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ARTICLE

Perchlorate, Nitrate, and Iodine Uptake and Distribution in Lettuce (*Lactuca sativa* L.) and Potential Impact on Background Levels in Humans

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Much focus has been placed on the impact of exposure to perchlorate (ClO_4^-) from drinking water. Recently, it has become more apparent that a significant percentage of the total ClO_4^- exposure may be due to ingestion of food. Most studies have only evaluated the uptake and distribution of ClO_4^- by plants without considering the potential for uptake of iodine (I) by the plant and the subsequent impacts on ClO_4^- uptake and distribution on human health. The objectives of this research effort were to evaluate the relative uptake of ClO_4^- and I supplied as either KI or KIO_3, the two major environmental forms of I in a standard hydroponic nutrient solution using butter head lettuce. No interaction of ClO_4^- uptake and distribution was found in the presence of I^- or IO_3^- relative to previous studies evaluating ClO_4^- alone. Bioconcentration factors for ClO_4^- and total I in butter head lettuce when coexposed to both anions were similar for outer (292 ± 17 and 294 ± 12 L kg^{-1} of dry weight, respectively) and inner (76 ± 18 and 60 ± 8 L kg^{-1} of dry weight, respectively) leaves but not for roots (23 ± 3.7 and 359 ± 1.7 L kg^{-1} of dry weight, respectively) when the iodine was supplied as I^-. The uptake of iodine was lower (BCF = 47 ± 3.8, 19 ± 0.6, and 189 ± 16, L kg^{-1} of dry weight for the outer and inner leaves and roots, respectively) for all tissues when iodine was supplied as IO_3^-, with the greatest accumulation by the roots. These results suggest that if lettuce is grown using fertilizers containing both ClO_4^- and I^-, then the final ratio of I_T/ClO_4 in the leaves will be essentially equal to the ratio in the fertilizer but lower if the I is supplied as IO_3^-. Therefore, the impact of the consumption of lettuce containing ClO_4^- may be mitigated if the lettuce is grown using fertilizer with an appropriate amount of I to maintain the existing ratio of serum I to total goitrogen load (TGL). Nevertheless, the TGL in lettuce appeared to be almost completely dominated by NO_3^- with only a minor contribution of ClO_4^-, even for the highest exposure to ClO_4^-.

KEYWORDS: Perchlorate; iodine; iodide; iodate; lettuce; *Lactuca sativa*; Chilean nitrate fertilizer; TGL; PEC

INTRODUCTION

Perchlorate (ClO_4^-) continues to be a chemical of concern in the United States. Perchlorate, like nitrate (NO_3^-) and thiocyanate (SCN), is a competitive inhibitor of iodide uptake by the sodium iodide symporter (NIS). The NIS is expressed in the thyroid, placenta, and mammary gland, where it plays a key role in iodide (I^-) transport. Insufficient levels of I^- can lead to thyroid dysfunction, but the larger concern is for sensitive subpopulations (e.g., gestating fetuses and infants) for which the thyroid plays a key a role in neurodevelopment (*1*). Although there are no current federal drinking water regulations for ClO_4^-, a reference dose (0.7 μg/kg/day) has been adopted that would equate to a drinking water concentration of 24.5 μg/L (assuming a 70 kg adult and drinking water as 100% of the exposure), and numerous states have issued some form of regulations with values ranging from 1 to 18 μg/L.

The sources of perchlorate have been extensively reviewed elsewhere but, in general, relate to its use as an oxidant in solid rocket propellant, flares, and fireworks, its natural presence in Chilean nitrate fertilizers (CNF), as a byproduct in hypochlorite (bleach) and chlorate salts, and finally natural atmospheric production and deposition (*2*). Perchlorate exposure is primarily by ingestion of affected drinking water or food. Perchlorate exposure of the general population appears to be ubiquitous at low levels (*3*), and a significant fraction of the exposure is likely from food, specifically vegetables and dairy products, rather than drinking water (see, e.g., ref *4*).

Perchlorate uptake into plants has been extensively studied, including laboratory studies, field studies, and market surveys, and a number of reviews have been recently published (*5*). Much like NO_3^-, ClO_4^- generally accumulates in highest concentration in regions of active transpiration (e.g., leaves of lettuce plants). Lower concentrations are generally observed in nontranspiring structures, such as roots and stems of many species (*6*). Perchlorate uptake is largely a function of the evapotranspiration rate, although, in general, it appears that perchlorate is partially

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excluded during uptake (*7*, *8*). Bioconcentration factors (BCF) for transpiring tissue (leaves) vary depending on the specific plant species, specific plant tissue evaluated (e.g., outer vs inner leaves), and growth conditions. For lettuce, maximum BCF values ranged from 4 to 40 (L kg^{-1} of fresh weight) depending on the specific lettuce type, with lower BCF values for middle and inner leaves (*8*). The impact of other common anions is as yet unclear. The presence of NO_3^-, SO_4^{2-}, and Cl^- had only a minimal impact on ClO_4^- uptake by smartweed exposed to relatively high ClO_4^- concentrations (*7*), whereas a significant negative impact by NO_3^- was observed for lettuce exposed to environmentally relevant concentrations of ClO_4^- (*9*). Once accumulated in vegetation, ClO_4^- is largely stable and is not extensively metabolized or translocated (*7*, *10*).

