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Contribution of tap water to chlorate and perchlorate intake: A market basket study ☆

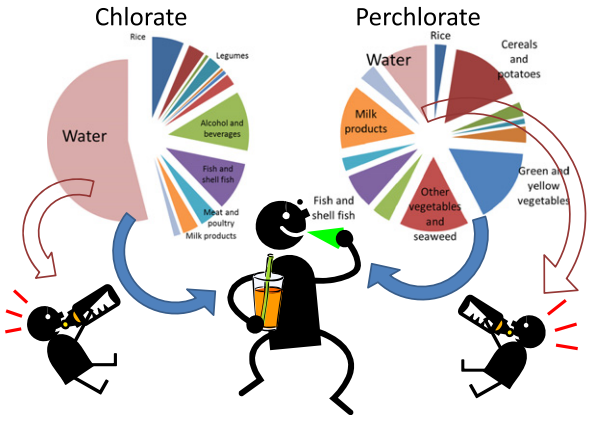
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HIGHLIGHTS

- Tap water contribution to total chlorate intake was first revealed.
- Cooking with tap water significantly influenced total chlorate intake.
- Chlorate intake from water is important especially when rice is major food.
- Total perchlorate intake was higher than the previous U.S. study due to vegetables.
- Total chlorate and perchlorate intake from baby formulas and water were high.

GRAPHICAL ABSTRACT



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ABSTRACT

The contributions of water to total levels of chlorate and perchlorate intake were determined using food and water samples from a market basket study from 10 locations in Japan between 2008 and 2009. Foods were categorized into 13 groups and analyzed along with tap water. The average total chlorate intake was 333 (min. 193–max. 486) μg/day for samples cooked with tap water. The contribution of tap water to total chlorate intake was as high as 47%–58%, although total chlorate intake was less than 32% of the tolerable daily intake, 1500 μg/day for body weight of 50 kg. For perchlorate, daily intake from water was 0.7 (0.1–4.4) μg/day, which is not high compared to the average total intake of 14 (2.5–84) μg/day, while the reference dose (RfD) is 35 μg/day and the provisional maximum tolerable daily intake (PMTDI) is 500 μg/day for body weight of 50 kg. The highest intake of perchlorate was 84 μg/day, where concentrations in foods were high, but not in water. The contribution of water to total perchlorate intake ranged from 0.5% to 22%, while the ratio of highest daily intake to RfD was 240% and that to PMTDI was 17%. Eight baby formulas were also tested — total chlorate and perchlorate intakes were 147 (42–332) μg/day and 1.11 (0.05–4.5) μg/day, respectively, for an ingestion volume of 1 L/day if prepared with tap water.

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1. Introduction

Chlorate and perchlorate are known as micropollutants in water. Chlorate is an impurity in sodium hypochlorite used as a disinfectant, and was added to the Japanese drinking water quality standard in November 2007 (in effect from April 2008) (MHLW, 2007). One of the known health effects of chlorate is oxidative damage to red blood cells, and the tolerable daily intake (TDI) was set to 30 μg/kg/day (MHLW, 2003). Chlorate is mainly thought to be present in water and its intake via the atmosphere seems unlikely (WHO, 2011). Therefore, 80% of TDI was allocated to drinking water, and the standard value of 600 μg/L was derived and established (MHLW, 2007). At present, 80% of TDI is also allocated to water in the guidelines issued by World Health Organization (WHO); due to the differences in standard body weight, the value in the WHO guideline is 700 μg/L (WHO, 2011).

Perchlorate is utilized for various purposes, including as a propellant for rocket fuel, explosives, fireworks, and airbags, and is also included in sodium hypochlorite (Kosaka et al., 2011). Perchlorate is known to suppress the uptake of iodine in the thyroid gland. In February 2005, the U.S. National Academy of Sciences (NAS) announced a perchlorate reference dose (RfD) of 0.7 μg/kg/day (NRC, 2005). In the same year, the U.S. Environmental Protection Agency (USEPA) announced a drinking water equivalent level (DWEL) of 24.5 μg/L (EPA, 2009) (when 100% contribution rate is assumed as 2 L of water a day consumed by an adult of body weight 70 kg). In 2008, the USEPA issued an Interim Health Advisory Level (HAL) of perchlorate of 15 μg/L (EPA, 2008). The USEPA has decided to regulate perchlorate under the Safe Drinking Water Act (SDWA) and is now developing a proposed national primary drinking water regulation for perchlorate and anticipates publication of the proposed rules for public review and comment in 2013 (EPA, 2012). JECFA (2011) established a the provisional maximum tolerable daily intake (PMTDI) of 0.01 mg/kg based on human data and including an uncertainty factor of 10 considering potentially vulnerable subgroups, such as pregnant women, fetuses, newborns and young infants.

In 2011, the Water Supply Division, Ministry of Health, Labour and Welfare, Japanese government, posed an evaluation value of 25 μg/L for perchlorate, assuming that the allocation of TDI to perchlorate in water is 10%, while it has been included in “the items for further study” as supplementary items to the Japanese Drinking Water Standard (MHLW, 2011).

Previously, we measured the concentrations of chlorate and perchlorate in bottled water and commercial beverages (Asami et al., 2009a), and also reported that the concentration of chlorate in some tap water exceeded 600 μg/L before the standard for chlorate was in effect (Asami et al., 2008) The highest chlorate concentration, 2900 μg/L was found due to high dose of sodium hypochlorite in 2006. Chlorate was present in degradation byproducts of sodium hypochlorite added in water purification process as an oxidative chemical and/or disinfectants (Kosaka et al., 2007). We also investigated the current state of chlorate and perchlorate in the Tone River basin in Japan, a main water source for Tokyo. The results indicated that perchlorate was present in environment water, drinking water, and water supplies in a wide region in Tone River basin due to environmental contamination mainly attributable to industrial effluents from few specific sources including a chlorate and perchlorate manufacturer and a facility conducting electrolysis processes. Takatsuki et al. (2009) made a survey on perchlorate contamination in leafy vegetables sold in Tokyo. Among 82 leafy vegetable samples tested, perchlorate was detected in the range of 0.3 ng/g and 29.7 ng/g in 79 samples. It was found at relatively high concentration in spinach and leafy green vegetables. Although it is not clear why they have higher concentration, it may have been possibly affected from water used for cultivation, as one of the sources of perchlorate.

In setting the guideline value for chlorate, the allocation ratio to water is 80% as one of disinfection byproducts, which is much higher than the default assumption of 10%–20% for other items, since chlorate was not considered to be exposed from other sources than water (WHO, 2011). To authors' knowledge, there is no data on total chlorate intake, therefore, intake survey through food is important, especially when considering tap water.

In 2008, the U.S. Food and Drug Administration reported the results of a perchlorate intake survey in the USA (Murray et al., 2008). However, the intake in Japan has yet to be investigated where cooking (boiling) and eating of rice at home is common, which seems a little different from that in the USA and European countries and which might be affected by constituents in tap water. The contribution of tap water is important to consider the allocation ratio to water based on the diet and, to our knowledge, there have been no previous surveys of chlorate intake.

