

## Fireworks Displays and Production as a Perchlorate Emission Source

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**Abstract**—This study investigated the perchlorate contamination relating to fireworks display and manufacture. Sampling surveys were conducted during and after fireworks display in Japan to estimate the discharge levels of perchlorate into a river and changes in concentrations. Groundwater contamination by fireworks manufacturing in India was also investigated. Aqueous samples were analyzed using ion chromatography-tandem mass spectrometry (IC-MS/MS). Perchlorate concentrations in river water before fireworks ranged from 0.12 to 0.84  $\mu\text{g/L}$  and then increased up to 33  $\mu\text{g/L}$  within 1.5 hours of fireworks event, but decreased to background levels (0.19–2.52  $\mu\text{g/L}$ ) within 2 hours after the end of the events. This suggests that perchlorate was washed out with river flow due to its high water solubility. The concentrations of perchlorate in the groundwater samples from India were <0.005–7700  $\mu\text{g/L}$ . The highest levels were found in Sivakasi followed by Chennai > Trichy > Mumbai > Madurai > Kolkata. Levels in groundwater near fireworks factories were significantly higher than those in the other locations. In Sivakasi, where more than 7000 fireworks factories are located, 41% of the analyzed groundwater samples contained perchlorate levels exceeding the proposed guideline for drinking water (6  $\mu\text{g/L}$ ), indicating that further epidemiological investigation on human health effects is needed.

Keywords: fireworks, perchlorate, groundwater, India, Japan

### INTRODUCTION

Perchlorate salts are inorganic compounds used in explosives and rocket fuel as oxidant to promote combustion and explosion. Human health effects of perchlorate are of public concern because it is known to inhibit iodine uptake by the sodium-iodide symporter (NIS) of thyroid gland consequently leading to decrease in the production of thyroid hormones (T4) and triiodothyronine (T3) (Dohan *et al.*, 2007). NIS is also exist at some extrathyroidal tissues, including lactating

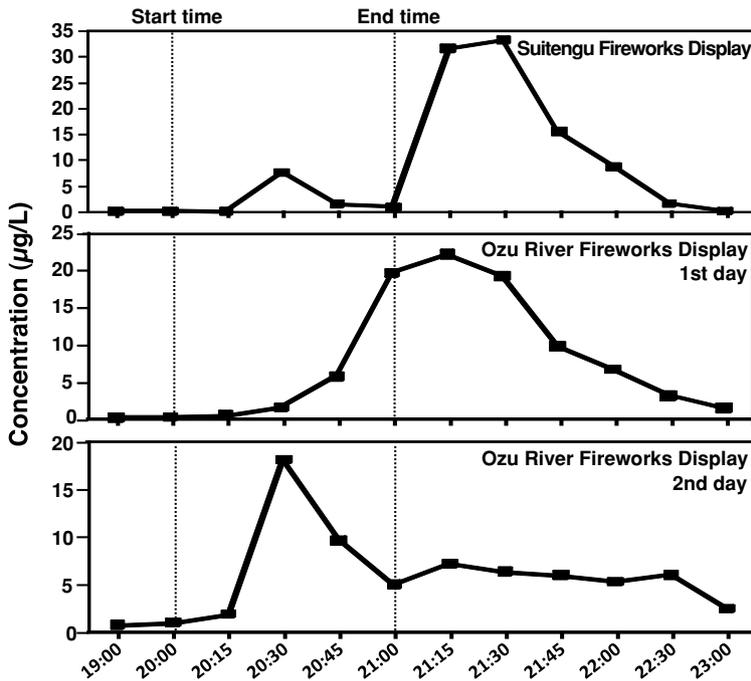


Fig. 1. Temporal variations of perchlorate concentrations during fireworks displays in Ozu city, Japan (2010).

mammary gland since iodine would be essential to the breastfed infant. Perchlorate competitively inhibits iodide uptake by NIS with 30 times greater affinity than iodide (Dohan *et al.*, 2007) and is selectively transferred to mammary gland (Dasgupta *et al.*, 2008). National Academy of Sciences (NAS) proposed 0.7 µg/kg/day as a reference dose (RfD) for perchlorate (NAS, 2005). Although arguments on safety level of perchlorate still remain, United States Environmental Protection Agency (USEPA) proposed a drinking water standard of 15 µg/L. In the U.S. an increasing risk of hypothyroidism by perchlorate exposure was reported (Greer *et al.*, 2002). Environmental and drinking water contamination by perchlorate are reported in certain countries such as the U.S. and Japan. However, only limited information on perchlorate pollution is available in Asia (Kannan *et al.*, 2009). In this study, perchlorate contaminations relating to fireworks display and manufacture were investigated. The discharge levels of perchlorate into a nearby river and changes in concentrations during and after fireworks display were estimated in Japan. Groundwater contamination by fireworks manufacturing were also investigated in India.

