Experimental investigation of water quality responses to inorganic pollutants for the establishment of a contamination warning system

Sukmin Yoon, Seong-Su Kim and No-Suk Park

ABSTRACT

In this study, batch and simulated pipeline experiments were conducted to investigate the response of water quality parameters (pH, conductivity, residual chlorine, turbidity, total organic carbon, UV 254, and oxidation reduction potential (ORP)) to various concentrations of four inorganic pollutants (Cd, Cr, Mn, and Pb). In addition, the possibility of detecting incidents of contamination in the actual water supply system was evaluated by deriving the response intensities of each factor to the concentrations of the pollutants. As a result, pH and ORP were identified as the major water quality parameters responsive to the four inorganic pollutants in this study. The responses were more intense (more sensitive) in pure water than in tap water. The results of the batch and simulated pipeline experiments for tap water showed almost identical tendencies, except for the second level of Mn injection (concentration 0.5 mg/L).

Key words | batch experiment, inorganic pollutants, response intensity, simulated pipeline experiment, water quality parameters

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INTRODUCTION

Contamination warning systems (CWSs) offer a novel approach to the detection of contamination incidents in water distribution systems (Boberson & Morely 2005). Concerns about drinking water quality contamination during water distribution raise a need for real-time monitoring and rapid contamination detection. Early warning systems are a potential solution (Dejus *et al.* 2018). Especially, security of water distribution networks (WDNs) through early warning systems has been one of the topics of research over the last two decades to safeguard human health and the environment against accidental and intentional contamination (Rathi *et al.* 2015). The United States Environmental Protection Agency (USEPA) has made significant efforts to develop a CWS architecture integrating multiple monitoring and surveillance strategies, including the monitoring of the security of distribution facilities and on-line water quality as well as the surveillance of customer calls and public health indicators (Allgeier *et al.* 2011). Accurate sensors for water quality parameters (such as residual chlorine, total organic carbon (TOC), conductivity, and pH) should be deployed, among other CWS components, throughout the water distribution system (USEPA 2010). If the water quality monitoring system, including sensors and analyzing equipment, is not adequate, very serious contamination incidents may occur such as in the case of Flint, Michigan, USA. The elevated levels of lead found in drinking water in Flint residences have had a profound effect on the level of trust between the community and the state, the economy of the region, and the health and well-being of the residents of Flint and surrounding communities (Masten *et al.* 2016).

Advancements in real-time water monitoring technologies permit rapid detection of in-stream, in-pipe water quality, and alert of threats from waste loads (Capodaglio 2016). Contamination detection potential refers to the detectability strength,

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and type of pollutant – key factors in designing hazardous material analysis and monitoring systems that constitute a CWS (McKenna *et al.* 2008). Previous USEPA studies have shown that at least one water quality parameter – residual chlorine, pH, turbidity, conductivity, temperature, and TOC – should change significantly for the system to be activated. These parameters are related to the ability of the system to identify the type of pollutant that can cause a contamination incident in a water distribution system (USEPA 2014a, 2014b, 2014c). It is impossible to directly detect a contamination incident by a specific pollutant. It takes a lot of time and hardware to monitor the substance and concentration of pollutants in real time. However, the above-mentioned water quality parameters in each pipe and reservoir are always monitored and the data are accumulated. An 'agent library' is defined as a library combining a material database and laboratory-scale experimental results, with the purpose of allowing a quick search for the type of incidents and pollutant classification. A 'plant library' is a set of data on actual water quality behavior obtained by installing the event detection system at the specific pilot plant or site. The agent library is generalized and is transferable from site to site. The plant library is site-specific (Ahuja 2013).

In order to develop the agent library as the first step in establishing a CWS, we experimentally investigated the response of water quality parameters to four inorganic pollutants that are likely to cause contamination incidents in Korea. The selected inorganic pollutants are associated with water quality accidents that have occurred in Korea in the past. In addition, six water quality parameters except UV 254 are always monitored and stored in Korea. The standard upper limits of Cd, Cr, Mn and Pb, which were used as inorganic pollutants, in Korea are set at 0.005, 0.05, 0.05, and 0.01 mg/L, respectively. In addition, the possibility of detecting accidents was evaluated by deriving the intensity of the response of each factor to pollutant concentrations.

Table 1 | Automatic water quality instruments used in this study

Instrument	Model	Manufacturer
TOC analyzer	TOC-4110	Shimadzu Corp.
Residual chlorine analyzer	OR 100	C-mac Corp.
UV 254 analyzer	Spectra Academy	K-mac Corp.
Multi-sensor meter (pH, temperature, turbidity, conductivity, ORP)	MC-P1	M-cubic Corp.

MATERIALS AND METHODS

Water quality instruments

Table 1 presents the models and manufacturers of the automatic water quality instruments used in this study.

Table 2 | Inorganic pollutants and injection concentrations

			Injection concentration (mg/L)			
Experiment	Water source	Pollutants	Dosing 1	Dosing 2	Dosing 3	Sampling time
Batch	Pure water	Cd	0.005	0.050	0.500	2 minutes
		Cr	0.050	0.500	5.000	
		Mn	0.050	0.500	5.000	
		Pb	0.010	0.100	1.000	
	Tap water	Cd	0.005	0.050	0.500	
		Cr	0.050	0.500	5.000	
		Mn	0.050	0.500	5.000	
		Pb	0.010	0.100	1.000	
Pipeline	Tap water	Cd	0.005	0.050	0.500	
		Cr	0.050	0.500	5.000	
		Mn	0.050	0.500	5.000	
		Pb	0.010	0.100	1.000	

The TOC analyzer, a low-temperature combustion oxidation system, can measure TOC in water from 0 to 20,000 mg/L every 4 minutes. The residual chlorine analyzer can measure to a minimum concentration of 0.05 mg/L every 3 minutes. The UV 254 analyzer can measure wavelengths from 200 to 900 nm every minute. UV 254 was not a parameter but measured to observe the correlation with TOC response and evaluate the possibility of TOC replacement. In addition, the multi-sensor meter can measure five water quality parameters every minute.

