



CASE STUDY

Decarbonizing gas emissions from petrochemical production using microalgae

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ABSTRACT

BACKGROUND AND OBJECTIVES: Greenhouse gas emissions are the primary cause of global warming. Under the Paris Agreement, all countries have developed programs to reduce anthropogenic impact on the environment. In the petrochemical industry, for example, isoprene, is a major contributor to the production of carbon dioxide, generating large amounts of acidic and hydrocarbon gases that are burned and released into the atmosphere. This study aimed to investigate the absorption of greenhouse gases from isoprene production by the marine microalgae *Isochrysis galbana* and *Tetraselmis suecica*, as well as the freshwater microalgae *Chlorella vulgaris*.

METHODS: Microalgae cells were cultured in a bioreactor. The grown microalgae strains and mineralized water were fed to the bioreactor. Gases discharged from isoprene production were passed through the bioreactor. Inlet and outlet gas compositions were monitored by chromatography.

FINDINGS: Absorption of gases discharged from isoprene production by microalgae was studied for the first time. *Chlorella vulgaris* microalgae reduced methane and carbon dioxide contents by an average of 20 times. A mixture of microalgae *Tetraselmis suecica* and *Isochrysis galbana* reduced methane and carbon dioxide contents by a factor of 10 but completely absorbed hydrocarbon gases from methane to pentane.

CONCLUSION: The results indicate that microalgae cultivation can be used as a reliable and stable technology for the biofixation of the gases discharged in isoprene production. This technology can eliminate the combustion stage of hydrocarbon gases in isoprene production and significantly reduce carbon dioxide emissions into the atmosphere.

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INTRODUCTION

Anthropogenic blow-off gases emitted into the atmosphere by industrial and energy enterprises significantly increase the amount of greenhouse gases. The greenhouse gas used to record the emissions of fossil fuel combustion products into the atmosphere is carbon dioxide (CO₂). The emissions of CO₂ determine the amount of greenhouse gases according to the Kyoto Protocol and other agreements. According to numerous studies and obtained technical solutions (Mitsubishi Heavy Ind. Ltd., 1991; Yilong et al., 2015), the concentration of CO₂ in the atmosphere has already exceeded 420 ppm in April 2021. The International Group of Experts on Climate Change predicts that by 2100, CO₂ concentrations will reach 570 ppm, leading to an increase in the average temperature of the Earth's surface by 1.9 degrees Celsius (°C) (Dissanayake et al., 2019). It has been reported (Li et al., 2023) that about 60 percent (%) of the Earth's inhabitants experience record-high annual temperatures. Excessive CO₂ emissions are generally considered the primary cause of global warming. Moreover, CO₂ emissions account for about 80% of all greenhouse gases. Human activities are the main cause of CO₂ emissions into the atmosphere, with fossil fuel combustion, agricultural activities, and industrial processes (Hussain et al., 2018) playing a leading role. In particular, since the Industrial Revolution, the use of fossil fuels in the power generation sector has been the main source of CO₂ emissions (Ahmed et al., 2019). The Paris Agreement on reducing greenhouse gas emissions has been signed by most countries. Microalgae are a good choice for use in the biological capture of CO₂ and other greenhouse gases because they are universal photosynthetic microorganisms and, most importantly, can capture the heat and fine dust emitted by blow-off and exhaust gases (Kamyab et al., 2019). The high emissions in the Northern Hemisphere are due to the large number of industrial establishments in Eurasia and North America. Moreover, large populations and big-scale transportation systems consume significant amounts of energy in this part of the world. There is another important factor, which is the climatic specialties of the regions that require a long heating season. In addition, climate affects all aspects of people's lives, including energy consumption (Arredondo, 2023), the efficiency of machinery, and industry in