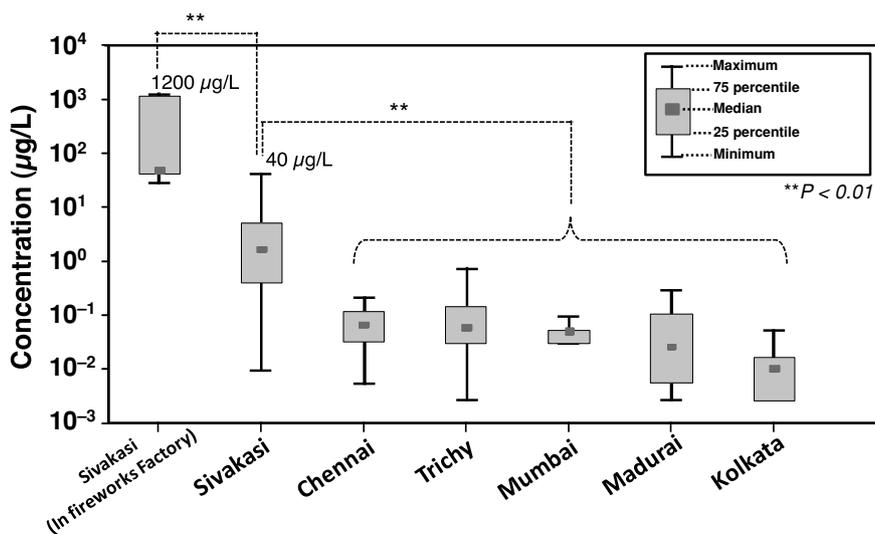


Fig. 2. Perchlorate concentrations in groundwater from 6 cities/towns in India.

## MATERIALS AND METHODS

### Sample collection

Total 36 surface water samples from Hijikawa River in Ehime, Japan were collected during 3 fireworks display events during July and August 2010. In each fireworks display, about 2000 fireworks were launched. We collected the river water samples an hour before and after the firework display and also collected the samples at 15 minutes interval during the 2 hours after the start of the fireworks event. All the samples were collected from the downstream of the river. To investigate the status of groundwater, we collected 184 groundwater samples from 6 cities (Sivakasi, Madurai, Trichy, Mumbai, Kolkata, Chennai) in India between October 2008 and January 2009. Sivakasi is a small town with a population of about 72,000 and is called as “A town of three industries”, known for fireworks, safety match-making and printing. There are several thousands factories scattered in and around Sivakasi town producing 80% and 90% of India’s total safety matches and fireworks, respectively. In addition, we also chose other two suburb cities (Madurai, Trichy) and three metropolises (Mumbai, Kolkata, Chennai) to compare with Sivakasi.

