

# Perchlorate in Tap Water, Groundwater, Surface Waters, and Bottled Water From China and its Association with Other Inorganic Anions and with Disinfection Byproducts

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**Abstract** Perchlorate is a potent thyroid hormone-disrupting compound. Drinking water is one of the major sources of human exposure to perchlorate. Little is known about the occurrence of perchlorate in waters from China. In this study, water samples ( $n = 300$ ) collected from 15 locations in 13 provinces and municipalities were analyzed for the presence of perchlorate. In addition, other inorganic anions that commonly occur in water—iodide, bromide, and nitrate—and the disinfection byproducts, bromate, chlorate, and chlorite were determined by high-performance liquid chromatography interfaced with tandem mass spectrometry. Perchlorate was detected in 86% of the samples analyzed, at concentrations ranging from  $<0.02$  to  $54.4 \mu\text{g l}^{-1}$  (mean  $\pm$  SD  $2.20 \pm 6.39 \mu\text{g l}^{-1}$ ; median  $0.62 \mu\text{g l}^{-1}$ ). Mean concentrations of perchlorate in tap water, groundwater, surface waters, and bottled water were 2.46, 3.04, 2.82, and  $0.22 \mu\text{g l}^{-1}$ , respectively. Significant positive correlations were found between the

concentrations of perchlorate and nitrate, perchlorate and chlorate, bromide and iodide, and nitrate and iodide.

Perchlorate is produced and used in the form of salts of ammonium, sodium, and potassium as an oxidizer in solid rocket propellants, missiles, flares, and fireworks (Urbansky 1998). Perchlorate salts are also used as components or additives in nuclear reactors, vehicle airbag inflators, electronic tubes, lubricating oils, leather tanning and finishing processes, electroplating and aluminum refining, and paint and enamel production (Urbansky 1998). In the United States, large-scale production of perchlorate started in the 1940s, during World War II, and great volumes of the compound have been disposed of in various states since the 1950s. In addition to anthropogenic sources, natural sources, such as sodium nitrate deposits in Chile (Urbansky et al. 2001) and formation in the atmosphere, have been reported (Dasgupta et al. 2005). Perchlorate can disrupt the sodium iodide symporter function of the thyroid gland, thereby interfering with the gland's uptake of iodide, and consequently impairing production of the thyroid hormones triiodothyronine (T3) and thyroxine (T4) (Wolff 1998). Neurodevelopmental effects have been shown to be associated with T3 and T4 deficiency during pregnancy, and these effects are exacerbated by low iodine intake (Li et al. 2000).

Perchlorate has been reported to occur in drinking water, groundwater, and surface waters across the United States (United States Environmental Protection Agency [USEPA] 2004; Snyder et al. 2005; Parker et al. 2008). Since 1997, perchlorate has been listed as a candidate for drinking water-monitoring programs (USEPA 1998). Occurrence of perchlorate in drinking water, groundwater, and surface waters has been documented in Japan (Kosaka et al. 2007),

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Korea (Quinones et al. 2007), and India (Kannan et al. 2009). Perchlorate is also present in foodstuffs, especially leafy vegetables and bovine milk (Kirk et al. 2003, 2005; Sanchez et al. 2008). Human exposure to perchlorate by way of food and drinking water has been documented (Murray et al. 2008). Presence of perchlorate in urine, breast milk, saliva, and serum sampled from the United States population suggested widespread human exposure to this thyroid hormone-disrupting contaminant (Kirk et al. 2005; Blount et al. 2007; Oldi & Kannan 2009a, 2009b).

In 2005, the USEPA established a reference dose of  $0.7 \mu\text{g kg}^{-1} \text{bw d}^{-1}$  and an interim health advisory level in drinking water of  $15 \mu\text{g l}^{-1}$  for perchlorate (USEPA 2005a). Several states in the United States have set advisory levels for perchlorate in the range of 1 to  $18 \mu\text{g l}^{-1}$  (USEPA 2005b). The California Department of Health Services proposed  $6 \mu\text{g l}^{-1}$  as the maximum contaminant level (MCL) for perchlorate in drinking water, whereas the Massachusetts Department of Environmental Protection proposed a level of  $2 \mu\text{g l}^{-1}$  as acceptable (USEPA 2005a).

China is the world's largest producer of fireworks, with thousands of tons of fireworks being produced every year, and perchlorate is used in the production of fireworks. Nevertheless, few studies have investigated the occurrence of perchlorate in China (Shi et al. 2007). Analysis of sewage sludge, rice, bottled water, and milk from China did show contamination by perchlorate (Shi et al. 2007). However, a comprehensive survey of perchlorate in tap water, groundwater, and surface waters in China is lacking. In the present study, we describe the occurrence of perchlorate in tap water, groundwater, and surface waters sampled from 15 locations across China. In addition, several inorganic anions (nitrate, bromide, and iodide) and disinfection byproducts (chlorate, chlorite, and bromate) were analyzed in water samples to enable examination of the relation of perchlorate concentration to the concentrations of inorganic anions and disinfection byproducts (note that nitrate was measured as concentrations of nitrate-N). This is the first study to report the simultaneous measurement of chlorate, chlorite, bromate, bromide, iodide, and nitrate in water by high-performance liquid chromatography interfaced with tandem mass spectrometry (HPLC-MS/MS).

