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Reevaluation of the global warming impacts of algae-derived biofuels to account for possible contributions of nitrous oxide

Sarah K. Bauer[a], Lara S. Grotz[a], Elizabeth B. Connelly[b], Lisa M. Colosi[a,*]

[a] Department of Civil and Environmental Engineering, University of Virginia, 351 McCormick Road, P.O. Box 400742, Charlottesville, VA 22904, United States
[b] Department of Systems and Information Engineering, University of Virginia, 151 Engineer's Way, P.O. Box 400747, Charlottesville, VA 22904, United States

HIGHLIGHTS

- LCAs of algae biofuels have overlooked a possible key contributor to GWP: N_2O.
- Experiments show min N_2O emissions under oxic conditions with nitrate N-source.
- Experiments show max N_2O emissions under anoxic conditions with nitrite N-source.
- Min N_2O emissions mediate <1% increase in GWP compared to existing estimates.
- Max N_2O emissions mediate an increase in existing GWP estimated by roughly 25%.

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ABSTRACT

The environmental impacts of algae biofuels have been evaluated by life-cycle assessment (LCA); however, these analyses have overlooked nitrous oxide (N_2O), a potent greenhouse gas. A literature analysis was performed to estimate algal N_2O emissions and assess the impacts of growth conditions on flux magnitudes. Nitrogen source and dissolved oxygen concentration were identified as possible key contributors; therefore, their individual and combined impacts were evaluated using bench-scale experiments. It was observed that maximum N_2O emissions (77.5 μg/g algae/day) occur under anoxic conditions with nitrite. Conversely, minimum emissions (6.25 μg/g algae/day) occur under oxic conditions with nitrate. Aggregated N_2O flux estimates were then incorporated into a LCA framework for algae biodiesel. Accounting for "low" N_2O emissions mediated no significant increase (<1%) compared to existing GWP estimates; however, "high" N_2O emissions mediate an increase of roughly 25%, potentially jeopardizing the anticipated economic and environmental performances of algae biofuels.

1. Introduction

Energy is one of the most critical resources of our time. The bulk of energy used across the globe currently comes from a finite supply of fossil fuels, which emit harmful greenhouse gas (GHG) emissions when they are consumed, contributing significantly to climate change. Therefore, there is a growing need for domestically-sourced, climate-neutral fuels. Algae-derived biofuels are attractive in this vein, because they have the potential to be carbon-neutral; they do not compete with agricultural resources and land that could be otherwise devoted to food production; and they can grow in salty or brackish water, thereby relieving pressure on already strained freshwater resources (Clarens et al., 2010; Liu et al., 2012; Peccia et al., 2013). Together, these advantages position algae-derived biofuels as a promising source of alternative energy.

The environmental impacts of hypothetical systems producing algae-derived biofuels have been extensively evaluated by life-cycle assessment (LCA), a technique used to assess the environmental impacts associated with a product throughout all stages of its life cycle (e.g., raw resource extraction, manufacturing, distribution, use, end-of-life, etc.). The global warming potential (GWP) of algae-derived biofuels has been especially well-studied, in part because the U.S.'s regulatory framework, as embodied by the so-called *Renewable Fuel Standard* (RFS2), provides financial incentives for reducing life-cycle GWP compared to conventional petroleum fuels through the market for Renewable Identification Numbers (RINs) (Schnepf and Yacobucci, 2013). A recent analysis by Connelly et al. (2015) suggests that the GWP of algae-derived diesel produced via the process of hydrothermal liquefaction (HTL) is 41.3 g CO_2 equivalents (eq) per MJ (Connelly et al., 2015). This

* Corresponding author.
E-mail address: lmcolosi@virginia.edu (L.M. Colosi).

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represents a decrease of roughly 59% compared to the benchmark GWP value for conventional petroleum diesel as of 2005 (93.6 g CO_2eq/MJ) (Han et al., 2011; Soratana et al., 2012; US Congress, 2007). Because this reduction is greater than 50%, algae-derived biodiesel produced via the HTL pathway theoretically qualifies as "biomass-based diesel" under RFS2 (Soratana et al., 2012; Zhang et al., 2013). Thus, previous LCAs on algae-derived biofuels have been seemingly indicative of a promising future for the emerging algae biofuels industry.

We hypothesize, however, that existing LCA analyses, including Connelly et al. (2015) and others, have overlooked nitrous oxide (N_2O) emissions as a possible key contributor to life-cycle GWP for algae-derived biofuels (Frank et al., 2012; Singh and Olsen, 2011; Stephenson et al., 2010). To date, these emissions have not been accounted for in any significant algae LCA study; however, it has been demonstrated that appreciable N_2O is produced by algae in both natural and engineered settings (Fagerstone et al., 2011; Ferrón et al., 2012; Guieysse et al., 2013; Mengis et al., 1997; Wang et al., 2006). For example, Mengis et al. (1997) and Wang et al. (2006) reported significant emissions of N_2O from natural, eutrophic lakes exhibiting algal blooms and identified algae as the possible source of these emissions.

