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Occurrence of perchlorate, chlorate and bromate in drinking water in Shenzhen and related human exposure risks

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ABSTRACT

Perchlorate, chlorate and bromate are ubiquitously present in the environment. Perchlorate and chlorate could affect thyroid functions, while bromate is carcinogenic and has been listed as a possible human carcinogen in group 2B by the International Agency for Research on Cancer (IARC). This study aimed to determine the occurrence of perchlorate, chlorate and bromate in three types of drinking water (n=226) in Shenzhen, and assess potential human exposure risks. The detection rates of chlorate and perchlorate were both greater than 60%, and they were positively correlated in both bottled water and tap water, indicating similar sources. Bromate and chlorate were negatively correlated in tap water, indicating that the production of them in tap water disinfection might restrict each other. The hazard quotient (HQ) and hazard index (HI) values of perchlorate, chlorate and bromate in drinking water were less than 1 regardless of age groups. However, for bromate some individual excess cancer risk (ICER) values in drinking water exceeded the maximum acceptable level, indicating potential cancer risk to Shenzhen residents.

1. Introduction

Perchlorate (ClO_4^-) is a strong oxidant (Pleus and Corey, 2018), and widely used in the manufacture of fireworks, propellants, explosives, signal flares, fertilizers, leather, drying agents and electronic tubes (Siglin et al., 2000; Steinmaus, 2016). It is water-soluble, mobile and persistent in the environment (Calderón et al., 2017), and has broad occurrences in soil (Ye et al., 2013), dust (Gan et al., 2014) and water (Can et al., 2016). A previous study has shown that perchlorate could be produced through the process of disinfecting water (Maffini et al., 2016). The ions of perchlorate and iodide have the same numbers of extra-nuclear electrons and similar ionic radius (Kumarathilaka et al., 2016). In human bodies, the affinity of perchlorate to the sodium/iodide symporter (NIS) is even higher than that of iodine, which could affect thyroid hormones and thyroid functions, especially for people who are sensitive to perchlorate (Blount et al., 2006; Charnley, 2008). Fetus, infants and children are sensitive to thyroid hormones which are closely related to the intelligence and neurodevelopment (Pleus and Corey, 2018). The United States Environmental Protection Agency (USEPA) set the perchlorate reference intake dose (RfD) to be 0.7 μg/kg bw/day (USEPA, 2005). Until now, China has not set a safety limit of perchlorate in water.

Chlorate (ClO_3^-) is a strong oxidizing anion and formed by water treatment with chlorine dioxide (ClO_2) (Al-Otoum et al., 2016; Smith et al., 2012). It also presents as sodium chlorate during the production of explosives, solid fuel rockets, pesticides and paper pulp bleaching agents (Ader et al., 2001; Ali et al., 2018b; Constantinou et al., 2019). Humans could be exposed via drinking water and dietary intake. Consuming too much chlorate could affect the functions of thyroid, intestine and kidney (Ali et al., 2017; Ali et al., 2018b; Hooth et al., 2001). The World Health Organization (WHO) and China set 700 μg/L as the guideline value of chlorate in drinking water (MOHPRC, 2006; WHO, 2011).

Bromate (BrO_3^-) usually exists in water as a disinfection by-product (DBP) that is generated by using ozone to disinfect water, and has also been used illegally or legally in processed food and cosmetics (Ali et al., 2018a; Gilchrist et al., 2016). Humans could be exposed to bromate by drinking water or consuming food. It was reported that bromate has potential risks to the liver, kidney, thyroid gland, central nervous system and mesothelium (Ajarem et al., 2016; Ben Saad et al., 2018; Crosby et al., 2000; Karbownik et al., 2005). The International Agency for Research on Cancer (IARC) has classified bromate in the 2B carcinogen group (IARC, 2018), which based on lots of animal experiments. The

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USEPA and Minister of Health of the People's Republic of China (MOHPRC) have set the safety concentrations of bromate in water as 10 μg/L (MOHPRC, 2006; USEPA, 2002). Bromate was frequently detected in food and water (Okolie and Osarenren, 2003; Raúl et al., 2019). However, some studies found that the levels of bromate exceed its safety concentrations (10 μg/L) Alomirah et al (2020a). reported that the mean concentration in bottled water from Kuwait was higher than 10 μg/L; Snyder et al (2005) reported that bromate concentrations in some bottled water from the United States exceeded the reference intake concentration (10 μg/L) set by USEPA and the maximum was up to 76 μg/L (only found in a bottled water).

