



Stable isotopic composition of perchlorate and nitrate accumulated in plants: Hydroponic experiments and field data

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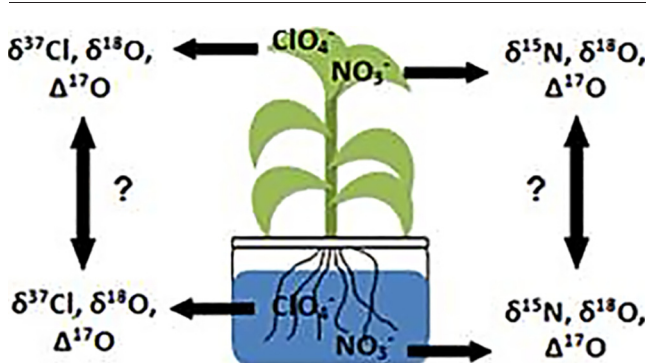
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HIGHLIGHTS

- Methods were developed to extract perchlorate from plants for isotopic analysis.
- Perchlorate and nitrate entered bean plants with little or no isotopic fractionation.
- Nitrate was fractionated isotopically within plants, whereas perchlorate was not.
- Data provided no evidence that plants cause isotopic variation of natural perchlorate.
- Perchlorate and nitrate isotopes in vegetables may reflect fertilizer and irrigation sources.

GRAPHICAL ABSTRACT



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ABSTRACT

Natural perchlorate (ClO_4^-) in soil and groundwater exhibits a wide range in stable isotopic compositions ($\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$), indicating that ClO_4^- may be formed through more than one pathway and/or undergoes post-depositional isotopic alteration. Plants are known to accumulate ClO_4^- , but little is known about their ability to alter its isotopic composition. We examined the potential for plants to alter the isotopic composition of ClO_4^- in hydroponic and field experiments conducted with snap beans (*Phaseolus vulgaris* L.). In hydroponic studies, anion ratios indicated that ClO_4^- was transported from solutions into plants similarly to NO_3^- but preferentially to Cl^- (4-fold). The ClO_4^- isotopic compositions of initial ClO_4^- reagents, final growth solutions, and aqueous extracts from plant tissues were essentially indistinguishable, indicating no significant isotope effects during ClO_4^- uptake or accumulation. The ClO_4^- isotopic composition of field-grown snap beans was also consistent with that of ClO_4^- in varying proportions from irrigation water and precipitation. NO_3^- uptake had little or no

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effect on NO_3^- isotopic compositions in hydroponic solutions. However, a large fractionation effect with an apparent ε ($^{15}\text{N}/^{18}\text{O}$) ratio of 1.05 was observed between NO_3^- in hydroponic solutions and leaf extracts, consistent with partial NO_3^- reduction during assimilation within plant tissue. We also explored the feasibility of evaluating sources of ClO_4^- in commercial produce, as illustrated by spinach, for which the ClO_4^- isotopic composition was similar to that of indigenous natural ClO_4^- . Our results indicate that some types of plants can accumulate and (presumably) release ClO_4^- to soil and groundwater without altering its isotopic characteristics. Concentrations and isotopic compositions of ClO_4^- and NO_3^- in plants may be useful for determining sources of fertilizers and sources of ClO_4^- in their growth environments and consequently in food supplies.

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1. Introduction

Perchlorate (ClO_4^-) is a ubiquitous trace inorganic constituent in the environment with both natural and anthropogenic sources. Widespread occurrence of natural ClO_4^- has been documented and there are numerous anthropogenic sources of ClO_4^- (Rajagopalan et al., 2009; Rao et al., 2007; Kounaves et al., 2010; Böhlke et al., 2009; Jackson et al., 2015a, 2015b). Because of its potential impact on thyroid function, the U.S. Environmental Protection Agency (EPA) is currently in the process of establishing a maximum contaminant level (MCL) for ClO_4^- in drinking water (Greer et al., 2002; “Drinking Water,” 2011). Leafy edible plants (e.g. lettuce and spinach), fruits and vegetables, and forage species are also an exposure route for humans, either from direct ingestion or when used for dairy feed that can lead to elevated concentrations of ClO_4^- in human breast milk and animal milk (Dasgupta et al., 2006; Jackson et al., 2005; Kirk et al., 2003, 2007; Sanchez et al., 2005).

Differentiating between various sources of ClO_4^- is possible based on the stable isotopic composition of ClO_4^- . The Cl and O stable isotopic composition of ClO_4^- has been shown to vary among samples representing different major sources or geographic areas (Jackson et al., 2010; Sturchio et al., 2011). Natural ClO_4^- has variable but generally positive $\Delta^{17}\text{O}$ values reflecting formation reactions involving ozone (O_3) and is thought to be derived largely from atmospheric deposition (Jackson et al., 2010; Sturchio et al., 2011). However, isotopic variation of natural ClO_4^- indicates that multiple production mechanisms may exist, or that post-depositional alteration (fractionation and/or exchange) can alter the original isotopic composition. Processes that could alter ClO_4^- isotopic compositions in the environment include microbial transformation, diffusion, isotope exchange with water, and plant uptake/transformation (Jackson et al., 2010; Van Aken and Schnoor, 2002; Sturchio et al., 2007; Hatzinger et al., 2009).

