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695

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Flow behavior of perchlorate from a source lake to a water supply tap following fireworks displays

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Abstract

Perchlorate is an oxidizer used in fireworks. Though fireworks displays are held over Lake Biwa, which supplies water to Kyoto, the city's water treatment process lacks the ability to remove perchlorate. This study investigated perchlorate contamination in source and tap water resulting from a fireworks display. During 2016, the perchlorate concentration in the source water increased to 22.3 μg/L during the 19 hours following the display and then decreased to <0.5 μg/L during the 43 hours following the display. The perchlorate concentration in the tap water increased to 13.6 μg/L during the 35 hours following the display, and then gradually decreased. To evaluate the state of mixing through the water treatment process, a model for chemical reactors was applied to concentration time-courses in the source and tap water. The model showed that perchlorate was dispersed homogeneously by stirring as the water flowed downstream through the waterway and through the water purification plant.

Key words: fireworks display, Kyoto, Lake Biwa, perchlorate, tank-in-series model

INTRODUCTION

Perchlorate is a stable chemical substance in the aquatic environment and interferes with the production of thyroid hormones required for human metabolism (Srinivasan & Viraraghavan 2009). Though perchlorate is a health risk, perchlorate has been detected in various types of food including dairy products, leafy vegetables, and seafood (Jackson *et al.* 2005; Takatsuki *et al.* 2011). Perchlorate has been detected in drinking water (Asami *et al.* 2007). The guidelines of perchlorate are different between countries and governments, and Japan set its non-legally binding guideline to 25 μg/L in tap water (Ministry of Health Labour and Welfare 2019). Although WHO set its guideline to 70 μg/L, some local governments severely set its guidelines to 6 μg/L in California and to 2 μg/L in Massachusetts (WHO 2017; MassDEP 2019; OEHHA 2019).

Some types of perchlorate are used as oxidizers in propellants such as rockets and fireworks, and fireworks displays are considered to cause perchlorate contamination in source water (Munster *et al.* 2009; Wu *et al.* 2011). Perchlorate concentrations have increased approximately 1,000 times compared to the mean baseline value in a small lake in the U.S. within just 14 hours following a fireworks display (Wilkin *et al.* 2007). In Japan, where over 200 fireworks displays are held annually (Japan Pyrotechnics Association 2019), perchlorate contamination has also been reported in a dammed lake (Yamada *et al.* 2010). Attempts have been made to remove or decompose perchlorate in the environment (Hori *et al.* 2012).

Lake Biwa, the largest lake in Japan, has northern and southern parts. The volume and residence time of water are 27.3 billion m^3 and 5.5 years in the northern part, and 0.3 billion m^3 and 15 days in the southern part (Somiya 2000). Lake Biwa is the main water resource of Kyoto with more than 1,000,000 residents. The 7.4-km-long waterway termed the 'Lake Biwa Waterway No. 2' carries the

Water Practice & Technology Vol 14 No 3
doi: 10.2166/wpt.2019.053

raw water to Kyoto, and water spends approximately 2 hours in this waterway. Keage Water Purification Plant in Kyoto has a water treatment process that includes particular active carbon absorption, coagulation-sedimentation, and rapid sand filtration (Figure 1). Near the waterway inlet, 10,000 fireworks are launched in a fireworks display every summer. Following the display, perchlorate is considered to be discharged into the lake water and to flow into the water purification plant through the waterway. This study investigated perchlorate contamination in the source and tap water resulting from the fireworks display. In this study, the hydraulic behavior of the water purification plant was also simulated on the basis of the experimental data of perchlorate concentration trends. We assumed that perchlorate was dispersed by mixing as it flowed downstream through Lake Biwa Waterway No. 2 and the Keage Water Purification Plant, because this chemical substance is stable in response to degradation and absorption. The 'tank-in-series model for complete-mixing' was applied to the dynamics of perchlorate. This tank-in-series model describes the state of mixing and evaluates the efficiency of a chemical reaction in a reactor (Gesui shiken houhou 2012). The tank-in-series model is often used to optimize activated sludge processes in a sewage system and to improve the performance of chlorine contact tanks and bypasses in a water supply system (Dominguez *et al.* 2005; Segawa *et al.* 2006; Sarathai *et al.* 2010; Rauen *et al.* 2012).