Drinking water is critical to maintain human life activities (Jéquier and Constant, 2010). Chinese Nutrition Society (CNS) recommended the daily intake of water to be 1500-1700 mL for adults (CNS, 2016). Perchlorate, chlorate and bromate are all water soluble, making them easily present in the water during the discharge processes (Cao et al., 2019; Kettlitz et al., 2016; Raúl et al., 2019). In addition, chemical disinfectants such as chlorine, ozone and chlorine dioxide are broadly used to kill harmful microorganisms in drinking water (Zheng et al., 2018). This may form perchlorate, chlorate, and bromate in the disinfected water as water DBPs (Jahan et al., 2021; Li and Ni, 2012): gaseous ClO_2 or chlorine (Cl_2) is used for water disinfection, which combines with water to synthesize $HClO_4$ and hypochlorous acid(HClO) or HClO and hydrochloric acid (HCl), which then undergo a series of chemical reactions to generate ClO_4^- (Niziński et al., 2021); ozone is used for disinfection water and combines with bromide ion (Br^-) generates bromate by a four-steps combination (von Gunten, 2003); another view of BrO_3^- existing in water is that ozone and Br- synthesize BrO_3^- through free radicals synthesized (Fischbacher et al., 2015). All the relevant chemical equations of generating perchlorate, chlorate and bromate in water are shown in the **supplementary materials**.

Although the use frequency and scope of perchlorate are higher than that of chlorate and bromate owing to the stability and strong oxidizing properties of perchlorate. Perchlorates, chlorates and bromates are the common halogenated acid salt and could be produced during disinfection. Thus, the present study aimed to assess the occurrence of perchlorate, chlorate and bromate in different types of drinking water from the city of Shenzhen, located in South China, which is one of the most economically and technologically developed cities in China (Lu et al., 2016). Specific objectives were to explore: (1) the concentrations and correlations of perchlorate, chlorate and bromate in drinking water in Shenzhen; and (2) the estimated daily intakes (EDI), hazard quotient (HQ), hazard index (HI) and individual excess cancer risk (ICER) of these chemicals via drinking water. To our knowledge, this is the first study simultaneously assessing human exposure to these chemicals from consuming drinking water in China.

2. Materials and methods

2.1. Chemical and reagents

The reference standards of perchlorate and chlorate were purchased from Cambridge Isotope Laboratories (Andover, MA, USA), and that of bromate was from Coast Hongmeng (Beijing, China). The $^{18}O_4^-$-labeled perchlorate ($Cl^{18}O_4^-$) was applied as an internal standard (IS) and was obtained from the Europe Reference Laboratory (Fellbach, Baden-Wurttemberg, Germany), and $^{18}O_4^-$-labeled chlorate ($Cl^{18}O_3^-$) and bromate ($Br^{18}O_3^-$) were both obtained from Cambridge Isotope Laboratories (Andover, MA, USA). High performance liquid chromatography (HPLC) grade regents, including methanol, acetonitrile, formic acid and ammonium formate were purchased from Fisher Scientific (Houston, TX, USA).

2.2. Sample collection

All water samples (n=226), including tap water (n=96), bottled water (n=116) and source water (n=14), were collected in Shenzhen, China from February to July 2021. Tap water is the water that people use through taps in their homes, bottled water is the water that is processed by a company and then bottled and sold in stores, and the source water is water collected in reservoirs (Geerts et al., 2020). For Shenzhen, the source of tap water is the source water: after source water has been treated by the relevant water treatment steps in the water plant, the water becomes tap water. According to the report of Shenzhen Water Group (SGWZ), there was still 0.14% of residents in Shenzhen are not using tap water (SGWZ, 2020).

Tap water samples were obtained from the homes of local residents, which were collected after turning on the tap for at least 3 min to remove deposit existing in the residual water from the pipeline. Source water samples were collected from reservoir water, which is also the source of tap water in Shenzhen. Source water samples were collected from 0.5 m deep below the water surface, which prevented the influence of other substances on the surface of the reservoir water. Bottled water samples included a variety of brands and were purchased from local supermarkets. The details were showed in the **supplementary materials.**

2.3. Sample treatment protocols

For each sample, 1.0 mL of water and 10.0 μL of a mixture of isotopically labeled internal standards ($Cl^{18}O_4^-$, 200 μg/L, $Cl^{18}O_3^-$, 1000 μg/L, $Br^{18}O_3^-$, 1500 μg/L) were added sequentially into a 15 mL plastic tube. The sample was vortexed for 10 seconds and filtered through a 0.22 μm regenerated cellulose filter membrane to a 9 mm thread screw neck vial. The final extract was determined on a high performance liquid chromatography coupled with a tandem mass spectrometry (HPLC-MS/MS).

2.4. Instrumental analysis

The HPLC-MS/MS consisted of a 20A HPLC system and a Q-Trap 5500 mass spectrometer (MS/MS), which was used to determine the concentrations of perchlorate, chlorate and bromate. The conditions of instrumental analysis have been introduced in a previous study (Chen et al., 2021), and the details are summarized in the **supplementary materials**.