## Materials and Methods

### Sample Collection

Water samples were collected from November through December 2008 and in December 2009. Grab samples ( $n = 300$ ) of tap water, bottled water, groundwater (or well water), surface waters (from rivers, lakes, and springs), and

water from drinking water-treatment plants (WTPs) were collected from 15 locations (Beijing, Shanghai, Tianjin, Harbin, Shenyang, Jinan, Tai'an, Zhengzhou, Kaifeng, Nanchang, Hengyang, Chengdu, Linfen, Kunming, and Shenzhen), in 13 provinces and municipalities, based on the availability and accessibility (Fig. 1). Tap water samples were randomly collected from homes, schools, restaurants, and hotels. In this study, tap water denotes water that was distributed through publicly owned WTPs (i.e., after water treatment) and that was intended for drinking or food processing. Groundwater samples were collected from public or private wells or from pumps or taps directly connected to groundwater supplies that did not undergo any water treatment. Surface-water samples were collected from rivers, lakes, and mountain springs. Water from public WTPs was sampled from either influent or effluent. Various well-known brands of bottled water were purchased from local retail stores. All of the samples were collected in clean glass vials. Samples were stored at  $4^\circ\text{C}$  until analysis.

### Standards and Reagents

Ammonium perchlorate (99.999%) and methylamine (40 wt% solution in water) were obtained from Sigma Aldrich (St. Louis, MO). Sodium bromide, sodium nitrate, and potassium iodide solutions (purity  $>99.5\%$ ) were from AccuStandard (New Haven, CT). Chlorate, chlorite, and bromate standards were from APG (Belpre, OH). Stable isotope-labeled sodium perchlorate ( $\text{Cl}^{18}\text{O}_4 > 90\%$ ) was purchased from Cambridge Isotope Laboratories (Andover, MA).

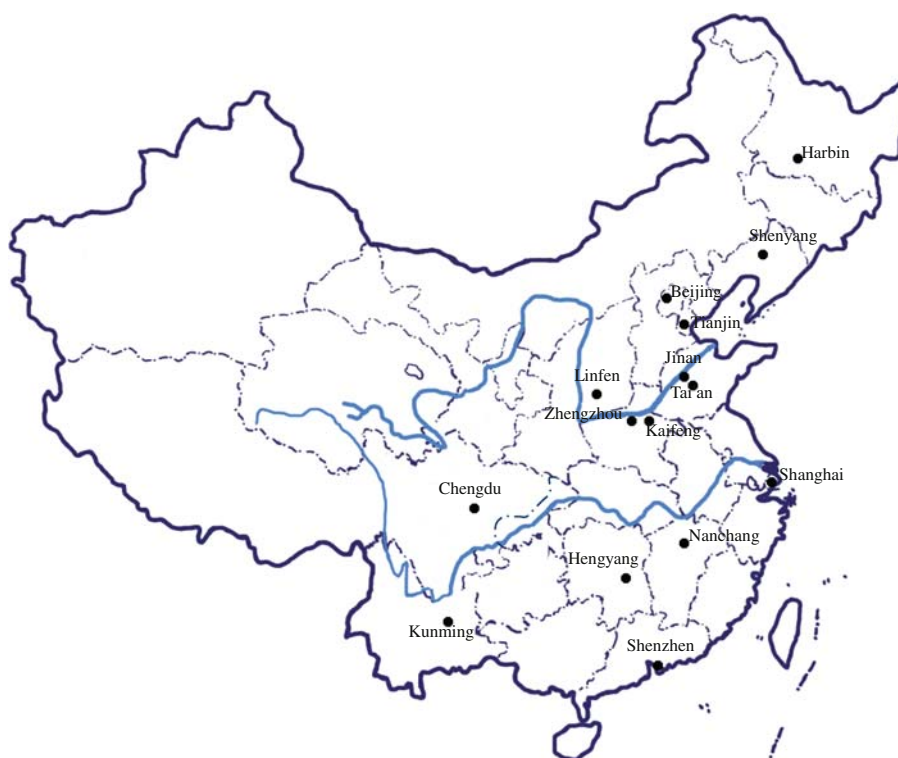
### Sample Preparation

The method for the analysis of perchlorate, chlorate, chlorite, bromate, bromide, nitrate, and iodide in water was similar to that described previously (Oldi & Kannan 2009a). Briefly, 2-ml water samples were filtered through a  $0.22\text{-}\mu\text{m}$  nylon filter. Precisely, 0.9 ml filtered water samples and 1 ng  $^{18}\text{O}$ -labeled perchlorate internal standard were added to sample vials. The samples were vortex mixed and then analyzed by HPLC-MS/MS.