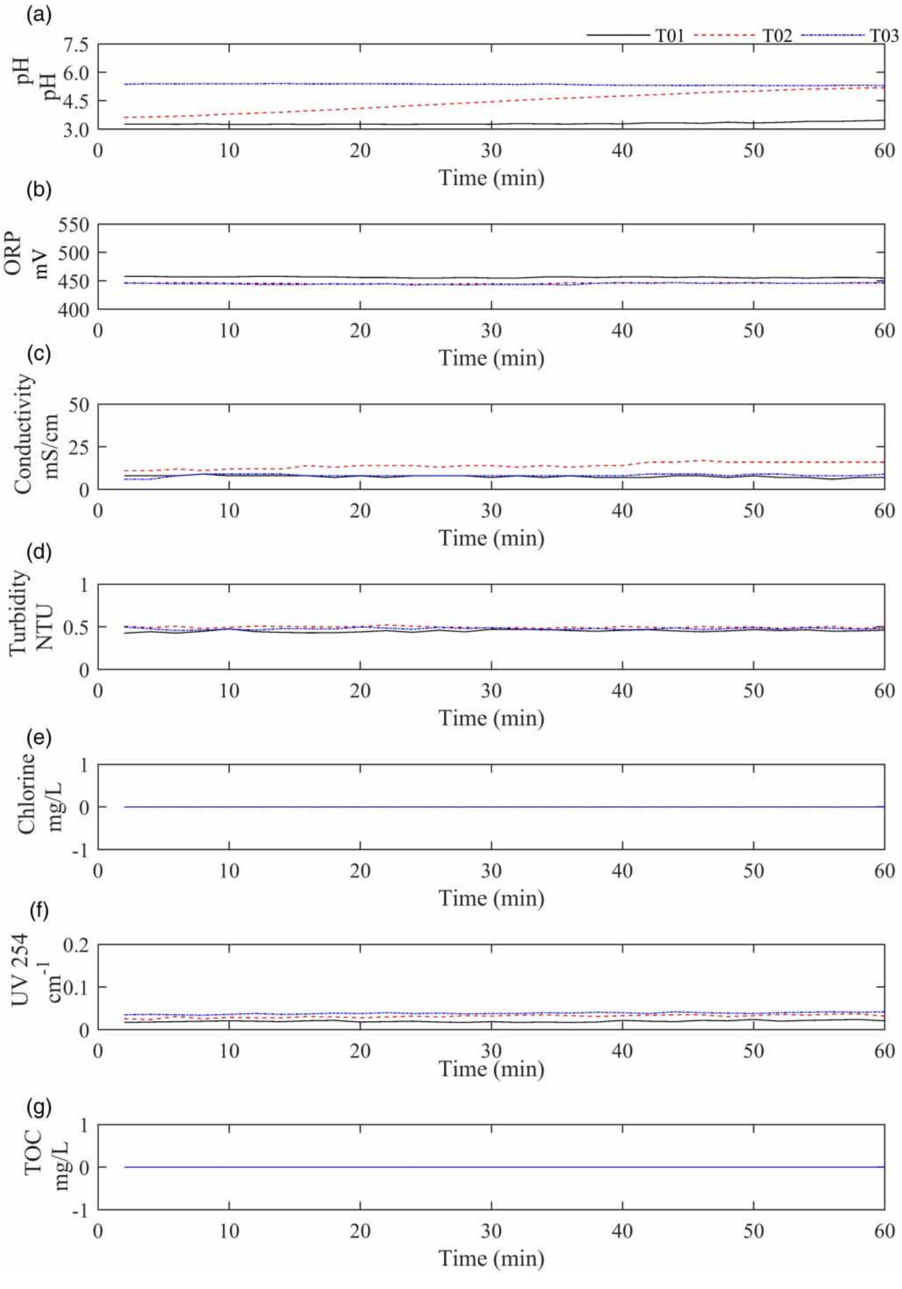

Figure 1 | Cd batch experiment results (pure water, 0.005 mg/L) (T01: 1st test, T02: 2nd test, T03: 3rd test).

Experimental method

Batch experiments

The batch experimental reactor was used to measure the baselines of tap water supplied to the laboratory and pure water. This batch reactor was also used to monitor the changes in water quality parameters with artificially injected pollutants. Two 5 L beakers were filled with tap water and pure water, slowly stirred, and the water quality parameters were measured at 2 min intervals for 100 min to determine the baseline. The measured water quality data was automatically stored on a computer. The tap and pure water experiments were conducted separately in order to

