Marine Pollution Bulletin 170 (2021) 112672

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Perchlorate in shellfish from South China Sea and implications for human exposure

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ARTICLE INFO

Keywords:
Perchlorate
Shellfish
Concentrations
Human exposure

ABSTRACT

Shellfish can absorb and accumulate contaminants. The consumption of shellfish could expose humans to pollutants and increase related health risk. Perchlorate (ClO_4^-) is a ubiquitous pollutant and could affect thyroid functions, especially for children and pregnant women. However, knowledge on the contamination of perchlorate in aquatic food such as shellfish remains limited. This study aimed to investigate the abundances of perchlorate in shellfish from South China Sea and to assess human exposure risks. A total of 178 shellfish samples from eight species were collected from offshore aquaculture waters in South China Sea. Perchlorate was detected in 99.4% of them, suggesting widespread pollution in coastal waters. Concentrations of perchlorate ranged from not detected (N.D.) to 71.5 μg kg^{-1}, with a median value of 4.33 μg kg^{-1}. Estimated daily intake (EDI) and hazard quotient (HQ) were used to assess human exposure dose and health risks, respectively. The HQ values were determined to be less than 1, indicating no significant health risks to local residents via shellfish consumption. To our knowledge, this is the first study to investigate perchlorate contamination in South China shellfish and assess potential human risks.

1. Introduction

Perchlorate (ClO_4^-) is a water-soluble and highly stable chemical (Levakov et al., 2019; Qin et al., 2014). Perchlorate is naturally formed by atmospheric processes and is frequently found in nitrate fertilizers (Dasgupta et al., 2006; Dasgupta et al., 2005). It is also widely applied as a strong oxidant in the manufacture of rocket propellants, fireworks, road flares and explosives (Dasgupta et al., 2006; Leoterio et al., 2017), owing to its +7 oxidation state of chlorine (Kumarathilaka et al., 2016). Due to the widespread applications, perchlorate has become a ubiquitous pollutant in the environment (Lee et al., 2012). Perchlorate was firstly detected in well water from California, indicating that perchlorate could penetrate the soil and contaminate ground water (Wagner et al., 2004). Since then, perchlorate has attracted mounting attention due to its potential risk to animals and humans. Perchlorate has been detected in water (Asami et al., 2013; Kannan et al., 2009), food (Asami et al., 2013; Gan et al., 2015; Shi et al., 2007; Sungur and Sangün, 2011), indoor dust (Gan et al., 2015; Zhang et al., 2015), soil (Calderon et al., 2014) and even in human saliva (Kannan et al., 2009), urine (Zhang et al., 2015), blood (Zhang et al., 2010) and breast milk (Wang et al., 2019). Humans may be exposed to perchlorate via pathways such as inhalation, drinking, and dietary intake, among which food consumption was generally believed to be the most important route (Dong et al., 2019).

Perchlorate can disrupt the synthesis of thyroid hormones and affect thyroid functions (Leung et al., 2010). It can also compete sodium/iodide symporter (NIS) with iodine (Eguchi et al., 2014) since perchlorate displays a higher affinity to NIS than iodide (Carr et al., 2015). Previous studies have suggested that the shortage of iodine could decrease serum thyroxine (T4) and tri-iodothyronine (T3) levels, while increasing serum thyrotrophin (TSH) levels in thyroid gland (Serrano-Nascimento et al., 2018; Wu et al., 2012). The decrease of thyroid hormones might influence vulnerable populations, including fetus, infants, children and pregnant women, as well as people who have thyroid deficiency (Wang et al., 2019). Oral exposure to perchlorate has been reported as causing hypothyroidism in pregnant rats, DNA damage and less sperm production in testicular of male rats (Jahagirdar et al., 2012; Yu et al., 2019).

As an important type of food to coastal residents, shellfish contain

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https://doi.org/10.1016/j.marpolbul.2021.112672
Received 30 April 2021; Received in revised form 21 June 2021; Accepted 22 June 2021
Available online 1 July 2021

high quality proteins, vitamins and minerals (Guerin et al., 2011; James et al., 2010). However, shellfish are filter-feeders and can absorb and accumulate contaminants from water and prey (Picot et al., 2011; Trabalon et al., 2017). Numerous studies have demonstrated that shellfish could accumulate heavy metals (Jia et al., 2018; Kang and So, 2016; Li et al., 2013; Liang et al., 2016; Liu et al., 2020), organochlorine pesticides (Lal et al., 2014; Li et al., 2020; Zhang et al., 2012; Zhou et al., 2008) and polychlorined biphenyls (Habibullah-Al-Mamun et al., 2019; Sagratini et al., 2008; Zhang et al., 2012). Perchlorate was widely detected in environment in China. Previous studies found that the mean concentration of perchlorate was 2.82 and 0.49 μg L^{-1}, respectively from surface water and sea water in China (Wu et al., 2010). It was reported that the concentration of perchlorate in outdoor dust ranged from 0.67 to 3.49 mg kg^{-1} in Guangdong Province and 0.01–921 mg kg^{-1} in China (Li et al., 2018). Especially during the Chinese Spring Festival, the concentration of perchlorate in outdoor dust was extremely high, which was 12.3–74.1 mg kg^{-1} in Guangdong Province and 0.132–5300 mg kg^{-1} in China (Gan et al., 2014). Perchlorate released from industrial emissions and fireworks display might contaminate sea water or shellfish diets, such as phytoplankton and seaweed (Kato et al., 2020). It was reported that the concentrations of perchlorate in seaweed ranged from 47 to 878 μg kg^{-1} (Martinelango et al., 2006). Shellfish might accumulate perchlorate via ingestion of these perchlorate-containing water or diets. Limited studies have also reported the occurrence of perchlorate in aquatic food including shellfish (Asami et al., 2013; Chang et al., 2020; Gan et al., 2015; Lee et al., 2012; Liao et al., 2020), indicating food consumption represents an important human exposure pathway.