### Instrumental Analysis

Sample injection was performed using a Gilson 215 liquid handler and a Gilson 819 injection module (Gilson, Middleton, WI) equipped with a  $100\text{-}\mu\text{l}$  injection loop. Separation of perchlorate, chlorate, chlorite, bromate, bromide, nitrate, and iodide ions in water was accomplished with an anion-exchange column (IonPac AS-21,  $250 \times 2 \text{ mm}$ ; Dionex, Sunnyvale, CA). Methylamine, 200 mM, was the

**Fig. 1** Map of China showing water sampling locations



mobile phase and was eluted isocratically at a flow rate of  $0.3 \text{ ml min}^{-1}$  with an Agilent 1100 HPLC system (Agilent, Santa Clara, CA). The injection volume was  $100 \mu\text{l}$ . Perchlorate, chlorate, chlorite, bromate, bromide, nitrate, and iodide eluted at 5.5, 3.4, 3.15, 3.1, 3.55, 3.7 and 4.6 min, respectively. The total runtime was 10 min. Target anions were introduced into a Micromass Quattro LC mass spectrometer (Waters, Milford, MA) in the negative electrospray ionization mode. Multiple reaction monitoring of the following mass transitions was used for identification and quantification of perchlorate, chlorate, chlorite, bromate, bromide, nitrate, and iodide:  $m/z$  99 ( $^{35}\text{ClO}_4^-$ )  $\rightarrow$   $m/z$  83 ( $^{35}\text{ClO}_3^-$ ),  $m/z$  101 ( $^{37}\text{ClO}_4^-$ )  $\rightarrow$   $m/z$  85 ( $^{37}\text{ClO}_3^-$ ),  $m/z$  107 ( $^{35}\text{Cl}^{18}\text{O}_4^-$ )  $\rightarrow$   $m/z$  89 ( $^{35}\text{Cl}^{18}\text{O}_3^-$ ),  $m/z$  83 ( $^{35}\text{ClO}_3^-$ )  $\rightarrow$   $m/z$  67 ( $^{35}\text{ClO}_2^-$ ),  $m/z$  85 ( $^{37}\text{ClO}_4^-$ )  $\rightarrow$   $m/z$  69 ( $^{37}\text{ClO}_3^-$ ),  $m/z$  67 ( $^{35}\text{ClO}_2^-$ )  $\rightarrow$   $m/z$  51 ( $^{35}\text{ClO}^-$ ),  $m/z$  69 ( $^{37}\text{ClO}_2^-$ )  $\rightarrow$   $m/z$  53 ( $^{37}\text{ClO}^-$ ),  $m/z$  127 ( $^{79}\text{BrO}_3^-$ )  $\rightarrow$   $m/z$  111 ( $^{79}\text{BrO}_2^-$ ),  $m/z$  129 ( $^{81}\text{BrO}_3^-$ )  $\rightarrow$   $m/z$  113 ( $^{81}\text{BrO}_2^-$ ),  $m/z$  79 ( $^{79}\text{Br}^-$ )  $\rightarrow$   $m/z$  79 ( $^{79}\text{Br}^-$ ),  $m/z$  81 ( $^{81}\text{Br}^-$ )  $\rightarrow$   $m/z$  81 ( $^{81}\text{Br}^-$ ),  $m/z$  62 ( $\text{NO}_3^-$ )  $\rightarrow$   $m/z$  46 ( $\text{NO}_2^-$ ), and  $m/z$  127 ( $\text{I}^-$ )  $\rightarrow$   $m/z$  127 ( $\text{I}^-$ ). A relative response of native standard to isotopically labeled internal standard and the ratio of  $^{35}\text{Cl}:^{37}\text{Cl}$  were used for the confirmation of perchlorate, chlorate, and chlorite. A ratio of ( $^{35}\text{Cl}:^{37}\text{Cl}$ )  $3.12\% \pm 25\%$  was considered acceptable. The relative response of  $^{79}\text{Br}:^{81}\text{Br}$  was used for the confirmation of bromate and bromide. A ratio of ( $^{79}\text{Br}:^{81}\text{Br}$ )  $1.03\% \pm 25\%$  was considered acceptable. Data acquisition was accomplished with Micromass MassLynx v. 3.5 software (Waters).

#### Quality Assurance and Quality Control

A 10-point calibration standard containing concentrations ranging from 0.01 to  $100 \mu\text{g l}^{-1}$  for perchlorate, from 0.14 to  $140 \mu\text{g l}^{-1}$  for chlorate, from 0.38 to  $380 \mu\text{g l}^{-1}$  for chlorite, from 0.09 to  $90 \mu\text{g l}^{-1}$  for bromate, from 0.05 to  $500 \mu\text{g l}^{-1}$  for bromide, from 0.02 to  $200 \mu\text{g l}^{-1}$  for iodide, and from 0.05 to  $500 \mu\text{g l}^{-1}$  for nitrate-N was injected with each batch of 25 samples. Calibration curves were generated at least weekly, and continuing calibration checks were performed daily before and after every batch of samples using a calibration standard to check the instrumental drift in response. Samples were diluted with milli-Q water if concentrations were above the calibration range. Along with every batch of samples, a laboratory reagent blank (LRB), a laboratory fortified blank, and a laboratory fortified duplicate were analyzed according to the procedure described for samples. The limit of quantitation (LOQ) was calculated as 10 times the LRB value. The LOQ for perchlorate was  $0.02 \mu\text{g l}^{-1}$ . The LOQs for chlorate, chlorite, bromate, bromide, nitrate-N, and iodide were 0.17, 1.4, 0.35, 2.5, 25, and  $0.05 \mu\text{g l}^{-1}$ , respectively.

Mean recovery of labeled internal standard ( $\text{Cl}^{18}\text{O}_4$ ) spiked into water samples was  $107\% \pm 23\%$ . The reported concentrations in samples were corrected for internal standard recoveries. Samples with concentrations below the LOQ were not included in the calculation of mean and median.

