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ARTICLE

Estimated Dietary Exposure of Canadians to Perchlorate through the Consumption of Fruits and Vegetables Available in Ottawa Markets

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There has been increasing concern over the contamination of drinking water and food with perchlorate. Studies have reported perchlorate in a variety of foods, including lettuce, milk, fruits, and juices. In this study, 150 food samples were analyzed by ion chromatography tandem mass spectrometry (IC-MS/MS) to determine the concentrations of perchlorate in imported and domestic fruits and vegetables available from retail outlets in Ottawa, Canada. Perchlorate was found in most of the tested food types with concentrations appearing to vary by commodity and country of origin. Levels ranged from nondetectable to 536 μg/kg, with Guatemalan cantaloupes (156 ± 232 μg/kg), United States spinach (133 ± 24.9 μg/kg), Chilean green grapes (45.5 ± 13.3 μg/kg), and United States Romaine lettuce (29.1 ± 10.5 μg/kg) having the highest concentrations. Dietary exposure to perchlorate from analyzed fruits and vegetables was estimated to be approximately 36.6 and 41.1 ng/kg bw/day for toddlers (1−4 yrs) and children (5−11yrs), respectively.

KEYWORDS: Perchlorate; fruit; vegetable; dietary exposure; IC-MS/MS

INTRODUCTION

Perchlorate occurs naturally in the environment (*1*), primarily near potash deposits and in arid regions (*2*). It can also originate from the use of perchlorate salts in military and industrial products such as solid rocket fuels, munitions, explosives and fireworks, road flares, air bag inflation systems, and some fertilizers (*3*−*5*). In the human body, the perchlorate anion can inhibit uptake of iodide, an essential trace element, at the sodium iodide symporter (NIS) by the thyroid gland (*6*, *7*). Sustained inhibition of iodide uptake can impair thyroid function by reducing the amount of iodide stored in the thyroid and, consequently, that which is available for production of the thyroid hormones triodithyronine (T_3) and thyroxine (T_4), leading to hypothyroidism (*8*). Thyroid hormones are responsible for regulating metabolic and developmental functions and are critical for normal fetal and neonatal development. Consequently, pregnant women and their fetuses, neonates, and people with iodine deficiency or with thyroid dysfunction are particularly at risk to perchlorate exposure.

Perchlorate contamination emerged as a public health concern in the late 1990s and has since been detected in various water supplies throughout the United States (*9*, *10*). This initiated the conduct of scientific studies and guideline development related to perchlorate in drinking water around the world. Currently, no enforceable national drinking water standards exist for perchlorate in the United States; however, various states have implemented respective guidelines or goals for perchlorate in drinking water ranging from 2 to 18 ng/g (*11*). In Canada, preliminary analysis of groundwater and surface water samples showed nondetectable or very low concentrations of perchlorate (*12*), indicating that perchlorate contamination of drinking water supplies is not expected to be a significant issue. Nevertheless, exposure to significantly high concentrations of perchlorate from sources, such as food, has the potential to cause adverse health effects. Several recent studies have shown that plant species are able to absorb perchlorate from soil and irrigation water, where elevated levels of perchlorate have been found in food crops (*13*, *14*), including lettuce (*15*), fish (*16*), seaweed (*17*, *18*), and some beverages (*19*). Studies from different regions of the United States (*20*), Chile (*21*), Japan (*22*), and China (*23*) also reported detectable levels of perchlorate in milk samples.

A number of epidemiological and clinical studies have attempted to determine the relationship between oral exposure to perchlorate and adverse thyroid related effects in humans (*24*−*26*). An industry sponsored study of perchlorate ingestion in drinking water by 24 human volunteers over 14 days (*27*) was identified as a critical study by the United States National Academy of Science (U.S. NAS) and other regulators. In that study, statistically significant decreases of thyroidal radioactive iodide uptake (RAIU) were reported for the perchlorate dose groups receiving 0.02, 0.1, or 0.5 mg/kg bw/day. However, significant changes in serum thyroid hormone concentrations were not observed, which would be considered to have greater biological significance. The California Environmental Protection Agency (CAL/EPA) evaluated the study conducted by Greer et al. (*27*) and calculated a benchmark dose level ($BMDL_{05}$) (lower limit of a one-sided 95% confidence interval for a perchlorate