In addition, the diet of infants differs from that of adults. The WHO guideline specifies the amount of drinking water for children weighing 10 kg as 1 L per day, and that for infants weighing 5 kg as 0.75 L per day (WHO, 2011). The concentration of perchlorate in milk was investigated in both Japan and the USA (Dyke et al., 2007). A relatively high concentration of perchlorate was detected in Japan. As infants rely on breast milk or baby formula for their daily nutritional intake, data regarding the amounts of chlorate and perchlorate in breast milk and formula are required to allow estimation of their intake levels by infants; however, no such data have been reported in Japan.

In the present study, we analyzed samples for the Total Diet Study (TDS) in cooperation with the National Institute of Health Sciences, Japan, and local health science institutes, estimated the amounts of chlorate and perchlorate intake, and compared the levels of their intake derived from food and tap water. In addition, a purchase survey was conducted on baby formula.

2. Materials and methods

2.1. Reagents and solutions

All solutions were prepared from ultrapure water obtained using a Gradient A10 water purification system (Millipore, Bedford, MA). Calibration standards were prepared by diluting 1000 mg/L certified standard solutions of chlorate (Kanto Chemical, Tokyo, Japan) and perchlorate (GFS Chemicals, Columbus, OH) in ultrapure water.

2.2. Test samples

From 2008 to 2009, foods were purchased and collected using the market basket method at 10 different locations across Japan, and were prepared at each location for use as test samples. Locations were selected to cover throughout Japan considering geographical and cultural differences as in the National Nutrition Survey (MHLW, 2005). At each sampling location, about 150 kinds of food were purchased from local grocery stores according to the methods used by the National Nutrition Survey (MHLW, 2005). Local custom and preference were taken into account when food items were selected, so the composition of the composite food samples was a little different to each other. Based on the amount of food intake according to the survey, and using the same method as described previously in detail (Ohno et al., 2010), a wide variety of foods were divided into 13 different groups (Table 1). After appropriate pre-cooking (normally boiling or baking), the foods were mixed and homogenized to make composite samples. Tap water was used for the pre-cooking at six locations, and pure water was used at other four locations. Representative intake levels for each food group in this study are shown in Fig. 1. The 14th group consisted of tap water from municipal drinking water treatment plants that used surface water as the source. The amount of water intake was not included in the above-mentioned national survey, so the level is represented as 2 L based on normal assumptions

Table 1
Food groups in the survey.

Food group	Contents
1	Rice
2	Cereals and potatoes
3	Sugar and confectioneries
4	Oil and fats
5	Legumes
6	Fruits
7	Green and yellow vegetables
8	Other vegetables and seaweed
9	Alcohol and beverages
10	Fish and shellfish
11	Meat and poultry
12	Milk products
13	Seasoning
14	Water

used in establishing drinking water quality standards. The pure waters used for cooking in four locations and the travel blank samples were also analyzed. Food samples were stored at −20 °C and thawed at room temperature immediately before analysis.

For eight baby formula samples, powdered milk and an ionized water (a mineral water for infants) were purchased from a market in the Tokyo area then used as samples in the test (Table 2). Baby formulas were evaluated for their concentration based on the manufacturers' indications.

2.3. Analytical method: pretreatment and analysis

Chlorate and perchlorate concentrations were analyzed by ion chromatograph (IC)–tandem mass spectrometry (MS/MS) as described elsewhere (Asami et al., 2009a; Kosaka et al., 2007). As an internal

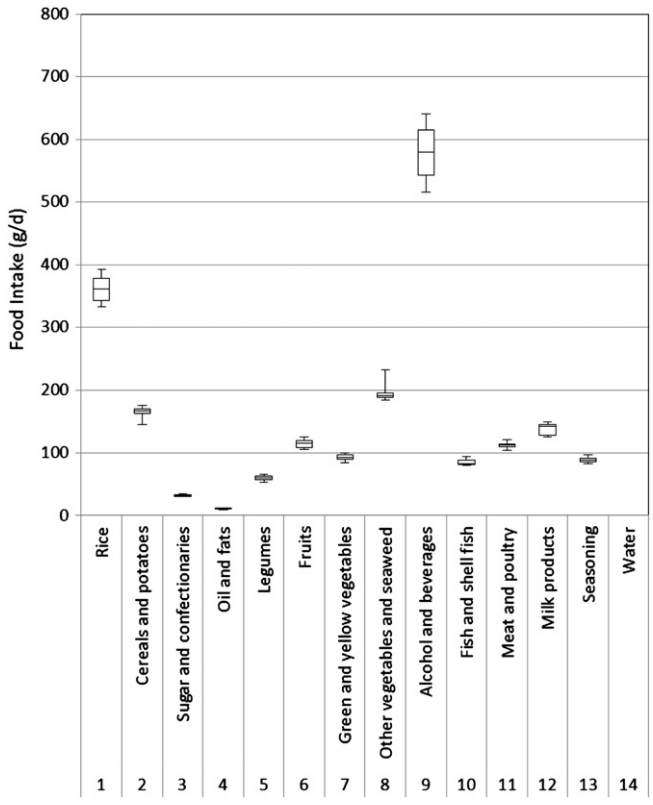


Fig. 1. Intake of each food group as determined by the methods of the National Nutrition Survey (MHLW 2004). Boxes represent 25%–75%quartile, while the center bars represent medians, and whiskers are maximum and minimum values. No data were available for group 14.

Table 2
Powdered milk.

No.	Manufacturer
I	WA
II	WA
III	MO
IV	MO
V	ME
VI	BS
VII	ME
VIII	ME

standard for perchlorate, ^{18}O-enriched $NaClO_4$ (Cambridge Isotope Laboratories, Andover, MA) was added to the samples immediately prior to analysis.

Samples of 1–5 g of each food group were placed in 50-mL tubes, and a standard solution of chlorate was added to a final concentration of 0, 1, or 2 μg/L. In addition, $^{18}O_4$-perchlorate was added as an internal standard to a final concentration of 1 μg/L. After adding 20 mL of solvent (mixed solution of distilled water: acetonitrile, 1:1 v/v), the samples were mixed and shaken at 75 rpm for 2 h. After shaking, the samples were separated by centrifugation (2000 rpm for 15 min), and 10 mL of the supernatant was collected and put into cartridges pretreated with methanol and distilled water (SepPak C18 1g; Waters, Milford, MA). The eluate was then filtered using hydrophilic polytetrafluoroethylene (PTFE) syringe filters (pore size 0.2 μm or 0.45 μm; Advantec, Dublin, CA), and the resulting solution was used as the test solution. For chlorate, the solution was further diluted by 10-fold and used as the test solution. For some food groups, preparation cartridges (OnGuardII Ba/Ag/H; Dionex) were used to avoid the effects of coexisting anions.

As pretreatment to determine the concentration of chlorate in baby formula, samples of 1 g were collected and the standard solution of chlorate was added to a final concentration of 0, 1, or 2 μg/L. Pretreatment to determine the concentration of perchlorate in baby formula was the same as described for food samples, and $^{18}O_4$-enriched perchlorate was added as an internal reference to a final concentration of 1 μg/L. Then, 10 mL of distilled water was added to dissolve the formula, after which 10 mL of 1% acetic acid solution was added and mixed thoroughly. Then, 20 mL of acetonitrile was added, mixed, and filtered using folded filter paper (2 V; Whatman, Kent, UK) that had been pretreated with distilled water. The filtrate was added to C18 cartridges and the samples for chlorate were diluted 10-fold, and then filtered again using anion-exchange cartridges or PTFE syringe filters.