Of particular relevance is the use of CNF (e.g., $NaNO_3$ and KNO_3) in the production of leafy edible vegetation (e.g., salads). CNF, as $NaNO_3$ is sometimes preferred due to its organic certification; however, it is mainly used as KNO_3 in fertigation and in soilless growing systems Historically, CNF contained up to 0.2% ClO_4^- and 0.2% I mainly in the form of IO_3^- with a total N (as NO_3^-) content of 10−20% (*11*). Around 2000, the largest CNF producer reduced the ClO_4^- content (< 100 mg kg^{-1}) and maintained proportional concentrations of total iodine (*2*, *12*). An analysis of one lot of CNF by the Texas Tech University laboratory confirmed the reported concentration of ClO_4^- (26 ± 3 mg kg^{-1}). The uptake and distribution of iodine and ClO_4^- into edible vegetation are extremely relevant, as the health impact of ClO_4^- to humans is a function not of the absolute exposure concentration, whether the exposure is from food or water, but rather of the relative ratio of I^- to ClO_4^- (*1*) in the consumed water or vegetation and, by extension, of the relative ratio of I^- to total goitrogen load (TGL).

Perchlorate is one of three significant goitrogens that inhibit I^- uptake by the thyroid. NO_3^- and thiocyanate (SCN) also inhibit I^- uptake by the NIS, but ClO_4^- has I^- uptake inhibition (IUI) potencies 9 and 150 times larger on a serum mass concentration basis than those of SCN and NO_3^-, respectively. On an ingested weight basis, due to differences in serum half-lives the ClO_4^- equivalent concentrations (PEC) of SCN and NO_3^- are 0.5 and 240, respectively (*13*). Inhibition by these goitrogens is competitive, and the total IUI is a function of the relative ratio of I^- to the total PEC (PEC_T). Therefore, evaluation of the impact of ClO_4^- exposure from lettuce (or other leafy vegetable) consumption must not only evaluate the intake of iodine but also take into account the existing iodine and goitrogen background levels.

The objectives of this research effort were to evaluate the relative uptake of ClO_4^- and iodine supplied as either KI or KIO_3, the two major environmental forms of iodine in a standard hydroponic nutrient solution using butter head lettuce. Uptake was evaluated with respect to initial concentration of total supplied iodine (I_T) and ClO_4^- at a constant ratio of ClO_4^- to I_T. We evaluated the final distribution and concentration of ClO_4^- and I_T within the plant. This is the first time that the impact of the form or presence of I_T on ClO_4^- uptake has been evaluated. The results are discussed in relation to the potential impact on iodine nutrition. The uptake and distribution of I reported in this study have been previously published (*14*) as they were part of a larger study that examined uptake of I^- and IO_3^- with and without ClO_4^- but are reproduced in part in this paper to examine the relationship between ClO_4^- and iodine uptake and distribution.

MATERIALS AND METHODS

Experimental Design. The relative uptake of I^- and IO_3^- with respect to ClO_4^- was evaluated in a hydroponic greenhouse study at the Wageningen University and Research Greenhouse Center in Bleiswijk, The Netherlands. The experimental design consisted of 10 treatments in which plants were exposed to various concentrations of total I (I_T) as either I^- or IO_3^- and ClO_4^- in a standard nutrient solution (described below). Nitrogen was supplied as $Ca(NO_3)_2$ and KNO_3 at a constant initial concentration (1060 mg as NO_3^- L^{-1}) for all treatments. Plants were exposed to four concentrations of I_T (12.9, 38.7, 64.5, and 90.3 μg L^{-1} as I), supplied as either KI or KIO_3. For each of the I^- and IO_3^- treatments, $KClO_4$ was supplied to produce four concentrations of ClO_4^- (25.8, 77.4, 129, and 181 μg L^{-1}) to achieve a concentration ratio of I_T/ClO_4^- of 0.5. The I_T/ClO_4^- ratio (0.5) to which the plants were exposed was chosen to be slightly higher than the I_T/PEC_T (~0.4) in the U.S. population according to the NHANES 2001−2002 database. As such, it would allow the study to evaluate whether plant uptake would affect the I_T/ClO_4^- ratio in plant tissue for an applied ratio in fertilizer. If the ratio were conserved through plant uptake and consumption of the plants, there would be no reduction of the I_T/PEC_T value of the population, assuming no change in SCN or NO_3^- exposure due to the presence of ClO_4^- in fertilizer. In addition, two control treatments were also evaluated. One control treatment consisted of plants grown in nutrient solution with no I or ClO_4^- exposure, whereas the other consisted of no plants at the highest I and ClO_4^- concentration evaluated (90 and 181 mg L^{-1}, respectively).