2.5. Quality assurance and quality control

The standard solutions of perchlorate, chlorate and bromate were spiked in water at three levels (1, 10, 40 μg/L) to evaluate the analytical recoveries. Their recoveries from analytical procedures ranged from 72% to 105%, 82% to 98% and 70% to 91%, respectively. Each batch of 15 samples was prepared and analyzed a blank sample. No detectable concentrations of perchlorate, chlorate and bromate were found in all blank samples. The relative standard deviations (RSD) of duplicate samples were lower than 10%. The limits of quantification (LOQs) of perchlorate, chlorate and bromate were defined as the responses of standards ten times the relevant noises, which were determined to be 0.1, 0.4 and 0.2 μg/L, respectively. Ten-point calibration curves were employed to cover the concentration ranges of perchlorate, chlorate and bromate from 0.2 μg/L to 50 μg/L, 0.4 μg/L to 200 μg/L and 2.0 μg/L to 100 μg/L, respectively. The regression coefficients (r^2) of calibration curves were all above 0.999.

2.6. Calculations and statistical analysis

The estimated daily intakes (EDIs) of a chemical from drinking water were used to assess human exposure, which were calculated based on the following equation (Alomirah et al., 2020b):

$$EDI = \frac{C \times C_W}{BW}$$

where EDI (μg/kg-day) is the estimated daily intake of perchlorate, chlorate or bromate from water; C (μg/L) is the chemical concentration in water; BW (kg) represents the human body weight, which was 8.1, 14.8, 38.2, 58.4 kg for infants (0-2 years), toddlers (2-5 years), children (5-17 years) and adults (>18 years), respectively (CAMEP, 2013a–c); C_w (mL/day) is the water consumption rate, which was set as 507.2, 748.2, 1150 and 1957 mL/day for infants, toddlers, children and adults, respectively (CAMEP, 2013d–f).

HQ and HI were used to assess the potential exposure risk to individual chemicals and the cumulative exposure risk, respectively (Ajay Kumar and Singhal, 2011; Chen et al., 2019):

$$HQ = \frac{EDI}{\frac{RfD}{TDIs}} \quad HI = HQ\,(ClO4-) + HQ\,(ClO3-) + HQ\,(BrO3-)$$

where *HQ* represents hazard quotient from drinking water, and *HQ* (ClO_4^-), *HQ* (ClO_3^-) and *HQ* (BrO_3^-) represent the hazard quotient of perchlorate, chlorate or bromate, respectively; *RfD* or *TDIs* (μg/kg bw/day) represents the reference dose proposed by USEPA or WHO, which are 0.7 μg/kg bw/day and 4 μg/kg bw/day for perchlorate and for bromate (USEPA, 2001b, 2005), and 30 μg/kg bw/day for chlorate (WHO, 2011); *HI* represents the cumulative exposure to these three chemicals; $HQ > 1$ or $HI > 1$ indicates a potential risk for humans.

Potential carcinogenic risk for bromate was estimated using the below equation (USEPA, 2001b):

$$ICER = UR_0 \times C$$

where ICER is the individual excess cancer risk; UR_0 is the risk factor for drinking water, which is 2×10^{-5} $(\mu g/L)^{-1}$; C (μg/L) is the concentration of bromate in drinking water.

If the detection concentration in water was lower than LOQ, a half value of LOQ was used for statistical analysis. SPSS 13.0 was used to analyze the data. Mann-Whitney U test and Kruskal-Wallis H test were used to find significant differences in concentrations and estimated daily intakes for different age groups, respectively. Spearman's correlation test was used to test the relationships between the three substances. The statistical significance level was set as 0.05 (p =0.05). Origin 8.0 and GraphPad Prism 8.0 were used to draw figures.

3. Results and discussion

3.1. Concentrations of perchlorate, chlorate and bromate in water

Table 1 shows the concentration distribution, such as mean, median, minimum, maximum, standard deviation and detection rate of perchlorate, chlorate and bromate in source water, bottled water and tap water. The concentration ranges of perchlorate, chlorate and bromate in overall drinking water were N.D. (not detected, which is same as 0)-2.49, N.D.-198 and N.D.-7.12 μg/L, respectively. The limits of chlorate and bromate in drinking water allowed by the Minister of Health of the People's Republic of China (MOHPRC) were 700 μg/L and 10 μg/L, respectively (MOHPRC, 2006). China has no limit on the concentration of perchlorate in drinking water, but the USEPA has set 56 μg/L as the safety limit (USEPA, 2005). Thus, the concentrations of the target chemicals did not exceed the standard limits in all water samples. Compared with tap water and source water, bottled water contained relatively lower concentrations of perchlorate (median: 0.308 μg/L) and chlorate (median: 0.563 μg/L), but higher levels of bromate (0.218 μg/L).

We compared our results with the data from previous studies (**Tables 2–4**). As none has studied these three substances in source water, we used surface water data for the comparison with our drinking water data. The median concentration of perchlorate in our study (0.695 μg/L) was much higher than that in Austria (0.33 μg/L) (Vejdovszky et al., 2018), the United States (0.15 μg/L) (Borjan et al., 2011), and Turkey (0.365 μg/L) (Sungur and Sangün, 2011), but far lower than that reported in the large-scale fireworks manufacturing area of China (3.99 μg/L) (Zhang et al., 2015) (**Table 2**). The detection rate of perchlorate was 99.6%, which was higher than that from other countries, such as Austria (4.49%) (Vejdovszky et al., 2018) and the United States (75%) (Borjan et al., 2011). Overall, the concentrations and detection rate of perchlorate in Shenzhen were both higher than those reported in most previous studies, indicating that perchlorate had widespread occurrence in Shenzhen water. Besides, the median concentration of perchlorate in source water (1.19 μg/L) was nearly four times higher than that in bottled water (0.308 μg/L) (**Table 2**) Snyder et al (2005). also found that the median concentration of perchlorate in surface water (0.30 μg/L) was much higher than that in bottled water (< 0.05 μg/L) in the United States. These may suggest elevated pollution of perchlorate in the environment due to human activities.