In the rice cooking test, 50 g of rice was boiled with 100 mL of tap or pure water. Tap water contained 93.7 μg/L of chlorate and pure water contained no chlorate. The boiled rice was then treated the same as the rice sample described above and compared with the calculated value adjusted by wet weight.

2.4. Analytical method: equipment used

Separation was performed using an IC system (ICS-2000; Dionex, Sunnyvale, CA) with an eluent generator (EG50; Dionex), guard column (IonPac AG20 column 2 × 50 mm; Dionex), separation column (IonPac AS20, 2 × 250 mm; Dionex), and suppressor (ASRS Ultra II, 2 mm; Dionex). The eluent was potassium hydroxide (KOH) at a flow rate of 0.25 mL/min with an injection volume of 100 μL. As a post-column solvent, a mixture of acetonitrile (high-performance liquid chromatography grade; Wako Chemical, Osaka, Japan) and ultrapure water (90/10 v/v) was supplied to the eluent at a flow rate of 0.2 mL/min.

An API 3200QTrap (Applied Biosystems, Foster City, CA) was used for MS/MS. Selected multiple reaction monitoring (MRM) transitions were set at m/z 83/67 (quantification) and 85/69 (confirmation) for

chlorate; m/z 99/83 (quantification) and 101/85 (confirmation) for perchlorate, and 107/89 for ^{18}O-enriched perchlorate.

The limits of quantification (LOQ) for the aqueous samples were set as 0.05 μg/L and 0.01 μg/L for chlorate and perchlorate, respectively. The LOQ for food samples varied for each group and each location depending on the collection quantity and concentration, and those for chlorate and perchlorate ranged between 0.2 and 10 ng/g-wet-weight and 0.05 and 0.2 ng/g-wet-weight, respectively. The LOQ for chlorate was higher than that for perchlorate because the former was measured using the standard addition method. Nevertheless, the concentration of chlorate was higher than the LOQ, and we were able to determine the concentration in all food groups. The concentrations of chlorate and perchlorate in the pure waters and the travel blank samples were all below LOQ.

With regard to accuracy, samples were analyzed twice for several food groups ($n = 2$). The relative standard deviation (RSD, %) for repeat accuracy was 0.86% minimum and 37.2% maximum for chlorate, while those for perchlorate were 0.6% and 8.5%, respectively. Samples were pretreated such that the additive recovery rate would be above 60% for chlorate and perchlorate. For some dairy products and baby formula samples, additive recovery rates of internal standard substance of chlorate and perchlorate did not reach 50%, however, their linearity and duplicability were high. Therefore, the standard addition method was employed for all samples to minimize the analytical errors.

3. Results and discussion

3.1. Concentrations of chlorate and perchlorate in tap water samples

The chlorate and perchlorate concentrations in tap water are shown in Table 3. Chlorate concentrations in tap water at the sampling locations were in the range of 34–140 μg/L. Chlorate is contained in sodium hypochlorite used for disinfection in the majority of water treatment processes. This range was almost the same level as our previous study on water supply, 25–120 μg/L contained in treated water (Asami et al., 2008). The concentration of perchlorate ranged from 0.03 to 0.23 μg/L at all except one location, which had a much higher concentration than the others (2.2 μg/L). As the degree of water contamination in the area including this location was previously shown to be high (Kosaka et al., 2007), perchlorate concentration in tap water represents source water contamination by perchlorate contamination in that area which may be affected by river water contamination.

3.2. Chlorate and perchlorate concentrations in food and water samples

The concentrations of chlorate and perchlorate in each group for food samples and water are shown in Figs. 2 and 3, respectively. Measured concentrations in food samples were converted for each sample as the concentration per kilograms wet weight.

Chlorate concentration varied from <0.02 μg/kg to 920 μg/kg. Among food sample groups, legumes (group 5), seafood (group 10), and meat and poultry (group 11) had rather high average concentrations of chlorate. The concentration of chlorate in sugar and confectioneries (group 3) was specifically high at one location, 150 μg/kg. The concentration in rice (group 1) was low (between 0.30 and 8.0 μg/kg) at locations A, B, G and I where food samples were cooked with pure water. In other locations, the values varied between 28 and 91 μg/kg, probably because tap water was used for cooking these samples. The concentrations of chlorate in cereals and potatoes (group 2) were between 30 and 110 μg/kg, which were similar to those in rice cooked with tap water. The cereals and potatoes group included potatoes and noodles, which require tap water for cooking. The concentrations in the legumes (group 5) were relatively high, ranging between 70 and 140 μg/kg. This group included many foods that may have used tap water during processing in commercial factories, such as tofu.

In general, the concentration of perchlorate was lower than that of chlorate (Fig. 3), but was highest at 350 μg/kg in vegetables and seaweed (group 8) at location B, followed by green and yellow vegetables (vegetables rich in colors, group 7) at location B with 110 μg/kg. The vegetables and seaweed group (group 8) included a total of 16 items: vegetables with light colors, such as lettuce, bean sprouts, Chinese cabbage, eggplant, as well as Japanese radish, onions, mushrooms, and seaweed. It is not considered that these concentrations were affected from water since tap water was not used in location B. The concentration in the cereals and potatoes (group 2) was 2.8–28 μg/kg, that in sugar and confectioneries (group 3) was 1.3–27 μg/kg, and that in fish and seafood (group 10) was 1.3–23 μg/kg, all of which were relatively high. In these groups, the concentrations of some food samples varied greatly depending on the locations. The concentrations were the highest in location B followed by location D.

3.3. Comparison of food items cooked using pure water and tap water

In this study, pure water was used for cooking at 4 of 10 locations (A, B, G and I) and tap water was used at 6 locations. When chlorate concentrations of each sample were divided into two groups; those cooked with pure water and those cooked with tap water, the measured chlorate concentrations were higher in locations that used tap water for cooking compared to the other locations where pure water was used (Fig. 2). The difference between samples prepared with pure water and tap water was statistically significant in rice and green and yellow vegetables (group 1 and 7, $P < 0.05$).

For perchlorate, it seems that the difference was found among foods themselves, not in waters used for cooking, because perchlorate concentration was higher in foods cooked with pure water.

In food groups of 2, 7 and 8, perchlorate concentrations in food cooked with pure water were mostly higher than those in cooked with tap water. Based on the fact that the perchlorate was not contained in pure water, perchlorate concentrations in some food items were considered higher at some locations.

These observations suggested that chlorate in tap water used for cooking affected the food concentration. It was not clear how each of these groups were prepared or cooked, such as boiling or baking. The way of cooking varies among food groups and location, and they should have been cooked in a 'common' way at each location. Among these food groups, it seems rice is Japan's most staple food and should have prepared with water at home as a rice cooker is found in most Japanese households. Therefore chlorate concentration in rice and that in tap water was compared. Among the 6 locations

Table 3
Chlorate and perchlorate in tap water in the study areas.