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dose that reduces mean thyroidal iodide uptake by five percent) of 3.7 μg/kg bw/day using the Hill model (*28*),which is lower than the lowest dose tested in the same study (7.0 μg/kg bw/day). From the same study, U.S. NAS recommended an oral reference dose (RfD) of 0.7 μg/kg bw/day based on a no observed effect level (NOEL) of 7 μg/kg bw/day for the inhibition of RAIU and an uncertainty factor of 10, which was adopted recently by the United States Environmental Protection Agency (U.S. EPA). Health Canada currently uses the $BMDL_{05}$ value of 3.7 μg/kg bw/day in its perchlorate risk assessments involving food exposures.

Our primary objective in this study was to explore the occurrence and concentrations of perchlorate in imported and domestic fruits and vegetables available from retail food outlets in Ottawa, Canada, since there are very limited published data available regarding concentrations of perchlorate in foodstuffs available to Canadians. An additional objective was to estimate the possible human exposure to perchlorate through the consumption of fruits and vegetables in Canada.

MATERIALS AND METHODS

Chemicals. Acetonitrile, OmniSolv HPLC grade, was purchased from EMD Chem. Inc. (Gibbstown, NJ). Ammonium acetate was obtained from Sigma (St. Louis, MO). Stable isotope labeled sodium perchlorate, $Na^{18}O_4Cl$, was purchased from Icon Stable Isotopes (Mt. Marion, NY). Sodium perchlorate ($NaClO_4$, >98.0%) as sodium perchlorate monohydrate was purchased from Alltech (Deerfield, IL). Deionized (DI) water from a water purification system (Barnstead Diamond nanopure grade, Barnstead Intern., Dubuque, Iowa) was used to prepare all the solutions.

Sample Collection. Fruit and vegetable samples were purchased from three retail food outlets in Ottawa from February to April of 2006 (5 weeks). Approximately 3−5 types of fruit and vegetables were purchased each week from these stores. The minimum weight of one sample was 454 g. Six individual samples were purchased for each fruit and vegetable in the same store.

Sample Preparation. Approximately 100 g of each individual sample, mixed fruit, or vegetable was homogenized in a food processor. Samples were prepared by weighing 10 g of each homogenized food sample into 50 mL polypropylene centrifuge tubes. To each sample, 20 μL of 10.0 mg/kg $^{18}O_4$-labeled perchlorate was added as a stable isotope labeled internal standard to correct for matrix effects on measured signals. Subsequently, 10 mL of DI water was added to serve as an extraction reagent. After shaking the samples on a vortex for 1 min, samples were centrifuged at 3000 rpm for 25 min. An aliquot of the supernatant was then filtered through a 0.20 μm Acrodisc Nylon syringe filter (Pall life Sciences, NY) into a 2 mL vial. The filtered samples were stored at −20 °C until analysis. For quality control purposes, matrix spiked samples, which contained 10.0 μg/kg native perchlorate, were analyzed for each batch (every six samples).

Analytical Method. An ion chromatography tandem mass spectrometry (IC-MS/MS) system was used for sample analysis. An Agilent HPLC 1100 system (Palo Alto, CA) was coupled to a Waters Quattro Ultima triple quadrupole mass spectrometer (Manchester, UK) with Z-spray electrospray (ESI) interface. The HPLC separation system consisted of a G1312A binary pump, a G1322A degasser, a G1329A temperature controlled (15 °C) autosampler, a G1316A thermostat column oven (30 °C), and an analytical column (AS16, 2 mm × 250 mm, Dionex, Sunnyvale). A guard column (AG16, 2 mm × 50 mm, Dionex, Sunnyvale) was installed before the analytical column. The mobile phase contained 30% of 100 mmol L^{-1} ammonium acetate in water and 70% of acetonitrile. The injection volume was 60 μL. A 6-port Rheodyne model MX9900−000 (Rheodyne, Rohnert Park, CA) divert valve and a shimadsu LC-600 (Shimadsu, Kyoto, Japan) were used to divert the waste out of MS detector at the first and the last 6 min of one chromatograph run (total 17 min). The operational parameters of ESI MS/MS were as follows: polarity, negative ion mode; capillary voltage, −2.5 KV; cone voltage, 40 V; source temperature, 140 °C; desolvation temperature, 340 °C; cone gas flow, 160 L/h; desolvation gas flow, 510 L/h; ion energy for quadrupole 1, 0.7; ion energy for quadrupole 2, 1.6.

