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Potential utilization of waste nitrogen fertilizer from a fertilizer industry using marine microalgae

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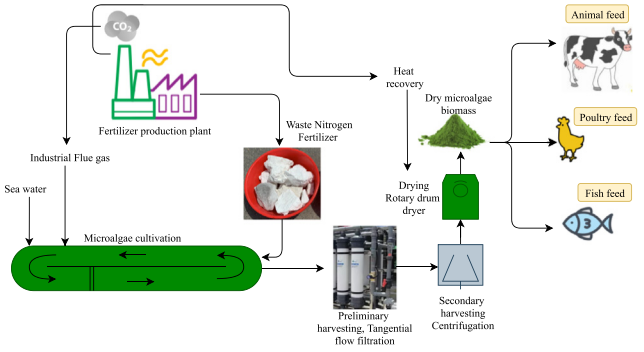
HIGHLIGHTS

- Microalgal utilization of waste nitrogen fertilizers (WNFs) of QAFCO was explored.
- A marine microalga, *Tetraselmis* sp., could efficiently utilize the WNFs.
- Waste nitrogen fertilizers did not affect the metabolites profiles of *Tetraselmis* sp.
- Different waste streams of QAFCO could lower biomass production energy demand.
- Environmental impact of landfilling WNFs could be reduced by growing algae with it.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated the feasibility of microalgal biomass production using waste nitrogen fertilizers (WNFs) generated by the Qatar Fertiliser Company (QAFCO). From the plant, three types of WNFs (WNF1, WNF2, and WNF3) were collected; WNF1 and WNF2 had high solubility (e.g., 1000 g/L) whereas WNF3 had low solubility (65 g/L). For a lower dosage (i.e., 100 mg N/L) of these WNFs, >98% of nitrogen was soluble in water for WNF1 and WNF2; however, 52 mg N/L was soluble for WNF3. Nitrogen content in these wastes was 44, 43, and 39% for WNF1, WNF2, and WNF3, respectively. As these WNFs were used as the sole nitrogen source to grow *Tetraselmis* sp., *Picochlorum* sp., and *Synechococcus* sp., *Tetraselmis* sp. could utilize all the three WNFs more efficiently than other two strains. The biomass yield of *Tetraselmis* sp. in a 100,000 L raceway pond was 0.58 g/L and 0.67 g/L for mixed WNFs (all WNF in equal ratio) and urea, respectively. The metabolite profiles of *Tetraselmis* sp. biomass grown using mixed WNFs were very similar to the biomass obtained from urea-added culture – suggesting that WNFs produced *Tetraselmis* sp. biomass could be used as animal feed ingredients. Life cycle impact assessment (LCIA) was conducted for six potential scenarios, using the data from the outdoor cultivation. The production of *Tetraselmis* sp. biomass in QAFCO premises using its WNFs, flue gas, and waste heat could not only eliminate the consequences of landfilling WNFs but also would improve the energy, cost, and environmental burdens of microalgal biomass production.

1. Introduction

The landfilling of municipal sewage sludge and municipal solid waste is linked with the release of greenhouse gas (GHG) emission, eutrophication, and many other categories of environmental pollution

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(Lombardi et al., 2017; Rajcoomar and Ramjeawon, 2017; Torrente-Velásquez et al., 2020). While the degradation of organic components could mainly lead to the release of GHG, the release of other elements (e.g., nitrogen, phosphorus, etc.) could be linked with eutrophication (Boeykens et al., 2017; Huang et al., 2017; Strokal et al., 2020). Qatar Fertiliser Company (QAFCO) is one of the world's largest urea fertilizer production industries located in the southern part of Qatar. Throughout the year, QAFCO produces a large volume of waste nitrogen fertilizers (WNFs) whenever there is a shutdown of the production line due to scheduled maintenance or any other reasons. As these WNFs are different in morphology, form, and color compared to the desired product, these are not sold commercially and instead landfilled in a designated area (Prajapati et al., 2010). However, there is a potential of leaching soluble nitrogen-rich compounds from this waste, which could result in an uncontrolled algal bloom in the surrounding aquatic environment (Guo et al., 2019; Peng et al., 2017; Torrente-Velásquez et al., 2020).