Shenzhen, a central city in Guangdong Province, is located in the eastern part of the Pearl River Delta and near Hong Kong (Wang et al., 2018). Along with rapid urbanization and industrialization in the region over the past 40 years (Xia et al., 2017; Yi et al., 2018), local environments and ecosystems have also stressed from anthropogenic contamination (Liu et al., 2018; Mai et al., 2019; Yu et al., 2018; Zhao et al., 2018). Microplastics were frequently detected in surface water and fish from this region (water: 7571 items m^{-3}; fish: 1.0–14.0 items $individual^{-1}$) (Wang et al., 2020). High levels of heavy metals such as chromium (Cr) (mean value: 99 mg kg^{-1}) and lead (Pb) (mean value: 33 mg kg^{-1}) (Liang et al., 2016), as well as organic pollutants such as organophosphorus flame retardants (2.3–30 ng g^{-1} wet weight) (Liu et al., 2019), polychlorinated biphenyls (30–4200 ng g^{-1} lipid weight) and polybrominated diphenyl ethers (6.9–690 ng g^{-1} lipid weight) were also reported in fish or shellfish (Sun et al., 2016). According to the sixth nationwide census of China in 2010, the number of births in Guangdong Province was the largest in China. Besides, Shenzhen is a very young city with a history of only 40 years. Residents in Shenzhen are relatively young and the number of vulnerable populations, such as pregnant women and children, is large. As mentioned above, perchlorate could cause negative effects on the thyroid function of pregnant women and the neurodevelopment of children (Glinoer, 2007). However, to our knowledge, nothing has been conducted to determine perchlorate contamination in marine aquaculture from this region.

Thus, this study investigated the occurrence of perchlorate in shellfish from South China Sea. Major objectives were to: (1) determine the abundances of perchlorate in major shellfish species and spatial distribution; and (2) estimate the daily intakes by local residents via shellfish consumption and associated health risks.

2. Materials and methods

2.1. Chemicals and reagents

A standard solution of perchlorate (ClO_4^-, 1000 μg mL^{-1}, purity: 100%) was purchased from Sigma-Aldrich (St. Louis. MO, USA). The internal standard of perchlorate ($Cl^{18}O_4^-$, 200 μg L^{-1}, purity >98%) was obtained from Cambridge Isotope Laboratories (Andover, MA, USA). Methanol, acetonitrile, formic acid and ammonium formate were high performance liquid chromatography (HPLC) grade (purity >99.5%) and purchased from Fisher Scientific (Houston, TX, USA). Ultra-pure water was produced from a Millipore water purification system (Billerica, MA, USA). Solid phrase extraction (SPE) cartridges (Oasis PRiME HLB, 3 mL 150 mg^{-1}) were purchased from Waters (Milford, Massachusetts, USA).

2.2. Sample collection

Sample collection was conducted from August 2014 to December 2016. Shellfish species with relatively high consumption frequencies by local residents were selected (Table S1). A total of 178 shellfish samples from eight species, including *Pinctada margaritifera* ($n = 16$), *Cyrenodonax formosana* ($n = 15$), *Crassostrea ariakensis* ($n = 42$), *Mimachlamys nobilis* ($n = 31$), *Mytilus galloprovincialis* ($n = 13$), *Babylonia areolata* ($n = 11$), *Haliotis diversicolor* ($n = 28$) and *Mactra mera* ($n = 23$), were purchased from four aquatic markets in Shenzhen, including Dongshan Pearl Island (DP), Yangmeikeng (YM), Xiexia Bay (XX) and Nan'ao Street skew Bay (NA) (Fig. S1, Table S2). After collection, shellfish samples were rinsed, took out the edible parts which need to test the concentrations of perchlorate, and then lyophilized completely in the laboratory. Water contents of individual shellfish samples were measured by gravimetric method. Dried shellfish samples were grounded to powder and store at −20 °C for further analysis.

2.3. Sample treatment protocols

Briefly, 0.5 g of shellfish powder was transferred into a 15 mL falcon-type plastic tube. After adding 100 μL internal standard ($Cl^{18}O_4^-$, 200 μg L^{-1} in ultra-pure water), the shellfish sample was added sequentially with 7 mL methanol and 3 mL ultra-pure water, and shaken for 20 min by a vortex oscillator (IKA® MS3 type vortex oscillator, IKA, Germany). The mixture was centrifuged at 10000 rpm for 10 min (Beckman Coulter AllegraTM X-22R tabletop high-speed centrifuge, Beckman, USA) and the supernatant was transferred into a new plastic tube. The supernatant was cleaned through a SPE cartridge and then a 0.45 μm PTFE filter. The first 1 mL elutant was discarded and the rest of filtered solution was collected for instrumental analysis.

2.4. Instrumental analysis

Perchlorate was determined by a 20A HPLC system (Shimadzu, Japan) equipped with a Q-Trap 5500 tandem mass spectrometer (MS/MS, Applied Biosystems, Foster City, CA, USA). Perchlorate was separated on a Trinity P1 column (100 mm × 2.1 mm × 3 μm, Thermo Fisher Scientific, USA). The column was maintained at 35 °C. The mobile phases included acetonitrile and 20 mmol L^{-1} ammonium formate. The mobile phase gradient program was set as fellows: 0–0.2 min, 70% acetonitrile; 0.2–3.0 min, 70%-90% acetonitrile; 3.0–7.0 min, 90%-70% acetonitrile; 7.0–9.0 min, 70% acetonitrile. The flow rate of mobile phases was 0.5 mL min^{-1}. An aliquot of 3 μL shellfish extraction was injected. Negative mode of electron spray ionization (ESI^-) and multiple reaction monitoring (MRM) mode were used to quantitatively determine perchlorate. Ion spray voltage, ion source temperature and scanning residence time were −4500 V, 550 °C and 50 ms, respectively.

2.5. Quality assurance and quality control

A blank sample was processed along with each batch of 20 samples in order to monitor contamination from experimental procedures. Concentrations of perchlorate in blank samples were all below the limit of detection (LOD). Internal standard ($Cl^{18}O_4^-$) was spiked into each shellfish sample in order to ensure the accuracy of quantification. The recoveries of perchlorate were measured by spiking perchlorate at different levels (1.0, 5.0, 20.0 ng mL^{-1}), which ranged between 70.3% and 101%. The relative standard deviation (RSD) of perchlorate was less than 10%. Limit of quantification (LOQ) of perchlorate was defined as a signal to noise ratio of ten, which is 0.1 ng mL^{-1}. The calibration curve for quantification ranged from 0.2 ng mL^{-1} to 50 ng mL^{-1} (0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, and 50.0 ng mL^{-1}). The correlation coefficient (R^2) of the calibration curve was 0.999.

