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Monitoring of perchlorate in diverse foods and its estimated dietary exposure for Korea populations

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HIGHLIGHTS

- Total 663 samples belonging to 39 kinds of food groups were analyzed for perchlorate.
- Perchlorate was detected in 411 samples with over 61% detection frequencies.
- The estimated dietary exposure to perchlorate for Korean is lower than the RfD.

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ABSTRACT

The perchlorate concentrations in various Korean food samples were monitored, and 663 samples belonging to 39 kinds of food were analyzed. The analysis results revealed that dairy products contain the highest average concentration of 6.34 μg/kg and high detection frequency of over 85%. Fruit and vegetables showed the next highest perchlorate concentration with an average of 6.17 μg/kg. Especially, with its average concentration of 39.9 μg/kg, spinach showed the highest perchlorate level among all target food samples studied. Tomato was followed by spinach, which showed a high perchlorate average concentration of 19.8 μg/kg, and over 7 μg/kg was detected in ham and sausage (avg. 7.31 μg/kg) and in instant noodles (avg. 7.58 μg/kg). Less than 2 μg/kg was detected in fishes, meats and beverages. The exposure dose of perchlorate in Korean by food intake was calculated on the basis of the analyzed perchlorate levels in this study. The daily perchlorate dose to which Korean adults are exposed is 0.04 μg/kg bw/day, which is lower than the RfD (0.7 μg/kg bw/day) value suggested by US NAS. This result indicates that Korean people's current exposure to perchlorate from domestic food consumption is evaluated as safe.

1. Introduction

Perchlorate is regarded as a new emerging pollutant and detected everywhere in environment [1–3]. It is well known that perchlorate competes with iodine ions inside the human body and interrupt the hormonal production of thyroid gland [4]. This disorder of the thyroid function may lead to a metabolic disorder in adults and an anomalous growth in children and fetuses [5]. Perchlorate is detected everywhere because of its diverse usage and inert property. Many researchers have reported that perchlorate is detected in soil [6,7], in water [6,7], and even in human urine [8]. Moreover, perchlorate has also been found in food and it is suggested that the main pathway of perchlorate is ingestion [5,9–11].

Since 2003, the perchlorate concentration of food samples has been reported, and most studies focused on investigating the levels of perchlorate in dairy samples. The first study about perchlorate in milk samples was reported by Kirk et al. [12], and they extended the perchlorate monitoring to various dairy samples and human milk. After these initial studies, many advanced studies about perchlorate levels in food samples have been reported. Krynitsky et al. [13] calculated perchlorate in lettuce, cantaloupe, bottled water, and milk (<1.0–53.8 ppb, μg/kg for lettuce and cantaloupe, μg/L for bottled water and milk), and Sanchez et al. [14] analyzed 21 kinds of leafy vegetables (18.0–628 μg/kg). Wang et al. [15] have estimated the dietary exposure of Canadians to perchlorate through the consumption of 10 kinds of samples belonging to fruits and vegetables. Recently, except milk and vegetables, different foods like rice, beverage bottled water, dietary supplements and flavor enhancing ingredients were monitored to find the perchlorate levels in these samples [16–20]. In 2004, US FDA (United States Food and Drug Administration) conducted a nationwide perchlorate survey, monitoring 775 samples consisting of 27 food groups and

Abbreviations: avg., average; DWEL, drinking water equivalent level; EPA, Environmental Protection Agency; FDA, Food and Drug Administration; HPLC, high-performance liquid chromatography; LC–MS/MS, liquid chromatography tandem quadrupole mass spectrometry; LOD, limit of detection; LOQ, limit of quantitation; MRM, multiple reaction monitoring; NAS, National Academy of Sciences; ND, not detected; PTFE, polytetrafluoroethylene; RfD, reference dose; RSD, relative standard deviation; SPE, solid phase extraction; US, United States.

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calculating the perchlorate dietary exposure for general American population. The estimated perchlorate exposure by foods intake was 0.053 μg/kg bw/day, which was below the RfD (reference dose) value (0.7 μg/kg bw/day) of perchlorate proposed by NAS (National Academy of Sciences), but several foods samples were contaminated with high level of perchlorate (e.g. greens: 92.4 μg/kg and cantaloupes: 28.6 μg/kg, etc.), indicating a high potential risk of perchlorate exposure. Since most previous studies on perchlorate in food samples have focused on dairy and vegetable samples except for the US FDA survey, estimation of human exposure to perchlorate through food intake is highly limited.

In June 2007, a dangerously high 34.1 μg/L of perchlorate was detected in tap water in Korea, which exceeded the US EPA (Environmental Protection Agency) DWEL (drinking water equivalent level, 24.5 μg/L), and perchlorate in the environment has become a social issue in Korea [21]. Korea's Ministry of Environment added perchlorate on the water pollutants list, and perchlorate drinking water advisory criteria was set to 15 μg/L in June 2010. However, an extremely high 411 μg/L of perchlorate is still being detected in the treated wastewater flowing into the Nakdong River [22], and papers by Korean researchers continue to report perchlorate detection in the water system [23–25]. Since perchlorate can reach ground water, agricultural products as well as livestock products, use of soil or irrigation water contaminated with perchlorate can pollute agricultural and livestock products which are hazardous to humans. However, no research has been reported on the measurement of human exposure to perchlorate in Korea despite the urgent need. Thus, we conducted a nationwide monitoring of perchlorate levels in 663 food samples to measure the level of perchlorate to which Koreans are exposed.