Butterhead lettuce seeds were sown on May 26, 2008, in vermiculite prerinsed with distilled water and incubated for 21 days in dilute nutrient solution (electrical conductivity (EC) ~ 1.6 dS m^{-1}). The plants were then transferred to 30 L polyethylene tubs with PVC covers wrapped in polyethylene sheets to reduce evaporation and equipped with plant holes. The containers were initially filled with 28 L of nutrient solution containing I^- or IO_3^- and ClO_4^- depending on the specific treatment. Each treatment consisted of 5 growth containers, and each growth container supported 6 plants, for a total of 30 plants per treatment. Growth containers were randomly arranged in a climate-controlled greenhouse. The growth solution in each container was continuously sparged with air to maintain oxygen in the root zone, which mimics the aerating effect of the continuous circulation of nutrient solution in a commercial growing operation. The growth solution was tested weekly for pH and EC and, if needed, corrected by adding HNO_3 (0.1 M), KOH (0.1 M), or $KHCO_3$ (0.1 M). On day 19, all growth containers with plants received an additional 5 L of diluted nutrient solution (EC = 1.1 dS m^{-1}) but no additional I^-, IO_3^-, or ClO_4^-. Plants were harvested 31 days after transplanting.

Samplings. Nutrient solution samples were taken for I_T and ClO_4^- analysis on days 0, 15, and 31. For each treatment, samples were pooled from replicates 1 and 3 and replicates 4 and 5, but not replicate 2. Therefore, for each of the 10 treatments, there were 3 samples analyzed. Samples were shipped on ice overnight for analysis as described below. Four plants from each growth container were individually removed and cut in half. The roots, outer leaves (unfolded green mature leaves), and inner leaves (folded yellow leaves) were separated, rinsed with surfactant solution as described in ref *15*, and centrifuged dry. The inner and outer leaves from four half-plants were randomly selected and weighed. All root material was weighed. After weighing, the material was dried at 80 °C for 48 h and reweighed. The dried plant material was pooled from replicates 1 and 3 as well as replicates 4 and 5, whereas replicate 2 was sampled individually. The dried material from each of the three pools (e.g., 1−3, 4−5, and 2) was subsampled. Subsampled material was analyzed for ClO_4^- and I_T analysis as described below. One sample per treatment of pooled dried material of both inner and outer leaves from all five replicates was analyzed for nitrate and Kjeldahl-N.

Analysis. Iodine analysis in nutrient solutions and in plant tissue extracts was conducted by ICP-MS by UT2A, the analytical laboratory of Pau University (France). With this method no discrimination between I^- or IO_3^- is possible. Tissue extracts were prepared according to the method in ref *16*, which is a total organic matter destruction, resulting in determination of total I. The detection limit for the nutrient solution was 0.1 μg L^{-1}, and for I in plant tissue the detection limit was 0.01 mg kg^{1-}. Perchlorate analysis was performed by ion chromatography with conductivity detection by Broughton Laboratories in Northshire, U.K. Plant extraction, sample preparation, and analysis followed those described in ref *17*. Approximately 600 mg of dried plant material was combined with 30 g of ultrapure water in a capped centrifuge tube and placed in a boiling