2.6. Data analysis

The estimated daily intake (EDI) of perchlorate via shellfish consumption was calculated according to a previous study (Smith et al., 2006):

$$EDI = \frac{Cs \times CR}{BW}$$

where EDI (ng kg^{-1} bw day^{-1}) represents the estimated daily intake of perchlorate; Cs (μg kg^{-1} wet weight) represents the concentration of perchlorate in shellfish; CR (g day^{-1}) represents the daily consumption rate of shellfish, which is 34.0, 50.5, 63.8, 64.4, 117.5 and 94.6 g day^{-1} for urban toddlers, rural toddlers, urban children, rural children, urban adults and rural adults, respectively (CAMEP, 2013d, 2013e; Huang et al., 2015); BW (kg) represents the body weight, which is 15.8, 15.2, 39.0, 38.2, 59.5 and 57.2 kg for urban toddlers, rural toddlers, urban children, rural children, urban adults and rural adults, respectively (CAMEP, 2013a, 2013b, 2013c).

In order to assess the health risks to perchlorate caused via shellfish consumption, hazard quotient (HQ) was determined as (Li et al., 2014). A half of LOQ was assigned for statistical analysis if a concentration measurement was below the LOQ:

$$HQ = \frac{EDI}{RfD}$$

where HQ is hazard quotient; RfD (ng kg^{-1} bw day^{-1}) is the reference dose proposed by the United States Environmental Protection Agency (USEPA, 700 ng kg^{-1} bw day^{-1}) (USEPA, 2005). A HQ greater than 1 indicates a potential risk.

A half of LOQ was assigned for statistical analysis if a concentration measurement was below the LOQ. The differences in shellfish kinds, spatial distribution and urban-rural differences were analyzed by the Kruskal-Wallis H test and Mann-Whitney *U* test (SPSS 13.0). The statistical significance level was set at $p < 0.05$.

3. Results and discussion

3.1. Detection frequencies and concentrations of perchlorate

The detection frequencies and concentrations of perchlorate in shellfish samples are summarized in Table 1. Perchlorate was detected in all shellfish samples except for one. The high detection frequency (99.4%) suggested ubiquitous presence of perchlorate in shellfish from South China Sea. By contrast, perchlorate was much less frequently detected in aquatic food from other regions, e.g., 18.2% in shellfish and 35.6% in seafood from Taiwan, China (Chang et al., 2020) and 12% in seafood from Korea (Lee et al., 2012). The wide occurrences of perchlorate in shellfish in the present study might be attributed to the ubiquitous pollution of perchlorate in South China.

Concentrations of perchlorate ranged from not detected (N.D.) (*Crassostrea ariakensis*) to 71.5 μg kg^{-1} (*Haliotis diversicolor*), with a median concentration of 4.33 μg kg^{-1} (Table 1). The median concentration in the present study was lower than those in Hebei (6.6 μg kg^{-1}), and twice lower than the levels reported from Beijing (9.1 μg kg^{-1}) and Tianjin (10.6 μg kg^{-1}) (Liao et al., 2020) (Table 2). However, it was much higher than those in Taiwan, China (<LOQ) (Chang et al., 2020). The mean concentration of perchlorate in the present study (7.96 μg kg^{-1}) was slightly higher than the mean value reported in Chengdu (7.34 μg kg^{-1}) (Gan et al., 2015) and one order of magnitude higher than those in Korea (0.95 μg kg^{-1}) (Lee et al., 2012). These comparisons also revealed a relatively high abundance of perchlorate in shellfish from South China Sea.

3.2. Perchlorate in different shellfish species

The species-dependent concentrations of perchlorate are presented in Table 1 and Fig. 1. Among the eight species of shellfish, the highest median concentration of perchlorate was found in *Mimachlamys nobilis* (9.04 μg kg^{-1}), followed by *Haliotis diversicolor* (7.25 μg kg^{-1}). *Mimachlamys nobilis* contained significantly greater concentrations than other species ($p < 0.05$), except for *Haliotis diversicolor*. This suggested species-specific accumulation of perchlorate.

However, to our knowledge, the comparison of perchlorate

Table 2
Perchlorate concentrations from different countries and regions (μg kg^{-1}).

Countries or regions	Samples	N	Range	Mean	Median	Reference
Shenzhen, China	Shellfish	178	N.D.-71.5	7.96	4.33	This study
Beijing, China	Aquatic products	20	0.52–30.9	8.2	9.1	(Liao et al., 2020)
Tianjin, China	Aquatic products	20	0.19–32.6	9.8	10.6	(Liao et al., 2020)
Hebei, China	Aquatic products	20	0.48–34.4	5.9	6.6	(Liao et al., 2020)
Chengdu, China	Seafood	20	3.17–15.8	7.34	–[c]	(Gan et al., 2015)
Taiwan, China	Seafood	45	LOQ-5.59	0.704	<LOQ	(Chang et al., 2020)
Korea	Fish and shellfish	100	N.D.-21.50	0.95	–[c]	(Lee et al., 2012)
Japan	Fish and shellfish	–[a]	1.3–23	–[b]	–[c]	(Asami et al., 2013)

[a] The article did not provide an accurate value in the number of fish and shellfish samples.
[b] The article did not provide an accurate data on the overall mean.
[c] The article did not provide an accurate data on the overall median.

Table 1
The concentrations of perchlorate in different species of shellfish (μg kg^{-1}).