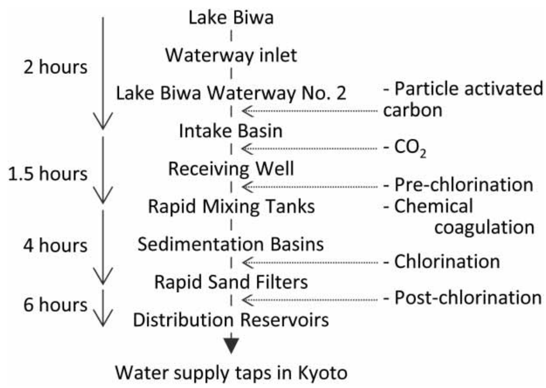

Figure 1 | Water treatment process of Keage Water Purification Plant.

Although perchlorate poses a health risk, water treatment processes including ozonation cannot remove perchlorate because of its persistence in water. However there are several reports to monitor perchlorate in tap water following fireworks displays in Japan (Kosaka *et al.* 2007). And some papers monitored perchlorate concentration at daily intervals (Wilkin *et al.* 2007), but we thought that monitoring at shorter intervals were needed to understand the behavior of perchlorate following a fireworks display in datail. In this study, perchlorate concentration was measured in the source and tap water at bihourly intervals following a fireworks displays in Lake Biwa from 2010 to 2015. The perchlorate concentration trend was also analyzed with a chemical reactor model to comprehend the diffusion of perchlorate as it flows downstream through the waterway and the water purification plant.

MATERIALS AND METHODS

Sampling water and measuring perchlorate

The investigation was carried out from 2010 to 2015, and the fireworks display was held from 19:30 to 20:30 each year. In 2010, the display was held on 6 Aug, and water was sampled in Lake Biwa on 9 Aug. In 2011, the display was held on 8 Aug, and water was sampled in the basins in Keage Water Purification Plant and in the water supply taps in Kyoto. The display was held on 8 Aug in 2014

Water Practice & Technology Vol 14 No 3
doi: 10.2166/wpt.2019.053

and on 7 Aug in 2015, and water was sampled in the waterway inlet and in the distribution reservoir in the plant using automatic water samplers (LYSAM-Ps, NKS Co., Ltd) in 2014 and 2015.

Perchlorate was measured using LC-MS in 2010 and LC-MS/MS from 2011 to 2015 (Table 1) (based on Yamada *et al.* 2010). The standard solution was prepared by dilution of 100 mg/L sodium perchlorate solution (Cambridge Isotope Laboratories, Inc.) and the internal standard solution was prepared by dilution of 100 mg/L $_{18}O^{4-}$ sodium perchlorate solution (Cambridge Isotope Laboratories, Inc.). Collected samples were filtered using a 0.2-μm membrane filter (GL Sciences Inc.) and stored at 4 °C (Wilkin *et al.* 2007).

Table 1 | Perchlorate measurements using LC-MS/MS

LC	Instrument	ACQUITY UPLC (Waters Corp.)	
	Column	ACQUITY UPLC BEH C18 (Water Corp.)	
	Column temp.	40 °C	
	Mobile phase A	5 m mol/L Ammonium acetate (Kanto Chemical Co., Inc)	
	Mobile phase B	Methanol (Nacalai tesque Inc.)	
	Gradient	0%B (0 min) → 25%B (2 min) → 25%B (2.5 min)	
	Flow speed	0.2 mL/min	
	Injection vol.	5 μL	
MS/MS	Instrument	Quattro Premier XE (Waters Corp.)	
	Ionization	ESI (Negative mode)	
	Monitering ion (*m/z*)	ClO_4^-	98.7 > 82.7
		$^{18}O_4 - ClO_4^-$	106.7 > 88.7

Modeling the chemical reactor

The dimensionless time θ was obtained by dividing the time t by the mean residential time T. C(θ) was the normalized tracer concentration at dimensionless time θ. Residence time distribution E(θ) was determined as a function of a time course of C(θ) in response to an impulse input at $\theta = 0$ (Equation (1)). The tank-in-series model assumes that a chemical reactor consists of N complete-mixing sequence tanks, and provides a residence time distribution E(θ) as Equation (2) as follows.