The presence of perchlorate in samples was quantified by isotope dilution mass spectrometry. Four transitions from both ^{35}Cl and ^{37}Cl containing species were monitored under multiple reaction monitoring (MRM) mode: m/z 98.9 → 82.9 and 100.9 → 84.9 for $[^{35}ClO_4]^-$ to $[^{35}ClO_4 - {}^{16}O]^-$ and $[^{37}ClO_4]^-$ to $[^{37}ClO_4 - {}^{16}O]$, respectively; m/z 106.9 → 88.9 and 108.9 → 90.9 for $[^{35}Cl^{18}O_4]^-$ to $[^{35}Cl^{18}O_4 - {}^{18}O]^-$ and $[^{37}Cl^{18}O_4]^-$ to $[^{37}Cl^{18}O_4 - {}^{18}O]^-$, respectively. The calibration curve was constructed by analyzing standard solutions containing a mixture of stable isotope labeled perchlorate at a constant concentration of 10 μg/L and native perchlorate at the following concentrations: 0.5, 2.0, 5.0, 10.0, 25.0, and 50.0 μg/L. The calibration curve was plotted on the basis of the relative response ratios between native perchlorate and the labeled perchlorate versus native perchlorate concentrations.

Quality Assurance and Quality Control. To ensure the linearity of the calibration curve, four or more standard solutions were analyzed and a correlation coefficient, $r^2 > 0.99$, was required. Quality of the data was assured by the following criteria: the ratio of the peak area of the quantitative MRM transition (^{35}Cl containing ion pair) to that of the qualitative MRM transition (^{37}Cl containing ion pair) for both native analyte, and the internal standard should be 2.91 with a tolerance of 20%; the peak width of both native ion pairs should be the same as that of the internal standard ion pair; the retention time of the native analyte should not deviate more than ±0.2 min of the internal standard. The samples having a concentration over the highest calibration standards were diluted with DI water and reanalyzed. The instrument limit of detection (LOD) was defined as the concentration at which the ratio of analyte signal to peak-to-peak noise (S/N) was 3:1 for the primary ion transition (m/z 98.9 → 82.9). The method LOD was obtained on the basis of the instrumental LOD in consideration of matrix effects and recovery correction. The limit of quantification (LOQ) was defined as three times that of the LOD. Additional quality assurance was provided by the analysis of matrix spiked samples (MSP), method blank samples (MB), and duplicate samples (DUP) for each individual food commodity.

Data Analysis. Masslynx (Waters Corp. Version 4.0) was used to analyze mass spectrometry data. Concentrations were expressed as mean ± standard deviation (SD). An ANOVA and t-test were conducted using Microsoft Excel 2007. p-values < 0.05 were considered statistically significant between the compared groups.

RESULTS AND DISCUSSION

Method Performance. Several methods have been developed for the analysis of perchlorate, including capillary electrophoresis (*29*) and Raman spectrometry (*30*). Ion chromatography (IC) is currently the most popular method (*31*). The EPA method 314.0 (*32*) is a widely used IC method for the determination of the perchlorate ion in drinking water using conductivity detection. However, in more complicated matrices, the analysis of perchlorate with IC using conductivity detection suffers from some serious challenges, including a high conductivity from matrix effects and a lack of sensitivity (*33*). To improve the selectivity and sensitivity of perchlorate analysis, tandem mass spectrometry has been coupled to IC (IC-MS/MS), with the use of isotope labeled internal standards. IC-MS/MS has significantly improved perchlorate detection with detection limits reported to be 0.5−5 ng/L in deionized water and 1−15 ng/g in various matrices, including urine, amniotic fluid, wine, and food (*19*, *17*, *34*). Therefore, IC-MS/MS was adapted for perchlorate analysis of fruits and vegetables in this study, where the reported instrument LOD was 22.5 ng/kg.