	Minimum	Maximum	Mean	Median	5th percentile	95th percentile	SD	DF (%)
Pinctada margaritifera (n = 16)	2.76	13.7	5.99	4.11	2.76	12.8	3.74	100
Cyrenodonax formosana (n = 15)	<LOQ	13.4	5.64	4.06	<LOQ	12.4	4.13	100
Crassostrea ariakensis (n = 42)	N.D.	39.2	7.40	3.88	<LOQ	32.8	9.15	97.6
Mimachlamys nobilis (n = 31)	2.22	48.4	14.0	9.04	2.87	42.9	12.2	100
Mytilus galloprovincialis (n = 13)	<LOQ	11.2	4.45	4.36	<LOQ	6.34	2.66	100
Babylonia areolata (n = 11)	<LOQ	4.16	2.33	2.22	<LOQ	4.16	1.24	100
Haliotis diversicolor (*n* = 27)	2.12	71.5	11.6	7.25	2.21	56.5	14.3	100
Mactra mera (n = 23)	<LOQ	18.0	4.22	2.96	<LOQ	16.6	3.89	100
All samples (n = 178)	N.D.	71.5	7.96	4.33	<LOQ	31.2	9.67	99.4

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

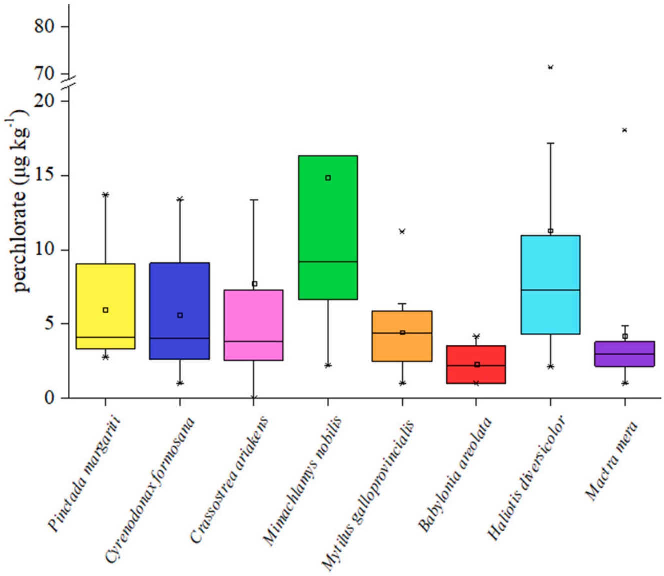

Fig. 1. The concentrations (μg kg^{-1}) of perchlorate in different kinds of shellfish.
(The line in the box represents the median value; the small square represents the mean value; the bottom and top of each box represent 25th and 75th percentiles, respectively; the top and bottom of each whisker represent 10th and 90th percentile, respectively; the asterisks represent means outliers.)

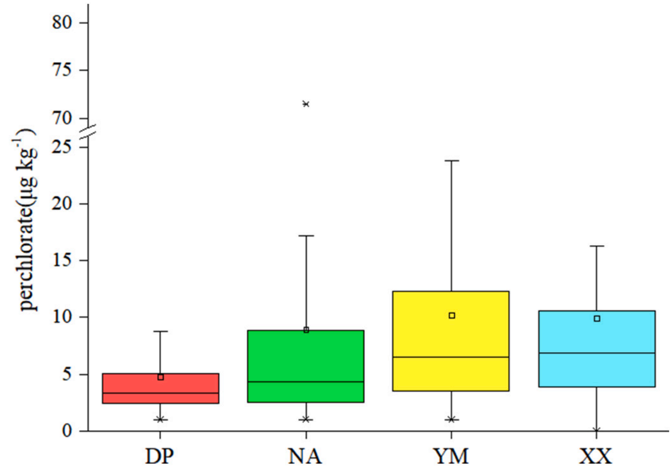

Fig. 2. The concentrations (μg kg^{-1}) of perchlorate in shellfish from different sampling sites.
(The line in the box represents the median value; the small square represents the mean value; the bottom and top of each box represent 25th and 75th percentiles, respectively; the top and bottom of each whisker represent 10th and 90th percentile, respectively; the asterisks represent means outliers.)

concentration in different kinds of shellfish has not been conducted before. Comparison of different shellfish species has been investigated for other types of pollutants. Liu et al. (2020) found that *Crassostrea ariakensis*, *Mytilus galloprovincialis* and *Mactra mera* contained higher concentrations of cadmium (Cd) and *Mimachlamys nobilis* contained elevated levels of Pb than other kinds of shellfish in Shenzhen, China. Xie et al. (2019) found that *Mytilus edulis* and *Ostrea gigas* (*Crassostrea ariakensis* in this category) contained high levels of pharmaceuticals and personal care products (PPCPs) in the Pearl River Delta. Gong et al. (2020) found that *Babylonia areolata* contained high levels of inorganic arsenic (iAs) and copper (Cu) in Shenzhen, China. These findings suggest species-specific accumulation of various pollutants in shellfish. This may likely be due to the influences by age, life cycle, living conditions, growth and development habits and other influencing factors.

3.3. Spatial distribution of perchlorate in shellfish

Perchlorate concentrations in shellfish from the four sampling sites were compared to investigate spatial distribution (Fig. 2 and Table S3). The median concentrations of perchlorate in shellfish from DP, YM, XX and NA were 3.32, 6.54, 6.86 and 4.30 μg kg^{-1} in shellfish, respectively. Concentrations of perchlorate in shellfish from DP were significantly lower than those from other sites ($p < 0.05$). The median perchlorate concentration of shellfish in XX was twice higher than in DP. As mentioned above, shellfish was recognized as "ecosystem engineers" in coastal environment (Gutiérrez et al., 2003). Thus, the concentration of perchlorate in shellfish may reflect the pollution status in coastal waters of the studied region.

Among the four different sites, the median concentration of perchlorate in shellfish from YM and XX were both above 6.5 μg kg^{-1}. There are some factories around XX, likely constituting potential sources. YM is a one of the famous tourist attractions in Shenzhen, where tourists and local residents often set fireworks to celebrate festivals. DP exhibited the lowest perchlorate contamination compared with other sites ($p < 0.05$). This may due that DP has municipal nature reserves. This study may use as a reference to control the perchlorate contamination in the different sites of Shenzhen.