general (Farajzadeh, 2023). Anthropogenic blow-off gas emitted by industrial and energy enterprises significantly increases the amount of greenhouse gases in the atmosphere. These greenhouse gases include carbon oxides, water vapor, sulfur oxides, nitrogen oxides, polycyclic aromatic hydrocarbons, fluoride compounds, and solid particles (Laptev et al., 2022). Currently, several methods have been proposed for the disposal of carbon dioxide. Some of these methods have been successfully implemented. An example is the possibility of using compressed carbon dioxide as dry ice. However, this technology cannot be fully utilized as CO₂ returns to the atmosphere during its use (De Morais et al., 2007). Other methods of CO₂ waste utilization include a variety of physicochemical methods; however, the main problem common to all options is the cost of CO₂ absorption technology. Absorption, transportation, and storage of CO₂ are very costly, thus undermining the cost-effectiveness of the projects. Currently, the biological absorption of CO₂ through photosynthesis using *Chlorella vulgaris* is the only promising method. One way to reduce CO₂ levels is by passing the exhaust gases through photobioreactors containing microalgae (Aryal et al., 2021). The vital role and main life activity of microalgae is photosynthesis, during which the microalgae consume CO₂ and solar radiation energy. In addition, the biomass remaining during and after cultivation can be used for the biotechnological production of biofuels, fertilizers, etc (Samimi et al., 2023). Microalgae are a promising source of biomass thanks to their fast reproductive rates. They can produce up to 70 tons per hectare per year (t/ha/y) of biomass when using open ponds (even though poplar biomass is 10–13 t/ha/y) (Balagurumurthy et al., 2013). An important characteristic of microalgae is that they do not require land cultivation or significant expenditure on freshwater (either salt-rich water or wastewater can be used). Furthermore, they can absorb significant amounts of CO₂ (Culaba et al., 2020). Microalgae have been found to have the highest CO₂ fixation efficiency compared to terrestrial plants (Cheah et al., 2015). This can be explained by the faster rate at which substances are transported through algal cell membranes (Zeng et al., 2012) than through plant capillaries, rapid metabolism, and cell division (on average, each cell divides once a day), and the ability of unicellular organisms to mutate and adapt to environmental conditions (Chen et

al., 2013). Microalgae have been shown to capture approximately 1.8 kilogram (kg) of carbon dioxide per kilogram of microalgae (kg-CO₂/1 kg) of biomass produced. Microalgae biomass is a source of lipids and carbohydrates (CHO) and is a production material for alternative motor fuels (biodiesel and bioethanol) (Culaba *et al.*, 2020), hydrogen (H₂), propylene glycol (Otsuka, 1961), formic acid, cosmetics, and some other products (Arenas *et al.*, 2016). The combination of biotechnological and catalytic processes to obtain such products is carried out in the bioprocessing of complex plant materials (Gong *et al.*, 2014; Samimi and Nouri, 2023). Taking these into account, microalgae cultivation technology can be used to absorb blow-off gases to obtain useful by-products and minimize greenhouse gas, heat, and dust emissions into the atmosphere (Slegers *et al.*, 2020). The main objective of this research was to use microalgae culture to develop industrial blow-off gas utilization technology in order to reduce CO₂ emissions. This technology can significantly reduce greenhouse gas emissions from the petrochemical industry, hence reducing anthropogenic impact on the environment. This work studied the absorption capacity of the marine microalgae *Tetraselmis suecica* and *Isochrysis galbana*, as well as the freshwater *Chlorella vulgaris* during gas purification from the catalytic processing of isoprene petrochemical production from CO₂-containing impurities of methane (CH₄) and other hydrocarbon gases. This study aimed to investigate the absorption of greenhouse gases from isoprene production by the marine microalgae *Isochrysis galbana* and *Tetraselmis suecica*, as well as the freshwater microalgae *Chlorella vulgaris*. The study was conducted in 2023 at the Ufa State Petroleum Technical University in Ufa, Republic of Bashkortostan, Russia.

MATERIALS AND METHODS

According to the literature (Cho *et al.*, 2020; Deamicis *et al.*, 2019; Duarte *et al.*, 2016), decarbonizing blow-off gases and exhaust gases of oil refineries using microalgae strains in laboratory conditions is typically based on creating a gas model and selecting a narrow range of carbon dioxide concentration in an inert solvent medium. In turn, in actual production conditions, the contents of CO₂ and hydrocarbon gases in the discharged gases change, affecting the microalgae absorption properties. *Isochrysis galbana*, *Tetraselmis suecica*, and *Chlorella vulgaris* are widely