## Results and Discussion

### Occurrence of Perchlorate in Waters From China

Concentrations of perchlorate in water samples from China are presented in Table 1 and Fig. 2. Perchlorate was detected in 259 (86%) of 300 water samples analyzed, at concentrations above the LOQ of  $0.02 \mu\text{g l}^{-1}$ . Perchlorate concentrations ranged from  $<0.02$  to  $54.4 \mu\text{g l}^{-1}$  (mean  $2.20 \pm 6.39 \mu\text{g l}^{-1}$ ; median  $0.62 \mu\text{g l}^{-1}$ ). Ten water samples contained perchlorate concentration  $>10 \mu\text{g l}^{-1}$ . The highest concentration ( $54.4 \mu\text{g l}^{-1}$ ) was found in a surface (river) water sample from Hengyang city, Hunan province. The other nine samples with concentrations  $>10 \mu\text{g l}^{-1}$  were from Hengyang city (Hunan province) ( $n = 4$ ), Tai'an city (Shandong province) ( $n = 1$ ), and Nanchang city (Jiangxi province) ( $n = 4$ ); three were tap water samples, two were groundwater samples and, four were surface water samples. Among water samples collected from 15 cities, samples from Hengyang showed the highest mean concentration ( $36.5 \pm 18.2 \mu\text{g l}^{-1}$ ) of perchlorate followed by Nanchang ( $4.70 \pm 4.62 \mu\text{g l}^{-1}$ ). Samples from Chengdu and Shenzhen had the lowest mean concentrations ( $0.14 \pm 0.07 \mu\text{g l}^{-1}$  for Chengdu and  $0.14 \pm 0.03 \mu\text{g l}^{-1}$  for Shenzhen) of perchlorate. The high mean concentrations of perchlorate in Hengyang and Nanchang are explained by the large fireworks manufacturing operations in these two provinces.

To enable examination of differences in perchlorate concentrations among various sources of water, we categorized the samples as tap water ( $n = 101$ ), groundwater ( $n = 24$ ), surface waters ( $n = 94$ ), bottled water ( $n = 69$ ), and other ( $n = 12$ ; i.e., water samples from WTPs). The respective mean concentrations of perchlorate in drinking water, groundwater, surface waters, bottled water, and other were  $2.46 \pm 6.59$ ,  $3.04 \pm 6.73$ ,  $2.82 \pm 7.63$ ,  $0.22 \pm 0.23$ , and  $0.69 \pm 0.88 \mu\text{g l}^{-1}$ , respectively (Table 2 and Fig. 3). The highest concentrations of perchlorate in tap water, groundwater, and surface waters were all from Hengyang at  $31.4 \pm 21.3$ ,  $22.1$ , and  $51.3 \pm 4.4 \mu\text{g l}^{-1}$ , respectively. Bottled water samples also contained perchlorate; 42 of 69 bottled water samples had perchlorate levels  $>0.02 \mu\text{g l}^{-1}$ . The highest concentration of perchlorate in bottled water was from Shenyang ( $0.73 \mu\text{g l}^{-1}$ ), and the second highest concentration was from Beijing ( $0.70 \mu\text{g l}^{-1}$ ). Seven samples representing five brands of bottled water had perchlorate concentrations  $>0.5 \mu\text{g l}^{-1}$ .

### Occurrence of Chlorate, Chlorite, Bromate, Bromide, Nitrate, and Iodide in Waters From China

Concentrations of chlorate, chlorite, bromate, bromide, nitrate-N, and iodide in water samples from China are

listed in Table 1. Chlorate, chlorite, bromate, bromide, nitrate-N, and iodide were, respectively, detected in 217 (72%), 9 (3%), 51 (17%), 227 (76%), 284 (95%), and 202 (67%) of the 300 samples analyzed. The concentrations ranged from  $<0.17$  to  $343 \mu\text{g l}^{-1}$  for chlorate; from  $<1.4$  to  $44.4 \mu\text{g l}^{-1}$  for chlorite; from  $<0.35$  to  $28.4 \mu\text{g l}^{-1}$  for bromate; from  $<2.5$  to  $112 \mu\text{g l}^{-1}$  for bromide; from  $<25$  to  $8490 \mu\text{g l}^{-1}$  for nitrate-N; and from  $<0.05$  to  $22.8 \mu\text{g l}^{-1}$  for iodide. The highest mean concentrations of chlorate, chlorite, bromate, bromide, nitrate-N and iodide were, respectively, found in samples from Beijing ( $28.5 \pm 78.7 \mu\text{g l}^{-1}$  chlorate), Jinan ( $44.4 \mu\text{g l}^{-1}$  chlorite; note that SD was not calculated because only one sample was higher than the LOQ), Shenyang ( $6.96 \pm 3.36 \mu\text{g l}^{-1}$  bromate), Shanghai ( $39.1 \pm 33.2 \mu\text{g l}^{-1}$  bromide), Hengyang ( $2154 \pm 330 \mu\text{g l}^{-1}$  nitrate-N), and Kaifeng ( $6.13 \pm 5.60 \mu\text{g l}^{-1}$  iodide).