3.4. EDI of perchlorate and potential health risk assessment

This study divided populations into toddlers (2–5 years old), children (6–7 years old) and adults (≥18 years old) by age. Infants (0–2 years old) were not considered because they basically consume breast milk or formula milk powder and hardly consume shellfish. The median and maximum EDI were estimated based on the median and maximum concentration of perchlorate in shellfish (Table 2), which were in the range of 4.90–30.0 ng kg^{-1} bw day^{-1} and 6.81–238 ng kg^{-1} bw day^{-1}, respectively. The highest median EDI was through the consumption of *Mimachlamys nobilis*, followed by *Haliotis diversicolor*, *Mytilus galloprovincialis*, *Pinctada margaritifera*, *Cyrenodonax formosana*, *Crassostrea ariakensis*, *Mactra mera* and *Babylonia areolata*. The median EDI values determined in our study were more than twice higher than those in Chengdu, China (Gan et al., 2015) and slightly higher than in North China (Liao et al., 2020), and three order of magnitude higher than in Taiwan, China (Chang et al., 2020), indicating relatively greater exposure risk in Shenzhen residents (Table 3).

When consuming the same kinds of shellfish, rural toddlers exhibited greater EDI than other age groups in both urban and rural area ($p < 0.05$). This may be related to the relatively low body weight of toddlers and high daily consumption of shellfish. This result agrees well with the study in Chengdu (Gan et al., 2015). However, for the same age group, there is no significant difference in the EDI of perchlorate between rural and urban residents in Shenzhen ($p > 0.05$). This might be related to the small difference in daily shellfish intake and body weight between urban and rural residents (CAMEP, 2013a, 2013b, 2013c, 2013d, 2013e; Huang et al., 2015).

To further evaluate human exposure risks via shellfish consumption, hazard quotient (HQ) was calculated by using the maximum EDI value of perchlorate (Fig. 3). The determined HQ for urban and rural residents ranged from 0.01 to 0.34, indicating that perchlorate in shellfish could not cause a potential health risk to humans in Shenzhen. By contrast, Liu et al. (2020) reported that the HQs of Cd and As in *Crassostrea ariakensis* and *Babylonia areolata* from Shenzhen both exceeded 1, which may cause exposure risks. Gong et al. (2020) found that *Babylonia areolata* contained inorganic arsenic (iAs) exceeding the maximum permissible limit, and children consuming *Argopecten irradians* and *Chlamys farreri* could be subjected to non-carcinogenic risks in Shenzhen. Thus, the content of other pollutants in shellfish in Shenzhen should be studied to find whether those pollutants exceed the tolerable daily intake or not.

Table 3
Estimate of daily intakes of perchlorate via shellfish consumption (ng kg^{-1} bw day^{-1}).

		Urban			Rural		
		Toddlers	Children	Adult	Toddlers	Children	Adult
Pinctada margaritifera (n = 16)	Median	8.84	6.72	8.12	13.6	6.93	6.80
	Maximum	29.5	22.4	27.0	45.5	23.1	22.7
Cyrenodonax formosana (n = 15)	Median	8.74	6.64	8.02	13.5	6.84	6.71
	Maximum	28.8	21.9	26.5	44.5	22.6	22.2
Crassostrea ariakensis (n = 42)	Median	8.35	6.35	7.66	12.9	6.54	6.42
	Maximum	84.4	64.1	77.4	130	66.1	64.8
Mimachlamys nobilis (n = 31)	Median	19.4	14.8	17.8	30.0	15.2	14.9
	Maximum	104	79.2	95.6	161	81.6	80.0
Mytilus galloprovincialis (n = 13)	Median	9.38	7.13	8.61	14.5	7.35	7.21
	Maximum	24.1	18.3	22.1	37.2	18.9	18.5
Babylonia areolata (n = 11)	Median	4.78	3.63	4.38	7.38	3.74	3.67
	Maximum	8.95	6.81	8.22	13.8	7.01	6.88
Haliotis diversicolor (*n* = 27)	Median	15.6	11.9	14.3	24.1	12.2	12.0
	Maximum	154	117	141	238	120	118
Mactra mera (n = 23)	Median	6.37	4.84	5.85	9.83	4.99	4.90
	Maximum	38.7	29.4	35.6	59.8	30.4	29.8
All samples (*n* = 178)	Median	9.32	7.08	8.55	14.4	7.30	7.16
	Maximum	154	117	141	238	120	118

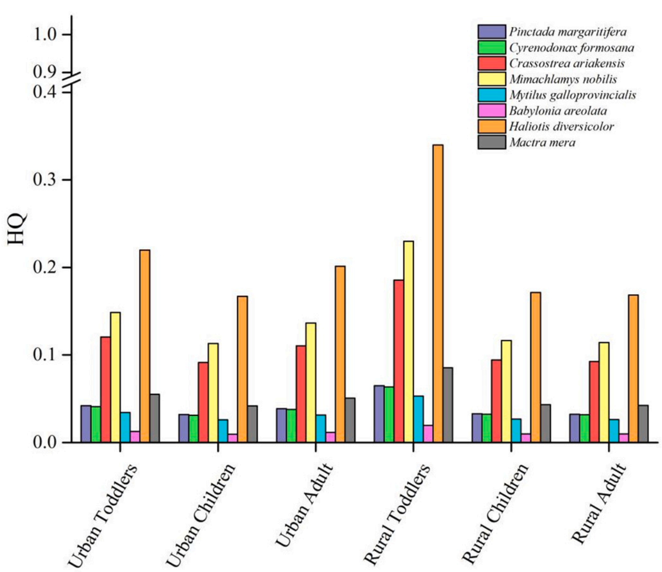

Fig. 3. Hazard quotient of perchlorate via shellfish consumption.

4. Conclusions

This study investigated the concentrations of perchlorate in different species of shellfish from South China Sea and assessed human health risks via shellfish consumption. High detection frequencies of perchlorate indicated ubiquitous contamination in coastal water and broad exposure in local residents. Among the eight species of shellfish, *Mimachlamys nobilis* and *Haliotis diversicolor* were observed with the highest median concentrations of perchlorate, indicating species-specific accumulation of this chemical. The EDI values of perchlorate from different shellfish species were all lower than the RfD (HQ < 1), suggesting no significant health risk to local residents via shellfish consumption.