used as experimental subjects, having passed the stages of pilot testing and being applied in practice. Thus, these species were chosen to investigate their CO₂ absorption capacity in blow-off gases that contain the components of methane series ranging from C₁ to C₅. *Isochrysis galbana* is a marine microalga used in the aquaculture industry (Coutinho *et al.*, 2006). This microalga is characterized by high division rates and lipid accumulation, leading to high lipid productivity and a significant increase in valuable chemicals such as omega-3 fatty acids. In addition, Bhatti *et al.* (2002) reported that *Isochrysis galbana* assimilates carbon by the active transfer of CO₂ and bicarbonate ions (HCO₃⁻) through expressing a coenzyme carbonic anhydrase. *Tetraselmis suecica* is a marine green alga belonging to the prasinophytes and is widely used in hatcheries as food for bivalves, shrimp larvae, and rotifers (Muller-Feuga, 2004). It is also produced on an industrial scale for sale in the aquaculture market (Tredici *et al.*, 2009). These marine microalgae present a wide range of antimicrobial properties (Austin *et al.*, 1990; Austin *et al.*, 1992) and have high potential as probiotics for fish (Irianto *et al.*, 2002). Due to the high content of vitamin E, *Tetraselmis suecica* is also used as a source of this vitamin for humans and animals (Carballo-Cárdenas *et al.*, 2003). *Chlorella vulgaris* with well-studied morphological and physiological characteristics is widely used as an experimental subject (Bajguz *et al.*, 2009). *Chlorella vulgaris* is a cosmopolitan species that inhabits both terrestrial and aquatic environments: freshwater and saltwater. *Chlorella vulgaris* can obtain energy to develop through photosynthesis (autotrophic method) and respiration process (heterotrophic method). In addition, *Chlorella vulgaris* can combine the two methods (mixotrophic method) (Masojídek *et al.*, 2014). This strain has been extensively studied, used in several industrial experiments, and found to be a fast-growing strain with the ability to capture CO₂ from blow-off gases (Van Den Hende, 2012). It is rich in proteins (51%–58%), carbohydrates (12–17%) and lipids (14–22%) (Cheah *et al.*, 2015). To study the ability of microalgae to absorb emission gas components free of harmful sulfur oxides and nitrogen oxides, the gases formed during the dehydrogenation of isopentane into isoprene were selected. The content of sulfur and nitrogen compounds was strictly regulated, ensuring their absence in the exhaust gas. The exhaust gases from

isoprene production were fed into a cooling system to reach a temperature of 45–55 °C to purify it from catalytic dust. The gases were then fed into a burner for combustion. Currently, the gases discharged in this way are released into the atmosphere. The experimental gas was selected before the burner. The gas was extracted into a rubber cylinder and delivered to the laboratory. The appearance of methane in blow-off gases during intermediate selections from the tap position 5. Fig. 1 shows the adaptation of microorganisms to the nutrient medium and the formation of microalgae methane-forming bacterial symbiotes. Marine microalgae strains were provided by the Department of Materials Science and Corrosion Protection, Ufa State Petroleum Technical University, Russia. Cells were cultured in silicate-free mineralized-33 g/L (Guillard, 1975) enriched artificial seawater. In each experiment conducted as part of this study, microalgae underwent two successive growth stages: a preparation stage and a cultivation stage. In the preparation stage, cells were periodically multiplied in 500-mL Erlenmeyer flasks containing 250 mL of solution and then transferred to 3-L Erlenmeyer flasks containing 1.75 L of solution. Cultivation flasks were maintained at 25°C, a photoperiod of 12:12 hours (h), and a light intensity of 70 square meter per second (m^2/s) under fluorescent lamps. The 500-mL Erlenmeyer flasks underwent the process of barbotage by blowing filtered air through an aquarium compressor at an airflow rate of 800 cm^3/min . These algal cultures were used as starter cultures in the late exponential growth phase of the cultivation stage in a laboratory photobioreactor. The scheme of the photobioreactor is shown in Fig. 1.