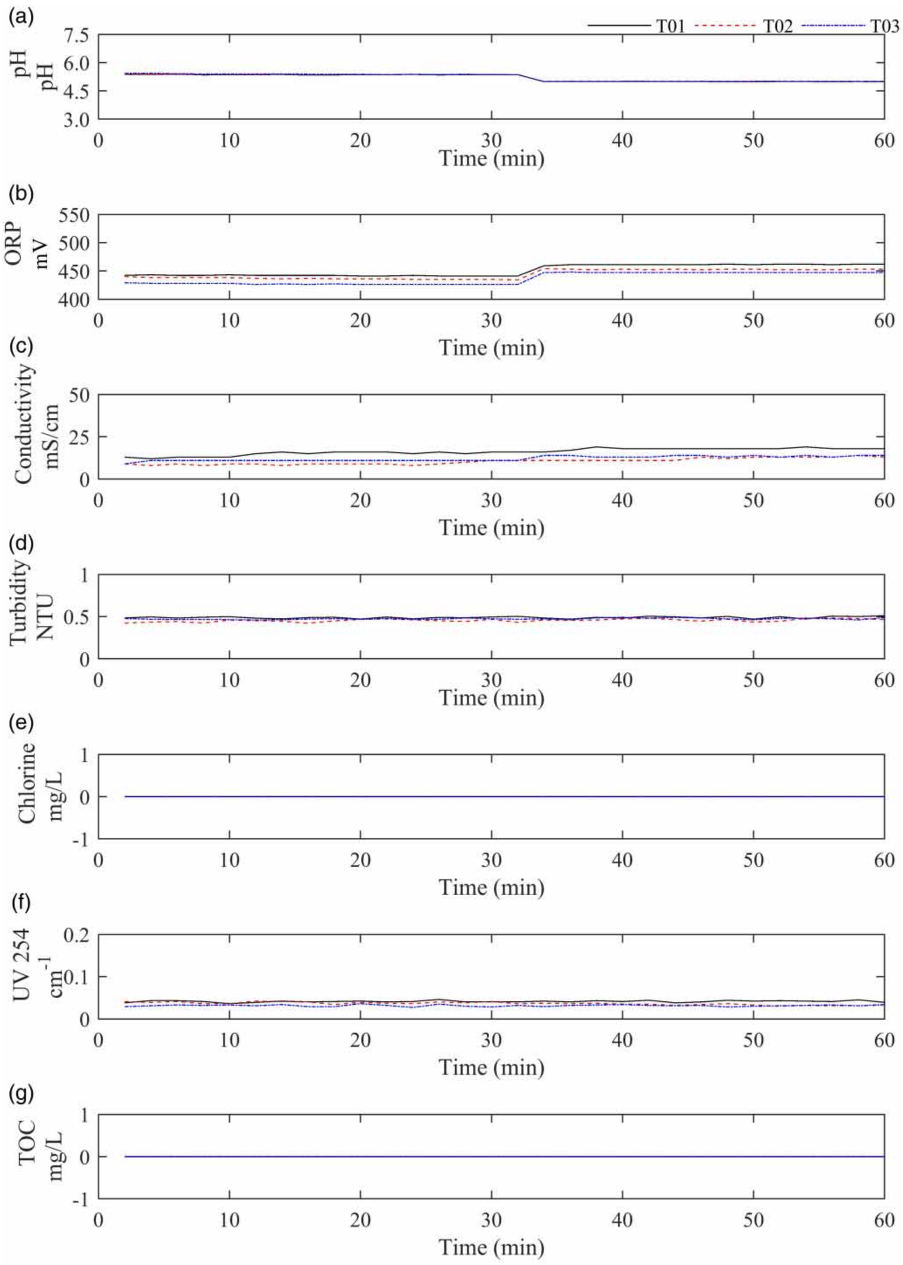

Figure 2 | Cd batch experiment results (pure water, 0.05 mg/L).

investigate the effects on water quality parameters of the residual chlorine in tap water. Especially, chlorine is widely used as the disinfectant in drinking water, which can be used as a surrogate parameter to provide indications of potential contaminants (Zhao *et al.* 2015).

Table 2 shows the pollutants and injection concentrations for the batch experiments. Cd, Cr, Mn, and Pb were selected as the inorganic pollutants and the injection concentration of the feed was increased to 10–100 times the reference concentration in the Korean Water Quality Standards for Drinking Water (Korean Ministry of Environment 2015). The standard solution was prepared based on the water quality standards. The changes in the water quality parameters were observed for