CRediT authorship contribution statement

Yining Chen: Investigation, Data analysis and Writing.
Zhou Zhu: Data analysis.
Yang Zhao: Investigation and Writing-Reviewing and Editing.
Xiaoling Wu: Investigation.
Qinru Xiao: Writing-Reviewing and Editing.
Yilan Deng: Writing-Reviewing and Editing.
Minhui Li: Writing-Reviewing and Editing.
Chun Li: Writing-Reviewing and Editing.
Hongmei Qiu: Writing-Reviewing and Editing.
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.

Acknowledgements

This study was supported by the National Natural Science Foundation of China (No. 42077385), the Fundamental Research Funds for the Central Universities of China (No. 20ykpy87), the 100 Top Talent Programs of Sun Yat-sen University, the Shenzhen Municipal Government Research Projects (No. JCYJ20180307102139795) and the Medical Scientific Research Foundation of Guangdong Province, China (No. A2018173).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2021.112672.

References

Asami, M., Yoshida, N., Kosaka, K., Ohno, K., Matsui, Y., 2013. Contribution of tap water to chlorate and perchlorate intake: a market basket study. Sci. Total Environ. 463-464, 199–208.

Calderon, R., Palma, P., Parker, D., Molina, M., Godoy, F.A., Escudey, M., 2014. Perchlorate levels in soil and waters from the Atacama Desert. Arch. Environ. Contam. Toxicol. 66, 155–161.

CAMEP, 2013a. Body Weight, Exposure Factors Handbook of Chinese Population (0-5years), p. 1015.

CAMEP, 2013b. Body Weight, Exposure Factors Handbook of Chinese Population (6-17years), p. 852.

CAMEP, 2013c. Body Weight, Exposure Factors Handbook of Chinese Population (Adults), p. 762.

CAMEP, 2013d. Dietary Intake, Exposure Factors Handbook of Chinese Population (0-5years), pp. 269–270.

CAMEP, 2013e. Dietary Intake, Exposure Factors Handbook of Chinese Population (6-17years), p. 313.

Carr, J.A., Murali, S., Hu, F., Goleman, W.L., Carr, D.L., Smith, E.E., Wages, M., 2015. Changes in gastric sodium-iodide symporter (NIS) activity are associated with differences in thyroid gland sensitivity to perchlorate during metamorphosis. Gen. Comp. Endocrinol. 219, 16–23.