Method of the gas composition analysis - In

the exhaust gas, the volume fractions of non-hydrocarbon gases, such as H_2 , nitrogen (N_2), oxygen (O_2) carbon monoxide (CO), CO_2 , and methane, were determined through absolute calibration using the LHM-8MD gas chromatograph with a flame ionization detector. The gas chromatograph is equipped with a chromatograph control unit and a chromatograph information processing unit. The chromatographic column was 2-m long and 3–4 mm internal diameter. Molecular sieve zeolite NaX (fraction 0.25–0.5 mm) was calcined at $T = 300^\circ\text{C}$. The mass fractions of C_2 – C_5 hydrocarbons were measured in the same gas chromatograph equipped with a thermal conductivity detector, a chromatographic column of 6-m length, and 3–4 mm internal diameter. The liquid phase was triethylene glycol dibutylate, and diatomite was used as the solid carrier. The method for the continuous cultivation mode on gas absorption experiments was based on existing production methods. Gas bubbling was performed sequentially through a cascade of 4 flasks passing through a layer of microalgae suspension. To obtain isoprene dehydrogenation of isopentane, the experiments were conducted using waste gas from petrochemical production. The bioreactor consisted of seven 3-L Erlenmeyer flasks with the gas supply tube down, to each flask was added 10–14 mL microalgae suspension, and the height of the liquid column was 10 cm. The tests were conducted during the daytime. Cylinders were placed at the inlet of the first four flasks and the outlet of the last four flasks (Fig. 1). Gas from storage tank 1 was pumped by peristaltic pump 2 at a flow rate of 200 mL/min . After the gas was completely pumped from cylinders 1 to 6 (1 run), they were rearranged, and bubbling continued. Gas sampling for component

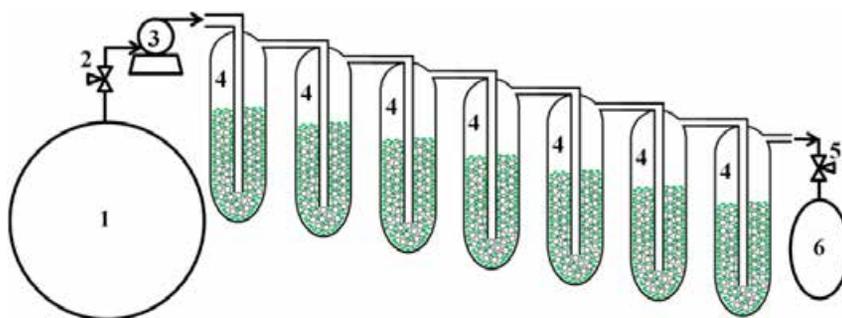


Fig. 1: Schematic of the bioreactor: 1- Cylinder with discharged gases, 2- Intake valve, 3- Peristaltic pump, 4- three-liter Erlenmeyer flasks containing microalgae, 5- Sampling outlet, 6- Intake cylinder.

Table 1: Changes in the composition of blow-off gas components before and after passing through the photobioreactor

Product	Cell volume, (cm ³)	Cell	Components composition (wt.%)															
			H ₂	O ₂	N ₂	CH ₄	CO	CO ₂	Ethane	Propane	Propylene	Isobutane	Butane	α-isobutane	β-transbutane	β-transbutane	Isopentane	Neopentane
Initial blow-off gas	57	before	15.43	0.375	42.13	24.66	2.47	2.42	6.97	2.45	2.68	0.241	0.0018	0.15	0	0.021	0.0034	0.0015
Blow-off passed through barboters with marine microalgae	53	after 7 runs	16.05	1.07	49.54	23.98	1.38	1.34	3.98	1.20	1.30	0.106	0.00057	0.064	0	0.0071	0.0011	0.0007
Tetraselmis suecica	55	after 24 h	0.934	27.75	70.82	0	0	0.105	0.38	0	0.0061	0.0007	0	0.00075	0	0.00048	0	0
Initial blow-off gas	57	before	15.43	0.375	42.13	24.66	2.47	2.42	6.97	2.45	2.68	0.241	0.0018	0.15	0	0.021	0.0034	0.0015
Blow-off passed through barboters with marine microalgae	52	after 7 runs	17.02	0.61	47.52	27.46	1.97	1.07	2.69	0.767	0.782	0.071	0.00018	0.036	0	0.0042	0	0.0001
Isochrysis galbana	54	after 24 h	0.96	30.35	67.30	0	0	0.104	1.28	0	0.0034	0.00053	0	0.00063	0	0.00041	0	0
Initial blow-off gas	50	before	11.1	8.2	42.36	18.19	1.09	1.84	7.61	2.81	3.02	0.694	0.182	2.57	0.018	0.025	0.18	0.103
Blow-off passed through barboters with marine microalgae	54	after 7 runs	15.28	0.38	39.66	30.54	2.11	1.46	4.91	1.87	1.88	0.416	0.081	1.26	0.0079	0.010	0.074	0.063
Tetraselmis suecica and Isochrysis galbana	55	after 24 h	1.28	29.94	67.10	0.28	0	0.16	1.23	0	0	0	0	0.0018	0	0	0	0

composition analysis was performed from cylinders 1 to 6 (Fig. 1).

