more than 300 μg/L of Fe only once throughout the entire experiment. Therefore, the water was contaminated by Fe leaching from stainless steel coupons only during nitrification.

Accidentally, highly linear correlation was theorized between iron and manganese ion released from steel materials ($R = 0.9373$). Iron-to-manganese ratio that is close to 60:1, which precisely conformed to proportion they added during pipeline manufacture, possibly indicated that metals released from alloy may accord with its composition.

3.3.3. Other metals released in RDRs

In addition to primary metals being released from the pipe, other trace metals might exist in pipe materials. These metals could increase the risk to human health by negatively affecting various organs and bodily systems, including the kidney, nervous system, gastrointestinal tract, hematopoietic system, skin, and respiratory system [25]. Table 2 displays the concentration of trace metals that leaked during nitrification. The Al remained below 200 μg/L except for the RDR with stainless steel coupons. This reactor displayed an Al concentration of 256 μg/L during nitrification. Al possibly came from aluminum salt coagulants used in water plant under improper operational conditions. The content of Pb in all apparatuses exceeded the standard during nitrification. The concentrations of Pb were 11.9 μg/L in the PVC RDR, 18.9 μg/L in the Cu RDR, 17.7 μg/L in the galvanized steel RDR, and 45.1 μg/L in the stainless steel RDR (Table 2). The reduction of the pH during nitrification may affect the amount of Pb that is released [16]. The primary source of Pb in drinking water was identified to be plumbing materials [26]. In the case of Ni, slight differences in the concentration were observed in the reactors, and the concentration of Ni was considerably below the drinking water standard.

3.4. Correlation analysis of the nitration factors

A Pearson correlation coefficient was calculated in SPSS to clarify the relationship between nitrification and the release of metals. As seen in Table 3, the pH maintained a strong negative correlation with NH_4^+-N ($r = -0.634$; $p < 0.01$), NO_3^--N ($r = -0.630$; $p < 0.01$), and AOB ($r = -0.580$; $p < 0.01$). The increase in AOB numbers is also accompanied by an increase in NO_2-N and HPC, and a reduction in NH_4^+-N. AOB was significantly correlated with NH_4^+-N ($r = 0.977$; $p < 0.01$), HPC ($r = 0.799$; $p < 0.01$), and NH_4^+-N ($r = -0.437$; $p < 0.05$) (Table 3). The conversion processes occurring during nitrification were described by the Pearson correlation coefficient, as shown in Table 3.

Table 2
Amounts of Al, Pb, and Ni released from four plumbing materials

		Al (μg/L)	Pb (μg/L)	Ni (μg/L)
China's Drinking Water Sanitary Standard (GB 5749-2006)		200	10	20
PVC	Non-nitrification	21.397	5.242	1.368
	Nitrification	87.282	11.922*	1.814
Cu	Non-nitrification	23.095	5.267	2.252
	Nitrification	115.860	18.899*	1.875
Galvanized steel	Non-nitrification	52.984	8.121	2.324
	Nitrification	85.978	17.663*	4.491
Stainless steel	Non-nitrification	13.196	9.166	2.622
	Nitrification	256.007*	45.070*	1.783

*Metal concentration exceeding China's Drinking Water Sanitary Standard (GB 5749–2006).

Table 3
Pearson correlation matrix for pH, metal, microbiological indicators, and nitrogen

Area of state		NH_4^+-N	NH_4^+-N	NO_3^--N	HPC	AOB	pH
NH_4^+-N	Pearson	1	−0.399**	−0.322*	−0.297	−0.473*	0.278
	Sig. (2-tailed)		0.004	0.023	0.231	0.020	0.087
NO_2-N	Pearson	−0.399**	1	0.551**	0.641**	0.977**	−0.634**
	Sig. (2-tailed)	0.004		0.000	0.004	0.000	0.000
NO_3-N	Pearson	−0.322*	0.551**	1	−0.037	0.389	−0.630**
	Sig. (2-tailed)	0.023	0.000		0.885	0.060	0.000
HPC	Pearson	−0.297	0.641**	−0.037	1	0.799**	−0.333
	Sig. (2-tailed)	0.231	0.004	0.885		0.003	0.177
AOB	Pearson	−0.473*	0.977**	0.389	0.799**	1	−0.580**
	Sig. (2-tailed)	0.020	0.000	0.060	0.003		0.009
Al	Pearson	−0.147	0.208	0.122	0.316	0.206	−0.256
	Sig. (2-tailed)	0.379	0.211	0.467	0.201	0.398	0.137
P	Pearson	−0.091	0.407	0.812**	0.372	0.237	−0.970**
	Sig. (2-tailed)	0.678	0.054	0.000	0.412	0.483	0.000
Mn	Pearson	−0.110	0.255	0.084	−0.206	−0.054	−0.546*
	Sig. (2-tailed)	0.509	0.122	0.616	0.412	0.828	0.014
Fe	Pearson	0.054	−0.103	−0.066	−0.251	−0.467*	0.673**
	Sig. (2-tailed)	0.749	0.539	0.692	0.315	0.044	0.003
Ni	Pearson	−0.056	0.935**	0.337	−0.161	−0.589	−0.443
	Sig. (2-tailed)	0.877	0.000	0.341	0.839	0.599	0.319
Cu	Pearson	−0.101	0.120	0.211	−0.277	−0.415	−0.761*
	Sig. (2-tailed)	0.552	0.480	0.209	0.266	0.077	0.030
Zn	Pearson	0.447**	−0.307	−0.271	−0.137	−0.231	0.568**
	Sig. (2-tailed)	0.006	0.064	0.105	0.586	0.341	0.000
Pb	Pearson	0.348*	−0.404*	−0.348*	−0.148	−0.400	0.351*
	Sig. (2-tailed)	0.035	0.013	0.035	0.558	0.100	0.039
Al	Pearson	−0.147	0.208	0.122	0.316	0.206	−0.256