A total of 150 samples were analyzed in 25 batches. Each batch contained six individual food samples and one composite food sample which was prepared by homogenizing equal amounts of these six food samples. For quality assurance, the following quality control samples were included in each batch of analysis: one MB sample, one DUP sample, one MSP sample, one blank spiked sample (BS), and two calibration continue verification samples (CCV). The relative percentage difference (RPD) in DUP samples ($n = 25$) ranged from 0 to 14.1%, and the mean value was 2.93 ± 4.39%. The mean recovery in MS samples ($n = 25$) was 95.1±8.42%, and the range of recovery was 80.2−115%. The mean value of recovery in BS samples ($n = 25$) was

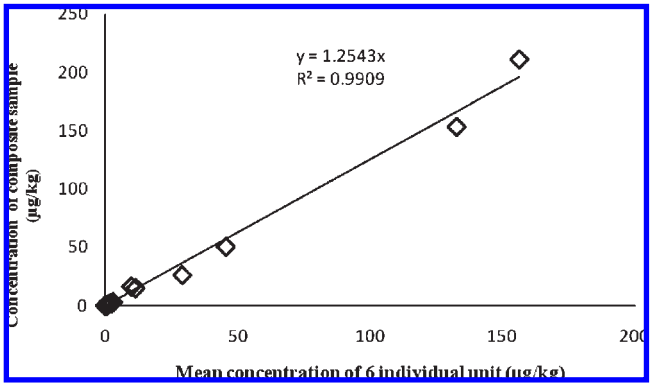

Figure 1. Correlation between the mean values of results obtained from the six individual food samples and the results obtained from composite samples.

95.1 ± 5.71% and ranged from 85.9 to 106%. The mean deviation of all CCV samples ($n = 50$) was 3.91 ± 2.32%, and the range was 0.22−9.74%. Although the use of isotope dilution is able to largely eliminate matrix effects, these effects cannot be completely mitigated because of the wide variety of sample types and the unique matrix component of each fruit or vegetable. To further adjust for matrix effects, the method LOD was estimated on a per sample basis. The mean method LOD was estimated to be 0.39 ± 0.28 μg/kg with a median value of 0.31 μg/kg.

When developing a sampling plan to monitor for the presence of a chemical contaminant in foods, one must consider the best sample collection and preparation method in order to obtain results that are most representative of the typical occurrence of that contaminant in those foods and available resources, as well as the purpose for which the data are being collected. One such consideration is whether to analyze composite or individual samples. For example, if we intend to determine the perchlorate concentration in a food commodity, such as, apple, is it better to perform six individual analyses from six different apples and calculate a mean value or to mix the same amount of sample from each apple into a composite sample and then perform one analysis? To help clarify this question, we carried out parallel experiments for perchlorate analysis on six individual samples and on one composite sample. **Figure 1** shows the correlation between the mean values obtained from the six individual food samples and the results obtained from the composite samples. A strong correlation ($r^2 = 0.991$) was found between the two data sets. A paired *t*-test was also performed where $T = 1.48$ and two-tail *p*-value = 0.15 ($n = 25$), which indicated that there was no significant difference between results from the two experiments. Hence, in the future, for this particular analyte, it would seem appropriate to analyze composite samples rather than each individual sample in order to obtain a mean value, since the analytical cost is significantly reduced, while the sample representativeness appears to be maintained.

Concentration of Perchlorate in Fruits and Vegetables. Table 1 lists the mean ± SD perchlorate concentrations in fruits and vegetables analyzed in this study, regardless of genotype and country of origin. A wide variety of perchlorate concentrations were found among the selected groups of fruits and vegetables. Quantifiable amounts of perchlorate were found in 58% (87 of 150) of the total samples analyzed, with 42% (63 of 150) being below the LOQ. Among the 63 samples with perchlorate concentrations below the LOQ, 29 contained "trace" amounts (between LOD and LOQ). In terms of each individual food commodity, perchlorate was not detected in any of the potato samples ($n = 24$), regardless of the country of origin or genotype.