	A*	B*	C	D	E	F	G*	H	I*	J
	(μg/L)									
Chlorate	130	59	45	83	80	130	34	140	56	67
Perchlorate	0.05	0.21	0.16	2.2	0.13	0.18	0.03	0.23	0.13	0.12

* Pure water was used for food preparation all of which contained no chlorate (<0.05 μg/L) or perchlorate (<0.01 μg/L).

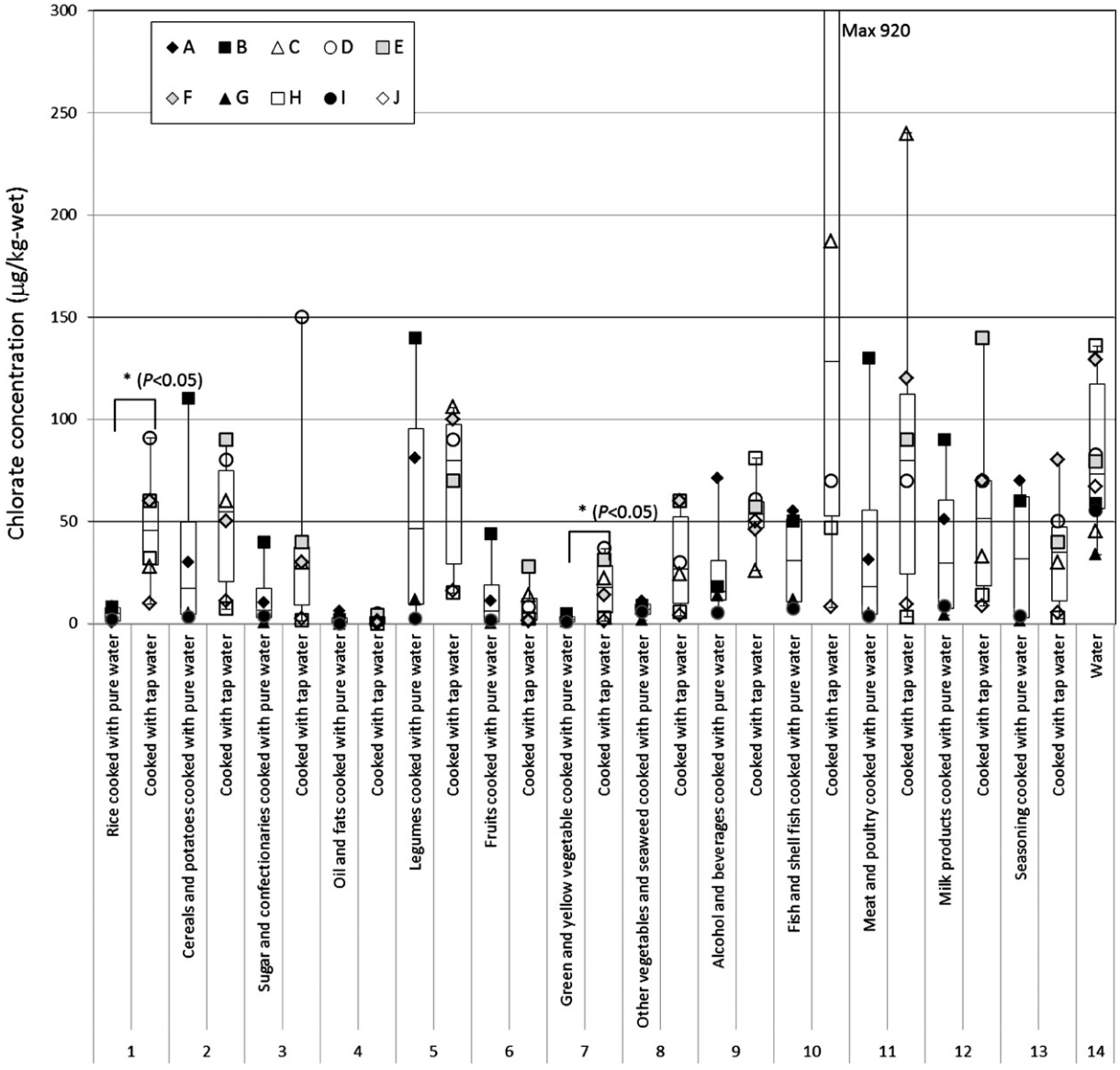


Fig. 2. Chlorate concentrations of each food group. Boxes represent 25%–75% quartile, the center bars represent medians, and whiskers are maximum and minimum values; * indicates significant difference between samples cooked with pure water and those with tap water at $P < 0.05$.

where tap water was used for cooking, the chlorate concentration in rice increased/decreased in proportion to that in tap water (Fig. 4). Chlorate in cooked rice correlated with cooked with tap water ($r^2 = 0.498$, $n = 6$).

3.4. Rice cooking test

Rice cooking test was separately conducted in the lab using ultrapure water and tap water. The levels of chlorate and perchlorate were lower in rice cooked with pure water than with tap water. Neither chlorate nor perchlorate was detected in rice samples cooked with pure water. Chlorate concentration in rice cooked with tap water with a content of 93.4 μg/L was 55.6 μg/kg, where rice contains 71% water. This value was close to the estimated chlorate concentration in rice of 57.1 μg/kg calculated from the tap water concentration. The same relationship was found for perchlorate, where the concentration was 2.3 μg/kg in cooked rice and the estimated concentration was 2.0 μg/kg. The above observations indicated that cooking food with tap water directly affects the levels of chlorate and perchlorate intake from food, because neither is present in rice but both are stable in water and non-volatile.

3.5. Daily intake of chlorate and perchlorate from food and water

Table 4 shows the average daily intakes of chlorate and perchlorate from food by multiplying the measured concentrations of the two compounds by the average daily intake of each food group based on the national nutrition survey (Fig. 1). The amount of water intake was not included in the above national survey, so the level is represented as 2 L based on normal assumptions used in establishing drinking water quality standards. Although this amount was presumed to include water used for cooking, it was used because no data are currently available. Authors are now conducting a national survey on water intake and it is tentatively elucidated 2 L can be considered to err on the side of safety for majority of population (in preparation).