Microbial degradation produces a well-described mass-dependent effect on $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$, but degradation alone cannot explain the isotopic variation among different geographic locations (Sturchio et al., 2007; Hatzinger et al., 2009; Sturchio et al., 2003). Isotopic fractionation of ClO_4^- by transport-related processes (dissolution/precipitation and diffusion) has not been thoroughly investigated, but such effects are likely to be smaller than the observed isotopic variations of natural ClO_4^- (Desaulniers et al., 1986; Kaufmann et al., 1993; Ransom et al., 1995). Isotope exchange of O between ClO_4^- and coexisting substances such as water, could affect ClO_4^- isotopic composition, but experiments indicate the $\text{ClO}_4^- - \text{H}_2\text{O}$ exchange half-life is > 100 years in the absence of catalysts (Böhlke et al., 2005; Hoering et al., 1958).

The effect of plant uptake on ClO_4^- isotopic compositions is not yet clear. Numerous soil and hydroponic exposure experiments (Sanchez et al., 2005; Seyfferth and Parker, 2007; Seyfferth et al., 2008a, 2008b; Ha et al., 2011; Voogt and Jackson, 2010) have indicated the potential for plants to uptake and accumulate ClO_4^- . It is possible that plants could change the ClO_4^- isotopic composition through a variety of mechanisms including: transport carriers in the root; diffusion limitations through the root; reduction of ClO_4^- within the plant; translocation within the plant; and exchange of O between ClO_4^- and H_2O or other compounds catalyzed by plant enzymes. It is well-known that physiological and physicochemical processes (fixation, assimilation, and

diffusion) in plants can cause isotopic fractionation of carbon (Marshall et al., 2007; Farquhar et al., 1989; Schmidt et al., 2015) ($^{13}\text{C}/^{12}\text{C}$) and nitrogen ($^{15}\text{N}/^{14}\text{N}$) (Schmidt et al., 2015; Evans, 2001; Mariotti et al., 1982; Werner and Schmidt, 2002); likewise, intracellular processing of ClO_4^- within plants may also affect ClO_4^- isotopic compositions. There are conflicting published results concerning ClO_4^- reduction in plants (Van Aken and Schnoor, 2002; Seyfferth et al., 2008b). Understanding whether or not plants can alter the isotopic composition of ClO_4^- is important because such alteration could introduce complications for determining sources of ClO_4^- in plants, soils, and groundwaters.

In the current study, controlled experiments were conducted to develop procedures for analyzing the isotopic composition of ClO_4^- extracted from plants and to determine whether isotopic exchange or fractionation (by transport or degradation) might alter the isotopic composition of ClO_4^- accumulating in plants. This was accomplished by comparing the stable isotopic compositions of ClO_4^- accumulated in hydroponically grown snap bean plants (*Phaseolus vulgaris* L.) with those of the starting reference materials and growth solutions. Results were interpreted in part by contrasting the isotopic fractionation of ClO_4^- and NO_3^- in the same experiments. This is important because isotopic fractionation effects of enzymatic reactions may not fully be expressed in residual reactants (i.e. in heterogeneous systems where reactions are transport-limited). Therefore, a lack of observable isotope effects in extractable ClO_4^- might not be a reliable indicator of ClO_4^- stability unless extractable NO_3^- exhibited substantial fractionation effects. We also evaluated ClO_4^- isotopic composition in plants and source water for field-grown snap beans to validate the applicability of our methods in a more realistic setting. In order to demonstrate how our methods can be used to identify sources of ClO_4^- in the food chain, we analyzed commercially grown spinach and snap bean plants exposed only to background concentrations of ClO_4^- .

2. Materials and methods

2.1. Hydroponic snap bean studies

Hydroponic greenhouse studies were conducted at the Texas Tech University Greenhouse Complex in Lubbock, TX. Snap beans (*Phaseolus vulgaris* L.) were grown hydroponically in a nutrient solution containing commercial ClO_4^- and/or a USGS ClO_4^- standard. Snap beans were selected for the hydroponic study as part of more comprehensive ongoing growth studies by the Agricultural Research Service (ARS) of the U.S. Department of Agriculture (USDA), which are described in the snap bean field studies section below. Details regarding the growth, collection, and analysis of the snap bean plants in the hydroponic study are described below.

Two hydroponic experiments were conducted with multiple treatments in each experiment (Table 1). Treatments generally consisted of snap beans (*Phaseolus vulgaris* L.) grown in nutrient solutions containing ClO_4^- (0.01, 2, and 10 mg/L) along with NO_3^- (235–274 mg $\text{NO}_3^-/\text{N/L}$). The 2 and 10 mg/L ClO_4^- treatments were used in order to reduce the amount of plant mass needed to be extracted for isotopic analysis while the 0.01 mg/L ClO_4^- treatment was used to approximate realistic values of ClO_4^- observed in nature (Rajagopalan et al., 2009; Rao et al.,

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