### Global Comparison of Perchlorate in Waters

Very few studies have reported the occurrence of perchlorate in waters from any country other than the United States. Perchlorate was analyzed in 3865 public water supplies in the United States between 2001 and 2005. The mean and median concentrations of perchlorate for the samples with positive detections were  $9.85 \mu\text{g l}^{-1}$  and  $6.40 \mu\text{g l}^{-1}$ , respectively, and ranged from  $4 \mu\text{g l}^{-1}$  to  $420 \mu\text{g l}^{-1}$  (USEPA 2008). In a watershed contaminated by perchlorate from industrial sources in Japan, 19 of 27 tap water samples had perchlorate concentrations  $>1 \mu\text{g l}^{-1}$ , and 13 of those had concentrations  $>10 \mu\text{g l}^{-1}$  (Kosaka et al. 2007). In Korea, tap water samples contained perchlorate concentrations ranging from  $0.15$  to  $35 \mu\text{g l}^{-1}$ , with a mean concentration of  $10.4 \mu\text{g l}^{-1}$  (Quinones et al. 2007). A recent study showed that the mean concentration of perchlorate in tap water sampled from India was  $0.1 \mu\text{g l}^{-1}$  (Kannan et al. 2009). In the present study, the mean concentration of perchlorate in tap water from China was  $2.46 \pm 6.59 \mu\text{g l}^{-1}$ , an order of magnitude higher than what was reported for samples from India but lower than the concentrations found in waters from potential point-source areas in Japan, Korea, and the United States.

The USEPA established an interim health advisory level for perchlorate in drinking water of  $15 \mu\text{g l}^{-1}$  (USEPA 2005a). Several states in the United States have set advisory levels of perchlorate in the range of  $1$  to  $18 \mu\text{g l}^{-1}$  (USEPA 2005b). In the present study of Chinese samples, 3 of 101 (3%) tap water samples exceeded the USEPA's interim health advisory level; 13 of 101 (12.9%) tap water samples contained perchlorate levels above the maximum contaminant level (MCL; i.e., the highest allowed in drinking water) in drinking water that was set by the California Department of Health Services ( $6 \mu\text{g l}^{-1}$ ); and 18 of

**Table 1** Perchlorate, chlorate, chlorite, bromate, bromide, and nitrate-N concentrations in water samples from China stratified by city

City	N	Perchlorate ( $\mu\text{g l}^{-1}$ )			Chlorate ( $\mu\text{g l}^{-1}$ )			Chlorite ( $\mu\text{g l}^{-1}$ )			Bromate ( $\mu\text{g l}^{-1}$ )		
		Range	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
Beijing	25	<0.02–6.24	1.12	1.61	<0.17–343	28.5	78.7	<1.4–3.59	2.75	0.72	<0.35–13.7	4.17	4.76
Shanghai	34	<0.02–8.44	2.18	2.59	<0.17–107	21.3	35.2	<1.4–2.25	1.90	0.33	<0.35–28.4	4.84	9.49
Tianjin	20	<0.02–3.14	0.63	0.67	<0.17–1.7	0.74	0.38	<1.4			<0.35		
Harbin	15	<0.02–0.59	0.26	0.17	<0.17–9.1	1.55	2.39	<1.4			<0.35		
Shenyang	23	<0.02–7.00	1.36	2.40	<0.17–23.1	7.17	7.71	<1.4			<0.35–11.1	6.96	3.36
Jinan	19	<0.02–2.87	1.08	0.79	<0.17–44.4	9.22	22.9	<1.4–44.4	44.4		<0.35–2.1	2.12	
Tai'an	20	<0.02–20.8	2.27	4.56	<0.17–6.1	1.38	1.89	<1.4			<0.35		
Zhengzhou	20	<0.02–1.25	0.83	0.46	<0.17–6.8	4.18	2.46	<1.4			<0.35		
Nanchang	25	0.02–15.6	4.70	4.62	<0.17–71.3	16.4	20.0	<1.4			<0.35–2.84	1.08	1.00
Hengyang	6	6.8–54.4	36.5	18.2	8.0–33.2	23.5	9.9	<1.4			<0.35–2.5	2.03	0.46
Kaifeng	18	<0.02–2.53	0.82	0.77	<0.17–5.1	3.01	2.37	<1.4			<0.35		
Chengdu	17	<0.02–0.22	0.14	0.07	<0.17–14.0	8.09	5.65	<1.4			<0.35–7.31	4.93	3.21
Linfen	29	<0.02–1.44	0.84	0.43	<0.17–309	16.1	64.0	<1.4			<0.35		
Kunming	20	<0.02–0.44	0.18	0.11	<0.17–57.7	9.13	18.0	<1.4–2.36	2.36		<0.35–3.54	1.50	1.51
Shenzhen	9	<0.02–0.17	0.14	0.03	<0.17–16.2	4.73	4.79	<1.4			<0.35–0.76	0.56	0.29
Overall	300	<0.02–54.4	2.20	6.39	<0.17–343	11.8	35.5	<1.4–44.4	7.04	14.0	<0.35–28.4	4.08	5.75
City	N	Bromide ( $\mu\text{g l}^{-1}$ )			Nitrate-N ( $\mu\text{g l}^{-1}$ )			Iodide ( $\mu\text{g l}^{-1}$ )					
		Range	Mean	SD	Range	Mean	SD	Range	Mean	SD			
Beijing	25	<2.5–23.4	9.42	7.88	30.8–2462	590	715	<0.05–0.86	0.23	0.23			
Shanghai	34	<2.5–94.1	39.1	33.2	<25–3578	859	1090	<0.05–12.4	2.98	3.60			
Tianjin	20	5.39–83.1	36.3	18.6	<25–1819	384	409	<0.05–8.43	1.76	2.47			
Harbin	15	<2.5–16.7	11.2	4.80	101.3–4065	1060	1280	<0.05–4.42	1.04	1.57			
Shenyang	23	<2.5–30.7	12.0	9.41	<25–1164	414	317	<0.05–3.28	1.63	1.36			
Jinan	19	2.98–112	16.9	24.5	59.03–2252	1120	784	<0.05–21.4	3.62	7.03			
Tai'an	20	<2.5–12.5	7.08	2.92	53.3–8491	1750	2070	<0.05–1.44	0.48	0.45			
Zhengzhou	20	<2.5–43.7	15.5	11.6	<25–4941	988	1480	<0.05–1.38	0.33	0.35			
Nanchang	25	<2.5–32.6	11.7	5.61	144.6–3161	1430	881	<0.05–9.73	1.84	2.77			
Hengyang	6	6.4–49.4	19.6	19.0	1868–2709	2154	330	1.9–6.6	3.51	1.70			
Kaifeng	18	3.52–42.2	18.3	9.35	<25–2046	641	636	<0.05–22.8	6.13	5.60			
Chengdu	17	<2.5–3.95	3.73	0.31	46.57–1597	408	463	<0.05–0.11	0.07	0.02			
Linfen	29	<2.5–28.5	9.70	5.51	33.76–3627	1050	931	<0.05–16.7	2.26	4.40			
Kunming	20	<2.5–8.32	5.32	2.09	35.31–1659	775	528	<0.05–0.14	0.10	0.03			
Shenzhen	9	<2.5–10.2	7.95	1.27	<25–318.1	246	98	<0.05–0.63	0.28	0.17			
Overall	300	<2.5–112	17.1	18.8	<25–8491	911	1061	<0.05–22.8	1.97	3.58			