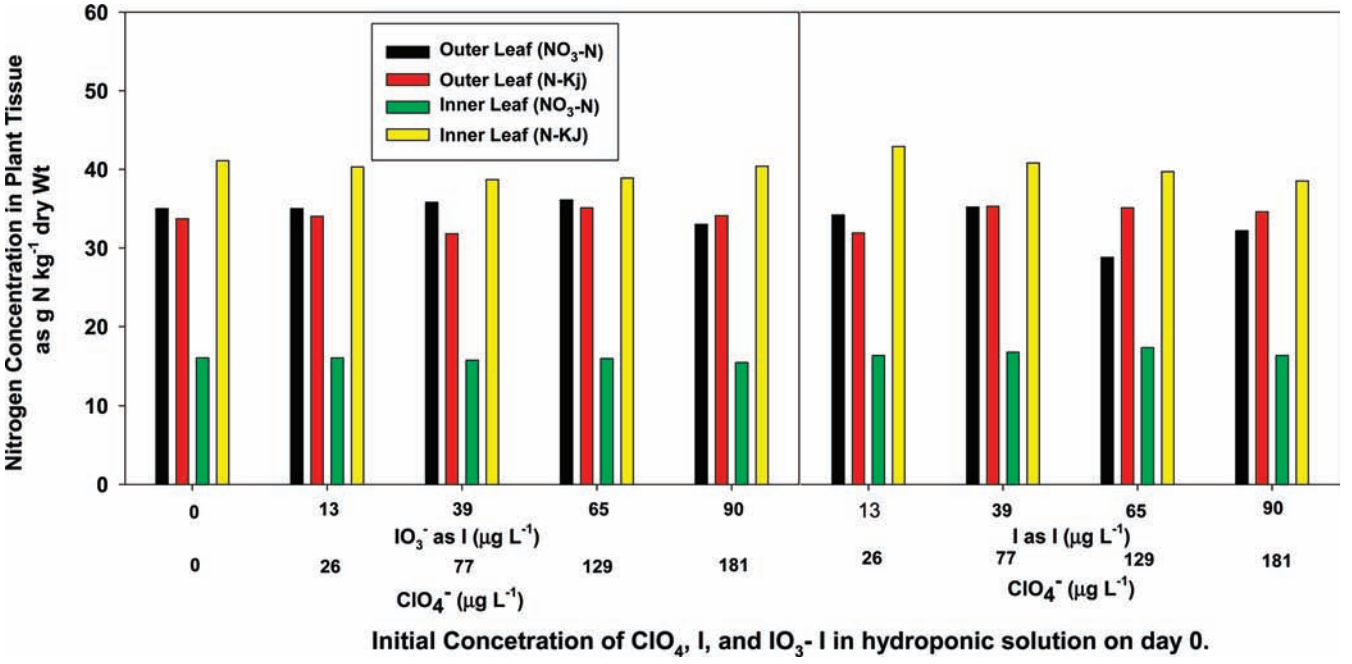

Figure 1. Variation in Kjeldahl-N and NO_3-N content in plant tissue with respect to I^- or IO_3^- and ClO_4^- concentrations in hydroponic growth solution.

water for 30 min. The samples were allowed to cool, shaking every 2 h for 6 h, and allowed to settle at 3 °C overnight. Each sample was then centrifuged at 20000*g* for 30 min and the supernatant filtered through a 0.2 μm syringe filter. One milliliter of extract was combined with activated alumina and left overnight at 3 °C. Nine grams of ultrapure water was added, and the supernatant was filtered through a second 0.2 μm syringe filter with an attached Dionex OnGuard RP cartridge preactivated with 5 mL of methanol followed by 10 mL of ultrapure water. After the first 2 mL of plant extract was discarded, the remaining volume was collected and stored for analysis. Perchlorate analysis for both nutrient solution and plant extracts was performed using a Metrohm 850 IC system equipped with a Metrosep ASUPP7-250 analytical and guard column. A 0.5 M sulfuric acid and 0.1 M oxalic acid in 10% acetone with a 90:10 water/acetonotrile solution was used as the suppressor regenerant. The eluent was a 50:50 acetonitrile/water solution with 6 mM $NaCO_3$.

Nutrient Solution. The nutrient solution was a standard nutrient solution for commercial lettuce production with a few modifications. KNO_3 was omitted from the basic recipe with the standard commercial fertilizers and added as chemically pure KNO_3 (Merck). The final solution had a pH of 5.5 and a conductance of 2.5 dS m^{-1}. $KClO_4$, KI, and KIO_3 were added individually to each container on the basis of the desired final concentration. Initial concentrations (mM) of macro- and micronutrients were K, 10.2; Na, 0.3; Ca, 4.2; Mg, 1.1; NO_3, 17.1; Cl, 0.1; SO_4, 1.1; P, 2; Si, 0.01; Fe, 0.021; Mn, 0.0055; Zn, 0.0040; B, 0.027; Cu, 0.0007; and Mo, 0.0001.

RESULTS

The impact of I^- and IO_3^- on the relative uptake and distribution of ClO_4^- was part of a larger study evaluating I^- and IO_3^- plant uptake in hydroponic cultivation. Details of the uptake and distribution of I^- and IO_3^- have been previously described (*14*) for this study but are reproduced here in part to determine the potential interactions with the uptake and distribution of ClO_4^- that were evaluated in a subset of the experiments comprising the overall study. The presence of I^- or IO_3^- and ClO_4^- at concentrations up to 90 (as I_T) and 180 μg L^{-1}, respectively, had no impact on the overall biomass production compared to the controls (*14*). Nitrogen (Kjeldahl and NO_3^-) distribution within the plant was also similar for both the controls and all tested concentrations of applied I^- or IO_3^- and ClO_4^- (**Figure 1**). NO_3^- accounted for ~25% of the total N in inner leaves and ~50% in outer leaves.

Uptake of ClO_4^- and I^- or IO_3^-. Water loss for each container was similar (19.8 ± 0.51 kg), suggesting similar total evapotranspiration supported by the similarity in total biomass between treatments. The percent mass loss of ClO_4^- from solution was also similar regardless of treatment. Perchlorate concentration was essentially unchanged (107 ± 6%) in the final hydroponic solution after adjustment for the addition of water on day 19. This suggests that ClO_4^- is largely taken up and transported by the plant by mass flow. Iodide concentration, like ClO_4^-, was essentially unchanged in the final solution (108 ± 26%), also indicating transport by mass flow, whereas IO_3^- accumulated (210 ± 24%), indicating some hindrance in the uptake process (*14*). The final recovered masses of ClO_4^-, I^-, and IO_3^- in the system (water and plant) were not quantitatively recovered, with percent recoveries averaging 81 ± 7.1, 84 ± 7.9, and 81 ± 13, respectively (**Tables 1** and **2**).

