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Spatial distribution of perchlorate, iodide and thiocyanate in the aquatic environment of Tianjin, China: Environmental source analysis

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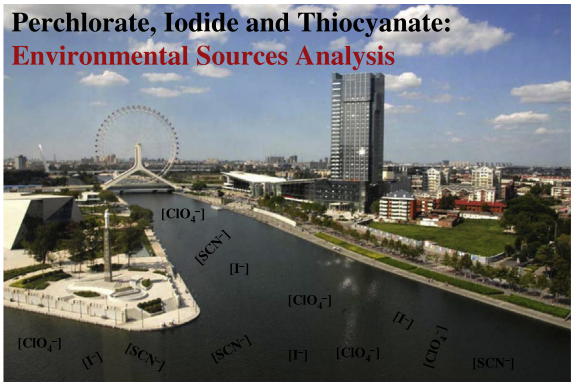
HIGHLIGHTS

- Perchlorate, iodide and thiocyanate concentrations were measured in rain-surface runoff pairs for the first time in China.
- Spatial variations were presented in surface environment.
- Precipitation may be one of the important sources for perchlorate, iodide and thiocyanate in the surface water.

GRAPHICAL ABSTRACT



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ABSTRACT

Although China is the largest producer of fireworks (perchlorate-containing products) in the world, the pathways through which perchlorate enters the environment have not been characterized completely in this country. In this study, perchlorate, iodide and thiocyanate were measured in 101 water samples, including waste water, surface water, sea water and paired samples of rain water and surface runoff collected in Tianjin, China. The concentrations of the target anions were generally on the order of rain > surface water ≈ waste water treatment plant (WWTP) influent > WWTP effluent. High concentrations of perchlorate, iodide and thiocyanate were detected in rain samples, ranging from 0.35 to 27.3 (median: 4.05), 0.51 to 8.33 (2.92), and 1.31 to 107 (5.62) ng mL^{-1}, respectively. Furthermore, the concentrations of the target anions in rain samples were significantly ($r = 0.596–0.750$, $p < 0.01$) positively correlated with the concentrations obtained in the paired surface runoff samples. The anions tested showed a clear spatial distribution, and higher concentrations were observed in the upper reaches of rivers, sea waters near the coast, and rain-surface runoff pairs sampled in urban areas. Our results revealed that precipitation may act as an important source of perchlorate, iodide and thiocyanate in surface water. Moreover, iodide concentrations in the Haihe River and Dagu Drainage Canal showed a good correlation with an ideal marker (acesulfame) of domestic waste water, indicating that input from domestic waste water was an important source of iodide in the surface waters of Tianjin.

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1. Introduction

Perchlorate (ClO_4^-) is an extremely water soluble and environmentally stable anion. Perchlorate has been used as an oxidizer in solid propellants, rockets, missiles, fireworks, and some munitions (Attanasio et al., 2011). Since the 1950s, the total production of perchlorate over 4×10^8 kg in the U.S. has been estimated (Dasgupta et al., 2006). In 1997, perchlorate concentrations up to 260 ng mL^{-1} were found in some water wells in eastern California (Wagner et al., 2004). Since then, perchlorate has been detected extensively in different countries around the world, with concentrations ranging from <0.1 to 2300 ng mL^{-1} in surface water (Kosaka et al., 2007; Kannan et al., 2009; Wu et al., 2010), from <0.1 to 35 ng mL^{-1} in drinking water (Quinones et al., 2007; Kannan et al., 2009; Blount et al., 2010), and from <0.07 to 0.35 ng mL^{-1} in sea water (Martinelango et al., 2006). Perchlorate was also reported in wet precipitation samples from the U.S. (Dasgupta et al., 2005; Furdui and Tomassini, 2009; Munster et al., 2009) and China (Ye et al., 2013) at concentrations between <0.01 and 5.5 ng mL^{-1}. The widespread presence of perchlorate in food and even in human beings has been well documented (Kirk et al., 2005; Sanchez et al., 2005; Blount et al., 2006; Dyke et al., 2006; Blount et al., 2007; Kannan et al., 2009; Oldi and Kannan, 2009; Zhang et al., 2010; Lee et al., 2012). Anthropogenic contamination with perchlorate results from the extensive use of perchlorate-containing products (Mendiratta et al., 2005; Wilkin et al., 2007; Shi et al., 2011; Wu et al., 2011). Atmospheric processes and the exploitation of nitrate deposits in Chile's Atacama Desert as fertilizer are known to be natural sources of perchlorate (Urbansky et al., 2001; Kounaves et al., 2010). For a specific environment, therefore, source analysis is needed to find the primary source so that the pollution can be controlled effectively.