101 (17.8%) tap water samples contained perchlorate levels above the values proposed by the Massachusetts Department of Environmental Protection ( $2 \mu\text{g l}^{-1}$ ).

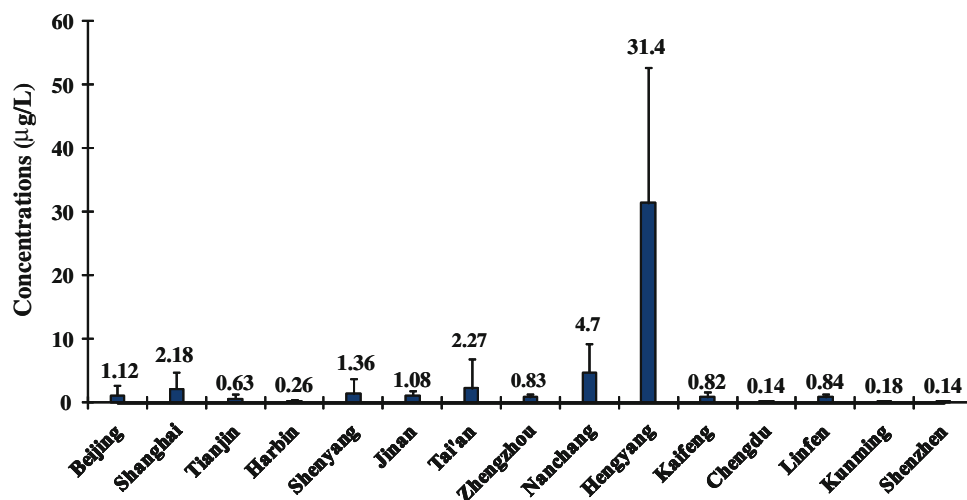
No earlier study has reported the occurrence of perchlorate in groundwater or surface waters from China. A survey of groundwater in the United States reported that 45% of 326 samples contained perchlorate at levels  $<0.04 \mu\text{g l}^{-1}$ ; 13% of the samples contained levels between 0.04 and  $0.12 \mu\text{g l}^{-1}$ ; and 42% contained levels  $>0.12 \mu\text{g l}^{-1}$  (Parker et al. 2008). The reported mean concentration of perchlorate in groundwater sampled from India was  $1.0 \mu\text{g l}^{-1}$  (Kannan

et al. 2009). In the present study, perchlorate concentrations in groundwater from China varied widely ( $<0.02$  to  $22.1 \mu\text{g l}^{-1}$ ), with a mean value of  $3.04 \mu\text{g l}^{-1}$ . Seven of 24 (29%) groundwater samples contained perchlorate levels  $<0.04 \mu\text{g l}^{-1}$ ; 1 of 24 (4%) samples contained perchlorate levels between 0.04 and  $0.12 \mu\text{g l}^{-1}$ ; and 16 of 24 (67%) samples contained perchlorate levels  $>0.12 \mu\text{g l}^{-1}$ . Perchlorate levels in groundwater from China were comparable with those cited previously for the United States and India.