Perchlorate uptake into the roots, inner leaves, and outer leaves was highly linear (r^2 = 0.64−0.98) with respect to initial ClO_4^- concentration in the root environment regardless of whether I was present as I^- or IO_3^- (**Figure 2**). Consequently, there was no apparent difference in the bioconcentration factor (BCF = (mg kg^{-1} of dry mass)/(mg L^{-1})) of ClO_4^- whether in the presence of I^- or IO_3^- even up to I_T concentrations of 90 μg L^{-1}. The BCF of ClO_4^- was highest for the outer leaves (292 ± 17 and 269 ± 12 L kg^{-1}) irrespective of the presence of I as I^- or IO_3^-, lower for inner leaves (62 ± 3.6 and 76 ± 18, respectively), and lowest for the roots (23 ± 3.7 and 21 ± 1.7, respectively) (**Figure 2**). These values are comparable to previous studies of ClO_4^- uptake by a variety of plants (*6*, *7*) and reasonably similar to previous studies investigating lettuce (*8*), assuming a dry matter content of ~5%. Iodide uptake with respect to exposure concentration (BCF) was essentially the same as ClO_4^- for the outer (294 ± 25 L kg^{-1}) and inner leaves (60 ± 8.4) but clearly different for root tissue (359 ± 1.7) (**Figure 2**). Iodate uptake (BCF) with respect to I^- was much lower for all plant tissue (47 ± 3.8, 19 ± 1.6, and 189 ± 16 L kg^{-1} for the outer leaves, inner leaves, and roots, respectively) (**Figure 2**).

Perchlorate distribution within the plant was similar for all initial exposure concentrations regardless of the presence of I^- or IO_3^- (**Figure 3**). Of the ClO_4^- recovered in the plant, the highest

Table 1. Unaccounted Quantity of ClO_4 (Absolute and as Percentage) in the Mass Balance, As Calculated from the Initial ($Solution_I$) and Final ($Solution_F$) Quantities in the Plant Containers and the Uptake by the Plant[a]

treatment			total mass of ClO_4				
ClO_4 ($\mu g\ L^{-1}$)	I ($\mu g\ L^{-1}$)	IO_3 ($\mu g\ L^{-1}$)	$solution_I$ (μg)	$solution_F$ (μg)	plant (μg)	unaccounted (μg)	% unaccounted
26	0	13	618 (34)	204 (15)	400 (143)	13	2
78	0	39	2370 (300)	675 (80)	1217 (156)	480	20
129	0	65	3790 (260)	1234 (120)	1851 (622)	708	19
181	0	90	4980 (140)	1570 (170)	2178 (75)	1234	25
26	13	0	635 (15)	194 (24)	314 (48)	126	20
78	39	0	1930 (83)	595 (62)	936 (186)	402	21
129	65	0	3390 (110)	1050 (85)	1521 (441)	829	24
181	90	0	5010 (47)	1600 (108)	2633 (315)	1015	19

[a] In μg per container, standard deviation in parentheses.

Table 2. Unaccounted Quantity of Iodine (Absolute and as Percentage) in the Mass Balance, As Calculated from the Initial ($Solution_I$) and Final ($Solution_F$) Quantities in the Plant Containers and the Uptake by the Plant[a]

treatment			total mass of I				
ClO_4 ($\mu g\ L^{-1}$)	I ($\mu g\ L^{-1}$)	IO_3 ($\mu g\ L^{-1}$)	$solution_I$ (μg)	$solution_F$ (μg)	plant (μg)	unaccounted (μg)	% unaccounted
26	0	13	462 (28)	337 (13)	138 (31)	14	3
78	0	39	1660 (271)	858 (96)	223 (21)	575	35
129	0	65	2190 (149)	1485 (105)	308 (146)	401	18
181	0	90	3020 (169)	1964 (156)	385 (90)	669	22
26	13	0	400 (7)	173 (19)	203 (24)	24	6
78	39	0	1070 (76)	345 (71)	492 (83)	231	22
129	65	0	1720 (14)	442 (51)	893 (81)	388	23
181	90	0	2410 (83)	554 (58)	1519 (166)	334	14

[a] In μg per container, standard deviation in parentheses.

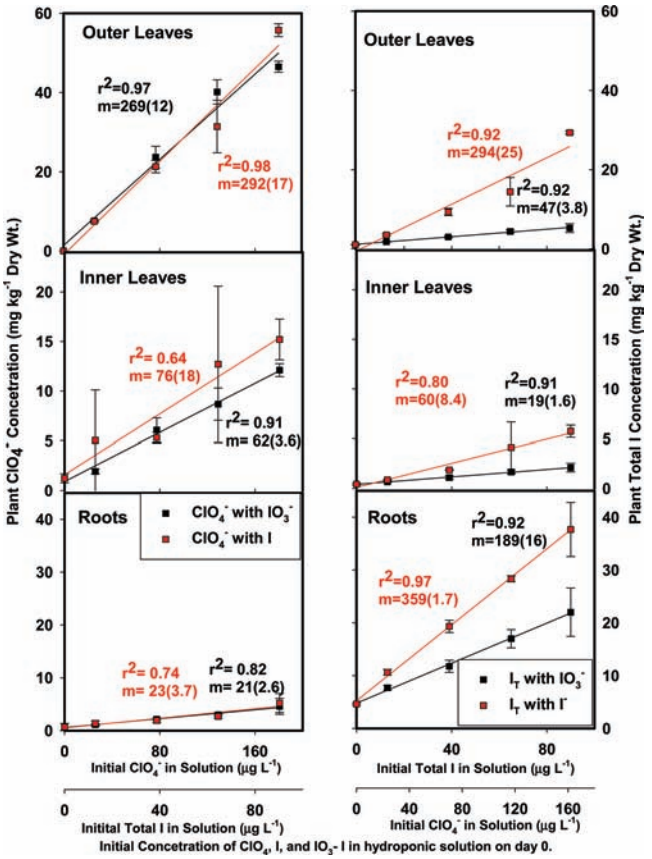

Figure 2. Relationship between exposure concentration of I^- or IO_3^- and ClO_4^- and plant tissue concentration. The slope of the line (m) is equal to the BCF ($L\ kg^{-1}$).