Among many alternative approaches to landfilling waste materials, the recycling or recovery of useful components from the waste materials could be an alternative strategy to reduce the volume and minimize the impact of pollution (Chung and Poon, 1996; Das et al., 2020; Fernández-Braña et al., 2020; Ferronato et al., 2019). In addition, conventional techniques such as incineration, pyrolysis, and gasification are being utilized for solid waste treatment (Matsakas et al., 2017; Phan et al., 2013; Velghe et al., 2011). In the context of a circular economy, the ultimate aim is to recycle the atoms (Breure et al., 2018; Stahel, 2016; Velvizhi et al., 2020). Microalgal ability to recover nutrients (Nitrogen, Phosphorus, and other elements) from different wastewaters were previously reported (Christenson and Sims, 2011; Das et al., 2018a; Ji et al., 2015; Shahid et al., 2020). Microalgae are capable of utilizing a variety of nitrogen sources such as (i) inorganic nitrate, nitrite, ammonium, and (ii) organic urea, aromatic compounds having nitro, amino groups, etc. (Lu et al., 2020; Markou et al., 2014; Zhao et al., 2019). The energy requirement of nitrogen fertilizer production could vary from 76.3 to 79.5 MJ/kg nitrogen (Mudahar and Hignett, 1985), which is also associated with the release of up to 540 kg CO_2 eq./tonne N production (Worrell et al., 1995). According to published literature, microalgae could be utilized to treat liquid waste, either pretreated or as in original form, from different industries (Nie et al., 2020; Scarcelli et al., 2020). Besides, leachates released from landfilled solid waste could also be treated with microalgae (Dogaris et al., 2020; Nawaz et al., 2020). However, the ability of microalgae to directly utilize semi-soluble solid by-products from a fertilizer industry as a nutrient source was not explored earlier. Recycling of nitrogen from the waste sources could have multiple benefits: avoiding the landfilling and utilization of the nitrogen that was fixed as WNFs using energy. Therefore, one of the objectives of this study was to determine the efficiency of microalgal nitrogen recycling from the different WNFs of QAFCO. The other objective of this study was to determine the life cycle impact assessment of producing microalgal biomass using WNFs to determine the environmental burden of the overall process.

2. Materials and methods

2.1. Characterization of the waste materials

Three types of waste nitrogen fertilizer samples (WNFs: WNF1, WNF2, and WNF3) were collected, based on the texture and color, from the waste container at the QAFCO fertilizer production facility. While the final product of the fertilizer company was granular urea, these waste samples were large and irregular shape solids, each weighing several kilograms (see Figs. S1.1, and S1.2). Once these samples were brought to the Algal Technology Program (ATP) labs, the rocks of similar texture and color were grind together to make powder, followed by sieving using 1 mm screen before conducting any experiment. The elemental composition of C, H, and N contents in these WNF samples directly was determined using Flash 2000 CHN analyzer (ThermoFisher Scientific, USA); the oxygen content was determined by deducting the combined C, H, and N content from 100%. Since these waste materials were collected from a urea fertilizer plant, the Fourier transmission infrared spectra for all the WNFs were compared with commercial urea using Agilent technologies Cary 600 Series FTIR spectrometer (K8006A, Malaysia). A known amount of these samples were digested in nitric acid, and the concentration of various contaminating metals in the digested samples were determined using Agilent 7700 series inductively coupled plasma – optical emission spectra (ICP-OES) machine. A known amount of each of these WNFs (100 mg N/L) was added in 2 L conical flasks containing 1 L DI water and mixed using magnetic stirrers for 5 days. The concentration of soluble nitrogen was determined, at a specific interval of time, using HACH TKN 139 kits and DR3900 HACH spectrophotometer.