2. Materials and methods

2.1. Sample collection

A total of 663 samples belonging to 39 kinds different food groups were collected from Korean markets that are located in Busan, the second largest city of Korea. The selected food groups were staple foods of Korean population, and all samples were randomly purchased from supermarkets from May to September, 2010. Specifically, 5 species of fish samples, 5 kinds of meats, 16 kinds of fruits and vegetables, 5 kinds of beverages, 3 kinds of dairy products, and 5 kinds of processed food products were selected. All the food samples were originated from the different regions of Korea and the processed and packaged foods samples such as milk, ham and yogurt, etc. manufactured by top five food production companies by sales in Korea were collected. The detailed information of the samples is listed in Table 1. All the collected samples were stored at refrigerator, and edible parts of each food were used for test portion and analyzed within 14 days.

2.2. Materials

A certified perchlorate standard solution was purchased from AccuStandard (New Haven, CT, USA). The $^{18}O_4$-labeled perchlorate as internal standard (IS) was obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). HPLC grade of acetonitrile and reagent water were purchased from J.T. Baker (Phillipsburg, NJ), 40% methylamine solution from Yakuri Pure Chemicals Co, Ltd. (Japan), and acetic acid from Waco Pure Chemical Industries, Ltd. (Japan). For clean-up procedure, Supelclean™ Envi™-Carb (500 mg, 6 cc) was purchased from Supelco (Bellefonte, PA, USA).

2.3. Sample preparation

The pretreatment method of perchlorate in food samples was conducted by modified US FDA and EPA methods [26,27]. The samples were treated differently according to its water contents, and four different pretreatment methods were applied to the samples of four categories of foods: (1) fruits and vegetables that have high moisture; (2) fish, meat and processed products that have low moisture; (3) dairy products (including steamed rice and tofu); (4) beverage and alcohol samples

Table 1
Target food samples and theirs levels in samples (unit for alcohol and beverage, μg/L; for other samples, μg/kg).

Commodity	n[b]	Mean	Median	Min[c]	Max	Commodity	n[b]	Mean	Median	Min[c]	Max
Fruit and vegetables		6.17				Meat and egg		0.98			
Apple[a]	14/25	1.22	1.06	<LOQ	6.81	Beef[a]	3/20	0.62	2.07	<LOD	2.87
Citrus[a]	4/20	1.55	3.06	N.D.	9.41	Pork[a]	2/20	0.32	1.62	<LOD	2.11
Watermelon	20/20	4.42	3.41	1.34	10.40	Chicken[a]	3/20	0.77	3.35	<LOD	4.12
Pear	16/20	1.72	1.04	<LOQ	8.03	Duck	5/20	0.69	1.82	<LOD	5.08
Tomato[a]	16/20	19.80	4.96	<LOQ	116.00	Egg[a]	17/20	2.50	2.48	<LOQ	6.54
Chinese cabbage[a]	20/20	4.08	2.73	1.22	16.80	Alcohol and beverage		1.59			
Onion[a]	18/20	1.01	0.90	<LOQ	2.84	Soju[a]	9/10	1.38	0.72	N.D.	4.53
Radish[a]	20/20	4.20	2.33	0.89	22.70	Beer[a]	10/10	1.04	0.97	0.46	2.29
Potato[a]	10/20	2.61	2.55	<LOQ	23.40	Soda[a]	17/20	1.28	1.03	<LOD	6.28
Spinach[a]	25/25	39.90	17.80	1.47	190.00	Fruit drink[a]	19/20	4.15	2.08	N.D.	35.90
Grape	5/5	0.79	0.83	0.60	0.95	Bottled water	10/10	0.11	0.07	0.03	0.24
Cabbage	0/5	0.49	0.75	N.D.	<LOQ	Dairy		6.34			
Bean sprouts[a]	2/5	0.56	0.35	N.D.	1.12	Milk[a]	23/23	5.63	6.49	1.02	11.40
Cucumber[a]	5/5	4.12	1.70	1.05	12.62	Yogurt[a]	17/20	3.42	3.86	<LOD	7.85
Carrot	4/5	0.63	0.59	<LOQ	1.04	Baby formula	5/5	9.98	6.78	5.21	22.56
Green pumpkin[a]	2/5	11.60	3.93	<LOQ	37.60	Processed product		3.65			
Fishes and shellfishes		0.95				Steamed rice[a]	20/20	1.18	1.17	0.64	1.61
Mackerel	7/20	0.87	2.43	<LOD	3.37	Tofu[a]	7/20	1.14	2.59	<LOD	5.54
Squid	5/20	0.33	0.92	<LOD	1.76	Instant noodles[a]	20/20	7.58	4.25	2.29	24.20
Hair tail	1/20	0.26	1.40	<LOD	1.40	Ham and sausage	20/20	7.31	3.89	1.83	39.00
Yellow corvina	5/20	1.83	3.49	<LOD	18.10	Snack	2/25	1.02	3.91	<LOD	3.94
Flounder	3/20	1.46	2.03	N.D.	21.50						

[a] Korean 30 favorite food (Report of In-Depth Analysis on the 3rd Korea Health and Nutrition Examination Survey, 2008).
[b] n: detection frequency (detected samples no./all samples no.).
[c] N.D.: not detected; <LOD: below LOD (limit of detection); <LOQ: below LOQ (limit of quantitation).