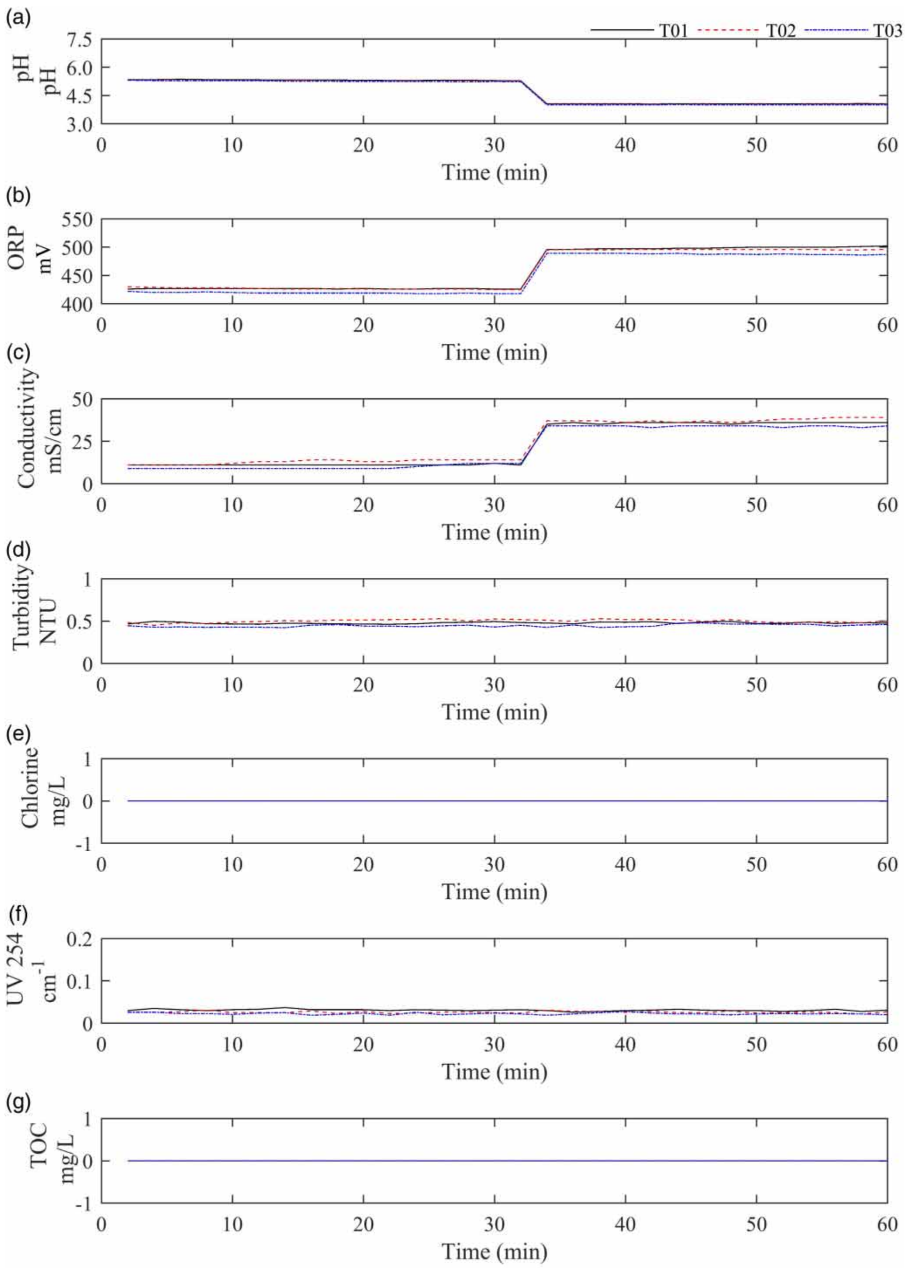

Figure 3 | Cd batch experiment results (pure water, 0.5 mg/L).

100 min at 2 min intervals, according to the injection concentration.

Simulated pipeline experiments

The simulated pipeline system consisted of a 10 m PVC pipe, a 50 L mixing tank, a circulation pump, a 5 L sampling vessel, and water quality sensors. The changes in the baseline and tap water quality parameters were continuously measured. The baseline was measured at 2 min intervals for 100 min before the injection of pollutants, and the prepared standard solution was subsequently injected into the mixing tank. After injection, the water quality parameters were monitored for 100 min at the

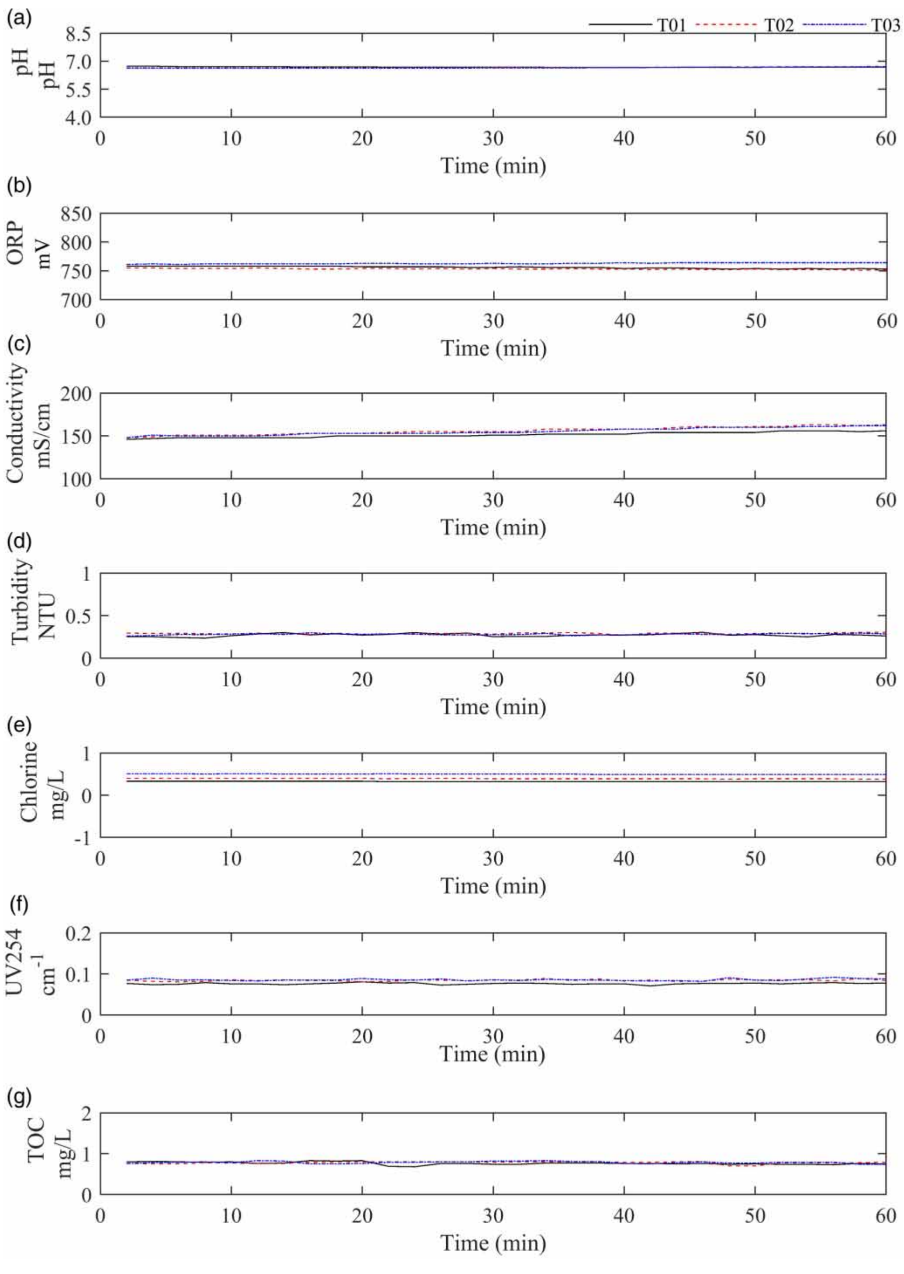

Figure 4 | Cd batch experiment results (tap water, 0.005 mg/L).

same intervals as those for the batch experiments. During the experiments, the pipe flow velocity was maintained at about 0.5 m/sec, which is within the flow rate range of the actual water distribution pipes. The difference between these experiments and the batch experiments was that a multi-stage injection was applied to increase the injection concentration at 10, 20, and 30 min intervals for all four pollutants.