Table 1. Mean and Range Values of Perchlorate Concentration in Fruits and Vegetables[a]

food product	sample number (*n*)	mean ± SD (μg/kg)	range (μg/kg)
apple	24	0.48 ± 0.60	ND−1.60
cantaloupe	18	56.1 ± 151	ND−536
carrot	12	1.31 ± 1.26	ND−3.08
grapes	12	27.7 ± 23.0	1.96−62.1
honeydew	6	0.30 ± 0.33	ND−0.66
lettuce	18	11.5 ± 14.2	1.27−46.7
oranges	12	0.50 ± 0.82	ND−2.89
potato	24	ND	ND
spinach	6	133 ± 24.9	99.4−175
tomato	18	0.30 ± 0.47	ND−1.38

[a] ND = not detected.

Table 2. Mean and Range Values of Perchlorate Concentrations in Fruits and Vegetables, Considering Genotype and Country of Origin[a]

commodity	country of origin	mean ± SD (μg/kg)	range (μg/kg)
apple, Empire	Canada	1.41 ± 0.17	1.17−1.60
apple, Macintosh	Canada	ND	
apple, Gala	U.S.	0.18 ± 0.15	ND−0.40
apple, Red Delicious	U.S.	0.32 ± 0.38	ND−0.81
cantaloupe	Costa Rica	0.61 ± 1.13	ND−2.90
cantaloupe	Guatemala	156 ± 99.5	ND−536
cantaloupe	Honduras	11.5 ± 7.50	ND−19.6
carrot	Canada	0.15 ± 0.17	ND−0.41
carrot	U.S.	2.47 ± 0.50	1.91−3.08
grape, green	Chile	45.5 ± 13.3	26.6−62.1
grape, red seedless	Chile	9.86 ± 15.1	1.96−40.5
honeydew	Costa Rica	0.30 ± 0.33	ND−0.66
lettuce, Romaine	U.S.	29.1 ± 11.5	13.9−46.7
lettuce, red leaf	U.S.	3.04 ± 0.42	2.49−3.53
lettuce, Boston	U.S.	2.39 ± 1.27	1.27−4.82
orange	U.S.	0.43 ± 0.37	ND−0.84
orange	U.S.	0.58 ± 1.15	ND−2.89
potato, white	U.S.	ND	
potato, red	U.S.	ND	
potato, red	Canada	ND	
potato, white	Canada	ND	
spinach	U.S.	133 ± 10.2	99.4−175
tomato, field	Mexico	ND	
tomato, field	U.S.	ND	
tomato, fine	Canada	0.90 ± 0.31	0.45−1.38

[a] Each category contains six Samples ($n = 6$). ND = not detected.

Tomato, apple, carrot, orange, and honeydew contained relatively lower levels of perchlorate, as the collective average was approximately 1 μg/kg. In contrast, lettuce, spinach, cantaloupe, and grape contained higher levels of perchlorate. The mean perchlorate concentration found in lettuce was 11.5 ± 14.2 μg/kg ($n = 18$, range 1.27−46.7 μg/kg). Spinach had a mean value of 133 ± 24.9 μg/kg perchlorate and ranged from 99.4 to 175 μg/kg ($n = 6$). Cantaloupe had a mean value of 56.1 ± 151 μg/kg and showed a perchlorate concentration up to 536 μg/kg ($n = 18$). Chilean grapes had a mean value of 27.7 ± 23.0 μg/kg perchlorate, and results ranged from 1.96 μg/kg to 62.1 μg/kg ($n = 12$).

Table 2 lists the mean and range of perchlorate concentrations in fruits and vegetables by genotype and country of origin. Higher

concentrations of perchlorate were found in cantaloupes from Guatemala, where the mean perchlorate concentration was 156 ± 99.5 μg/kg (n = 6). This was 13 times higher than the mean value of perchlorate in cantaloupes from Honduras (11.5 ± 7.50 μg/kg, n = 6). The perchlorate levels in cantaloupes from Costa Rica were negligible compared to these two countries. Perchlorate levels differed considerably between the two Chilean grape genotypes (green and red grapes). Green grapes had a mean perchlorate concentration of 45.5 ± 13.3 μg/kg (n = 6), whereas the mean concentration in red grapes was 9.86 ± 15.1 μg/kg (n = 6). A significant difference was found when a simple factor ANOVA was used to analyze these two groups of data (p-value = 0.001). Similarly, perchlorate concentrations in Romaine lettuce (mean value = 29.1 ± 11.5 μg/kg, n = 6) were higher than the mean values of perchlorate in the other two varieties of lettuce (red leaf, Boston) analyzed, even though all of the varieties were from the U.S. A simple factor ANOVA gave a p-value of 4.47×10^{-6}, indicating a statistically significant difference. However, it is not clear at this point whether genotype or country of origin play a more important role in determining the concentrations of perchlorate in fruits and vegetables.