RESULTS AND DISCUSSION

The CO₂ absorption efficiency for both microalgae species was 95.0% (Table 1). The marine microalgae *Tetraselmis suecica* and *Isochrysis galbana* showed the greatest affinity for hydrocarbons of the C₁–C₅ methane series. Moreover, the residual concentration of the gases at the outlet of the photobioreactor decreased completely as the number of carbon atoms in the chain increased. Assuming that the C₁–C₅ gases are components of the nutrient medium of the algal strains under study, the practical implementation of CO₂ absorption in production excludes the operation of flaring of these gases and further reduces CO₂ and water vapor emissions into the atmosphere. After 1 day, the total nitrogen and oxygen concentrations in the gas volume of the receiving chamber increased significantly from 42.51–48.13 weight percent (wt.%) to 97.65–98.57 wt.%. To simultaneously study the CO₂ absorption efficiency of the two algal strains, additional blow-offs were selected, hence the composition of the source gas was slightly different. The CO₂ absorption capacity of the microalgae mixture was 91.3%. A similar dependence was obtained for the absorption of hydrocarbons of the C₁–C₅ methane series by the mixture of algal strains. After 1 day, the gas volume in the receiving chamber showed a significant increase of 97.04 wt.% in the total percentage of nitrogen and oxygen. These results indicate that the use of strains of marine microalgae *Tetraselmis suecica* and *Isochrysis galbana* is a promising method for capturing CO₂ and C₁–C₅ methane series hydrocarbons in the blow-off gases of petrochemical and oil refinery plants.

Hydrogen is the lightest and most volatile gas. Numerous studies (Machinery et al. 2023) prove the release of biogenic hydrogen by algae, rather than its absorption. In our experiments, hydrogen diffused through a balloon. Studies on CO₂ absorption by the freshwater alga *Chlorella vulgaris* were conducted one month later using blow-off gases from the same technological installation, so the composition of the gas was different from the study period of marine microalgae (Table 2). The microalgae *Chlorella vulgaris* demonstrated significant absorption of C₁–C₅ methane series hydrocarbons. The microalgae *Chlorella vulgaris* demonstrated the ability to absorb CO₂ with an efficiency of 88.48%. After 1 day, a significant increase in the percentage of nitrogen and oxygen was observed, from a total of 16.50 to 92.74 wt.% by gas volume. Studies on changes in the genome, abundance, and other biological characteristics of the microalgae were not conducted due to the short duration of the experiment (24 h). Since microalgae cannot go through growth stages in such a short period of time, and the measured components show only slight changes, the composition of the aqueous medium in the initial and post-experimental conditions of the study with *Chlorella vulgaris* is presented for reference (Table 3). Studies conducted on CO₂ absorption for actual gases in the industrial production of isoprene did not correlate with the efficiency of the absorption capacity of all microalgae strains used when the gas components changed due to compositional differences. However, the data obtained provide general information on the feasibility of the CO₂ absorption method in the presence of C₁–C₅ methane series hydrocarbons. Therefore, it is possible to increase the efficiency of CO₂ and C₁–C₅ absorption by selecting the wavelength

Table 2: Changes in the composition of the blow-off gas after repeated passes through the photobioreactor

Components	Initial	After 3 runs	wt.%		
			After 5 runs	After 7 runs	After 24 h
H ₂	42.59	49.84	43.93	44.91	2.74
O ₂	6.89	4.80	4.40	5.49	9.61
N ₂	9.61	12.58	18.04	23.01	83.13
CO	2.35	3.58	2.71	2.57	0
CO ₂	7.64	3.88	4.26	2.97	0.88
CH ₄	13.89	16.43	18.31	16.63	0
Ethane	4.29	2.23	2.29	1.79	1.92
Derivatives of propane	8.02	4.38	4.03	1.95	0.85
Derivatives of butane	4.04	1.99	1.78	0.58	0.11
Derivatives of pentane	0.64	0.29	0.26	0.09	0

Table 3: Changes in the composition of the aqueous (nutrient) medium with *Chlorella vulgaris*