RESULTS AND DISCUSSION

Results of the batch experiments

Cadmium (Cd)

No significant changes in turbidity, residual chlorine, TOC, and UV 254 were observed from Cd injection batch

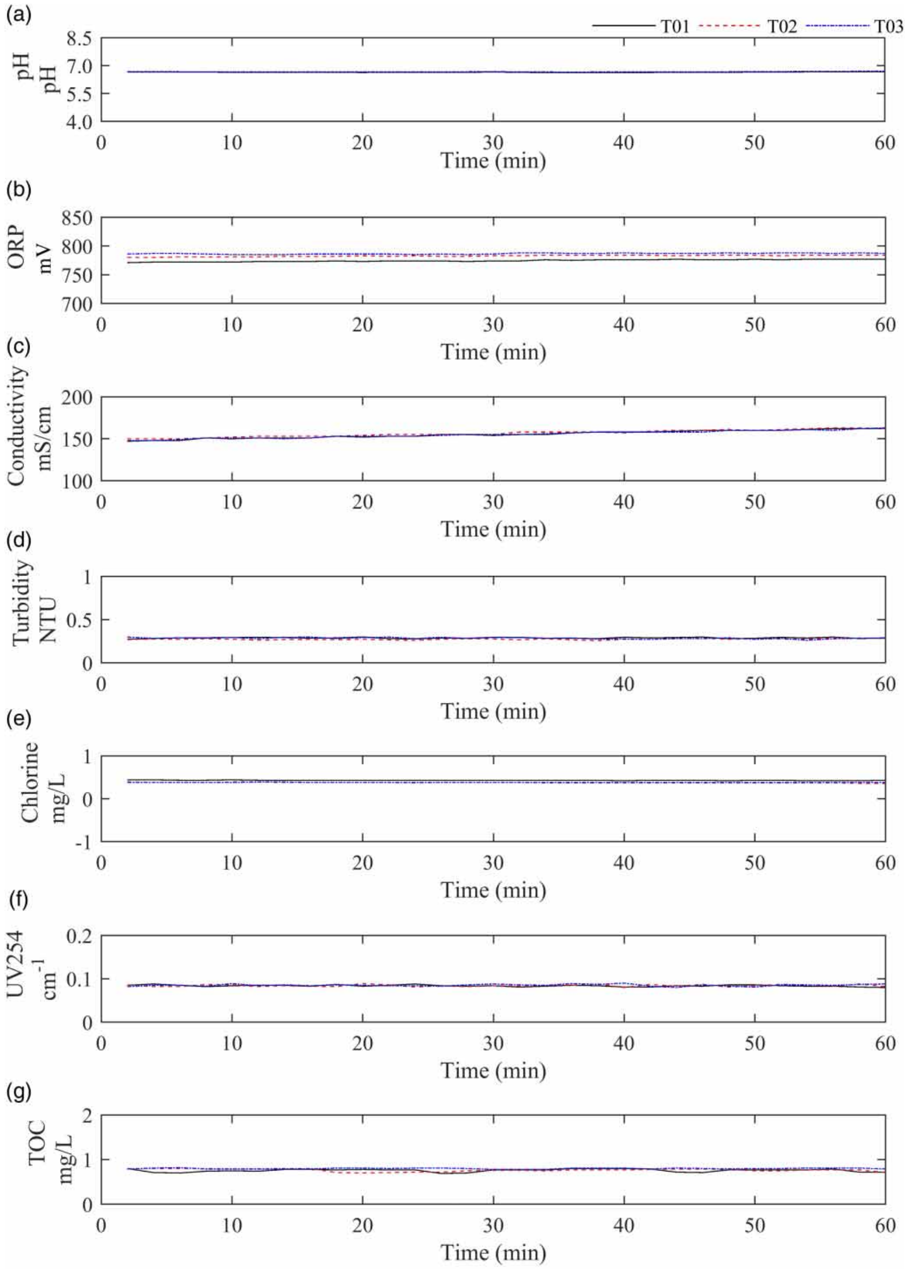

Figure 5 | Cd batch experiment results (tap water, 0.05 mg/L).

experiments in pure water. The pH and oxidation reduction potential (ORP) responded at 0.05 mg/L, which is the concentration limit according to the domestic water quality standard, and their most significant response was observed at the maximum concentration of 0.5 mg/L (Figures 1–3). Even though the conductivity response occurred at the maximum dosing concentration of 0.5 mg/L for pure water, there was no response at the same concentration for tap water. In addition, no significant responses in turbidity and residual chlorine were found in the Cd injection batch experiment for tap water, and only pH and ORP responded at the maximum concentration of 0.5 mg/L