The median concentration of chlorate in all drinking water was 3.80 μg/L, which was much lower than that in Europe (45 μg/L) (Kettlitz et al., 2016), Cyprus (150 μg/L) (Constantinou et al., 2019), the United States (160 μg/L) (Benjamin et al., 2011)and Spain (224 μg/L) (Garcia-Villanova et al., 2010) (**Table 3**). However, the median concentrations of chlorate (bottled water: 0.563 μg/L, source water: 68.1 μg/L and tap water: 46 μg/L) in this study were higher than those reported in Canada (bottled water: N.D. and tap water: N.D.) and another United States study (bottled water: 0.36 μg/L and surface water: 2 μg/L) (Djam et al., 2020; Snyder et al., 2005). Among the three types of drinking water, the median concentration of chlorate in source water (68.1 μg/L) was two orders of magnitude higher than that in bottled water (0.563

Table 1
The concentrations of perchlorate, chlorate and bromate in different types of drinking water (μg/L).

	Minimum	Maximum	Mean	Median	5th percentile	95th percentile	SD	DF (%)
Bottled water (n=116)								
perchlorate	N.D.	1.93	0.531	0.308	N.D.	1.34	0.539	73.3
chlorate	N.D.	74.3	11.2	0.563	N.D.	67.9	20.2	62.9
bromate	N.D.	7.12	1.09	0.218	N.D.	4.48	1.53	55.2
Source water (n=14)								
perchlorate	1.08	1.23	1.18	1.19	1.08	1.23	0.40	100
chlorate	21.7	70.9	58.3	68.1	21.7	70.9	19.8	100
bromate	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0
Tap water (n=96)								
perchlorate	<LOQ	2.49	0.806	0.760	<LOQ	2.21	0.676	100
chlorate	N.D.	198	45.5	46.0	N.D.	127	47.8	91.7
bromate	N.D.	5.57	0.426	<LOQ	N.D.	3.13	0.987	63.5
Drinking water (n=226)								
perchlorate	N.D.	2.49	0.688	0.695	N.D.	1.66	0.612	99.6
chlorate	N.D.	198	28.7	3.80	N.D.	104	39.1	77.4
bromate	N.D.	7.12	0.730	<LOQ	N.D.	3.79	1.32	55.3

SD: standard deviation; DF: detection frequency; LOQ: limits of quantitation; N.D.: not detected

Table 2
Perchlorate concentrations in drinking water from different countries and regions (μg/L).

Countries or regions	N	DR (%)	Range	Mean	Median	Reference
Bottled water						
Shenzhen	116	73.3	N.D.-1.93	0.531	0.308	This study
Istanbul	27	7.40	<LOD-0.19	<LOD	<LOD	(Can et al., 2016)
Kuwait	13	100	0.01–0.70	0.28	0.08	(Alomirah et al., 2016)
Taiwan, China	5	100	0.327-0.484	0.416	0.423	(Chang et al., 2020)
Chengdu, China	12	-	<LOQ-2.84	1.03	0.75	(Gan et al., 2015)
Korea	10	100	0.03-0.24	0.11	0.07	(Lee et al., 2012)
Canada	10	70	N.D.-5.098	0.58	0.092	(El Aribi et al., 2006)
South Korea	48	60.4	ND-0.29	0.07[a]	-	(Her et al., 2011)
United States	21	47.6	<LOD-0.74	0.12	<0.05	(Snyder et al., 2005)
Source water / Surface water						
Shenzhen	14	100	1.08-1.23	1.18	1.19	This study
Kuwait	16	100	0.14–7.02	2.12	1.91	(Alomirah et al., 2016)
Malta	28	63.9	ND-8.4	1.09	0.3	(Pace and Vella, 2019)
Tianjin, China	33	97.0	<LOQ-6.87	1.70	1.04	(Qin et al., 2014)
United States	11	90.9	<LOD-6.80	2.85	0.30	(Snyder et al., 2005)
Tap water						
Shenzhen	96	100	<LOQ-2.49	0.806	0.760	This study
Kuwait	168	100	0.02-18.6	0.49	0.10	(Alomirah et al., 2016)
Istanbul	27	58	<LOD-0.75	0.13	0.05	(Can et al., 2016)
Chengdu, China	51	100	0.57-1.61	0.86	0.83	(Gan et al., 2015)
Canada	12	-	0.016-2.983	0.317	0.065	(El Aribi et al., 2006)
Istanbul, Turkey	60	-	<0.01–0.48	-	0.08	(Erdemgil et al., 2016)
Ankara, Turkey	35	-	<0.01–3.45	-	0.07	(Erdemgil et al., 2016)
Sakarya, Turkey	20	100	0.03–0.05	-	0.04	(Erdemgil et al., 2016)
Isparta, Turkey	15	100	0.02–0.16	-	0.03	(Erdemgil et al., 2016)
Kayseri, Turkey	15	100	0.19–0.47	-	0.25	(Erdemgil et al., 2016)
Malta	54	51.8	ND-2.5	0.56	0.35	(Pace and Vella, 2019)
South Korea	520	79.8	ND-6.1	0.56[a]	-	(Her et al., 2011)
United States	3262	-	0.620-1.89[b]	0.714	1.16	(Blount et al., 2010)
Japan	30	100	0.06-37	-	-	(Kosaka et al., 2007)
Drinking water						
Shenzhen	226	99.6	N.D.-2.49	0.688	0.695	This study
Austria	89	4.49	N.D.-0.60[c]	0.39	0.33	(Vejdovszky et al., 2018)
China	61	100	0.26-280	-	3.99	(Zhang et al., 2015)
New Brunswick, United States	253	75	<LOD–1.04	0.17	0.15	(Borjan et al., 2011)
Hatay, Turkey	8	100	0.31-0.97	0.44	0.365	(Sungur and Sangün, 2011)
China	300	86.3	ND-54.4	2.20	0.62	(Wu et al., 2010)