Perchlorate can inhibit the uptake of iodide (I^-), which is required for the biosynthesis of the thyroid hormones, thyroxin, and triiodothyronine in mammals, thereby reducing the levels of these thyroid hormones in the body (Greer et al., 2002; Ting et al., 2006). Perchlorate has been reported to elicit developmental and neurobehavioral problems in infants and children (Travis and Sujatha, 2005). The toxic effect of perchlorate is exacerbated in individuals with low dietary iodine intake (Greer et al., 2002). In 2005, the U.S. Environmental Protection Agency (U.S. EPA) established a reference dose (RfD) of 0.7 μg kg^{-1} body weight day^{-1}, with a drinking water equivalent level (DWEL) of 24.5 ng mL^{-1} (National Academy of Sciences, 2005). Thiocyanate (SCN^-) can also act as a goitrogen by blocking iodide uptake by the sodium iodide symporter (NIS) in a competitive manner (Wyngaarden et al., 1953).

Excessive iodide intake can induce hypothyroidism during perinatal life (Theodoropoulos et al., 1979; Bourjeily et al., 2010). Several studies have investigated the occurrence of high levels of iodide in sea water, with concentrations greater than 46.8 ng mL^{-1} (Rong et al., 2013). A survey of North American and European rivers also indicated that the iodide concentrations varied from 5 to 212 ng mL^{-1} (Moran et al., 2002).

China is the world's largest producer of fireworks, with thousands of tons being produced every year. A few studies have reported perchlorate concentrations in surface water from China, with concentrations varying widely from 0.07 to 51.3 ng mL^{-1} (Wu et al., 2010; Ye et al., 2013). No study has yet explored the sources of perchlorate, iodide, and thiocyanate in surface waters of China. In this study, we investigated the occurrence of perchlorate, iodide, and thiocyanate in river water, sea water, rain water, and surface runoff in Tianjin, China. The spatial distribution and sources of the target anions were discussed. The source of perchlorate in the surface waters was primarily determined by comparing two potential sources, precipitation and discharges from WWTPs. To analysis the contribution of domestic waste water to the three target anions in surface water, an artificial sweetener, acesulfame, was used as an indicator of domestic waste water by correlative comparison (Buerge et al., 2009). To our knowledge, this is the first study to report the perchlorate, iodide and thiocyanate concentrations in waste water and rain-surface runoff pairs of China.

2. Materials and methods

2.1. Sample collection

A total of 101 environmental water samples, including surface water (n = 33), paired rain and surface runoff water (n = 25 pairs), waste water (n = 6), and sea water (n = 12), were collected in Tianjin, China. The surface water samples were collected in the Dahuangpu Wetland (DHP1-7, shown in Fig. 1a), the Haihe River (HR1-18, shown in Fig. 1b) and the Dagu Drainage Canal (D1-8, shown in Fig. 1b), respectively. The rain water (R1-25 shown in Fig. 1b) and surface runoff samples (S1-25, shown in Fig. 1b) were collected during one precipitation event on November 7, 2011. The surface water and waste water were collected during 5 d after the rainfall event; surface water were collected on November 9 to November 10, 2011, and waste water were collected on November 8, 2011. Waste water samples included three pairs of influent and effluent from three major WWTPs (WWTP#1–#3, shown in Fig. 1b) in Tianjin. Sea water samples were drawn in Bohai Sea on June 7, 2011 (B1-12, shown in Fig. 1c).

All water samples were collected using stainless steel buckets, which had been pre-cleaned by methanol and Milli-Q water. Precipitation was collected during the entire event (approximately 6 h), and well mixed for use as rainwater samples. The paired surface runoff samples were collected simultaneously from rain water drains or roadside puddles. The surface water and sea water samples were collected at a depth of approximately 0.50 m. All samples were stored immediately at −20 °C until arrival at the laboratory for analysis.

2.2. Sample preparation and instrumental analysis

The method for the extraction of perchlorate, iodide and thiocyanate from water was similar to the method described previously (Wu et al., 2011). The concentrations of perchlorate, iodide and thiocyanate were determined using two-dimensional ion chromatography and suppressed conductivity detection (2D-IC). Details regarding chemicals and reagents, sample preparation and instrumental analysis for the target anions are given in the Supplementary Material (SM).

The analysis of acesulfame was performed by solid phase extraction and HPLC-MS/MS, and the details can be found in our previous study (Gan et al., 2013a).

2.3. Quality assurance and quality control

Calibration curves were prepared every day at the beginning and at the end of each batch of 20 samples analyzed. The regression coefficient for the calibration standards, injected at concentrations ranging from 0.05 to 50 ng mL^{-1}, was >0.999. As a check for instrumental drift in the response factors, a midpoint calibration standard was injected after every 10 samples. The limits of quantitation (LOQs) of perchlorate, iodide, and thiocyanate were defined as the values associated with signal-to-noise ratios of 10. The LOQs of perchlorate, iodide, and thiocyanate were 0.09, 0.08, and 0.05 ng mL^{-1}, respectively.

Procedural blanks were prepared by substitution of 2.0 mL of Milli-Q water for environmental water, followed by passage through the entire analytical procedure. Pure solvent (Milli-Q