Chang, W.H., Chen, H.L., Lee, C.C., 2020. Dietary exposure assessment to perchlorate in the Taiwanese population: a risk assessment based on the probabilistic approach. Environ. Pollut. 267, 115486.
Dasgupta, P.K., Martinelango, P.K., Jackson, W.A., Anderson, T.A., Tian, K., Tock, R.W., Rajagopalan, S., 2005. The origin of naturally occurring perchlorate: the role of atmospheric processes. Environ. Sci. Technol. 39, 1569–1575.
Dasgupta, P.K., Dyke, J.V., Kirk, A.B., Jackson, W.A., 2006. Perchlorate in the United States. Analysis of relative source contributions to the food chain. Environ. Sci. Technol. 40, 6608–6614.
Dong, H., Xiao, K., Xian, Y., Wu, Y., Zhu, L., 2019. A novel approach for simultaneous analysis of perchlorate (ClO4(-)) and bromate (BrO3(-)) in fruits and vegetables using modified QuEChERS combined with ultrahigh performance liquid chromatography-tandem mass spectrometry. Food Chem. 270, 196–203.
Eguchi, A., Kunisue, T., Wu, Q., Trang, P.T., Viet, P.H., Kannan, K., Tanabe, S., 2014. Occurrence of perchlorate and thiocyanate in human serum from e-waste recycling and reference sites in Vietnam: association with thyroid hormone and iodide levels. Arch. Environ. Contam. Toxicol. 67, 29–41.
Gan, Z., Sun, H., Wang, R., Deng, Y., 2014. Occurrence and exposure evaluation of perchlorate in outdoor dust and soil in mainland China. Sci. Total Environ. 470-471, 99–106.
Gan, Z., Pi, L., Li, Y., Hu, W., Su, S., Qin, X., Ding, S., Sun, H., 2015. Occurrence and exposure evaluation of perchlorate in indoor dust and diverse food from Chengdu, China. Sci. Total Environ. 536, 288–294.
Glinoer, D., 2007. Clinical and biological consequences of iodine deficiency during pregnancy. Endocr. Dev. 10, 62–85.
Gong, Y., Chai, M., Ding, H., Shi, C., Wang, Y., Li, R., 2020. Bioaccumulation and human health risk of shellfish contamination to heavy metals and As in most rapid urbanized Shenzhen, China. Environ. Sci. Pollut. Res. Int. 27, 2096–2106.
Guerin, T., Chekri, R., Vastel, C., Sirot, V., Volatier, J.L., Leblanc, J.C., Noel, L., 2011. Determination of 20 trace elements in fish and other seafood from the French market. Food Chem. 127, 934–942.
Gutiérrez, J.L., Jones, C.G., Strayer, D.L., Iribarne, O.O., 2003. Mollusks as Ecosystem Engineers: The Role of Shell Production in Aquatic Habitats, 101, pp. 79–90.
Habibullah-Al-Mamun, M., Ahmed, M.K., Islam, M.S., Hossain, A., Tokumura, M., Masunaga, S., 2019. Polychlorinated biphenyls (PCBs) in commonly consumed seafood from the coastal area of Bangladesh: occurrence, distribution, and human health implications. Environ. Sci. Pollut. Res. Int. 26, 1355–1369.
Huang, W., Pan, L., Wang, Z., Zhang, J., Peng, C., Li, B., Sun, Q., Li, W., Jiang, L., You, J., 2015. Food consumption survey of residents in Shenzhen. Chinese Journal of Food Hygiene 27, 57–61.
Jahagirdar, V., Zoeller, T.R., Tighe, D.P., Wagner, C.K., 2012. Maternal hypothyroidism decreases progesterone receptor expression in the cortical subplate of foetal rat brain. J. Neuroendocrinol. 24, 1126–1134.
James, K.J., Carey, B., O'Halloran, J., van Pelt, F.N., Skrabakova, Z., 2010. Shellfish toxicity: human health implications of marine algal toxins. Epidemiol. Infect. 138, 927–940.
Jia, Y., Wang, L., Qu, Z., Yang, Z., 2018. Distribution, contamination and accumulation of heavy metals in water, sediments, and freshwater shellfish from Liuyang River, Southern China. Environ. Sci. Pollut. Res. Int. 25, 7012–7020.
Kang, C.H., So, J.S., 2016. Antibiotic and heavy metal resistance in Shewanella putrefaciens strains isolated from shellfishes collected from West Sea, Korea. Mar. Pollut. Bull. 112, 111–116.
Kannan, K., Praamsma, M.L., Oldi, J.F., Kunisue, T., Sinha, R.K., 2009. Occurrence of perchlorate in drinking water, groundwater, surface water and human saliva from India. Chemosphere 76, 22–26.
Kato, L.S., Ferrari, R.G., Leite, J.V.M., Conte-Junior, C.A., 2020. Arsenic in shellfish: a systematic review of its dynamics and potential health risks. Mar. Pollut. Bull. 161, 111693.
Kumarathilaka, P., Oze, C., Indraratne, S.P., Vithanage, M., 2016. Perchlorate as an emerging contaminant in soil, water and food. Chemosphere 150, 667–677.
Lal, V., Bridgen, P., Votadroka, W., Raju, R., Aalbersberg, W., 2014. Characterization of organochlorine pesticides, brominated flame retardants and dioxin-like compounds in shellfish and eel from Fiji. Sci. Total Environ. 491-492, 200–204.
Lee, J.W., Oh, S.H., Oh, J.E., 2012. Monitoring of perchlorate in diverse foods and its estimated dietary exposure for Korea populations. J. Hazard. Mater. 243, 52–58.
Leoterio, D.M., Paim, A.P., Belian, M.F., Galembeck, A., Lavorante, A.F., Pinto, E., Amorim, C.G., Araujo, A.N., Montenegro, M.C., 2017. Potentiometric perchlorate determination at nanomolar concentrations in vegetables. Food Chem. 227, 166–172.
Leung, A.M., Pearce, E.N., Braverman, L.E., 2010. Perchlorate, iodine and the thyroid. Best Pract. Res. Clin. Endocrinol. Metab. 24, 133–141.
Levakov, I., Ronen, Z., Dahan, O., 2019. Combined in-situ bioremediation treatment for perchlorate pollution in the vadose zone and groundwater. J. Hazard. Mater. 369, 439–447.
Li, J., Huang, Z., Hu, Y., Yang, H., 2013. Potential risk assessment of heavy metals by consuming shellfish collected from Xiamen, China. Environ. Sci. Pollut. Res. Int. 20, 2937–2947.
Li, Q., Yu, Y.J., Wang, F.F., Chen, S.W., Yin, Y., Lin, H.P., Che, F., Sun, P., Qin, J., Liu, J., Wang, H.M., 2014. Urinary perchlorate exposure and risk in women of reproductive age in a fireworks production area of China. Arch. Environ. Contam. Toxicol. 67, 42–49.
Li, Y., Liao, R., Gan, Z., Qu, B., Wang, R., Chen, M., Ding, S., Su, S., 2018. Seasonal variation and exposure risks of perchlorate in soil, indoor dust, and outdoor dust in China. Arch. Environ. Contam. Toxicol. 75, 367–376.
Li, W., Zhang, Z.M., Zhang, R.R., Jiao, H.F., Sun, A.L., Shi, X.Z., Chen, J., 2020. Effective removal matrix interferences by a modified QuEChERS based on the molecularly imprinted polymers for determination of 84 polychlorinated biphenyls and organochlorine pesticides in shellfish samples. J. Hazard. Mater. 384, 121241.
Liang, P., Wu, S.C., Zhang, J., Cao, Y., Yu, S., Wong, M.H., 2016. The effects of mariculture on heavy metal distribution in sediments and cultured fish around the Pearl River Delta region, south China. Chemosphere 148, 171–177.
Liao, Z., Cao, D., Gao, Z., Zhang, S., 2020. Occurrence of perchlorate in processed foods manufactured in China. Food Control 107.
Liu, Y., Chen, S., Xu, J., Liu, X., Wu, Y., Zhou, L., Cheng, J., Ma, H., Zheng, J., Lin, D., Zhang, L., Chen, L., 2018. The association between air pollution and outpatient and inpatient visits in Shenzhen, China. Int. J. Environ. Res. Public Health 15.
Liu, Y.E., Luo, X.J., Huang, L.Q., Zeng, Y.H., Mai, B.X., 2019. Organophosphorus flame retardants in fish from Rivers in the Pearl River Delta, South China. Sci. Total Environ. 663, 125–132.
Liu, S., Liu, Y., Yang, D., Li, C., Zhao, Y., Ma, H., Luo, X., Lu, S., 2020. Trace elements in shellfish from Shenzhen, China: implication of coastal water pollution and human exposure. Environ. Pollut. 263.
Mai, L., You, S.N., He, H., Bao, L.J., Liu, L.Y., Zeng, E.Y., 2019. Riverine microplastic pollution in the Pearl River Delta, China: are modeled estimates accurate? Environ. Sci. Technol. 53, 11810–11817.
Martinelango, P.K., Tian, K., Dasgupta, P.K., 2006. Perchlorate in seawater: bioconcentration of iodide and perchlorate by various seaweed species. Anal. Chim. Acta 567, 100–107.
Picot, C., Nguyen, T.A., Carpentier, F.-G., Roudot, A.-C., Parent-Massin, D., 2011. Relevant shellfish consumption data for dietary exposure assessment among high shellfish consumers, Western Brittany, France. Int. J. Environ. Health Res. 21.
Qin, X., Zhang, T., Gan, Z., Sun, H., 2014. Spatial distribution of perchlorate, iodide and thiocyanate in the aquatic environment of Tianjin, China: environmental source analysis. Chemosphere 111, 201–208.
Sagratini, G., Buccioni, M., Ciccarelli, C., Conti, P., Cristalli, G., Giardinà, D., Lambertucci, C., Marucci, G., Volpini, R., Vittori, S., 2008. Levels of polychlorinated biphenyls in fish and shellfish from the Adriatic Sea. Food Addit. Contam. Part B Surveill. 1, 69–77.
Serrano-Nascimento, C., Calil-Silveira, J., Dalbosco, R., Zorn, T.T., Nunes, M.T., 2018. Evaluation of hypothalamus-pituitary-thyroid axis function by chronic perchlorate exposure in male rats. Environ. Toxicol. 33, 209–219.
Shi, Y., Zhang, P., Wang, Y., Shi, J., Cai, Y., Mou, S., Jiang, G., 2007. Perchlorate in sewage sludge, rice, bottled water and milk collected from different areas in China. Environ. Int. 33, 955–962.
Smith, P.N., Severt, S.A., Jackson, J.W.A., Anderson, T.A., 2006. Thyroid function and reproductive success in rodents exposed to perchlorate via food and water. Environ. Toxicol. Chem. 25, 1050–1059.
Sun, R., Luo, X., Tang, B., Li, Z., Wang, T., Tao, L., Mai, B., 2016. Persistent halogenated compounds in fish from rivers in the Pearl River Delta, South China: geographical pattern and implications for anthropogenic effects on the environment. Environ. Res. 146, 371–378.
Sungur, Ş., Sangün, M.K., 2011. Ion chromatographic determination of perchlorate in foods consumed in Hatay region. Food Chem. 126, 326–331.
Trabalon, L., Vilavert, L., Domingo, J.L., Pocurull, E., Borrull, F., Nadal, M., 2017. Human exposure to brominated flame retardants through the consumption of fish and shellfish in Tarragona County (Catalonia, Spain). Food Chem. Toxicol. 104, 48–56.
USEPA, 2005. Perchlorate and perchlorate salts. https://cfpub.epa.gov/ncea/iris/iris_documents/documents/subst/1007_summary.pdf#nameddest=rfd.
Wagner, H.P., Suarez, F.X., Pepich, B.V., Hautman, D.P., Munch, D.J., 2004. Challenges encountered in extending the sensitivity of US Environmental Protection Agency method 314.0 for perchlorate in drinking water. J. Chromatogr. A 1039, 97–104.
Wang, Z., Pan, L., Liu, G., Zhang, H., Zhang, J., Jiang, J., Xiao, Y., Bai, W., Jiao, R., Huang, W., 2018. Dietary exposure to cadmium of Shenzhen adult residents from a total diet study. Food Addit. Contam. Part A Chem. Anal. Control Expo. Risk Assess. 35, 706–714.
Wang, Z., Sparling, M., Wang, K.C., Arbuckle, T.E., Fraser, W., 2019. Perchlorate in human milk samples from the maternal-infant research on environmental chemicals study (MIREC). Food Addit. Contam. Part A Chem. Anal. Control Expo. Risk Assess. 36, 1837–1846.
Wang, S., Zhang, C., Pan, Z., Sun, D., Zhou, A., Xie, S., Wang, J., Zou, J., 2020. Microplastics in wild freshwater fish of different feeding habits from Beijiang and Pearl River Delta regions, south China. Chemosphere 258, 127345.
Wu, Q., Zhang, T., Sun, H., Kannan, K., 2010. Perchlorate in tap water, groundwater, surface waters, and bottled water from China and its association with other inorganic anions and with disinfection byproducts. Arch. Environ. Contam. Toxicol. 58, 543–550.
Wu, F., Zhou, X., Zhang, R., Pan, M., Peng, K.L., 2012. The effects of ammonium perchlorate on thyroid homeostasis and thyroid-specific gene expression in rat. Environ. Toxicol. 27, 445–452.
Xia, X., Zhang, A., Liang, S., Qi, Q., Jiang, L., Ye, Y., 2017. The association between air pollution and population health risk for respiratory infection: a case study of Shenzhen, China. Int. J. Environ. Res. Public Health 14.
Xie, H., Hao, H., Xu, N., Liang, X., Gao, D., Xu, Y., Gao, Y., Tao, H., Wong, M., 2019. Pharmaceuticals and personal care products in water, sediments, aquatic organisms, and fish feeds in the Pearl River Delta: occurrence, distribution, potential sources, and health risk assessment. Sci. Total Environ. 659, 230–239.
Yi, L., Chen, J., Jin, Z., Quan, Y., Han, P., Guan, S., Jiang, X., 2018. Impacts of human activities on coastal ecological environment during the rapid urbanization process in Shenzhen, China. Ocean Coast. Manag. 154, 121–132.