DF: detection rate; LOD: limits of detection (The responses of standards three times the relevant noises.); LOQ: limits of quantitation. N.D.: not detected
[a] : based on positive set only.
[b] : The range of perchlorate concentrations is from 25th to 95th
[c] : The maximum range of perchlorate concentrations is 95th

Table 3
Chlorate concentrations in drinking water from different countries and regions (μg/L).

Countries or regions	N	DR (%)	Range	Mean	Median	Reference
Bottled water						
Shenzhen	116	62.9	N.D.-74.3	11.2	0.563	This study
Iran	168	12.5	ND-337	-	-	(Djam et al., 2020)
United States	21	100	<LOQ-5.4	1.39	0.36	(Snyder et al., 2005)
Canada	42	7	N.D.-260	6.9	N.D.	(Dabeka et al., 2002)
Source water / Surface water						
Shenzhen	14	100	21.7-70.9	58.3	68.1	This study
United States	11	100	<LOQ-270	30.4	2	(Snyder et al., 2005)
Tap water						
Shenzhen	96	91.7	N.D.-198	45.5	46	This study
Canada	11	9	N.D.-115	10.5	N.D.	(Dabeka et al., 2002)
Japan	10	100	34–140	82.4	74	(Asami et al., 2013)
Drinking water						
Shenzhen	226	77.4	N.D.-198	28.7	3.8	This study
Cyprus	284	69	N.D.-1100	190	150	(Constantinou et al., 2019)
Europe	39	74.4	<LOQ-83	-	45	(Kettlitz et al., 2016)
United States	7	100	<LOQ–1500	482.9	160	(Benjamin D. Stanford, 2011)
Spain	509	65.2	N.D.-4340	119[a]	224[a]	(Garcia-Villanova et al., 2010)
China	300	72.3	<LOQ-343	11.9	-	(Wu et al., 2010)

DR: detection rate; LOQ: limits of quantitation. N.D.: not detected
[a]: based on positive set only.

μg/L) Snyder et al (2005). also found that the median concentration of chlorate in surface water (2 μg/L) in United States was five times higher than that in bottled water (0.36 μg/L).

Bromate was detectable in bottled water and tap water, but not in source water (**Table 1**), indicating that bromate may be produced during water treatment. The median concentration of bromate in all drinking water was < LOQ (< 0.2 μg/L), which was at least one order of magnitude lower than that in Chile (24.9 μg/L) (Raúl et al., 2019) and Spain (12 μg/L) (Garcia-Villanova et al., 2010) (**Table 4**). Among the results listed in **Table 4**, the median concentration of bromate was 13.6 μg/L in tap water and 11.5 μg/L in surface water from Kuwait (Alomirah et al., 2020b), which were higher than the limit (10 μg/L) set by USEPA and MOHPRC (MOHPRC, 2006; USEPA, 2001a). Compared with other studies, the detection rate of bromate in this study was similar to that in other countries, but the concentrations were relatively low (Garcia--Villanova et al., 2010; Raúl et al., 2019), indicating that the production of bromate in drinking water in Shenzhen is relatively low. In the present study, bromate was not detected in source water. This is consistent with the findings from other studies (Raúl et al., 2019; Snyder et al., 2005). The median concentration in bottled water (0.218 μg/L) was higher than that in tap water (<LOQ) in the present study. However, Djam et al (2020) and Snyder et al (2005) found that the median concentrations of bromate in tap water (Kuwait: 13.6 μg/L, Canada: 0.7 μg/L) were higher than those in bottled water (Kuwait: 2.39 μg/L, Canada: 0.5 μg/L) in Kuwait and Canada, which may be related to different water treatment processes in different countries.