accumulations (67 ± 9.7 and $75 \pm 3.0\%$ in the presence of I and IO_3^-, respectively) were in the outer leaves, with insignificant accumulation in the roots ($<2\%$) for all treatments, similar to previous studies. Iodine distribution within the plant was dependent on the applied iodine form but not on total applied concentration (*14*). Similar to ClO_4^-, I_T distribution was highest in the outer leaves ($59.5 \pm 5.0\%$) when iodine was applied as I^-, but in contrast to ClO_4^-, the roots and inner leaves have similar mass distributions (23.6 ± 5.5 and $16.9 \pm 2.1\%$ respectively). I_T distribution when iodine was supplied as IO_3^- was also highest in the outer leaves ($44.9 \pm 1.5\%$), but root accumulation was higher than in inner leaves (33.4 ± 0.8 and $21.7 \pm 1.0\%$, respectively) (**Figure 3**).

The potential exposure impact due to the differential uptake and distribution of ClO_4^-, I^-, and IO_3^- can be best evaluated by a comparison of the ratio of I_T to ClO_4^- in the initial solution compared to the edible plant tissue (**Figure 4**). For the treatments with I^-, the final ratio of I_T to ClO_4^- (0.47 ± 0.03) in the outer leaves for all treatments was essentially the same as the ratio in the initial growth solution (0.54 ± 0.07), lower for the inner leaves (0.36 ± 0.3) (**Figure 4**), and greater for the roots (9.4 ± 1.5). For treatments with IO_3^- (initial fertilizer solution average ratio of $I_T/ClO_4^- = 0.66 \pm 0.08$), the final ratio of I_T to ClO_4^- was lower for the edible tissue (outer and inner leaves) (0.14 ± 0.06 and 0.22 ± 0.07, respectively) and higher for the roots (5.9 ± 0.8). There was no consistent pattern to the change in the I_T to ClO_4^- ratio in any plant tissue with respect to total applied concentration of I^- or IO_3^- and ClO_4^-, although the spent hydroponic solution did show a consistent pattern of I_T depletion with respect to applied ClO_4^- and I_T concentration.

DISCUSSION

The impact of ClO_4^- concentration, plant species, presence of some major coanions (e.g., NO_3^-), and evapotranspiration on

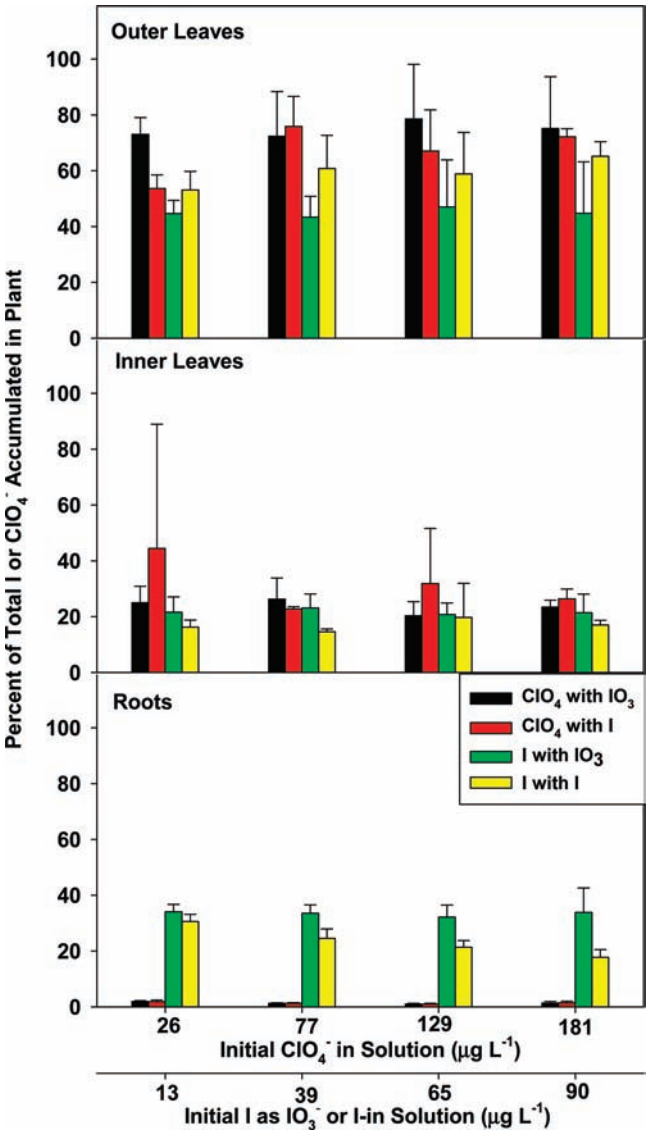

Figure 3. Distribution of I_T and ClO_4^- in lettuce expressed as a percent of the total uptake with respect to the concentration of I^- or IO_3^- and ClO_4^- in the hydroponic growth solution.