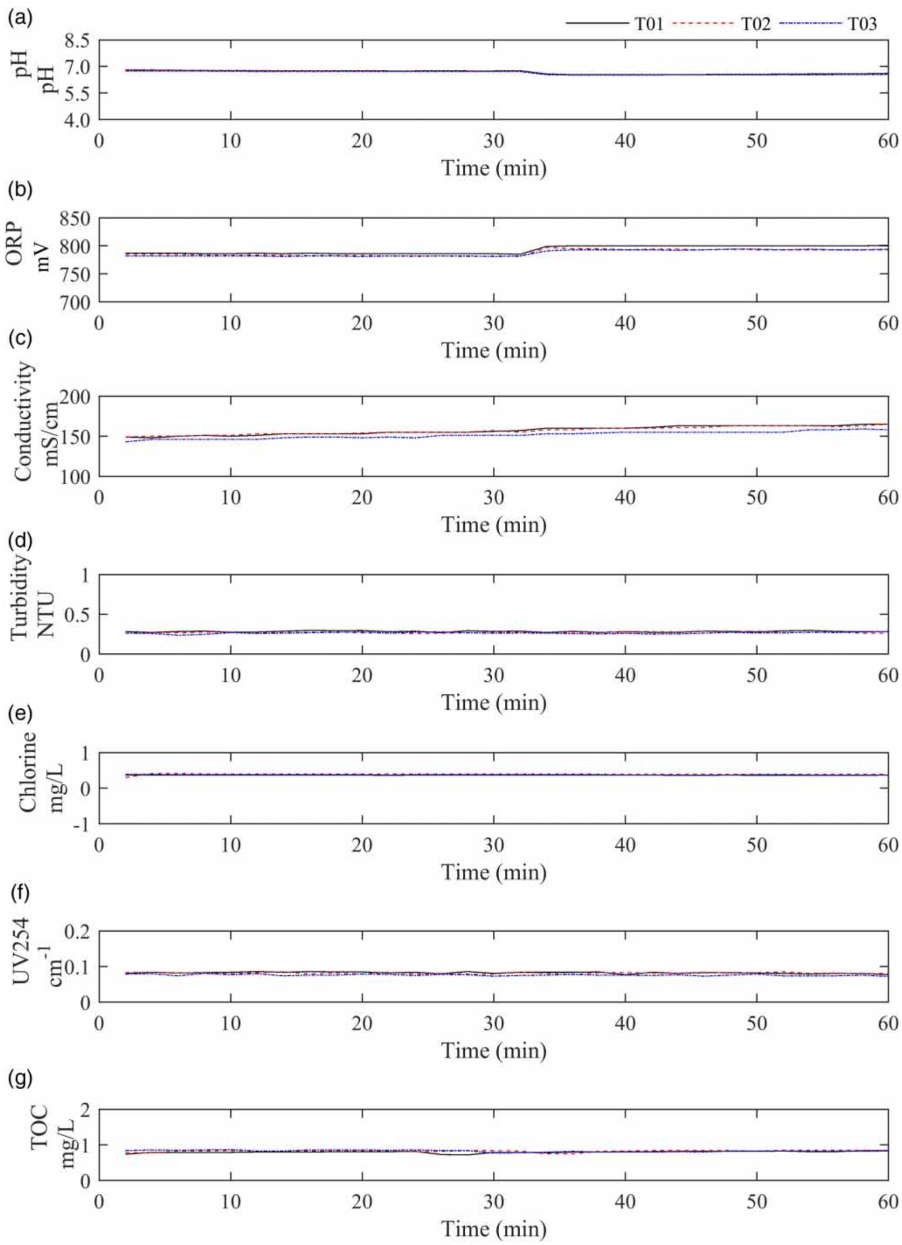

Figure 6 | Cd batch experiment results (tap water, 0.5 mg/L).

(refer to Figures 4–6). The response intensity of each water quality parameter to Cd injection could therefore be derived as shown in Table 3.

Chromium (Cr)

Cr injection experiments on pure water showed no significant responses in turbidity, residual chlorine, and UV 254. The pH and ORP responses were seen at 0.5 mg/L, which is 10 times the domestic water quality threshold. Furthermore, there was a significant basal change at 5 mg/L. For conductivity, the response was demonstrated at the maximum concentration of 5 mg/L. In addition, the results of the Cr injection experiment for tap water showed no significant response for turbidity, residual chlorine, TOC, and UV 254. The pH and ORP showed very small responses at a concentration of 0.5 mg/L, which is 10 times the threshold of the domestic standard: a similar result to the pure water experiment. At the maximum concentration of 5 mg/L, pH, ORP, and conductivity showed significant responses.

Manganese (Mn)

No significant responses in turbidity, residual chlorine, TOC, and UV 254 were observed in the results of the Mn injection experiment, whereas pH and ORP showed a response at 0.05 mg/L, which is the threshold level. For conductivity, the response appeared at the maximum concentration of 0.5 mg/L. The experimental results for tap water showed no significant responses for turbidity, residual chlorine, TOC, and UV 254. ORP showed a response at 0.05 mg/L. The pH, ORP, and conductivity showed significant responses at 5 mg/L.

Lead (Pb)

No significant responses in turbidity, residual chlorine, TOC, and UV 254 were observed as a result of the Pb injection experiment. Responses from pH, ORP, and conductivity were observed at the threshold concentration of 0.01 mg/L. At the 0.1 mg/L concentration, each parameter showed a remarkable response. No significant response in turbidity, residual chlorine, TOC, and UV 254 was observed in the experimental results for tap water, whereas ORP showed a small response at 0.1 mg/L, which is 10 times the threshold level. At the maximum concentration of 1 mg/L, pH, ORP, and conductivity demonstrated remarkable responses.