$^*p \le 0.05$.
$^{**}p \le 0.01$.

Table 4 indicates the presence of a negative correlation between several metals and pH. Therefore, the increase of soluble metals was associated with a decline in pH. The relationships between the metal concentrations and nitrification are shown in Tables 3 and 4. The results imply that the metal contamination of the water was partially induced by nitrification in the plumbing system.

3.5. Discussion

The aim of the present paper was to investigate the release of metal ions and water quality change during nitrification by simulate experiment. The study focused on determining the effects of nitrification on general water characteristics, such as DO and pH, and the metal ions that are released from different pipe materials.

Similar to Zhang et al. [15], nitrification occurred more readily in RDRs with polymer plastic pipes than metal pipes. For the materials involved in the four RDRs, the highest nitrification occurred in RDR with PVC followed by (in order) galvanized steel, stainless steel, and Cu. Nitrifiers were observed in inactive state in metal pipes than in PVC pipes. Therefore, alloy surfaces are unfavorable to nitrifier growth compared with inert surfaces, such as PVC. According to previous studies, some metals, such as Zn, Cu, Ni, and Pb, are toxic to nitrifiers [27,28]. However, because of the continuous operation of the RDRs, Cu potentially did not achieve a sufficiently high concentration in flowing water to interfere with nitrification. Ammonia loss during nitrification was as low as 40%, likely because the AOB culture medium that contained the nitrogen source was continually injected into the RDRs.

Metal pipes released more metal ions during nitrification. In this study, there were two reasons explaining metal release before nitrification. The first reason was the presence of electrochemical reactions that reduced nitrite and nitrate to ammonia through the oxidation of a metal to a metal ion form. This process was observed in all four RDRs at the onset of the

Table 4
Pearson correlation matrix of metal and turbidity

		Al	P	Mn	Fe	Ni	Cu	Zn	Pb
Turbidity	Pearson	0.130	−0.620*	−0.021	0.847**	−0.676	0.596**	0.251	0.764**
	Sig. (2-tailed)	0.508	0.024	0.916	0.000	0.528	0.001	0.197	0.000
pH	Pearson	−0.256	−0.970**	−0.546*	−0.673**	−0.443	−0.761*	−0.568**	−0.351
	Sig. (2-tailed)	0.137	0.000	0.014	0.003	0.319	0.030	0.000	0.039
Al	Pearson	1	0.182	−0.206	0.159	−0.230	0.250	−0.059	−0.035
	Sig. (2-tailed)		0.364	0.190	0.315	0.430	0.115	0.713	0.828
P	Pearson	0.182	1	0.356	−0.190	0.432	0.213	−0.564**	−0.272
	Sig. (2-tailed)	0.364		0.069	0.342	0.123	0.295	0.003	0.179
Mn	Pearson	−0.206	0.356	1	0.022	0.933**	0.109	−0.152	−0.144
	Sig. (2-tailed)	0.190	0.069		0.890	0.000	0.497	0.342	0.369
Fe	Pearson	0.159	−0.190	0.022	1	−0.350	0.646**	0.250	0.484**
	Sig. (2-tailed)	0.315	0.342	0.890		0.219	0.000	0.116	0.001
Ni	Pearson	−0.230	0.432	0.933**	−0.350	1	−0.317	−0.255	−0.538
	Sig. (2-tailed)	0.430	0.123	0.000	0.219		0.291	0.400	0.058
Cu	Pearson	0.250	0.213	0.109	0.646**	−0.317	1	−0.185	0.281
	Sig. (2-tailed)	0.115	0.295	0.497	0.000	0.291		0.247	0.079
Zn	Pearson	−0.059	−0.564**	−0.152	0.250	−0.255	−0.185	1	0.546**
	Sig. (2-tailed)	0.713	0.003	0.342	0.116	0.400	0.247		0.000
Pb	Pearson	−0.035	−0.272	−0.144	0.484**	−0.538	0.281	0.546**	1
	Sig. (2-tailed)	0.828	0.179	0.369	0.001	0.058	0.079	0.000	