accumulation of ClO_4^- has been documented (*7*–*9*). Our results are congruent with past studies in relation to ClO_4^- uptake and distribution. This study shows for the first time that neither I^- nor IO_3^- affects perchlorate uptake over an environmentally relevant range of concentrations in the root environment. The distribution of I_T in plant tissue is also similar to ClO_4^- with the exception of a higher accumulation in root mass for iodine. Ingestion of plants grown in hydroponic solution containing ClO_4^- and I^- or IO_3^- will result in exposure to both ClO_4^- and I. When plants are exposed to iodine as I^-, the ratio of I_T/ClO_4^- in the plants will be very similar to that of the root environment with respect to the above-ground biomass and increase for the roots. In cases when IO_3^- is present in the growth solution, the ratio will decrease in the above-ground biomass and increase in the roots. The varying uptake of I^- and IO_3^- may be related to the difference in their molecular diameters. Larger ions with the same valence are less easily taken up by plants than smaller ions (*18*). Another possible explanation for this phenomenon may be the requirement for chemical reduction of IO_3^- to I^-, prior to plant uptake (*19*). Results of this study cannot easily be extrapolated to field-grown lettuce, because the soil matrix may affect the availability of I^- and IO_3^- ions due to transformation and/or sequestration.

The relevance of ClO_4^- uptake and distribution in plants is primarily due to the potential for human exposure. Recent exposure surveys indicate that food, mainly vegetables and dairy products, may account for a significant portion of the U.S. population's ClO_4^- exposure (*4*). Dietary intake of fruits or vegetables, if iodine is present in the growth media used to produce them, can also be an important source of total iodine for the world population, especially for countries that do not use iodized salt, for individuals who choose to use noniodized salt, or for those people who follow a low-salt diet (*14*). However, the evaluation of human ClO_4^- exposure from plant ingestion should recognize that the absolute concentration of ClO_4^- is not as important to potential health effects but rather the ratio of I_T to ClO_4^-. As previously mentioned, ClO_4^- is a competitive inhibitor of I^- uptake at the NIS. As such, the impact of ClO_4^- is very dependent on the iodine status of the individual, which in turn is highly dependent on the individual's total I_T exposure.

When potential impacts on human health by exposure to ClO_4^- or other NIS inhibitors from the consumption of edible plants are evaluated, the selectivity of the human NIS must be taken into account. The PEC is the concentration of any inhibitor

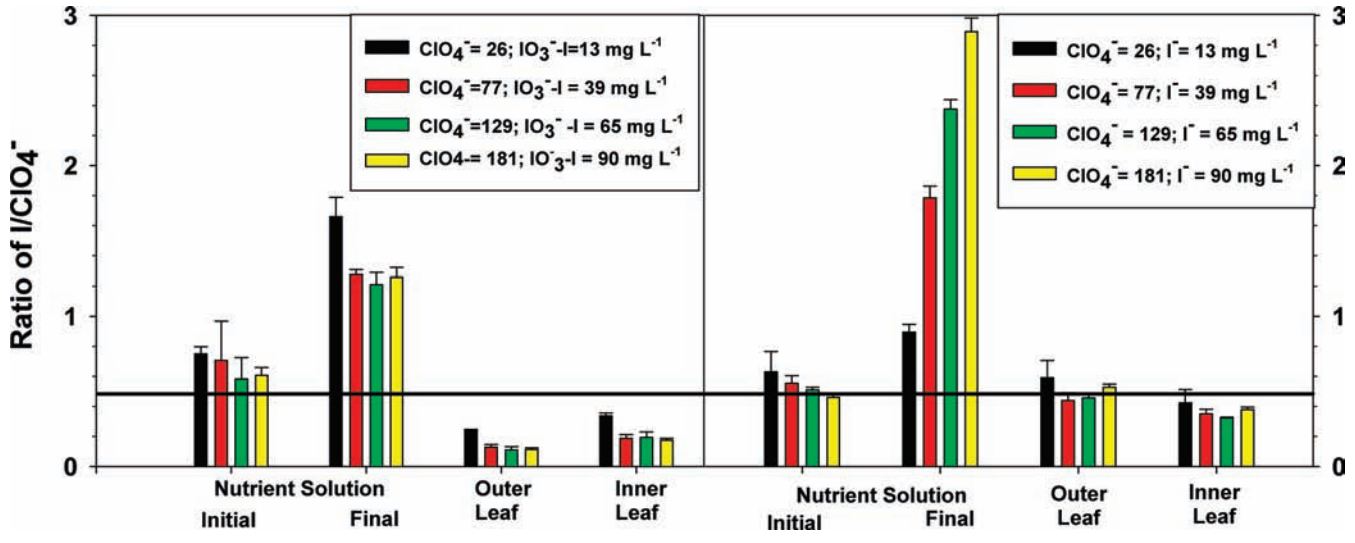

Figure 4. Ratio of I_T to ClO_4^- for edible lettuce tissue exposed to I as I^- or IO_3^- and ClO_4^- in the hydroponic growth solution and lettuce tissue.