Table 4
Bromate concentrations in drinking water from different countries and regions (μg/L).

Countries or regions	N	DR (%)	Range	Mean	Median	Reference
Bottled water						
Shenzhen	116	55.2	N.D.-7.12	1.09	0.218	This study
Kuwait	19	52.6	ND-7.99	2.89	2.39	(Alomirah et al., 2020b)
Indian	31	100	2-30	11.16	9	(Ajay Kumar, 2011)
Iran	168	23.8	ND-353	-	-	(Djam et al., 2020)
United States	21	100	<LOQ-76	6.46	0.70	(Snyder et al., 2005)
Canada	42	52	N.D.-76.9	5.5	0.5	(Dabeka et al., 2002)
Source water / Surface water						
Shenzhen	14	0	N.D.-N.D.	N.D.	N.D.	This study
Kuwait	16	50.0	ND-NA	ND	NA	(Alomirah et al., 2020b)
Chile	6	0	ND	ND	ND	(Raúl et al., 2019)
Nevada, United States	11	100	<LOQ-4.6	0.414	0.05	(Snyder et al., 2005)
Tap water						
Shenzhen	96	63.5	N.D.-5.57	0.426	0.1	This study
Kuwait	142	51.0	ND-89.3	19.6	13.6	(Alomirah et al., 2020b)
Canada	11	73	N.D.-5.4	1.8	0.7	(Dabeka et al., 2002)
Drinking water						
Shenzhen	226	55.3	N.D.-7.12	0.730	0.1	This study
Chile	43	41.9	ND-22.9	2.49	-	(Raúl et al., 2019)
Spain	509	66.4	N.D.-49	12	8	(Garcia-Villanova et al., 2010)

DR: detection rate; LOQ: limits of quantitation. N.D.: not detected

3.2. The relationships between perchlorate, chlorate and bromate levels in water

The relationships between the concentrations of the three target chemicals in different types of water are shown in **Fig. 1**. Perchlorate and chlorate were positively correlated in both bottled water ($r = 0.452$, $p < 0.01$) and tap water ($r = 0.585$, $p < 0.01$), indicating their similar sources. As the previously mentioned disinfection formulas for chlorine or chlorine dioxide, this may demonstrate the correlation of perchlorate and chlorate in bottled and tap water concerning water disinfection Wu et al (2010). also found a positive correlation between perchlorate and chlorate levels in drinking water ($r = 0.136$, $p < 0.01$). There is no correlation between perchlorate and chlorate in the source water due to the extensive production and use of perchlorate in daily life. However, bromate and chlorate were negatively correlated in bottled water ($r =$ -0.330, $p < 0.01$), indicating that the production of them in tap water disinfection might restrict each other. Until now there is no relevant chemical formula to prove this, but some studies have found that the initial stage of chlorination of natural water after ozonation is reduced (Hoigné and Bader, 1983; von Gunten, 2003).

Concentrations of three chemicals were significantly different ($p <$ 0.05) in different types of water, except for chlorate in tap water and source water and bromate in tap water and bottled water. The bromate concentrations in tap water and bottled water were not significantly different ($p >$ 0.05), indicating that the treatment of tap water and bottled water could be similar in some procedures.

3.3. The EDIs of perchlorate, chlorate and bromate from drinking water

Table 5 shows the EDIs of perchlorate, chlorate and bromate via drinking water for different age groups of people. The median and maximum concentrations of chemicals in drinking water were used to evaluate the median and maximum EDIs, respectively. The median EDIs of perchlorate, chlorate and bromate among three types of water were 0.009-0.074, 0.017-4.26 and 0-0.014 μg/kg-day, respectively. The mean EDI of perchlorate in drinking water was reported to be 0.003 μg/kg-day in Kuwait (Alomirah et al., 2016), which was one magnitude lower than that in Shenzhen (0.031 μg/kg-day). It was reported that the median EDI of perchlorate in drinking water for infants, children and adults in Austria was 0.0165, 0.0153 and 0.00991 μg/kg-day, respectively (Vejdovszky et al., 2018), much lower than the estimates in Shenzhen (infants: 0.044 μg/kg-day; children: 0.021 μg/kg-day and adults: 0.023 μg/kg-day). In the present study, the maximum EDIs of perchlorate, chlorate and bromate among three types of water were 0.037-0.156, 2.13-12.4 and 0-0.446 μg/kg-day, respectively. It was reported that the maximum intake of bromate from drinking water was 1.365 and 1.116 μg/kg-day in Chile and India (Ajay Kumar, 2011; Raúl et al., 2019), respectively, much higher than that in Shenzhen, indicating lower bromate exposure through drinking water for Chinese people.