*$p \leq 0.05$.
**$p \leq 0.01$.

experiment, notably for the Cu and galvanized steel RDRs (Eqs. (1–3)). In the RDR with Cu coupons, the ammonia concentration elevated abnormally from 0.67 to 1.24 mg/L with a near 85% loss of nitrate. These electrochemical reactions are likely attributed to this finding. Additionally, the increase in pH and the increase in the Cu concentration at the beginning of the study also corroborated this conjecture (Fig. 4).

$$NO_3^- + 7H_2O + 8e^- = NH_3 \cdot H_2O + 9OH^- \tag{1}$$

$$NO_2^- + 6H_2O + 6e^- = NH_3 \cdot H_2O + 7OH^- \tag{2}$$

$$\text{Metal} = \text{Metal}^{2+} + 2e^- \tag{3}$$

The second reason for metal release in this study is that the pH eventually becomes acidic as nitrification progresses. The metals displayed their maximum contaminant levels at these decreased pH levels. The production of nitrite and nitrate during nitrification has been predicted to increase metal corrosion [17]. The literature has reported the results of numerous studies on the interaction of nitrification and water chemistry. In this study, nitrification decreased the pH to acidic levels despite a rise at the beginning of the experiment. During nitrification, the amount of metals leaching from materials increased. Cu release was accompanied by a lower pH and an increase in NH_4^+-N concentration resulting from nitrification in RDR with Cu coupons. Moreover, the release of the Cu ion in the RDR with Cu coupons was slower than the Zn and Fe ions in the RDR with galvanized steel coupons, most likely because of the toxicity of Cu to the nitrifier. A similar trend was found for Fe and Zn with NH_4^+-N and pH in RDR with galvanized steel coupons. The release of Fe and Zn tripled during nitrification compared with non-nitrification. However, Fe contaminates water more easily than Zn in the RDR with galvanized steel. Fe was observed in the RDRs with galvanized and stainless steel. However, the Fe concentration in the RDR with galvanized steel was greater than that in the RDR with stainless steel. Surprisingly, the Fe and Mn released from steel were highly correlated ($r = 0.9373$). Additionally, the Fe-to-Mn ratio precisely conformed to the proportion added during the pipeline manufacturing process.

As for other trace metals, metal coupons released more metal ions during nitration. Moreover, metal coupons released more metal than plastic pipes. For example, the Pb released in RDRs displaying nitrification was threefold and fivefold more than the Pb released in RDRs without nitrification in Cu and stainless steel RDRs, respectively (Table 2).

A correlation analysis investigated the relationship among various parameters, including water quality, nitrification, and metal ions. This analysis determined the water quality parameters that affect metal ion release. As shown in Table 3, the pH presented a strong negative correlation with NH_4^+-N ($r = -0.634$; $p < 0.01$), NO_3^--N ($r = -0.630$; $p < 0.01$), and AOB ($r = -0.580$; $p < 0.01$). However, NH_4^+-N ($r = 0.977$; $p < 0.01$), HPC ($r = 0.799$; $p < 0.01$), and NH_4^+-N ($r = -0.437$; $p < 0.05$) were significantly correlated with AOB. The statistical analysis mentioned above demonstrated that a decrease in pH would occur when ammonia was transformed to nitrite and nitrate by nitrifying bacteria. Moreover, nitrite and HPC could be used as an indicator of nitrification because AOB displays a value in direct proportion to nitrite and HPC. A negative correlation is shown in Table 4 between the concentration of several metals and the pH. This indicates that an increase in soluble metals was associated with a decline in pH. The relationship between metal concentrations and nitrification (Tables 3 and 4) may imply that metal released into water was partially induced by nitrification occurring in the plumbing system.

With regard to DO consumption, the DO remained between 3.75 and 4.40 mg DO/mg NH_3-N, which was close to the stoichiometric level of 4.33 mg DO/mg NH_3-N for all RDRs except the Cu coupons RDR (10.47 mg DO/mg NH_3-N). This high DO/NH_3-N value may contribute to the relatively low ammonia conversion.

4. Conclusions

The extent of nitrification in the plumbing system depended on the pipe material; metal pipe materials were less favorable for the growth of nitrifiers than non-metallic pipe materials. In turn, nitrification exerts different influences on metal release to varying degrees in simulate reactors. The pH and DO concentration in the water decreased when ammonia was transformed to nitrite and nitrate by nitrifying bacteria. This process accelerated the release of metal ions from pipe materials by electrochemical reactions and through the acidic water environment. The pH did not recover after nitrification ceased. More metal ions were released from pipes when nitrification was detected. Among the metal materials that were analyzed, nitrification displayed the least influence on stainless steel. The correlation analysis demonstrated that an increase of soluble metals was associated with a decline in pH.

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