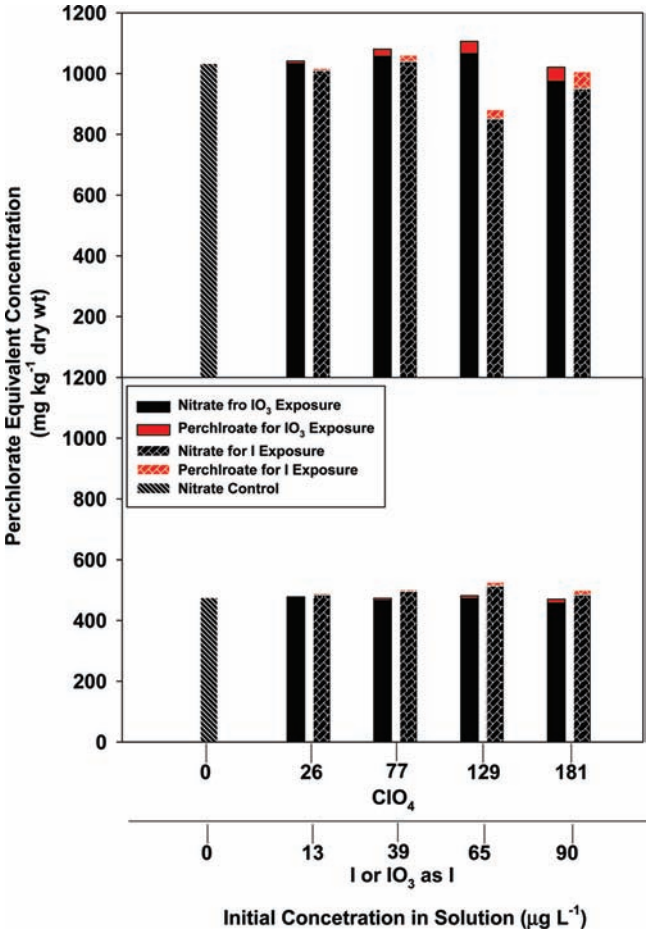

Figure 5. Relative impact of ClO_4^- and NO_3^- on the total perchlorate equivalent concentration with respect to the concentration of ClO_4^- in the hydroponic growth solution at a constant NO_3^- exposure of 1060 mg L^{-1}.

that is equivalent to a given dose of ClO_4^-. The PECs of ClO_4^-, SCN, and NO_3^- are 1, 15, and 150, respectively (*13*), and the TGL can be defined as the sum of all goitrogens expressed as their PEC (e.g., [NO_3^-/150 + SCN/15 + ClO_4^-] where all species are expressed as mg/L or mg/kg). Clearly, the use of N fertilizers that contain ClO_4^- (e.g., CNF) compared to N fertilizers that do not contain ClO_4^- will result in an increase of ClO_4^- in plant tissue. However, as highlighted by previous researchers NO_3^- exposure from consumption of edible leafy plants is generally considered to be much greater than ClO_4^- by orders of magnitude (*20*, *21*). The relatively minor impact of ClO_4^- as a contributor to TGL in lettuce (as a known accumulator a conduit for exposure) is highlighted by this study in which the TGL in the above-ground plant material (outer and inner leaves) is almost completely dominated by NO_3^- even for plants exposed to ClO_4^- concentrations as high as 180 μg L^{-1} (**Figure 5**). For plants that produce SCN (e.g., broccoli and cauliflower), the contribution of ClO_4^- would be even less (*22*). This is largely mirrored in the NHANES 2001−2002 urinary data for which the ClO_4^- accounts for $<1\%$ of the total TGL for the total population.

Regardless of the relative contribution of ClO_4^- to TGL, to evaluate the overall impact to human health from consumption of plants grown with ClO_4^--containing fertilizers, the ratio of I_T to ClO_4^- in the plant should also be considered. From the results of this study it appears that if I is present as I^- in the fertilizer, the plant foliage will largely reflect the relative ratio of I_T/ClO_4^- in the fertilizer, whereas if it is present as IO_3^-, the plant will have slightly lower ratios of I_T/ClO_4^- in the leaves. Therefore, when fertilizers with ClO_4^- (e.g., CNF) are compared to those that do not contain perchlorate, NO_3^--based or otherwise, the real issue is if the ClO_4^- in the fertilizer leads to a reduction in the I_T to TGL (I/TGL) in the plant. Iodine supplementation of fertilizers may also be a potential means of providing iodine to general populations and a means of offsetting general goitrogen exposure, although much more work is required to evaluate this concept.

ABBREVIATIONS USED

BCF, bioconcentration factor; CNF, Chilean nitrate fertilizers; IUI, iodine uptake inhibition; NIS, sodium iodide symporter; PEC, perchlorate equivalent concentration; SCN, thiocyanate; TGL, total goitrogen load; TSH, thyroid stimulating hormone; T4, total thyroxin.

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