$$E(\theta) = \frac{C(\theta)}{\int_0^{\infty} C(\theta)d\theta} \tag{1}$$

$$E(\theta) = \frac{N^N}{(N-1)!}\theta^{N-1}e^{-N\theta} \tag{2}$$

The tank-in-series model was applied to the flow behavior from the waterway inlet to the distribution reservoirs. The theoretical residential times of 2014 were 20 via the calculation with the volume and the flow rate of each tank of the plant. The perchlorate concentration was normalized using Equation (1). Though the tank-in-series model is premised on impulse input, perchlorate in the waterway inlet had a concentration distribution. Therefore, the input of continuous time impulse was assumed. The theoretical time-course curves in the distribution reservoirs were analyzed for $N = 1$, 2, 5, 10, and 20 using Equation (2) with the observed time-curves in the waterway inlet. The data were not recorded 15 and 17 hours after the end of the firework display in 2014. The missing data were complemented with the average values between the data of the adjacent sampling times. Perchlorate concentrations in the waterway inlet were regarded as zero following the last sampling time.

Water Practice & Technology Vol 14 No 3
doi: 10.2166/wpt.2019.053

RESULTS AND DISCUSSION

Perchlorate concentration in the water resource and the water supply taps

Perchlorate was detected near the launch site after 3 days following the fireworks display in 2010 (Figure 2), but it was not detected further north than the launch site because of the lake water flowing from the north to the south. In 2011, perchlorate was detected 13.7 μg/L in the waterway inlet in the following morning after the display, though it was not detected there in the morning of the display day. This indicated that the fireworks display caused perchlorate contamination in Lake Biwa.

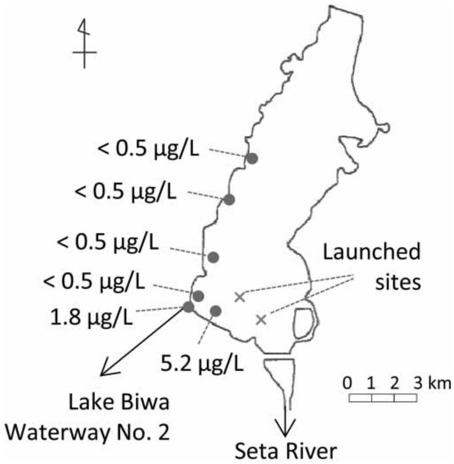

Figure 2 | Perchlorate concentration distribution in the southern part of Lake Biwa after 3 days following the fireworks display in 2010.

In 2011, the perchlorate concentration kept constant from the waterway inlet to the rapid sand filter at the same day (Figure 3). This result indicated that perchlorate could not be removed through the water treatment process including particular active carbon absorption, coagulation-sedimentation, and rapid sand filtration as the previous report said (Kosaka *et al.* 2007).

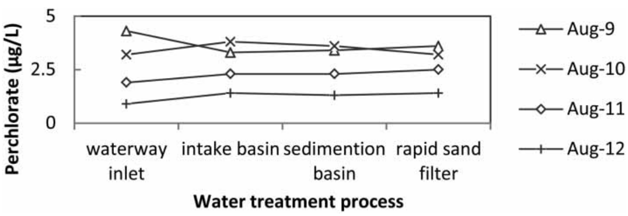

Figure 3 | Perchlorate concentrations through the water treatment process after 1–4 days following the fireworks display in 2011.

The perchlorate concentration in the tap water supplied from Keage Water Purification Plant was detected at 3.8 μg/L after 2 days following the fireworks display in 2011, and the concentration decreased to 0.6 μg/L after 10 days following the display (Figure 4). Kyoto had other three water purification plants taking water through the Lake Biwa Waterway No. 2 from Lake Biwa. In the tap water supplies from these plants, perchlorate was also detected at 3.3–5.7 μg/L after 2 days following the display, and perchlorate decreased to <0.2–0.4 μg/L after 10 days following the display. The contamination level was below its guideline in Japan, but perchlorate contamination lasted several days following the fireworks display.

Water Practice & Technology Vol 14 No 3
doi: 10.2166/wpt.2019.053

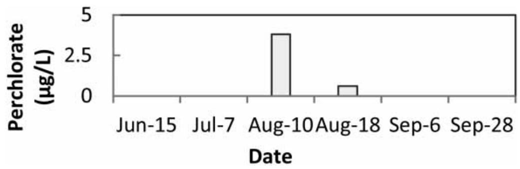

Figure 4 | Perchlorate concentrations in tap water from June to September in 2011. The fireworks display was held on 8 August.