Figure 7 presents the response intensities of pH and ORP to the four inorganic pollutants in tap and pure water; the graphs were derived based on the batch experimental results. The response intensities appear to be more sensitive in pure water compared to tap water. A significant response is observed at the first level (the reference concentration allowed for each pollutant) in pure water, whereas the response appears at the second stage (10 times the threshold) in tap water. In addition, the pure water exhibited more intense responses at all

Table 3 | Response intensities to Cd injection (batch experiments for pure and tap water)

	0.005 mg/L			0.05 mg/L			0.5 mg/L		
Parameters	T01	T02	T03	T01	T02	T03	T01	T02	T03
pH	–	–	–	0.37	0.36	0.37	1.22 (0.18)	1.22 (0.20)	1.22 (0.17)
ORP (mV)	–	–	–	18.00	20.00	21.00	70.00 (14.00)	70.00 (16.00)	71.00 (9.00)
Conductivity (mS/cm)	–	–	–	–	–	–	24.00 (–)	23.00 (–)	22.00 (–)
Turbidity (NTU)	–	–	–	–	–	–	–	–	–
Chlorine (mg/L)	–	–	–	–	–	–	–	–	–
UV254 (cm^{-1})	–	–	–	–	–	–	–	–	–
TOC (mg/L)	–	–	–	–	–	–	–	–	–

T01, T02, T03: experiment times; (number) is the response intensity value for tap water.

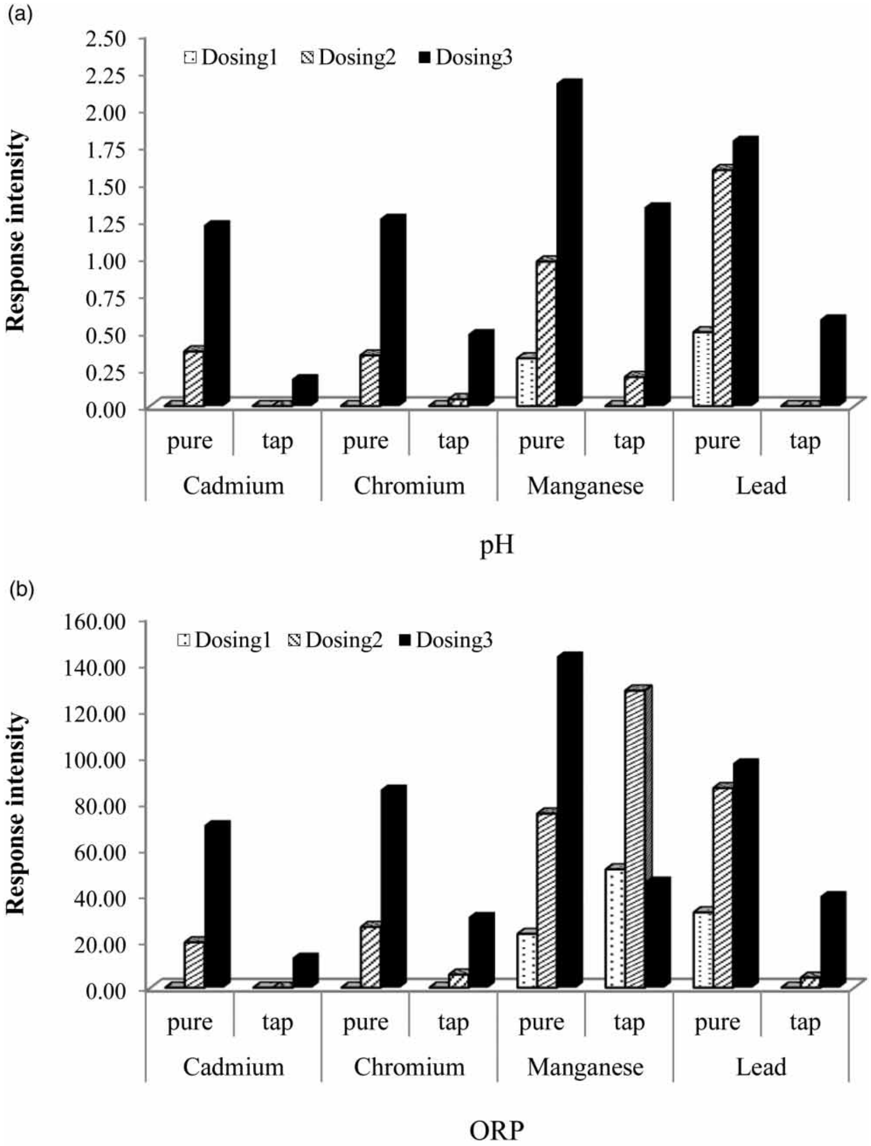

Figure 7 | (a) pH and (b) oxidation reduction potential (ORP) response intensity in the batch experiments.

stages. At the third level (100 times the threshold), where the pH and ORP responses were remarkable, the magnitude of the difference was 3.5 times or more on average. This is presumably due to the chlorine and organic matter contained in the tap water. It could be thought that the residual chlorine in the tap water is reacted with inorganic pollutants. The oxidized inorganic matters also cause reactions with the remaining organic matter in tap water. Depending on the type of pollutant, the pH and ORP response intensity was different. The response to Mn and Pb was higher than to Cd and Cr, and the difference was more than 2.5 times on average.

Results of the simulated pipeline experiments

Cadmium (Cd)

A Cd solution was injected at a concentration of 0.005 mg/L, 10 min after the start of the pipeline experiment, and increased to 0.05 mg/L after 30 min. The injection concentration was increased to 0.5 mg/L after a further 30 min. The multi-stage injection was applied in the simulated pipeline experiment to determine whether contamination incidents can be detected by monitoring fluctuations in the baseline of tap water. Results showed that no significant responses appeared for conductivity, turbidity, residual chlorine, TOC, and UV 254. pH and ORP responded at the maximum concentration of 0.5 mg/L.

Chromium (Cr)

The experimental results showed no significant response for turbidity, residual chlorine, TOC, and UV 254. Similar to the batch experiment results, the pH showed a slight response at 0.5 mg/L (10 times the threshold). pH, ORP, and conductivity showed a remarkable response at the maximum concentration of 5 mg/L.