2.2. Screening of microalgae

Three marine strains (e.g., *Tetraselmis* sp., *Picochlorum* sp., and *Synechococcus* sp.) were screened for their ability to utilize these waste sources as sources of nitrogen. The details of the two strains *Tetraselmis* sp. and *Picochlorum* sp. were given elsewhere (Das et al., 2016). *Synechococcus* sp. is a fast-growing marine cyanobacterium (1–2 μm length) capable of producing carotenoids (see Supplementary). Another reason for selecting these strains was that these strains could be grown at elevated salinity – as high as twice the salinity of natural seawater (unpublished). Sterile and filtered seawater (salinity 4.2% NaCl) was used to grow these microalgal strains. Each of these WNFs was used as the sole nitrogen source in the growth media such that the concentration of total nitrogen in each culture was 28 mg/L. As a control, each of these strains was also grown using urea as the source of nitrogen. For all the cultures, 10 mg/L KH_2PO_4 was added as a source of phosphorus. The trace metals were added as per Guillard f/2 nutrient recipe. Neither any silica nor any vitamin was added in these cultures. 25 mL inoculum of each strain was mixed with 975 mL of the growth media in a 1 L size PBR (dia: 8 cm). White fluorescent lighting was used to provide a light intensity of 600 μmol E/m^2/s on the wall of the PBR. The culture mixing inside the PBR was achieved by pumping compressed air, at a rate of 0.5 L/m, at the bottom of the PBR. After 7 days of growth, the difference between the final and initial biomass densities was determined. All the indoor growth experiments were triplicated and conducted inside a temperature-controlled portacabin (25 ± 1 °C). Based on the growth comparison, one strain was selected for large-scale cultivation.

2.3. Large-scale biomass production

Based on the microalgae screening experiment, as described in Section 2.2, *Tetraselmis* sp. was selected for large-scale outdoor cultivation. The selected microalga was then scaled-up to 20 L in indoor 2 plastic PBRs (10 L each). Next, these cultures were mixed with 180 L of seawater in a 1 m^2 (2.5 m × 0.4 m) raceway tank. Once the biomass density in this culture reached 0.5 g/L, the culture was split into two 5 m^2 raceway tanks and mixed with 900 L sterilized seawater. Next, the cultures in these two larger tanks were added to 23,000 L seawater in a 125 m^2 raceway pond. The growth of the strain was monitored daily by determining the biomass density. When the culture reached the stationary phase, 10,000 L of this culture was transferred to another 500 m^2 raceway pond and mixed with 90,000 L seawater. The powder samples of WNF1, WNF2, and WNF3 were mixed in an equal ratio before adding to the cultivation. The concentration of the nutrients used for outdoor cultivation was the same used for indoor screening work. The growth of the microalga in this raceway pond was also monitored daily. The details of these raceway ponds were presented earlier (Das et al., 2016, 2019a). All the outdoor cultures were periodically checked under the microscope to identify contamination from other microalgae and predators. For all the outdoor cultures, the seawater was sterilized by adding

a commercial-grade bleach solution (20 mL per 100 L), one day before inoculation. During the cultivation, the daily evaporation water loss in the raceway pond was compensated using seawater only. For all these growth trials, CO_2 was added continuously as 4 L/m and 12 L/m for 25,000 L and 100,000 L, respectively. The paddlewheels in all the outdoor raceway ponds were connected to motors with the same power ratings (1.6 kW). A portion of the culture was harvested using a modified pilot-scale membrane filter unit; the details of the previously used filter unit was given elsewhere (Das et al., 2019c).

2.4. Characterization of the biomass

The harvested biomass samples from the 100 m^3 raceway pond growth trials (both urea and WNFs) were freeze-dried. The quantification methods of lipid, protein, carbohydrate, and ash content in the biomass samples were described earlier (Das et al., 2016). The FAME profiles of the biomass samples were characterized at the ATP lab using the method described by Das et al. (2016). However, the biomass samples were sent to Eurofins India limited for characterizing the protein and sugar profiles using liquid chromatography coupled with refractive index detector, and liquid chromatography coupled with a fluorescent detector (Das et al., 2018b).

