Occurrence of Chlorate and Perchlorate in Bottled Beverages in Japan

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The concentrations of chlorate and perchlorate were examined by ion chromatography-tandem mass spectrometry (IC-MS-MS) in 106 bottled beverages purchased or obtained mainly in the Tokyo area to estimate exposure to these chemicals attributable to bottled beverages. The bottled beverages were classified into 5 categories: water from the water supply (n = 5), natural water (n = 49), bottled water (n = 10), tea (n = 25), and soft drinks (n = 17). Chlorate was detected in 85 bottled beverages (highest concentration, 700 μg/l), including all of the samples of bottled water from the water supply at levels ranging from 25 to 120 μg/l. Perchlorate was detected above the minimum reporting limit (*i.e.*, 0.05 μg/l) from 62 bottled beverages, with the highest concentration of 0.92 μg/l. As the average consumption of bottled beverages calculated from market statistics is approximately 400 ml/day per person, it seems important to take the amounts of chlorate and perchlorate ingested from bottled beverages into consideration for estimation of total intake of these chemicals.

Key words —— bottled beverages, chlorate, perchlorate, drinking water

INTRODUCTION

Chlorate, a known byproduct of chlorine dioxide disinfection, was introduced into the drinking water standards and set at a maximum level of 600 μg/l in April 2008 because of its oxidative effects on red blood cells in humans.[1] A national survey in 2005 indicated that chlorate concentrations exceeded 600 μg/l in 14 of 598 finished waters after treatment processing. In Japan, the principal criteria for drinking water standards are detection of compounds in finished water at concentrations close to or above one-tenth of the respective standard or guideline.

The tolerable daily intake (TDI) for chlorate issued by the Food Safety Committee of the Cabinet Office, Japan, is 30 μg/kg per day, calculated from the no-observed-adverse-effect level (NOAEL) of 30 mg/kg per day divided by an uncertainty factor of 1000. The World Health Organization (WHO) also set a guidelines stipulating a maximum concentration of 700 μg/l.[2,3]

Perchlorate has only recently been addressed as a contaminant of concern in drinking water. It has been used as a chemical propellant in rocket fuels and as an oxidizing agent in many products. The National Research Council (NRC) showed that perchlorate interferes with iodine uptake in the thyroid gland.[4] In 2005, the United States Environmental Protection Agency (US EPA) established an official reference dose (RfD) of 0.7 μg/kg per day of perchlorate and specified a drinking water equivalent level (DWEL) of 24.5 μg/l.[5] More recently, the US EPA set an interim health advisory level of perchlorate in drinking water of 15 μg/l.[6]

Considerably high concentrations of chlorate and lower concentrations of perchlorate have been found as impurities in sodium hypochlorite solution, which is the most common disinfectant agent used in 85% of water supply systems in Japan.[7] Chlorate and perchlorate have also been detected in Japanese aquatic environments, especially in the Tone River basin, which is one of the largest water sources for drinking water supply in the Tokyo Metropolitan Area.[8] The maximum concentrations of chlorate and perchlorate in the tributary directly downstream of the outlet of industrial effluents in the Tone River basin were reported to be 9000 μg/l and 3900 μg/l, respectively. In the previous study,[8] there were two main sources of chlorate and perchlorate discharge: a factory involved in the production of chlorate and perchlorate, and a factory using an electrolysis pro-

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cess that unintentionally produced perchlorate.

During the survey of chlorate and perchlorate in water before and after the drinking water treatment process in the Tone River basin, the highest concentration of chlorate in raw water was 78 μg/l and that of perchlorate was 40 μg/l.[9] As chlorate and perchlorate have hydrophilic properties, they could not be removed during the treatment process.

To date, there have been no reports of the occurrence of chlorate in foods. Most previous reports of the occurrence of perchlorate have been in the U.S.A. One study identified perchlorate in foods and beverages in many countries.[10] In Japanese samples, perchlorate contents were 0.103–14.85 μg/l in wine, beer, and sake (rice wine). Another study demonstrated a mean perchlorate concentration of 9.39 μg/l in Japanese milk.[11]

So far, we have collected data on concentrations of chlorate and perchlorate in drinking water from the water supply as described above. However, data on chlorate and perchlorate concentrations in bottled beverages are very limited. As the average consumption of bottled beverages is increasing, chlorate and perchlorate in bottled beverages were examined to compare their levels with those in the water supply system, and further to estimate chlorate and perchlorate exposure attributable to bottled beverages.

MATERIALS AND METHODS

From September to October of 2007, 106 bottles of commercial or distributed bottled beverages were purchased or obtained mainly in the Tokyo area. The bottled beverages were classified into 5 categories according to their labels: water from the water supply (n = 5), natural water (n = 49), bottled water (n = 10), tea (n = 25), and soft drinks including cider and juice (n = 17). Water sources of the water from water supply, natural and bottled waters were nationwide in Japan and some of them were imported from foreign countries. The number of the producing companies was 12 for tea (abbreviated as A, C, E, H, I, J, K, M, O, P, R, and S) and 8 for soft drinks (abbreviated as A, C, D, I, K, P, R and S). Natural water actually included 3 bottles of water that had been treated with chlorine and that should have been labeled as "water from the water supply" or "bottled water."