The EDI values of perchlorate from bottled water by children and adults were significantly higher than that for other age groups consuming different types of water ($p < 0.05$), and the EDI of bromate from bottled water by infants was significantly higher than that by other age groups consuming different types of water ($p < 0.05$). Besides, the EDI of chlorate from source water was significantly different among age groups ($p < 0.05$). Since the body weight and the estimated daily water consumption were applied as mean values in the formula, this outcome may be related to uneven concentration distributions.

3.4. Exposure risk of perchlorate, chlorate and bromate via drinking water

The HQ of perchlorate, chlorate and bromate via drinking water was

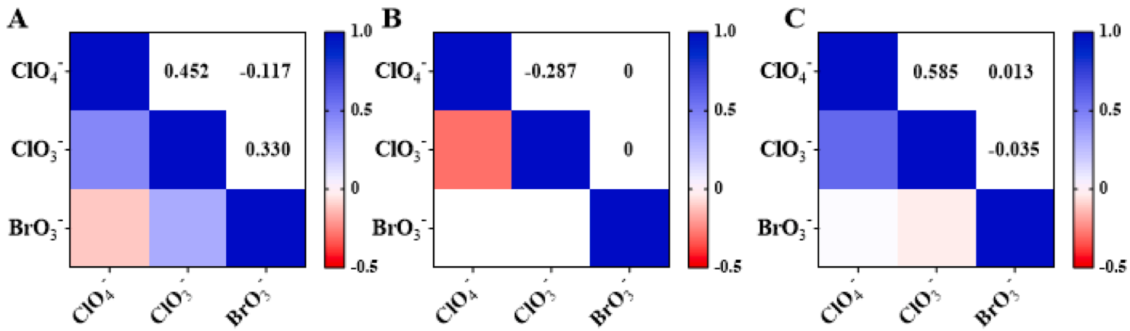

Fig. 1. Spearman correlation coefficients among in perchlorate, chlorate and bromate levels in bottled water (A), source water (B) and tap water (C).

Table 5
Estimated of daily intakes of perchlorate, chlorate and bromate in different types of drinking water (μg/kg-day).

		Bottled water		Source water		Tap water		Drinking water	
		Median	Maximum	Median	Maximum	Median	Maximum	Median	Maximum
Perchlorate	infants	0.019	0.121	0.074	0.077	0.048	0.156	0.044	0.156
	toddlers	0.016	0.098	0.060	0.062	0.038	0.126	0.035	0.126
	children	0.009	0.058	0.036	0.037	0.023	0.075	0.021	0.075
	adults	0.010	0.065	0.040	0.041	0.025	0.083	0.023	0.083
Chlorate	infants	0.035	4.65	4.26	4.44	2.88	12.4	0.238	12.4
	toddlers	0.028	3.76	3.44	3.58	2.33	10.0	0.192	10.0
	children	0.017	2.24	2.05	2.13	1.39	5.96	0.114	5.96
	adults	0.019	2.49	2.28	2.38	1.54	6.64	0.127	6.64
Bromate	infants	0.014	0.446	0	0	0.006	0.349	0.006	0.446
	toddlers	0.011	0.360	0	0	0.005	0.282	0.005	0.360
	children	0.006	0.214	0	0	0.003	0.168	0.003	0.214
	adults	0.007	0.239	0	0	0.003	0.187	0.003	0.239

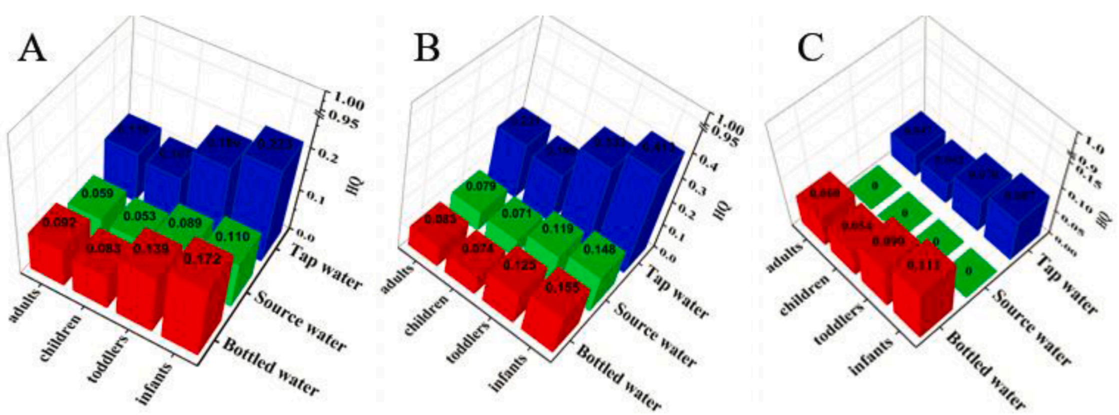

Fig. 2. Hazard quotient of perchlorate (A), chlorate (B) and bromate (C) in different types of drinking water.

determined using the maximum EDI value (Fig. 2, **Table S2)**. The HQ ranges of perchlorate, chlorate and bromate were 0.053-0.223, 0.074-0.413, and 0-0.111, respectively. All HQ values were far lower than 1, indicating no potential risk for Shenzhen people through drinking water.