2.5. LCIA studies

2.5.1. Impact of landfilling waste nitrogen fertilizer from QAFCO

The landfilling site was assumed to be 10, 25, and 50 km away from the QAFCO site. The environmental impact of landfilling waste nitrogenous fertilizer was conducted using GaBi version 9.2 software. CML (Centrum voor Milieukunde Leiden) impact assessment method was used to evaluate various environmental impact categories (Gabathuler, 1997). The impact results obtained from GaBi software were normalized using their respective normalization factors. The impact results were normalized using the formula, $I_N = I_i/N_i$, where I_N is normalized impact result, and I_i and N_i are impact result before normalization and normalization factor, respectively.

2.5.2. LCIA of biomass production

2.5.2.1. Energy calculation. The Life cycle impact assessment of producing microalgal biomass in QAFCO premises was conducted to understand the net greenhouse gas reduction potential per ton of WNFs utilization. In the base case (Scenario I), it was assumed that *Tetraselmis* sp. would be grown in QAFCO premises in open raceway pond and batch mode using the WNFs and the flue gas. As QAFCO is located next to the sea, seawater could be easily collected from the sea. The evaporation water loss would be compensated by adding seawater. The fertilizer requirement, CO_2 requirement, and energy requirement for cultivation per unit of biomass production would be taken from the 100,000 L cultivation experiment. An improved case (Scenario II; see Supplementary) was assumed where *Tetraselmis* sp. would be grown in semi-continuous cultivation with average areal biomass productivity of 25 g/m^2/d, the CO_2 utilization efficiency of 70% (Zaimes and Khanna, 2013), and the paddlewheel energy requirement of 0.02 MJ/m^2/d (Lundquist et al., 2010). For all the scenarios, the energy requirement for preliminary and secondary harvesting of biomass by the cross-flow unit, and industrial centrifuge, respectively. For the scenario I, the harvested microalgae biomass will be dried using a rotary drum drier. However, in Scenario II, waste heat from the QAFCO industrial process would be used to dry the wet biomass. Scenario III was assumed to be similar to Scenario I, except that the microalgal cultivation site would be (i) 10 km away from QAFCO, and (ii) 10 km away from the sea (see Supplementary). Similarly, Scenario IV would be similar to Scenario II, except the cultivation site would be 10 km outside of QAFCO. Two additional scenarios (Scenario V and Scenario VI) were assumed, where urea would be used as a source of nitrogen. The other parameters for Scenario V and Scenario VI would be similar to Scenario III and Scenario IV, respectively. For Scenario IV and VI, the harvested biomass (25% solid content) would be transported to the QAFCO site by a truck. The energy associated with the construction of different facilities and machinery were not considered for conducting the LCIA. In an earlier study, it was found that *Tetraselmis* sp. could utilize simulated flue gas (unpublished data). Hence, the flue gas from the QAFCO plant was considered as a source of CO_2 for all the scenarios. It was assumed that the concentrations of added phosphorus, iron, and other trace elements, for each all the scenario, remains the same although the batch cultivation of microalgae (scenario I, III, and V) would lose more nutrients compare to semi-continuous cultivation (scenario II, IV, and VI) with growth-media recycling.

2.5.2.2. Impact of microalgal biomass production in different scenarios. The environmental impact associated with the utilization of 1-ton waste nitrogen fertilizer for six different scenarios were computed using GaBi version 6.2 software. Furthermore, inventories were developed for energy and mass flows for six different scenarios. The inventory data was used as input for computing environmental impact using GaBi software. Eleven relevant environmental impact categories were selected, and their corresponding impacts were determined based on the CML database. These impact categories are abiotic depletion, acidification potential, eutrophication potential, freshwater aquatic toxicity potential, global warming potential (100 years), human toxicity potential, marine aquatic toxicity potential, ozone layer depletion potential, photochemical ozone creation potential, and terrestric ecotoxicity potential.