N_2O generation by axenic cultures of algae was first documented in the 1980s (Weathers, 1984; Weathers and Niedzielski, 1986). There was then relatively little work in this area for several decades, until the rise in popularity of algae-derived biofuels. More recently, Florez-Leiva et al. (2010) and Ferrón et al. (2012) measured N_2O emissions from industrial-scale open ponds of marine algae cultivated for biofuel production. Both studies observed a correlation between algae growth and N_2O production, whereby N_2O production was dependent upon nitrogen fertilizer availability. In the Florez-Leiva et al. (2010) study, N_2O production peaked at the senescence stage of algae growth (from 8 to 600 μmol/m^3). Fagerstone et al. (2011) measured N_2O production from freshwater algae under lab-scale conditions and found that altering the composition of the initial headspace, and thus, oxygenic state, produced significant change in N_2O production, whereby 0.5–0.8 ppm$_v$ N_2O was achieved during dark periods when the initial headspace was air under oxic conditions (i.e. high dissolved oxygen [DO]), as compared to 70–220 ppm$_v$ N_2O during dark periods for reactors with nitrogen gas (N_2) as the initial headspace under anoxic conditions (i.e. low DO). Other studies have also suggested that N_2O production decreases under conditions of high DO (Ferrón et al., 2012; Mezzari et al., 2013). More recently, studies have also shown the importance of the selection of nitrogen fertilizer (i.e. nitrate, nitrite, and ammonium) on the production of N_2O from algae. Several studies have shown that nitrite fertilizer availability strongly promotes N_2O production when compared to nitrate or ammonium (Alcántara et al., 2015; Guieysse et al., 2013; Weathers, 1984). It has also been suggested by literature that photosynthesis repression (dark conditions) promotes higher N_2O concentrations (Alcántara et al., 2015; Fagerstone et al., 2011; Guieysse et al., 2013). In contrast to many previous studies, Albert et al. (2013) reported that N_2O production from algae stimulated by nitrite and nitrate is primarily released during algae photosynthesis (light conditions).

To summarize, there is no clear quantitative articulation of how the selection of culture conditions or algae strain impacts overall emissions magnitude. Reported N_2O fluxes also vary dramatically among and within previous studies, making it difficult to determine what flux magnitude is typical. This lack of uniformity could explain why there has been no meaningful accounting for N_2O impacts in existing LCA framework to date, even though previous studies have called for LCA research on this front (Fagerstone et al., 2011; Florez-Leiva et al., 2010). This is potentially problematic given N_2O's very strong 100-year GWP, which is 298 times greater than that of CO_2 (Fagerstone et al., 2011). N_2O emissions from large-scale algae installations could, therefore, pose a severe threat to the environment even if relatively small amounts were emitted. This would dramatically undermine the perceived sustainability benefits and commercial appeal of algae-derived biofuels.

The overall objective of this research was to determine if accounting for N_2O production during algae cultivation would substantively change previous LCA-based estimates of life-cycle GWP for algae-derived diesel. The investigation was conducted in three parts: (1) thorough examination of literature measurements of N_2O emissions from algae grown under simulated cultivation conditions, to estimate fluxes and derive hypotheses about what conditions contribute to N_2O production; (2) bench-scale experiments to validate hypotheses about the individual and combined responsiveness of N_2O flux magnitudes to key cultivation conditions; and (3) integration of literature and experimental results into an existing LCA-based framework to assess the potential GWP impacts arising from N_2O emissions during production of algae-derived biofuels. Results from this research shed light on whether algae-derived biofuels can contribute to the achievement of national energy and climate change goals, as laid out in RFS2 and elsewhere.

2. Materials and methods

2.1. Literature review of N_2O emissions during algae cultivation

Several studies reporting measurements of N_2O production under simulated algae cultivation were reviewed, including (in chronological order): Weathers (1984), Weathers and Niedzielski (1986), Florez-Leiva et al. (2010), Fagerstone et al. (2011), Ferrón et al. (2012), Guieysse et al. (2013), Albert et al. (2013), and Mezzari et al. (2013). There was significant heterogeneity in the results from these eight papers. As such, it was necessary to apply a meta-analysis approach, so that the data could be standardized and aggregated together and then used to draw overall conclusions. In particular, it was necessary to collate information about cultivation conditions (i.e., pH, dissolved oxygen [DO] concentration, light intensity, medium composition, etc.), reactor size, headspace volume, and algae cell concentration, etc. from each study. These data were used to convert all measured N_2O fluxes into a single set of standardized units (μg N_2O/g algae/day) and to categorize commonalities between experimental conditions (e.g., high vs. low DO). A summary of information obtained from each study and an overview of how these data were converted to the standardized unit is provided in Section 2 of the S.I. document.

2.2. Experimental setup for simulated algae cultivation

A series of bench-scale cultivation experiments was performed to evaluate hypotheses about the impacts of seemingly critical growth conditions on the magnitude of N_2O emissions. These hypotheses, arising from a review of published studies, related to the DO concentration and the nitrogen (N) source in the growth medium. The model alga *Scenedesmus dimorphus* was used for these experiments on account of its widespread prevalence in temperate freshwater systems and its purported usefulness in commercial algae-to-energy production (Chisti, 2007; Zhang et al., 2014). This is a different algal species than what had been used in previous studies, which had been primarily *Chlorella* sp. (Alcántara et al., 2015; Guieysse et al., 2013; Mezzari et al., 2013; Weathers, 1984). Use of *S. dimorphus* was intended to diversify knowledge of N_2O emissions from different, commercially relevant algal species, so that it could be determined whether the