Pretreatment was different in each categories. For water from water supply, natural water and bottled water, dilution rate was 5 for chlorate analysis and no dilution was made for perchlorate analysis. For tea samples, the same rate of dilution was made for each analysis after filtration with 0.45 μm polytetrafluoroethylene (PTFE; Whatman) filter. For soft drinks, dilution rate was 20 for chlorate analysis and no dilution was made for perchlorate analysis after filtration with 0.2 μm or 0.45 μm PTFE filter. For some samples of natural water and bottled water in which chlorate was interfered by coexisting salts, such as chloride and sulfate, OnGuard II Ba/Ag/H cartridges (Dionex, Sunnyvale, CA) were used as pretreatment cartridges for chlorate analysis without dilution. Chlorate and perchlorate have been stable at least in the confirmed conditions with or without hypochlorite at the concentration below several mg/l. Using this method, alcohols could not be analyzed because the peaks were deformed due to organic acids contained. Therefore alcohols and "ionic" beverages which may contain high concentration of sugars were not included in this study.

Chlorate and perchlorate concentrations were analyzed by ion chromatography-tandem mass spectrometry (IC/MS/MS) (Dionex ICS-2000 and API 3200QTrap; Applied Biosystems, Foster City, CA) as described elsewhere.[8] As an internal standard for perchlorate, ^{18}O-enriched $NaClO_4$ (Cambridge Isotope Laboratories, Andover, MA) was added to the samples just prior to analysis.

Calibration standards were prepared by diluting 1000 mg/l certified standard solutions of chlorate (Kanto Chemical, Tokyo, Japan) and perchlorate (GFS Chemicals, Powell, OH) into ultrapure water purified with a Gradient A10 water purification system (Millipore, Bedford, MA). Separation was performed using an IC (ICS-2000; Dionex) with an eluent generator (EG50; Dionex), a guard column (IonPac AG20 column 2 × 50 mm; Dionex), a separation column (IonPac AS20, 2 × 250 mm; Dionex), and a suppressor (ASRS Ultra II, 2 mm; Dionex). The eluent was potassium hydroxide (KOH) at a flow rate of 0.25 ml/min. The injection volume was 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. Detection was performed by MS/MS (API 3200QTrap; Applied Biosystems) in the turbo-ion-spray ionization mode. Multiple reaction monitoring (MRM) transitions were m/z 85–66 for chlorate, m/z 99–83 (quantification) and

m/z 101–85 (confirmation) for perchlorate, and m/z 107–89 for ^{18}O-enriched perchlorate. The minimum reporting/limits (MRLs) for chlorate were 0.05 µg/l for water from the water supply, natural water, and bottled water. As the dilution rate differed, the MRLs were 0.25 µg/l for bottled tea and 1.0 µg/l for bottled soft drinks. The MRLs for perchlorate were all set at 0.05 µg/l. Each MRL was the minimum concentration for each calibration curve. For each compound, the limits of quantification calculated as $10\sigma'/a$ was lower than MRL [σ': standard deviation of response at 0.05 µg/l (the number of repetitions was five); a: slope of the calibration curve]. The maximum concentration of the calibration curve for each compound was 10 µg/l, and therefore the samples were diluted before analysis if necessary.

RESULTS

Table 1 shows the chlorate concentrations of 106 bottled beverage samples. Chlorate was detected in all of the samples of bottled water from the water supply at levels ranging from 25 to 120 µg/l. The concentration exceeded 10 µg/l in 3 natural water samples. A hearing by phone was conducted for the producing companies of the 3 natural waters, and consequently 2 bottles of the "natural water" were found to have originated from supplied water and the other employed a chlorination process, which should not have been labeled as "natural water."

Among the bottled water samples, the average concentration of chlorate was 14 µg/l, and the highest concentration was 100 µg/l. Among the bottled tea samples, the average concentration of chlorate was 30 µg/l and the highest concentration of chlorate was 700 µg/l, which was produced by company C as shown. Among the soft drinks produced by 8 different companies, chlorate was found in all 6 soft drinks produced by company C and 2 of 3 soft drinks produced by company A, at the same levels as water from the water supply, as shown in Fig. 1. The hearing by phone for company C revealed that the factory that produced the beverage containing the highest concentration of chlorate, 700 µg/l, used a mixture of water from underground and water supply followed by a treatment process in the factory. In addition, it is possible that they used chlorinating substances for washing the bottles although chlorate content in chlorinating substances other than sodium hypochlorite solution is unknown.[12] Although not clear for other factories, it was assumed that they employed original chlorination processes to treat the water. In this regard, the concentration of chlorate indicated that chlorination was employed in the process, because there is little chlorate contamination in natural water.