Perchlorate concentrations in river water from the middle and lower Tone River Basin, Japan, were between



**Fig. 2** Perchlorate concentrations ( $\mu\text{g l}^{-1}$ ) (mean/SD) in 15 locations from China.



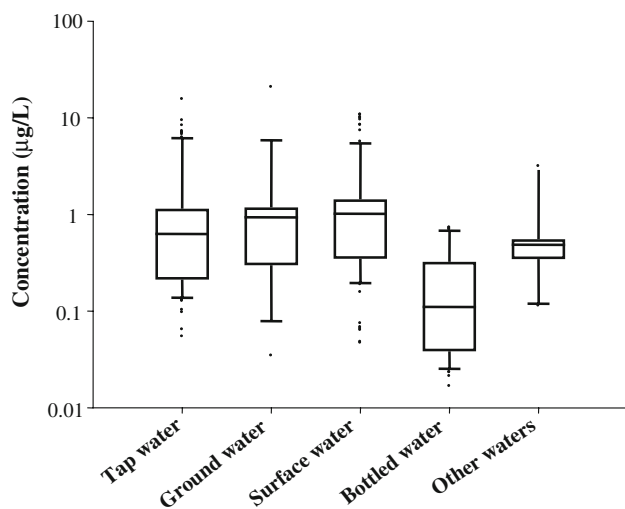
**Table 2** Perchlorate concentrations ( $\mu\text{g l}^{-1}$ ) in water samples from China stratified by category

City	Tap water		Groundwater		Surface water		Bottled water		Other water samples	
	N	mean $\pm$ SD	N	mean $\pm$ SD	N	mean $\pm$ SD	N	mean $\pm$ SD	N	mean $\pm$ SD
Beijing	9	2.04 $\pm$ 2.35			3	1.40 $\pm$ 0.18	7	0.21 $\pm$ 0.25	6	0.51 $\pm$ 0.06
Shanghai	8	2.43 $\pm$ 2.92			14	2.29 $\pm$ 2.60	12	0.41 $\pm$ 0.003		
Tianjin	12	0.44 $\pm$ 0.20			4	0.55 $\pm$ 0.19	3	<0.02	1	3.14
Harbin	5	0.21 $\pm$ 0.16			6	0.32 $\pm$ 0.19			4	0.23 $\pm$ 0.15
Shenyang	6	3.80 $\pm$ 3.40			3	0.07 $\pm$ 0.002	14	0.38 $\pm$ 0.26		
Jinan	7	1.02 $\pm$ 1.06	1	0.03	9	1.39 $\pm$ 0.48	2	0.40 $\pm$ 0.03		
Tai'an	12	1.35 $\pm$ 0.88	4	6.38 $\pm$ 9.62	1	1.32	3	0.07 $\pm$ 0.07		
Zhengzhou	9	1.00 $\pm$ 0.07	3	1.01 $\pm$ 0.13	4	1.13 $\pm$ 0.22	4	0.02 $\pm$ 0.005		
Nanchang	4	8.44 $\pm$ 6.18	3	0.39 $\pm$ 0.09	15	5.47 $\pm$ 3.91	3	0.11 $\pm$ 0.15		
Hengyang	3	31.4 $\pm$ 21.3	1	22.14	2	51.3 $\pm$ 4.4				
Kaifeng	2	0.71 $\pm$ 0.55	8	0.21 $\pm$ 0.17	7	1.05 $\pm$ 0.91	1	0.64		
Chengdu	6	0.18 $\pm$ 0.009			2	0.22 $\pm$ 0.005	9	0.07 $\pm$ 0.05		
Linfen	7	1.15 $\pm$ 0.23	4	0.61 $\pm$ 0.42	15	0.80 $\pm$ 0.41	3	0.03		
Kunming	5	0.20 $\pm$ 0.14			9	0.21 $\pm$ 0.10	6	0.11 $\pm$ 0.05		
Shenzhen	6	0.15 $\pm$ 0.02					2	0.09	1	<0.02
Overall	101	2.46 $\pm$ 6.59	24	3.04 $\pm$ 6.73	94	2.82 $\pm$ 7.63	69	0.22 $\pm$ 0.23	12	0.69 $\pm$ 0.88

10 and 20  $\mu\text{g l}^{-1}$  (Kosaka et al. 2007). The maximum concentrations of perchlorate in waters from the upper Tone River and the Usui River were 340 and 2300  $\mu\text{g l}^{-1}$ , respectively (Kosaka et al. 2007). River water samples from the Nakdong and Yeongsan Rivers in Korea also contained notable levels of perchlorate (<0.05 to 60  $\mu\text{g l}^{-1}$ ) (Quinones et al. 2007). In our study, perchlorate concentrations in surface water samples, from rivers, lakes and springs in China, ranged from 0.05 to 54.4  $\mu\text{g l}^{-1}$ , and these levels are comparable with or lower than the concentrations cited previously for river waters from Japan, Korea, and the United States.

A 2007 study reported concentrations of perchlorate in bottled water from China (range <0.002 to 2.01  $\mu\text{g l}^{-1}$ ;

mean 0.16  $\mu\text{g l}^{-1}$ ; Shi et al. 2007). In the United States, perchlorate was found in 10 of 21 bottled water samples at concentrations ranging from 0.07 to 0.74  $\mu\text{g l}^{-1}$  (mean 0.14  $\mu\text{g l}^{-1}$ ), whereas the remaining 11 samples had perchlorate levels <0.05  $\mu\text{g l}^{-1}$  (Snyder et al. 2005). In India, perchlorate was not detected (> 0.02  $\mu\text{g l}^{-1}$ ) in any of the bottled water samples analyzed (Kannan et al. 2009). Among the 69 Chinese bottled water samples analyzed in the present study, perchlorate was found at concentrations ranging from <0.02 to 0.73  $\mu\text{g l}^{-1}$ , and 61% of the samples had concentrations >0.02  $\mu\text{g l}^{-1}$  (mean 0.22  $\mu\text{g l}^{-1}$ ). The concentrations of perchlorate in bottled water from China are similar to the concentrations reported for samples from the United States.