Defined indicator	Initial media	After blow-off gases (after 24 h)	After smoke gases (after 24 h)
Potential of hydrogen (pH)	4.95	5.81	5.32
Nitrite ion: NO ₂ ⁻ milligram per gram (mg/L)	11.86	9.32	11.35
Nitrate ion: NO ₃ ⁻ (mg/L)	1095.60	1224.9	1156.85
Ammonium ion: NH ₄ ⁺ (mg/L)	8.51	77.22	14.14
Phosphate ion PO ₄ ³⁻ (mg/L)	98.0	101.0	97.0

of illumination, the temperature of the microalgae suspension, the bubbling rate, and the size of the gas bubbles.

CONCLUSIONS

Absorption of gases discharged from isoprene production by microalgae was studied for the first time. During isoprene synthesis by two-stage dehydrogenation of isopentane, waste gases such as light hydrocarbons C₁–C₅ and inert gases CO, CO₂, and N₂ were formed. Since the gas mixture was not utilized, the gases were sent to the furnace for combustion according to the technological scheme. Then, the combustion products of the waste gas and furnace gas were released into the atmosphere. Expert assessments on the calculation of CO₂ emissions from isoprene production are not presented in the literature. According to estimates, the carbon dioxide emissions are equivalent to 10,000 to 15,000 tons per year. Microalgae cultivation technology is recognized as the most effective and natural technology for utilizing carbon dioxide emissions to harness greenhouse gases. In this research, *Isochrysis galbana*, *Tetraselmis suecica*, and *Chlorella vulgaris* were selected to study the absorption capacity of CO₂ and hydrocarbon gases in the isoprene production discharged gases. Studies have shown that *Chlorella vulgaris* absorbs CO₂ and methane most effectively, reducing carbon dioxide content from 7.64 to 0.82 wt.% and methane content from 13.89 to 0 wt.%. All microalgae completely utilize carbon monoxide. C1–C5 hydrocarbon gases are absorbed most effectively by mixed strains of *Tetraselmis suecica* and *Isochrysis galbana*. Comparative studies on biological fixation of discharged gases indicate that the marine microalgae strains *Tetraselmis suecica* and *Isochrysis galbana* and their mixtures, as well as the freshwater microalgae strain *Chlorella vulgaris*, have the potential to serve as reliable and stable CO₂ biofixation mechanisms in the

purification of discharged gases. The development of disposal technologies for discharged gases can eliminate the need for a combustion stage, reduce CO₂ and combustion heat emissions by a factor of 10, reduce anthropogenic impacts on the environment, and slow down the pace of global warming.

AUTHOR CONTRIBUTIONS

F.B. Shevlyakov corresponding author, performed the main experiments, participated in the analysis of chromatography data, interpretation of the results, and preparation of the manuscript. O.R. Latypov organized, financed, and edited the work. A.B. Laptev prepared an experimental plan, translated and corrected the text of the article, and D.R. Latypova conducted laboratory studies.

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CONFLICT OF INTEREST

The author declares that there is no conflict of interest regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy have been completely observed by the authors.

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ABBREVIATIONS

%	Percent
°C	Degree Celsius
μl	microliter
C ₁ -C ₅	methane – pentane
C ₂ -C ₅	Ethane – pentane
CH ₄	Methane
cm ³	Cubic centimetre
cm ³ /min	Cubic centimeter per minute
CO	Carbon monoxide
CO ₂	carbon dioxide
H ₂	hydrogen
HCO ₃ ⁻	Hydro carbonate ion
h	Hour
g/L	Grams per liter
kg	Kilogram
kg CO ₂ /1 kg	Kilogram carbon dioxide per kilogram microalgae
micromole photons/(m ² s)	Micromole of photons per square meter per second
mg/L	Milligrams per liter
mL	Milliliter

mL/min	Milliliter per minute
mm	Millimeter
m ² /s	Square meter per second
N ₂	Nitrogen
NO ₂ ⁻	Nitrite ion
NO ₃ ⁻	Nitrate ion
NH ₄ ⁺	Ammonium ion
O ₂	Oxygen
pH	Potential of hydrogen
PO ₄ ³⁻	Phosphate ion
ppm	Part per million
t/ha/y	Tons per hectare per year
wt.%	Weight percent

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