### Chemical analysis

Water sample was passed through an ion-exchange cartridge (OnGuard II

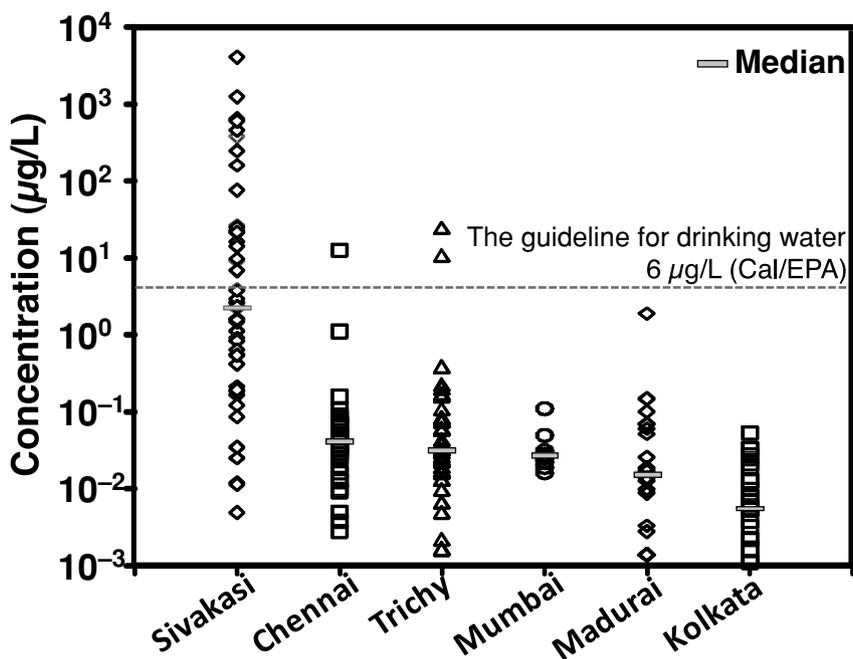


Fig. 3. Comparison of the drinking water standard of the perchlorate and its concentrations in groundwater from Indian cities/towns.

Ba/Ag/H, Dionex) and a 0.25- $\mu\text{m}$  membrane filter. One mL of purified sample was spiked with internal standard ( $\text{Cl}^{18}\text{O}_4^-$ : 0.1 ng) and analyzed using ion chromatography-tandem mass spectrometry (IC-MS/MS).

## RESULTS AND DISCUSSION

### *Effect of fireworks displays on perchlorate in river water*

Perchlorate concentrations in river water before the fireworks event ranged from 0.12 to 0.84  $\mu\text{g/L}$  and then increased up to 33  $\mu\text{g/L}$  within 1.5 hours after event started (Fig. 1). These results clearly indicate that perchlorate was discharged into river water by fireworks display. Subsequently, concentrations decreased to background levels (0.19–2.5  $\mu\text{g/L}$ ) within 2 hours after the end of the events (Fig. 1), suggesting that perchlorate was washed out with river water flow and/or dissipated due to its high water solubility. Sanchez *et al.*, (2009) reported high levels of perchlorate in farmland soil and crops around Colorado River in the U.S. because of discharge of perchlorate from rocket launches. Water from Hijikawa River is used for agriculture, so further study on the uptake of perchlorate by crops grown in the downstream of the river is warranted.

*Groundwater contamination of perchlorate by fireworks manufacturing industries*

Perchlorate contamination was monitored in groundwater from 6 cities in India. It was detected in almost all the groundwater samples analyzed (Fig. 2;  $<0.005\text{--}7700\ \mu\text{g/L}$ ), indicating widespread perchlorate contamination in India. Among the analyzed groundwater samples, the highest levels were found in Sivakasi ( $0.009\text{--}7700\ \mu\text{g/L}$ ) followed by Chennai ( $0.005\text{--}24\ \mu\text{g/L}$ )  $>$  Trichy ( $<0.005\text{--}46\ \mu\text{g/L}$ )  $>$  Mumbai ( $0.029\text{--}0.09\ \mu\text{g/L}$ )  $>$  Madurai ( $<0.005\text{--}3.5\ \mu\text{g/L}$ )  $>$  Kolkata ( $<0.005\text{--}0.09\ \mu\text{g/L}$ ). Median perchlorate concentration of  $1200\ \mu\text{g/L}$  was found in groundwater samples ( $n = 5$ ) sampled from inside the fireworks factory in Sivakasi, and was significantly higher than in water samples from outside the factory (median:  $40\ \mu\text{g/L}$ ,  $n = 24$ ). These results indicate that fireworks manufacturing industry is the major pollution source of perchlorate detected in groundwater. Perchlorate concentrations were compared with the guideline for drinking water in California ( $6\ \mu\text{g/L}$ ). Levels in groundwater from Chennai, Trichy, Mumbai, Madurai and Kolkata were below the guideline (Fig. 3). In Sivakasi, 22 groundwater samples showed concentrations higher than this guideline level among 54 samples (Fig. 3). Some workers in those factories may use those wells for drinking or cooking purposes. To our knowledge, there is no report on health effect around Sivakasi so far, but epidemiological study must be carried out as soon as possible. Decrease in thyroid hormone levels in pups of perchlorate exposed dams as well as dose-dependent deficits in hippocampal synaptic function was reported (Gilbert and Sui, 2008). It is also reported that maternal perchlorate exposure led to embryonic hypothyroidism in Japanese quail (Chen *et al.*, 2008). Therefore, detailed monitoring survey of perchlorate based on groundwater hydrology is warranted, to evaluate the toxicological risk and to prevent adverse effect on human or wildlife. Furthermore, education of residents in Sivakasi, public awareness raising and antipollution measure are necessary as administrative responsibilities for public health.

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