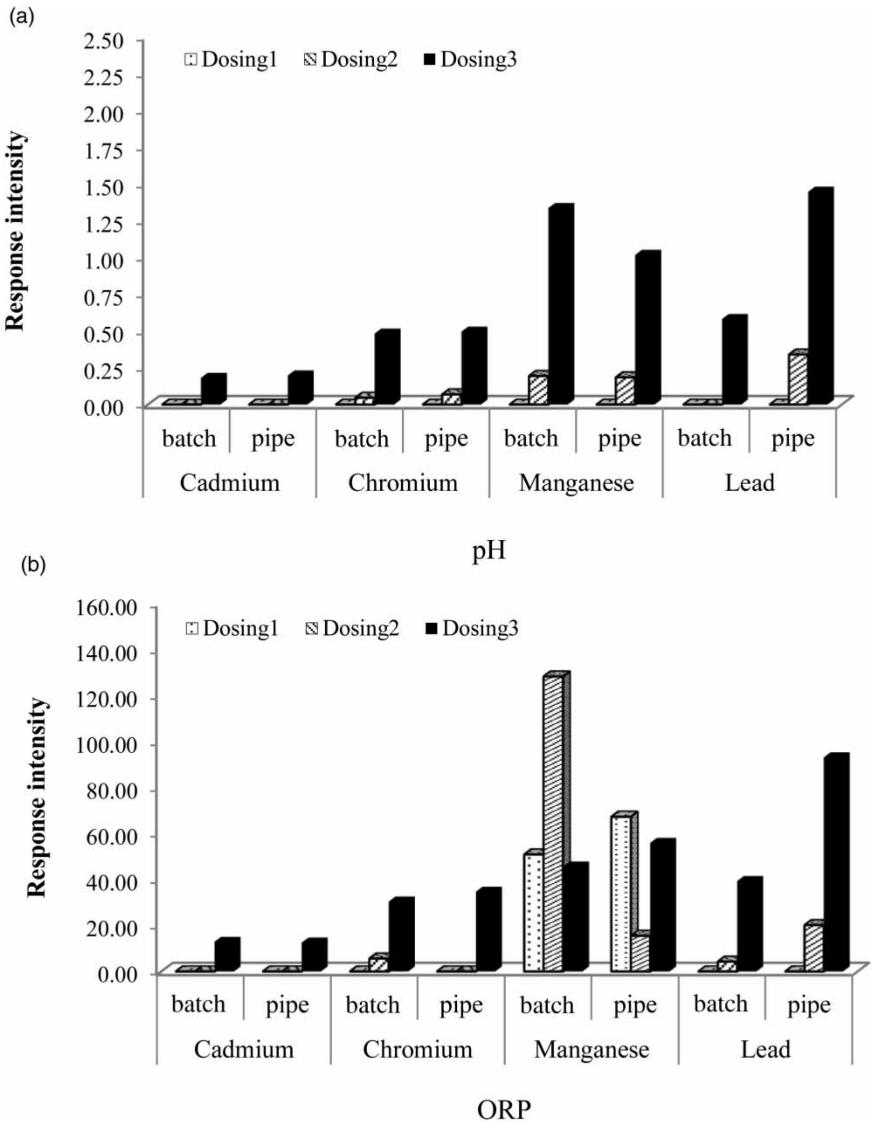

Figure 8 | (a) pH and (b) oxidation reduction potential (ORP) response from the batch and simulated pipeline experiments (tap water).

Manganese (Mn)

No significant responses were observed in turbidity, residual chlorine, TOC, and UV 254. ORP showed a response at 0.05 mg/L (threshold level) and pH responded at 0.5 mg/L (10 times the threshold). At the maximum concentration level of 5 mg/L, the pH, ORP, and conductivity showed a remarkable response.

Lead (Pb)

No significant responses in turbidity, residual chlorine, TOC, and UV 254 were observed in the experiment. The pH and ORP showed small responses at 0.1 mg/L (10 times the threshold). At the maximum concentration of 1 mg/L, pH, ORP, and conductivity showed a remarkable response.

Only pH, conductivity and ORP responded to high concentrations of heavy metal pollutants. It may be because of the pH, conductivity and ORP being among parameters that are associated with inorganic heavy metals. Figure 8 compares pH and ORP intensity for each pollutant, as derived by the batch and simulated pipeline experiments conducted on tap water. If organic pollutants were injected, all of the parameters would have responded. In the batch experiment, there was a single pollutant injection concentration for every condition, while a multi-stage injection was applied in the pipeline experiments. The reason for applying the different conditions in the experimental methods was to simultaneously evaluate the response intensities and possibilities of detecting various contamination incidents in the actual water supply system. Results show that both experiments for tap water showed almost identical tendencies, except for the second level of manganese injection (concentration 0.5 mg/L). However, the reasons for this difference remain unclear.

CONCLUSION

In order to develop a fundamental agent library to establish a CWS, the responses of water quality parameters to four inorganic pollutants in pure and tap water were investigated experimentally. The main findings of this study are as follows:

(1) The pH and ORP were identified as major water quality response parameters for the four inorganic pollutants studied. The responses in pure water appeared to be more sensitive, in terms of intensity, than those in tap water. In the pure water, a significant response was observed at the first level (the reference concentration allowed for each pollutant), whereas the response appeared at the second stage (10 times the threshold) in the case of tap water. Moreover, the pure water exhibited a higher strength at all stages.

(2) The results of the batch and simulated pipeline experiments for tap water showed almost identical tendencies, except for the second level of manganese injection (concentration 0.5 mg/L). However, the reasons for this difference remain unclear.

(3) To establish a complete CWS, it is necessary to extend the various agent libraries. For that, the response of inorganic, toxic and organic pollutants, which were not covered in this paper, should be investigated to achieve the database. In addition, research should also be conducted to analyze the behavior of other parameters.

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