**Fig. 3** Box plot of perchlorate concentrations in water samples from China

The relatively lower concentrations of perchlorate in tap water and bottled water than in groundwater or surface waters suggest removal of perchlorate from water during treatment by passage through ion-exchange resins, as has been suggested earlier (Kannan et al. 2009). In our study, six water samples collected from a drinking water treatment plant (four influent and two effluent samples) in Beijing had perchlorate levels in influent at  $0.55 \pm 0.01 \mu\text{g l}^{-1}$  and levels in effluent at  $0.44 \pm 0.001 \mu\text{g l}^{-1}$ .

#### Correlations Among Anions and Source Assessment

Pearson correlation coefficient was calculated to examine the relation between perchlorate and the other anions measured in the water samples (Table 3). Concentrations below the LOQ were set to zero for the correlation analysis. Chlorite and bromate were not included in the correlation analysis because these contaminants were detected in < 50% of the samples. Pearson correlation coefficients calculated between concentrations of perchlorate and nitrate and between perchlorate and chlorate were 0.268 ( $p < 0.001$ ) and 0.136 ( $p < 0.01$ ), respectively. Pearson correlation coefficients between bromide and iodide and

**Table 3** Pearson correlation coefficient between anions in waters in China

	$\text{ClO}_4^-$	$\text{ClO}_3^-$	$\text{Br}^-$	$\text{NO}_3^-$	$\text{I}^-$
$\text{ClO}_4^-$	1				
$\text{ClO}_3^-$	0.136**	1			
$\text{Br}^-$	-0.009	-0.08	1		
$\text{NO}_3^-$	0.268***	-0.05	0.052	1	
$\text{I}^-$	0.06	-0.06	0.370***	0.259***	1

\*\*  $p < 0.01$ , \*\*\*  $p < 0.001$

between nitrate and iodide were 0.370 ( $p < 0.001$ ) and 0.259 ( $p < 0.001$ ), respectively, suggesting significant association between the latter pairs of anions in waters. An earlier study from the United States showed that the water samples that contained the highest perchlorate concentration also contained the highest levels of chlorate and bromate (Quinones et al. 2007). A positive correlation coefficient in our study between perchlorate and chlorate suggests that chlorate is derived from similar sources or from degradation of perchlorate.

In the present study, water samples from Hengyang city (Hunan province) and Nanchang city (Jiangxi province) contained the two highest mean concentrations of perchlorate. This is explicable by the fact that the first and second largest fireworks manufacturing operations are located in these two provinces. As mentioned earlier, China is the world's largest fireworks manufacturing country; thus, firework production and display are important sources of perchlorate contamination in waters in China.

#### Human Exposure to Perchlorate and Other Anions by way of Water Consumption

Perchlorate can disrupt thyroid gland function by interfering with the gland's uptake of iodide, consequently impairing production of thyroid hormones T3 and T4. Water consumption is an important source of perchlorate exposure. Assuming a daily water consumption rate of 2 L and an average body weight of 60 kg for adults, the average daily intake of perchlorate in China by way of water is calculated to be  $0.08 \mu\text{g kg}^{-1} \text{d}^{-1}$ . Although drinking water is an important source of perchlorate to humans, diet, especially fruits and vegetables, can be another significant source of human exposure to perchlorate. In this study, water samples from Hengyang city (Hunan province) had mean perchlorate concentration of  $31.4 \mu\text{g l}^{-1}$ , which is two times higher than the USEPA's interim health advisory level for perchlorate ( $15 \mu\text{g l}^{-1}$ ), and the average daily intake of perchlorate by Hengyang citizens by way of water consumption is calculated to be  $1.05 \mu\text{g kg}^{-1} \text{d}^{-1}$ . The MCL values proposed by the USEPA for bromate, chlorite, and nitrate (measured as nitrogen) are 10, 1000, and 10000  $\mu\text{g l}^{-1}$ , respectively (USEPA 2009). In the present study, five bottled water samples from three cities in China contained bromate levels  $> 10 \mu\text{g l}^{-1}$ . Chlorite and nitrate-N levels in drinking water and bottled water samples from China were below the MCL proposed by the USEPA.

#### Conclusion

Perchlorate was detected in most of the water samples from China at notable concentrations. The maximum

concentration of perchlorate found in a tap water sample was  $44.1 \mu\text{g l}^{-1}$ , a value three times exceeding the interim health advisory level of  $15 \mu\text{g l}^{-1}$  that was proposed in the United States by the USEPA. Mean concentrations of perchlorate, by water category, were in the order of bottled water < other water < tap water < surface water < groundwater. Mean perchlorate concentration in Chinese tap water samples was  $2.46 \pm 6.59 \mu\text{g l}^{-1}$ , and calculated daily intake of perchlorate by way of drinking water is  $0.08 \mu\text{g kg}^{-1} \text{d}^{-1}$ , suggesting that drinking water is a nonnegligible source of human exposure to perchlorate in China. A significant positive correlation existed between concentrations of perchlorate and chlorate and between perchlorate and nitrate, suggesting similarities in the sources of these anions. Firework production and display could be an important source of contamination of perchlorate in waters in China.

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