In 2011, perchlorate concentration was also measured in the intake basin in Keage Water Purification Plant. The maximum concentration was 8.1 μg/L after 1 day following the display, and then decreased to <0.2 μg/L after 6 days. This result suggested that perchlorate contamination in the tap water decreased more slowly than the contamination in the intake basin.

The half-life of perchlorate was reported to be 29 days in a reflecting pond following a fireworks display, and perchlorate concentrations were decreased to the background levels in other lakes in 20–80 days (Wilkin *et al.* 2007; Wu *et al.* 2011). Unlike these studies, it took only 6 days to decrease perchlorate to <0.2 μg/L in the intake basin in Keage Water Purification Plant following the fireworks display in 2011. The one-direction flow from the north to the south might contribute to the decreasing rate of perchlorate in Lake Biwa.

Concentration trends in the waterway inlet and in the distribution reservoir

In 2014, the perchlorate concentration in the waterway inlet increased to 22.3 μg/L within 19 hours following the display, and the concentration in one of the distribution reservoir increased up to 13.6 μg/L within 35 hours following the display (Figure 5(a)). In 2015, perchlorate concentration in the waterway inlet increased up to 10.4 μg/L within 13 hours after the display, and the concentration in another distribution reservoir increased up to 6.4 μg/L within 25 hours following the display (Figure 5(b)). During 2014 and 2015, the perchlorate concentration time courses in the distribution reservoirs followed wide and low bell-shaped curves, and the maximum concentration in the distribution reservoirs was 61% of the maximum in the waterway inlet.

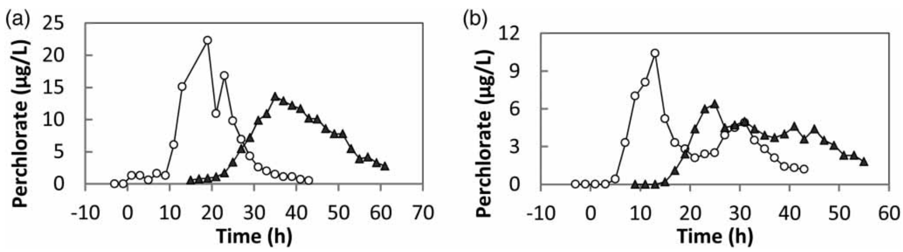

Figure 5 | Perchlorate concentration trends in the waterway inlet (○) and in the distribution reservoirs (▲). The fireworks display ended at 0 h. (a) Water was sampled in one of the distribution reservoirs in 2014. (b) Water was sampled at another distribution reservoir in 2015.

Rain and wind were considered to be the main reasons why the perchlorate concentration in 2014 was higher than that in the other years. The amounts of rainfall at the waterway inlet were 4 mm from 19:00 to 20:00 and 2.5 mm from 20:00 to 21:00 on the day of the fireworks display. In addition, an average 4.5 m/s wind blew from the north-northeast during the following 2 days after the display. Rainfall was considered to have prevented the propellants of the fireworks from spreading around the launched site, and the wind was considered to have carried the propellants into the waterway inlet.

There were two peaks in the perchlorate concentration trend in the waterway inlet in 2015 (Figure 5(b)) because of the change in the wind direction. During the following 2 days after the display, the day-time wind from the north-northeast (2–4 m/s) was considered to have carried

Water Practice & Technology Vol 14 No 3
doi: 10.2166/wpt.2019.053

perchlorate away from the waterway inlet, and the night-time wind from the south-southwest (1–2 m/s) was considered to have carried it back. This study indicated that rain and wind affected the behavior of perchlorate following the fireworks display, though Wilkin suggested that rain didn't decrease perchlorate concentration following fireworks displays (Wilkin *et al.* 2007).

The maximum perchlorate concentrations following fireworks displays were 519 μg/L in a reflecting pond and 44.2 μg/L in a small lake (Wilkin *et al.* 2007; Wu *et al.* 2011), but the maximum concentration was just 22.3 μg/L in this study. The south part of Lake Biwa has a total area of 55 km^2, and the lake water flows from the north to the south. These properties might contribute to disperse perchlorate in the lake water following the fireworks display.

Past studies monitored perchlorate concentration at daily intervals (Wilkin *et al.* 2007; Wu *et al.* 2011). Figure 5 showed that perchlorate concentration increased and then decreased during the 2 days following the fireworks display. This study indicated that the water should be sampled at hourly intervals to comprehend a behavior of perchlorate following a fireworks display in detail.