The concentrations of perchlorate in the bottled beverages are shown in Table 2. In all beverages, perchlorate concentration did not exceed 1 µg/l. Our previous study indicated that concentrations of perchlorate in the water supply are markedly dependent on the area of source water. However, neither clear differences nor area dependency of perchlorate concentration were observed in this study.

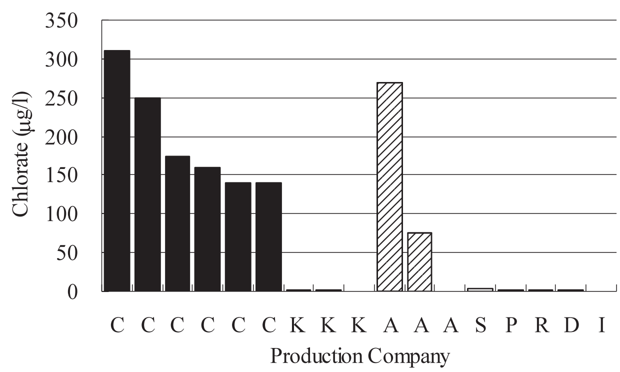

Fig. 1. Chlorate Concentrations in 17 Soft Drinks According to the Companies Responsible for Their Production

Table 1. Chlorate in Bottled Beverages (µg/l)

	n	detected	MRL[a]	max	ave[b]	< 10	< 100	< 600	≥ 600
Water supply	5	5	0.05	120	51	0	4	1	0
Natural[c]	49	34	0.05	100	4.5	46	2	1	0
Bottled water	10	9	0.05	110	14	8	1	1	0
Tea	25	23	0.25	700	30	23	1	0	1
Soft drink	17	14	1.0	310	91	9	1	7	0

a) MRL: Minimum Reporting/limit described in the text. *b*) Arithmetic mean. *c*) "Natural water" included 3 bottles of water that had been treated with chlorine and should have been labeled water from the "water supply."

Table 2. Perchlorate in Bottled Beverages (μg/l)

	n	detected	MRL[a]	max	ave[b]	< 0.1	< 0.5	< 1.0	≥ 1.0
Water supply	5	3	0.1	0.92	0.32	2	2	1	0
Natural[c]	49	29	0.1	0.57	0.09	35	12	2	0
Bottled water	10	5	0.1	0.53	0.13	7	2	1	0
Tea	25	19	0.1	0.62	0.15	11	13	1	0
Soft drink	17	7	0.1	0.18	0.04	15	2	0	0

a) MRL: Minimum Reporting/limit described in the text. *b*) Arithmetic mean. *c*) "Natural water" included 3 bottles of water that had been treated with chlorine and should have been labeled water from the "water supply."

DISCUSSION

For chlorate, bottled water from the water supply, which is usually subjected to a sodium hypochlorite treatment process, showed higher concentrations of chlorate. However, some beverages in other categories showed high concentrations of chlorate, and this was considered to indicate a history of chlorination process.

There are only limited data regarding real consumption of beverages for Japanese, which may depend on personal lifestyle, climate and other factors. In a survey of total beverage consumption in 2000 in Tokyo,[13] total beverage consumption was approximately 1.5 l/person per day in summer and 1.0 l/person per day in winter for all age distribution classes. Almost one third of total beverage consumption consisted of bottled natural water or soft drinks. The remaining portion was comprised of tea or coffee using water from the water supply, direct intake of supplied water, or that treated by home water treatment devices. According to the statistics published by the Japan Beverage Industry Association, beverage consumption was 19,000,000 kl in 2007, which is equivalent to 146 l/person per year or 400 ml/person per day.[14] Especially, the average mineral water consumption showed a yearly increase to 19.6 l/year or 53.7 ml/person per day.[15] Thus, an average person may consume 50–500 ml of bottled beverages per day. Assuming the maximum concentration of chlorate and the estimated consumption to be 500 ml, total daily intake of chlorate from one type of bottled tea was 175 μg/person per day; this is comparable to the hypothetical maximum daily intake of 2 l of supplied water containing 100 μg/l of chlorate, which is the one sixth of the drinking water standard, while this figure 1, 2 l, is assumed to include partial consumption *via* preparation of foods and beverages. This portion may increase due to personal preference and application of water, especially in cooking.

Normally drinking water from the water supply has been considered to be a main exposure pathway for chlorate due to the use sodium hypochlorite solution in disinfection processes and it is occasionally an important exposure pathway for perchlorate due to the contamination of the water sources. However, it is becoming important to collect the data in bottled beverages and their consumption because the amount of bottled beverages is increasing and because chlorination is applied for the water treatment at some factories of the beverage producing companies. It therefore seems important to take the chlorate and perchlorate intake from bottled beverages including tea, natural and bottled water into consideration for total intake of these chemicals.

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