The results indicated that the sum of daily chlorate intake from food (without water) at each location was within the range of 47–84 μg/day

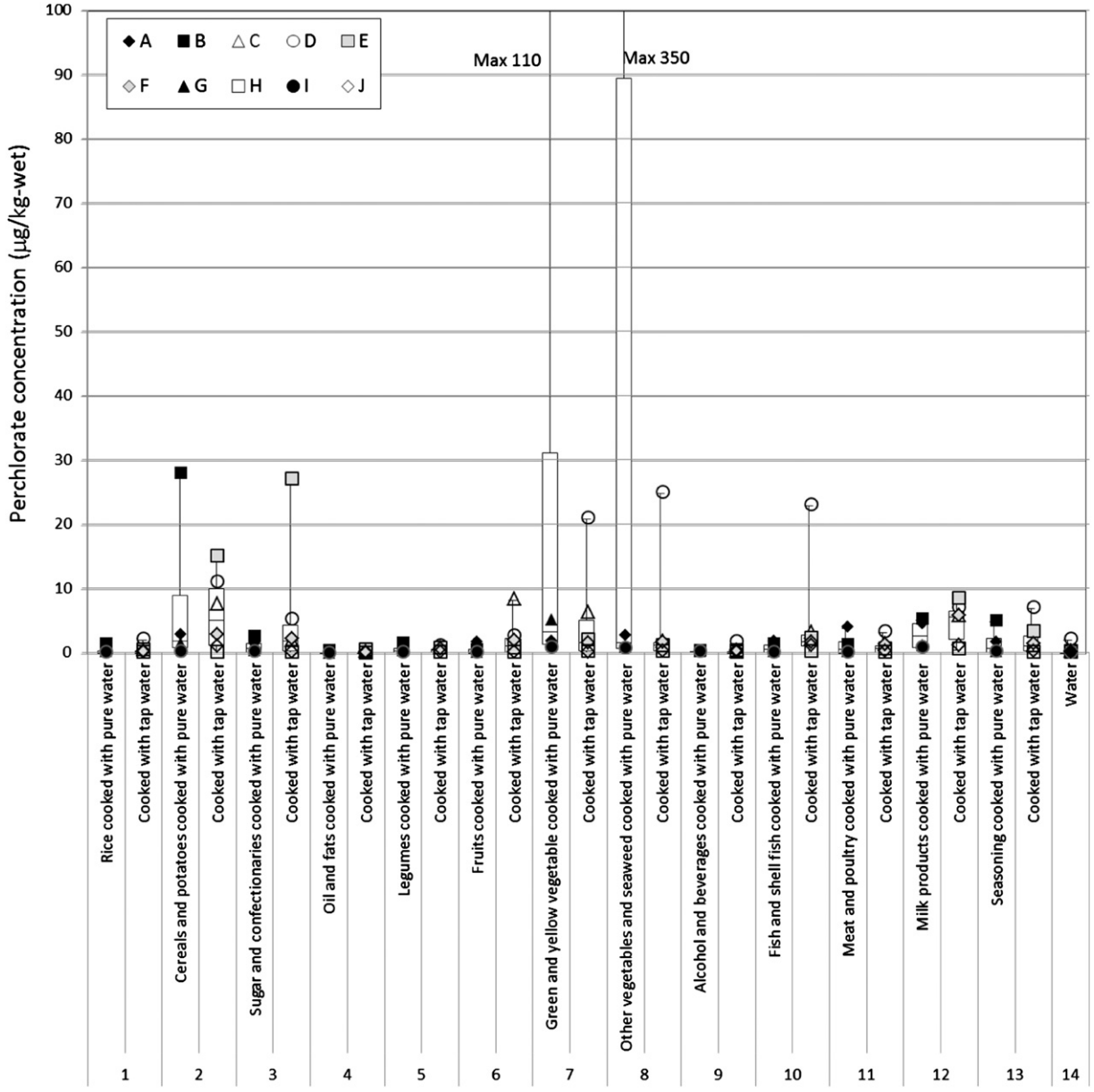


Fig. 3. Perchlorate concentrations of each food group. Boxes represent 25%–75% quartile, the center bars represent medians, and whiskers are maximum and minimum values.

for locations using pure water for cooking, and 102–214 μg/day for locations using tap water for cooking. The results of daily intake at each location were shown in Fig. S1. Among the food groups in average, rice (group 1), cereals and potatoes (group 2), alcohol and beverages (group 9), fish and shellfish (group 10), and meat and poultry groups (group 11) had high levels of intake.

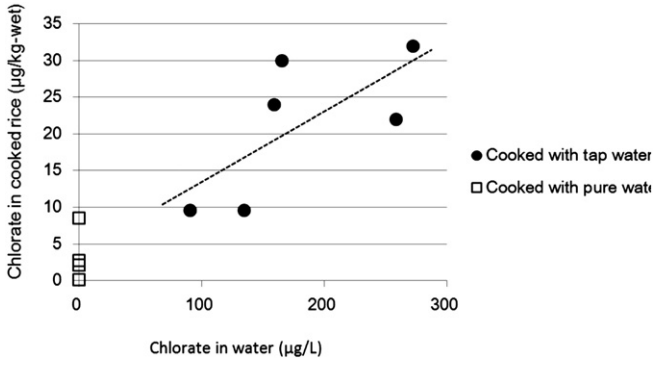


Fig. 4. Relationship of chlorate concentration in tap water to that in cooked rice. Chlorate in cooked rice had correlation with cooked with tap water ($r^2 = 0.498$, $n = 6$).

For rice, the amount of chlorate intake was higher in locations C, D, E, F, H, and J (9.6–32 μg/day) compared to other locations, which was considered to be because tap water was used to cook rice at these locations. In the cereals and potatoes group (group 2), the chlorate intake ranged from 3.2 to 19 μg/day, while in the fish and seafood group (group 10) the intake ranged from 4.1 to 81 μg/day, and that in the meat poultry group (group 11) ranged from 3.4 to 29 μg/day. These observations indicated differences in chlorate intake depending on location, but not on water used for cooking as a result of statistical analysis (Fig. 2). The sugar and confectioneries group (group 3) and legumes group (group 5) showed relatively high measured concentrations, but intake levels were not markedly high compared to other food groups when measured concentrations were multiplied by the daily intake. The preferred beverage group – alcohol and beverages (group 9) – showed relatively high intake values at all locations ranging from 5.3 to 81 μg/day.

Table 4
Daily intakes of chlorate and perchlorate from 13 food groups and water.