In cases of a 50-kg adult, a provisional tolerable daily intake of perchlorate was calculated to be 35 μg/d on the basis of the Reference Dose (0.7 μg/kg/d) announced by the National Resarch Council (National Research Council 2005). The maximum concentration of perchlorate was 13.6 μg/L in the distribution reservoir in 2014 in this study, and the daily intake was calculated to be 27.2 μg/d when drinking 2 L of 13.6 μg/L perchlorate-contaminated water. This calculation showed that drinking tap water in Kyoto was possibly acceptable even following the fireworks display in Lake Biwa.

Modeling the flow behavior of perchlorate

The perchlorate concentration decreased from the waterway inlet to the distribution reservoir. In this study, mixing was assumed to be the only factor decreasing the perchlorate concentration, because the water treatment process did not remove perchlorate (Figure 3). 'The tank-in-series model for complete mixing' was applied to analyze the behavior of perchlorate through the Lake Biwa Waterway No. 2 and Keage Water Purification Plant. This model also assumed that the flow path through the waterway and the plant was a chemical reactor consisting of N complete-mixing sequence tanks. In this model, a time-course has a wider and lower curve as N decreases, and it has a narrower and higher curve as N increases. You can evaluate the state of mixing on the basis of n when the theoretical time-course at $N = n$ fits the observation curve.

The amount of perchlorate was preserved from the waterway inlet to the distribution reservoir in 2014 and 2015. The mass balance equation showed that perchlorate was not decomposed. The theoretical time-course curves at $N = 10$ fitted the experimental curves of 2014 and 2015 most closely (Figures 6, data not shown in 2015)., The tank-in-series model well explained that mixing dispersed perchlorate in the water as it flowed downstream through the waterway and the plant.

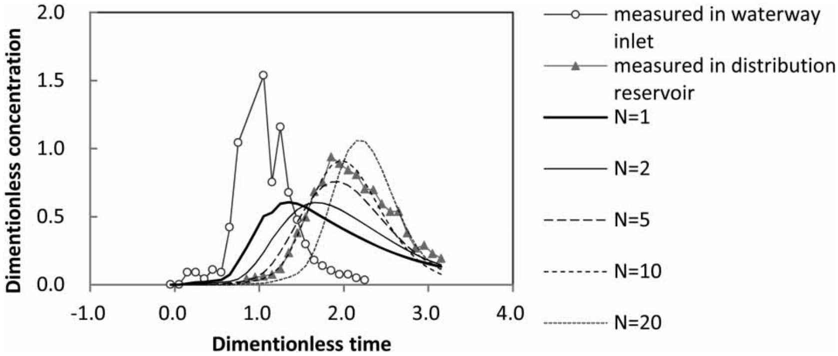

Figure 6 | Comparison of the experimental and theoretical curves for various numbers of tanks in 2014.

Water Practice & Technology Vol 14 No 3
doi: 10.2166/wpt.2019.053

CONCLUSION

This study from 2010 to 2015 investigated perchlorate contamination resulting from an annual fireworks display held over Lake Biwa, which supplies water to Kyoto. Though the rain and wind might affect the behavior of perchlorate, the maximum perchlorate concentration in the source water was 22.3 μg/L during the 19 hours following the fireworks display in 2014, and perchlorate was decreased to 0.5 μg/L during the 43 hours following the display. Perchlorate concentration drastically changed during the several days following the display. Perchlorate is expected to be monitored in the source water for several days following fireworks displays in order to comprehend the behavior of perchlorate. The maximum concentration in tap water was 13.6 μg/L during the 35 hours following the display in 2014. Although perchlorate concentration in the intake basin of Keage Water Purification Plant was decreased to <0.5 μg/L during 6 days following the fireworks display in 2011, it took 11–29 days to decrease its concentration in tap water in Kyoto to <0.5 μg/L. Perchlorate concentration attenuated more slowly in tap water than that in the source water. Perchlorate is expected to be monitored in the tap water during the months following fireworks displays.

The 'tank-in-series model for complete mixing' at $N = 10$ well described that the perchlorate concentration trend in the distribution reservoir had a wider and lower curve than the trend in the waterway inlet. This model indicated that perchlorate was not decomposed but dispersed by mixing as it flowed downstream though the waterway and the water purification plant.

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