Yu, H.Y., Chang, C., Li, F., Wang, Q., Chen, M., Zhang, J., 2018. Thallium in flowering cabbage and lettuce: potential health risks for local residents of the Pearl River Delta, South China. Environ. Pollut. 241, 626–635.

Yu, J., Dong, H.W., Shi, L.T., Tang, X.Y., Liu, J.R., Shi, J.H., 2019. Reproductive toxicity of perchlorate in rats. Food Chem. Toxicol. 128, 212–222.

Zhang, T., Wu, Q., Sun, H.W., Rao, J., Kannan, K., 2010. Perchlorate and iodide in whole blood samples from infants, children, and adults in Nanchang, China. Environ. Sci. Technol. 44, 6947–6953.

Zhang, J., Liu, F., Chen, R., Feng, T., Dong, S., Shen, H., 2012. Levels of polychlorinated biphenyls and organochlorine pesticides in edible shellfish from Xiamen (China) and estimation of human dietary intake. Food Chem. Toxicol. 50, 4285–4291.

Zhang, T., Chen, X., Wang, D., Li, R., Ma, Y., Mo, W., Sun, H., Kannan, K., 2015. Perchlorate in indoor dust and human urine in China: contribution of indoor dust to total daily intake. Environ. Sci. Technol. 49, 2443–2450.

Zhao, G., Ye, S., Yuan, H., Ding, X., Wang, J., Laws, E.A., 2018. Surface sediment properties and heavy metal contamination assessment in river sediments of the Pearl River Delta, China. Mar. Pollut. Bull. 136, 300–308.

Zhou, R., Zhu, L., Kong, Q., 2008. Levels and distribution of organochlorine pesticides in shellfish from Qiantang River, China. J. Hazard. Mater. 152, 1192–1200.