Food groups		All locations			Cooked with pure water			Cooked with tap water		
		Average	Min	Max	Average	Min	Max	Average	Min	Max
(a) Chlorate (μg/day)										
1	Rice	14.1	0.1	32.0	3.4	0.1	8.5	21.2	9.6	32.0
2	Cereals and potato	9.7	3.2	19.0	7.9	3.2	19.0	10.9	7.2	15.0
3	Sugar and confectionaries	1.8	0.3	4.8	1.5	0.3	3.7	2.0	0.9	4.8
4	Oil and fats	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1
5	Legumes	8.0	2.4	16.0	6.8	2.4	12.0	8.8	4.7	16.0
6	Fruits	1.7	0.2	5.0	2.0	0.2	5.0	1.6	0.2	3.4
7	Green and yellow vegetables	1.7	0.3	4.0	0.6	0.3	1.2	2.4	1.2	4.0
8	Other vegetables and seaweed	5.7	1.7	14.0	2.9	1.7	5.7	7.5	3.9	14.0
9	Alcohol and beverages	31.1	5.3	81.0	18.6	5.3	45.0	39.5	16.0	81.0
10	Fish and shell fish	22.1	4.1	81.0	6.9	4.1	12.0	32.2	5.9	81.0
11	Meat and poultry	9.8	3.4	29.0	6.6	3.5	14.0	12.0	3.4	29.0
12	Milk products	9.7	4.5	17.0	8.2	4.5	13.0	10.7	4.7	17.0
13	Seasoning	4.3	1.7	7.8	4.1	1.7	6.2	4.5	2.7	7.8
14	Water	163.6	68.0	272.0	139.2	68.0	260.0	179.8	90.4	272.0
	Total	283.2	135.2	486.2	208.6	135.2	339.2	333.0	192.8	486.2
Ratio of water (%)		*57.8*	*46.9*	*76.7*	*63.9*	*50.3*	*76.7*	*53.1*	*46.9*	*57.8*
Ratio of water and rice (%)		*62.7*	*51.9*	*76.7*	*66.1*	*56.6*	*76.7*	*59.4*	*51.9*	*66.9*
Water ratio compared to TDI (%)		*10.9*	*4.5*	*18.1*	*9.3*	*4.5*	*17.3*	*12.0*	*6.0*	*18.1*
Water and rice ratio compared to TDI (%)		*11.8*	*5.1*	*20.3*	*9.5*	*5.1*	*17.3*	*13.4*	*6.7*	*20.3*
Total ratio compared to TDI (%)		*18.9*	*9.0*	*32.4*	*13.9*	*9.0*	*22.6*	*22.2*	*12.9*	*32.4*
(b) Perchlorate (μg/day)										
1	Rice	0.2	0.0	0.7	0.2	0.0	0.5	0.2	0.0	0.7
2	Cereals and potato	1.4	0.1	4.8	1.7	0.2	4.8	1.2	0.1	2.5
3	Sugar and confectionaries	0.2	0.0	0.8	0.1	0.0	0.3	0.2	0.1	0.8
4	Oil and fats	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	Legumes	0.1	0.0	0.3	0.1	0.0	0.3	0.0	0.0	0.1
6	Fruits	0.2	0.0	1.0	0.1	0.0	0.2	0.3	0.1	1.0
7	Green and yellow vegetables	1.9	0.0	9.4	3.9	0.2	9.4	0.5	0.0	2.1
8	Other vegetables and seaweed	7.6	0.2	67.0	17.3	0.5	67.0	1.1	0.2	5.2
9	Alcohol and beverages	0.2	0.1	0.9	0.2	0.1	0.3	0.3	0.1	0.9
10	Fish and shell fish	0.4	0.1	1.9	0.2	0.1	0.2	0.6	0.1	1.9
11	Meat and poultry	0.2	0.0	0.5	0.2	0.0	0.5	0.2	0.1	0.4
12	Milk products	0.9	0.6	1.1	0.8	0.6	1.1	0.9	0.6	1.1
13	Seasoning	0.3	0.1	0.7	0.3	0.1	0.4	0.3	0.1	0.7
14	Water	0.7	0.1	4.4	0.2	0.1	0.4	1.0	0.2	4.4
	Total	14.1	2.5	83.9	25.2	2.9	83.9	6.8	2.5	19.7
Ratio of water (%)		*4.9*	*0.5*	*22.3*	*2.8*	*0.5*	*6.8*	*11.4*	*4.4*	*22.3*
Ratio of water and rice (%)		*6.2*	*1.0*	*25.9*	*4.0*	*1.0*	*7.2*	*14.1*	*6.5*	*25.9*
Water ratio compared to RfD (%)		*2.0*	*0.2*	*12.6*	*0.6*	*0.2*	*1.2*	*2.9*	*0.7*	*12.6*
Water and rice ratio compared to RfD (%)		*2.5*	*0.5*	*14.6*	*1.1*	*0.5*	*2.5*	*3.5*	*0.8*	*14.6*
Total ratio compared to RfD (%)		*40.4*	*7.2*	*239.6*	*71.9*	*8.4*	*239.6*	*19.4*	*7.2*	*56.2*

Group 9 included alcoholic beverages, bottled teas, juices, and instant coffee and the referred beverages contribute a high percentage of the daily intake. As the consumption of soft drinks has been increasing in recent years (Asami et al., 2009b), surveys of chlorate and perchlorate contents shall be continued for these soft drinks for future studies.

High concentrations of chlorate were detected in some bottled waters for various reasons; e.g., chlorinated water may be used as the raw source to produce the bottled water, or there may be certain factors that cause high concentration of chlorate in the production process, such as antiseptic washing and disinfection.

Fig. 5(a) shows the average proportions of daily chlorate intakes based on data of locations where used tap water for preparation of foods and the daily intake of tap water set as 2 L. As the contribution of water to food showed significant difference between samples cooked with tap water and those with pure water, the average proportions were calculated using data for all locations, tap water and pure water. The daily intake of chlorate ranged from 193 to 490 μg/day in these locations cooked with tap water and the percentage intake from tap water at each location ranged from 47% to 58% (Table 4). When the amount of water used to cook rice was considered as part of the intake from tap water, the value ranged from 52% to 78%. Besides the contribution of tap water was large, the sum of daily intake of chlorate ranged from 13% to 32% of the TDI proposed by JECFA, i.e. 1500 μg/day for an adult with a body weight of 50 kg, and was much lower than the TDI.

Fig. 5(b) shows the proportion of daily perchlorate intakes. The sum of daily intake of perchlorate at each location was within the range of 2.5–20 μg/day for all location, except one location, B, 84 μg/day, where other vegetables and seaweed showed high concentrations of perchlorate. The ratio of water contribution to the total intake ranged from 0.6% to 22%, while it was 0.5%, when excluding the location B. Because the location B contained extraordinary high sample, average proportion of all locations excluding B was also shown in the figure. Among all food groups, highest intake was observed for the other vegetables and seaweed group. Compared to chlorate, the daily intake of perchlorate varied markedly depending on location but there was no direct relationship with water.

As shown in Table 5, the perchlorate intake from food was specifically high at location B, and the perchlorate intake from tap water was high at location D compared to other locations. The perchlorate intake at location B was relatively high, because the food samples, especially in “other vegetables and seaweed”. As location B hasn't been known as a contaminated area, to the author's knowledge and the samples were analyzed in composite for each group, we couldn't identify in this study what and how food was contaminated. For location D, it was suspected vegetables grow in this area might have perchlorate contamination, because leafy vegetables in this