The results from our study were compared with the survey data of fruits and vegetables from the U.S. Food and Drug Administration's (U.S. FDA) exploratory survey (*35*). Perchlorate concentrations from these two studies showed good agreement for lettuce, spinach, apple, and potato, while perchlorate concentrations in tomato, cantaloupe, honeydew, and carrot showed considerable differences. Murray et al. (*36*) reported a similar concentration distribution in their total diet study (TDS) for perchlorate. In their comparison of different publications, it was found that perchlorate concentrations in certain commodities, such as lettuce and orange, were consistent between studies, while tomato and cantaloupe varied considerably. The heterogeneous distribution of perchlorate among different species may be related to the process of perchlorate uptake by plants and the interaction of parameters such as growth rate and location. Unfortunately, there are only a limited number of studies related to the uptake rate of perchlorate and factors influencing the accumulation of perchlorate in plants. Seyfferth and Parker (*37*) studied the uptake rates of perchlorate in different genotypes of lettuce and found that they exhibited a linear increase in tissue perchlorate accumulation with increasing perchlorate concentration in culture solutions. Therefore, they concluded that when considering the influence of genotype, in terms of species and production location, the location had a larger influence on perchlorate accumulation than did the genotype. Jackson et al. (*38*) studied the perchlorate uptake routes in forage and edible vegetation. They found that leaves generally accumulated more perchlorate than fruits. For example, perchlorate concentration in soybean leaf tissue (31 ± 2.9 mg/kg) was significantly higher than in pod (7.6 ± 3.3 mg/kg) or seed tissues (0.6 ± 0.05 mg/kg). Similarly, tomato leaves (11 ± 0.91 mg/kg) presented much higher concentration of perchlorate than the tomato fruits (0.18 ± 0.02 mg/kg). The results from their work may explain why in the current study, tomatoes, potatoes, carrots, oranges, and apples, which are all fruits of their respective plants, showed lower perchlorate concentrations than lettuce and spinach which are all leafy parts of individual plants. However, the reasoning for finding elevated perchlorate concentrations in grapes and cantaloupes are not clear at this point; although the geological location in which these plants are grown might be a possible explanation (*1*, *21*). In general, perchlorate uptake and accumulation in vegetables may relate considerably to the concentration and duration of exposure to perchlorate in the field (*39*).

Table 3. Estimated Average Daily Perchlorate Intake from Fruits and Vegetables

		estimated intake (ng/kg bw/day)		
age group	body weight (kg)	fruits	vegetables	total
toddlers 1−4 yrs	15	8.60	28.0	36.6
children 5−11 yrs	30	17.1	24.0	41.1
teenagers 12−19 yrs	60	8.00	23.2	31.9
women 18−34 yrs	66	3.80	24.1	27.9
all adults ≥20 yrs	70	4.30	24.1	28.4

Estimated Dietary Exposure to Perchlorate from Fruits and Vegetables. Dietary exposures to perchlorate from fruits and vegetables were estimated using a deterministic approach, in which average perchlorate concentrations reported in this study were combined with 24 h dietary recall food consumption data from the Nutrition Canada Food Consumption survey (*40*) (age group < 18 years) and the Nova Scotia Provincial Nutrition Survey (*41*) (adults > 18 years and women 18−34 years). Samples in which perchlorate was not detected were conservatively set to the detection limit of the analytical method in order to calculate average perchlorate concentrations for each fruit and vegetable type. Subsequently, these average perchlorate concentrations were combined with average consumption rates of each fruit and vegetable for all individuals surveyed (eaters and noneaters). Estimated exposures from each individual fruit and vegetable type were summed to generate an approximate exposure to perchlorate from the fruits and vegetables analyzed in this survey. Daily dietary perchlorate intakes on a body weight basis were calculated using body weight data obtained from the Canadian Community Health Survey Cycle 2.2 (*42*).