The maximum HI values for people at different ages consuming different types of water are shown in Fig. 3. The range of HI was 0.122-0.502. The HI values of bottled water were significantly lower than those of tap water for the same age group ($p < 0.05$), which indicates that tap water presents lower risks than bottled water. The HI values for infants was significantly higher than those for children and adults ($p < 0.05$), which was mainly related to their lower body weight. Another study also suggested that body weight was an important factor affecting human health risk assessment (Wang et al., 2018). In addition, the HI values were significantly different ($p < 0.05$) among different age groups of people via drinking source water.

The detection rate of bromate was low in Shenzhen, and the carcinogenic risk of bromate was from 2×10^{-6} to 1.42×10^{-4}. The maximum value of IECR exceeded the value of the maximum acceptable level (2×10^{-5}). Therefore, drinking water in Shenzhen may bring a potential cancer risk.

4. Conclusion

Perchlorate and chlorate exhibited widespread occurrence in drinking water in Shenzhen. Bromate in drinking water may originate from water disinfection process. Perchlorate and chlorate were positively correlated in bottled water and tap water, suggesting similar sources. HQ and HI in three types of drinking water among different age groups were less than 1, indicating no potential risk to humans. However, some IECR values of bromate in drinking water exceeded the value of the maximum acceptable level, indicating potential cancer risk to Shenzhen populations.

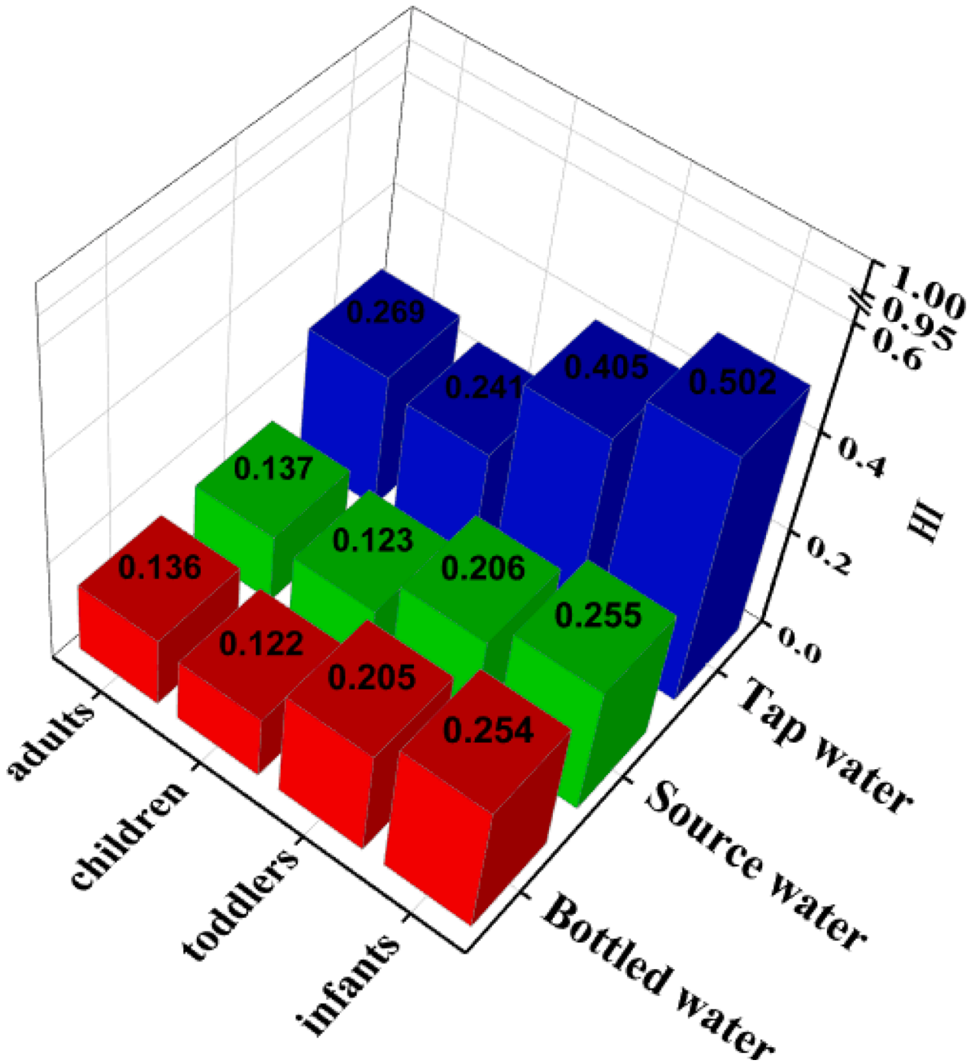

Fig. 3. . Hazard index in different types of drinking water.

CRediT authorship contribution statement

Yining Chen: Investigation, Data curation, Formal analysis, Writing – original draft. **Zhou Zhu:** Data curation, Formal analysis. **Hongmei Qiu:** Supervision. **Shaoyou Lu:** Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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