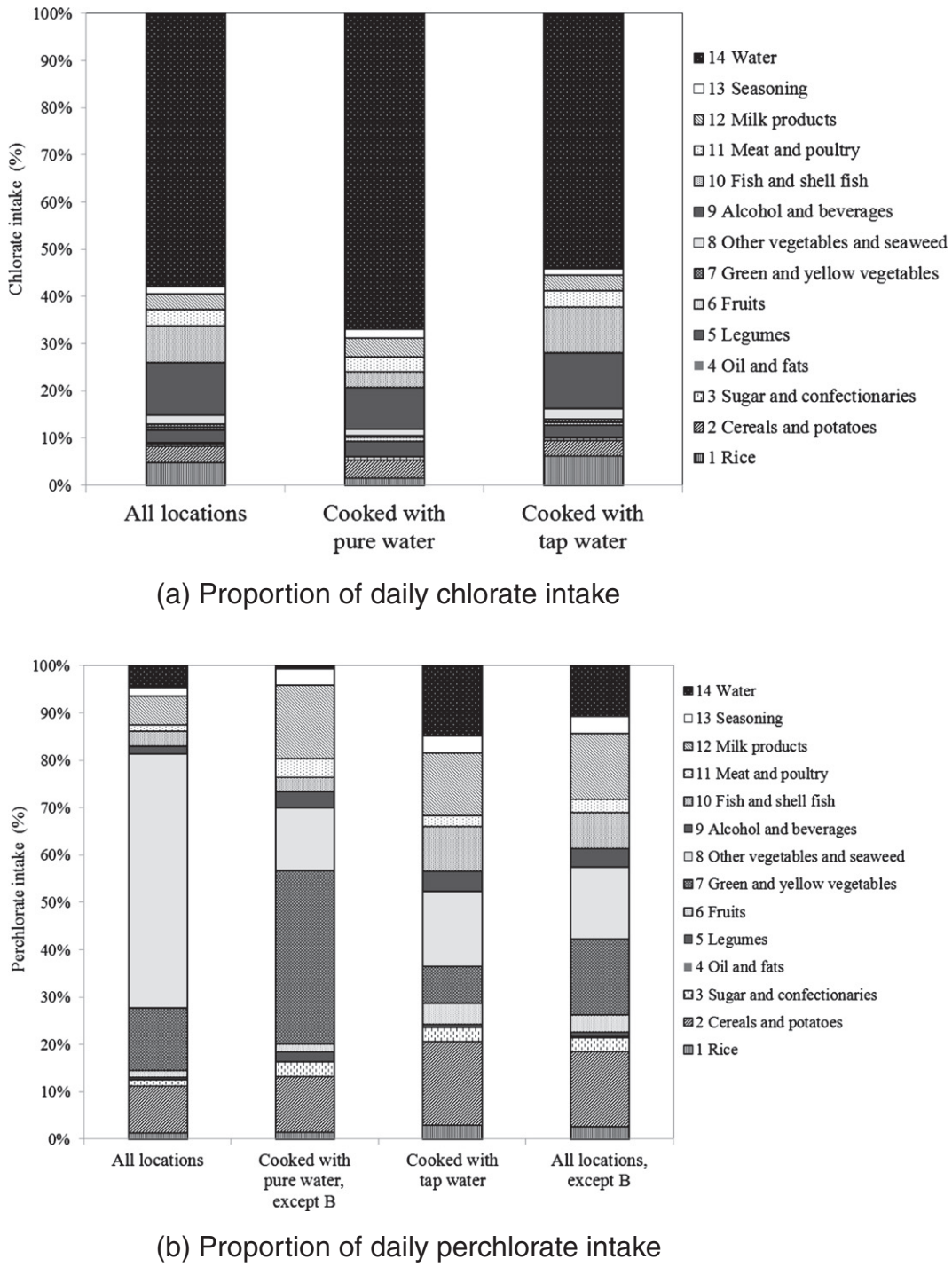


Fig. 5. Average proportion of daily chlorate (a) and perchlorate (b) intakes (%) from each food group. (a) Proportion of daily chlorate intake. (b) Proportion of daily perchlorate intake.

area were previously reported to contain relatively high concentration of perchlorate (Takatsuki et al., 2009). Among all locations, the daily intake from food was higher than that from tap water for perchlorate. At 9 of the locations, except the location B, the daily intake was less than 35 μg/day, the RfD (EPA, 2009b), i.e. for adults with a body weight of 50 kg; however, it exceeded this value by twofold at location B. Although the total perchlorate intake was 17% of the PMTDI value prepared by JECFA (2011), the total intake in this study (2.5–84 μg/day) is higher than the estimated dietary exposure mentioned in JECFA (2011), i.e. 0.7 μg/kg/day (highest) and 0.1 μg/kg/day (mean), or 35 μg/day (highest) and 5 μg/day (mean) assuming the body weight as 50 kg.

3.6. Chlorate and perchlorate concentrations in baby formula and water

Eight samples of baby formula were purchased from 4 major manufacturers for testing. Of the 8 samples, only VII was a liquid electrolyte. Measured concentrations in each sample other than the sample VII, were converted to the concentration in 1 g of dry weight of the sample powder. The measured concentration of chlorate was

Table 5
Chlorate and perchlorate daily intake from 13 food groups.

Food groups		A*	B*	C	D	E	F	G*	H	I*	J
1) Chlorate (μg/day)											
1	Rice	0.1	2.7	9.6	30.0	24.0	22.0	8.5	32.0	2.1	9.6
2	Cereals and potatoes	4.4	19.0	10.0	14.0	15.0	8.3	5.1	7.2	3.2	11.0
3	Sugar and confectionaries	0.3	1.3	1.1	4.8	1.2	0.9	0.7	1.5	3.7	2.3
4	Oil and fats	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1
5	Legumes	5.2	7.5	6.1	5.4	4.7	5.8	12.0	15.0	2.4	16.0
6	Fruits	1.2	5.0	1.7	1.0	3.4	0.2	0.2	2.2	1.5	1.0
7	Green and yellow vegetables	0.3	0.4	2.0	4.0	3.0	1.2	1.2	2.6	0.6	1.3
8	Other vegetables and seaweed	2.1	1.7	4.4	6.3	14.0	11.0	1.9	5.6	5.7	3.9
9	Alcohols and beverages	45.0	9.9	16.0	33.0	30.0	27.0	14.0	81.0	5.3	50.0
10	Fish and shell fish	4.4	4.1	15.0	5.9	36.0	81.0	12.0	47.0	7.2	8.2
11	Meat and poultry	3.5	14.0	29.0	7.8	9.4	13.0	5.4	3.4	3.6	9.2
12	Milk products	6.4	13.0	4.7	9.6	17.0	10.0	4.5	14.0	8.7	8.7
13	Seasoning	6.2	5.0	2.8	4.7	3.5	7.8	1.7	2.7	3.6	5.2
14	Water	2260.0	117	90.4	1165.4	1159.0	2258.0	68.0	272.0	111.2	134.2
	Total	3339.2	2201.3	1192.8	2292.0	3320.2	4446.2	1135.2	486.2	158.8	260.6
2) Perchlorate (μg/day)											
1	Rice	0.064	0.45	0.17	0.70	0.16	0.075	0.16	0.09	0.018	0.036
2	Cereals and potatoes	0.41	4.8	1.3	1.9	2.5	0.46	1.3	0.07	0.24	0.93
3	Sugar and confectionaries	0.039	0.080	0.067	0.17	0.83	0.067	0.32	0.06	0.14	0.05
4	Oil and fats	0.002	0.003	0.002	0.001	0.004	0.001	0.003	0.0009	0.002	0.0027
5	Legumes	0.045	0.080	0.04	0.066	0.047	0.035	0.28	0.04	0.043	0.048
6	Fruits	0.17	0.057	1.0	0.33	0.084	0.22	0.05	0.06	0.043	0.067
7	Green and yellow vegetables	0.17	9.4	0.58	2.1	0.19	0.13	5.1	0.15	0.79	0.036
8	Other vegetables and seaweed	0.51	67	0.33	5.2	0.26	0.29	0.91	0.19	0.78	0.16
9	Alcohols and beverages	0.13	0.15	0.12	0.92	0.069	0.21	0.17	0.37	0.25	0.1
10	Fish and shell fish	0.14	0.11	0.26	1.9	0.21	0.14	0.24	0.21	0.11	1.1
11	Meat and poultry	0.45	0.13	0.16	0.37	0.063	0.13	0.17	0.1	0.048	0.15
12	Milk products	0.56	0.76	0.83	0.96	1.0	0.83	1.1	0.63	0.9	1.1
13	Seasoning	0.14	0.42	0.10	0.67	0.29	0.13	0.23	0.08	0.22	0.23
14	Water	0.10	0.42	0.32	4.40	0.26	0.36	0.06	0.46	0.26	0.24
	Total	2.9	83.9	5.3	19.7	6.0	3.1	10.1	2.5	3.8	4.2