The estimated perchlorate daily exposures, from fruits and vegetables purchased in Canada, for various age groups, are listed in **Table 3**. In addition to the general adult population, exposures were estimated for the most sensitive subpopulations; toddlers, children, and women of approximate childbearing age (18−34). Perchlorate intakes from fruits ranged from approximately 3.8 to 17.1 ng/kg bw/day, while perchlorate intakes from vegetables varied little between each age and/or age−sex group (ranges from 24.0 to 28.0 ng/kg bw/day). These estimated intakes are comparable to results reported by the U.S. FDA in their assessment of perchlorate exposure using data from their TDS study (*36*). The U.S. FDA study estimates that perchlorate intakes from vegetables range from approximately 20 to 47 ng/kg bw/day for children 2 years of age up to adults 70 years and above. However, exposure estimates from fruit consumption in the U.S. are slightly higher than Canadian estimates. The U.S. FDA study estimated that perchlorate intakes from fruits range from approximately 4 to 58 ng/kg bw/day. Higher exposures on a body weight basis were observed in younger subpopulations due to their higher consumption of fruit relative to their lower body weights. Perchlorate exposures from fruit and vegetables were mostly influenced by perchlorate concentrations in the food rather than food consumption intakes. For example, although apples, oranges, and potatoes are consumed in much higher amounts than other fruits and vegetables, they contributed very little to the perchlorate exposure estimate. Cantaloupe and spinach were the most significant contributors to the daily exposure estimates due to the relatively higher concentrations of perchlorate in these foods. However, considering the fairly wide concentration range and standard deviation of perchlorate reported in some vegetables, such as cantaloupe, further study may be required to investigate the perchlorate levels in those fruits exhibiting a wide range of concentrations.

Moreover, food consumption intakes used for this assessment represent average consumption amounts for all individuals (eaters and noneaters surveyed). As such, the perchlorate intakes may not be representative for high-end consumers of a particular food. Therefore, this approach may underestimate exposure for people consuming large amounts of certain foods on a daily basis or population subgroups with specific nutritional requirements. Since 24 h dietary recall data were used, the intake amounts reported here do not include a correction for frequency of consumption. Consequently, these figures are assumed to represent daily consumption which may lead to a somewhat overestimated exposure for long-term intakes by the average consumer.

The selected fruits and vegetables analyzed in this study are expected to account for the majority of the perchlorate exposure from fruits and vegetables, according to the TDS data from the U.S. FDA. However, this deterministic exposure assessment of perchlorate in fruits and vegetables is considered preliminary since intake estimates were based on empirical data from only 10 fruits and vegetables, which were available during a specific sampling period and in retail markets from Ottawa. Consequently, total dietary exposure to perchlorate cannot be estimated using the limited variety of foods sampled in this study. According to the U.S. FDA TDS, perchlorate occurrence is widely distributed in the food supply. Detectable concentrations of perchlorate were found in 59% of all samples analyzed and in at least one sample in 74% of the 285 different U.S. TDS foods. Vegetables and fruits combined account for no more than 50% (between 27% and 50%) of the total estimated intake of perchlorate by teenagers and adults. This is a strong indication that more data are required on perchlorate concentrations as a result of seasonal availability of fruits and vegetables and in a greater variety of food commodities representing the majority of the Canadian diet. This would enable an accurate estimate of total dietary exposure to perchlorate.

Additionally, directed sampling of foods specific to the high risk groups, such as infant foods and infant formulas, should be planned. Furthermore, Dasgupta et al. (*43*) recently reported that perchlorate is excreted to a much greater degree in human milk than is iodide. Given the relatively rapid turnover and limited storage capacity for thyroid hormones, newborns must rely on a continuous dietary supply of iodide in order to produce their daily requirement of these critical hormones (*44*, *45*). Consequently, breastfed neonates may be particularly vulnerable to adverse effects due to perchlorate exposure. Future work is planned to determine the concentration of perchlorate and iodide in Canadian human milk in order to better inform a dietary risk assessment (*46*).

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