* Pure water was used for food preparation all of which contained no chlorate (<0.05 μg/L) or perchlorate (<0.01 μg/L).

highest in VIII (1400 ng/g dry weight) followed by VI (810 ng/g dry weight). The daily intake was calculated by multiplying the measured concentration by the amount of formula per feeding, and the daily intake in 1 L of formula was calculated. The daily intake of chlorate was within the range of 8.4–196 μg/day for each sample. The measured concentration of perchlorate was high in I (22 ng/g dry weight) followed by II and VIII (each 10 ng/g dry weight). The daily intake of perchlorate was calculated in the same way as for chlorate, and ranged from 0.02 to 2.3 μg/day.

Using the measured concentration of TDS sample tap water to make the formula, the amounts of chlorate and perchlorate intake were as shown in Tables 6 and 7. The average daily intake of chlorate was 147 (42–332) μg/day for an ingestion volume of 1 L/day if prepared with tap water. In comparison to the TDI value of 150 μg/day for infants and toddlers calculated weighing 5 kg, some samples had higher daily intake levels.

The average daily intake of perchlorate was 1.1 μg/day ranged from 0.05 to 4.5 μg/day also for an ingestion volume of 1 L/day if prepared with tap water. There was no correlation between samples with high levels of chlorate intake and those with high perchlorate intake. The amounts were almost lower compared to the RfD value of 3.5 μg/day for infants and toddlers weighing 5 kg, but if tap water from location D with high intake was used to prepare the formula, total intake exceeded the RfD value (some samples were for toddlers weighing over 8.5 kg, and the daily intake also changes as infants grow), although it is sufficiently below PMTDI.

Using the combination of the mean, minimum and maximum concentration of chlorate and perchlorate in tap water examined in this study, the contribution of water for baby intake were calculated as 56% (15–94) for chlorate and 31% (1.3–99) for perchlorate. The range greatly depends upon the concentration of the sample baby formula and the concentration of water. It is difficult to conclude the contribution of water, because the number of sample baby formula and water was limited in this study, but the intake greatly depends on concentration of chlorate and perchlorate in water.

Table 6
Chlorate and perchlorate in baby formula.

		Intake (μg/1 L)	
		Chlorate	Perchlorate
I	WA	33.6	2.3
II	WA	15.6	0.98
III	MO	50.7	0.57
IV	MO	88.2	0.42
V	ME	63.8	0.04
VI	BS (liquid)	113.4	0.60
VII	ME	8.4	0.02
VIII	ME	196	1.05
	Av.	71.2	0.75

4. Discussion

The present study was performed using samples from the total diet study to evaluate the concentrations of chlorate and perchlorate

Table 7
Chlorate and perchlorate in baby formula.

	Chlorate intake (μg/day as 1 L)			Perchlorate intake (μg/day as 1 L)		
	Av.	Min.	Max.	Av.	Min.	Max.
Baby formula*	65	8	196	0.77	0.02	2.3
Water	82	34	136	0.34	0.03	2.2
Total	147	42	332	1.11	0.05	4.5

* Average is calculated excluding sample VI.

in food and tap water from 10 locations and calculate the total levels of intake. In most cases, the concentrations of chlorate and perchlorate from the various food groups were higher than the lower limit of quantification.

For the chlorate ion, the percentage contribution of tap water to total intake was as high as 47%–77%, and the level of intake in some food samples probably included chlorate originating from tap water. For example, chlorate in the tap water used for boiling and simmering of rice, potatoes, and noodles may have affected the amount of chlorate in food. The sum of the intakes from food and tap water for adults was less than approximately 32% of TDI.

A survey of the total intake of perchlorate and iodine was performed by the FDA in the USA, and the presence of perchlorate was confirmed in a wide variety of foods, as also demonstrated in the present intake survey (Murray et al., 2008). In the USA, the main sources of perchlorate intake were milk and dairy products, as well as vegetables. The intake from vegetables was relatively high in both countries. The survey in the USA classified the subjects into 14 categories according to age group and gender, and the amounts of intake for each category were compared. The intake of perchlorate for a 2-year-old was approximately 50% of the RfD value, and it seemed that younger age groups had higher intake ratios. As the study in the USA indicated that the average concentration of perchlorate in breast milk is 5 times higher than that in cow's milk (Kirk et al., 2005), it may be necessary to investigate the intake of perchlorate from breast milk in future studies.

In the present study, the measured concentration of perchlorate in dairy products was relatively high; however, when converted to the amount of intake, the levels were not high. Vegetables, seaweed, cereals and potatoes showed specifically high perchlorate levels at certain locations. Location D, which had high levels of perchlorate intake from tap water, had relatively high total intake corresponding to 56% of the RfD, and this was considerably higher than at the other locations. There was no obvious relationship whether tap water was used to prepare food, but further studies are required regarding the concentrations in both tap water and food from the viewpoint of total intake.

The perchlorate intake from “other vegetables and seaweed” at location B was relatively high. Because the food samples were analyzed in composite for each group, this study was not able to further reveal which individual food(s) were actually of high perchlorate concentration. But it should be noted seaweed, which is generally known to contain high perchlorate and iodine (Martinelango et al., 2006, for example), was included in location B and other locations. Japanese diet normally includes a high proportion of seafood especially seaweeds, such as Wakame (*Undaria pinnatifida*). Although it is known that perchlorate interferes with iodine uptake, adverse health effect from iodine deficiency might not be occurred if iodine intake from foods is high and if perchlorate intake is relatively low. Because iodine uptake from Japanese normal diet is relatively higher than other countries (Kikuchi et al., 2008), so evaluation of both perchlorate and iodine intake should be conducted in future when considering perchlorate and iodine uptake.

To our knowledge, no detailed data are available regarding water consumption for drinking, cooking use, both only boiling and making soup, ice, and other uses for ingestion. Therefore, we are currently engaged in a national survey of water consumption.

The results of the present study revealed the total intake, as well as the percentage intake from water, of chlorate and perchlorate in Japan. With the studied areas being selected from across Japan, the percentage contribution of chlorate and perchlorate from water to the total amount of intake was first proved. The contribution of water used for preparation of food was also found as an important factor in the present study. The contribution of total daily intake of chlorate originated from water including water used for preparation of food in this study was lower than the current TDI allocation of chlorate to water (i.e., 80%) and also the total intake of chlorate was much the less than the TDI. The contribution of perchlorate and total perchlorate intake ranged widely, therefore it needs further studies when considering the current allocation (i.e., 10%).

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