3. Results and discussion

3.1. Characteristics of the waste nitrogen sources

Among the three different waste nitrogen sources, WNF3 had the lowest nitrogen content, whereas the other two had nitrogen content very similar to that of commercial urea (Table 1). The carbon content in the WNF3 was higher than the other two waste nitrogen sources. Among these waste nitrogen sources, both WNF1 and WNF2 had very high solubility in water (>98%) 15 min after mixing for dosing of 100 mg N/L; however, for the same dosage, about 47% of the WNF3 was water-soluble after 15 min. The solubility of the WNF3 increased to 51% after 5 days of mixing with the water. A follow-up experiment was conducted, where 100 g of these WNFs and urea were mixed with 100 mL DI, to understand the solubility of the WNFs. For example, the commercial urea has very high solubility (1079 g/L @ 20 °C) (Pinck and Kelly, 1925). 100 g of urea, WNF1, and WNF2 got solubilized in 100 mL DI water within 10 min of mixing, whereas WNF3 formed a white cloud with only 25.3 g N/L soluble nitrogen, which was only 6.5% of the added nitrogen. As an additional 100 mL of DI water was added in the same flask and mixed for another 15 min, only 8.3% of the added nitrogen was soluble (16.25 g N/L).

FTIR spectra of WNF2 was very similar to commercial urea (Madhurambal et al., 2010), whereas WNF1 and WNF3 were different compared to WNF2 and commercial urea (Fig. 1). The absorbance spectra for WNF1 was similar to urea, but the absorbance value was lower. FTIR of urea showed the presence of characteristic N—H bond

Table 1
Elemental composition (CHN) of different types of waste nitrogen sources.

Type	C (%)	H (%)	N (%)	O[a] (%)
WNF 1	20.4	6.4	45.1	28.1
WNF 2	19.6	6.7	45.8	27.9
WNF 3	24.4	4.3	39.1	32.2
Urea[b]	20	6.6	46.7	26.7

[a] By difference, and ignoring the other contaminants.
[b] From the chemical formula.

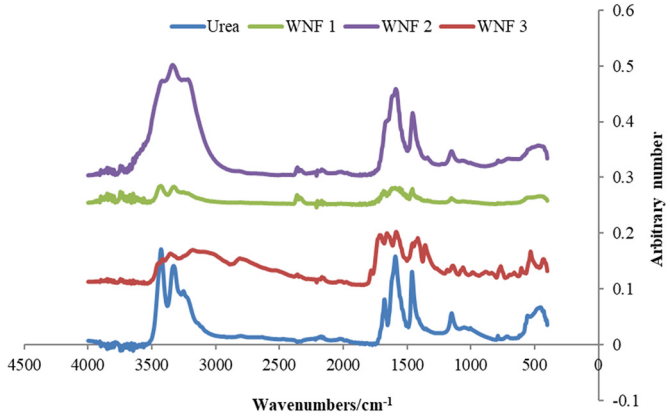

Fig. 1. FTIR spectrum of urea and waste nitrogen fertilizers.

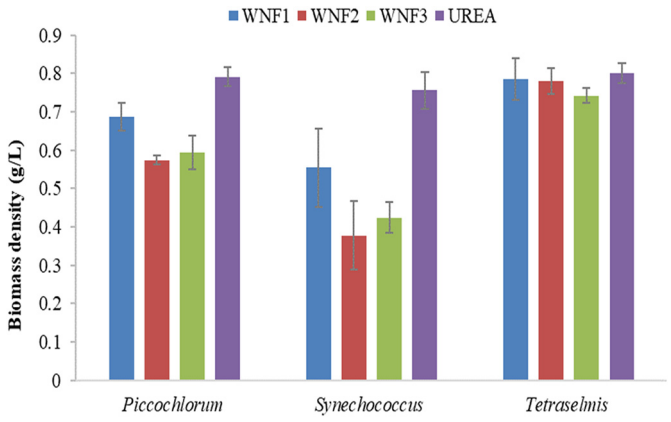

Fig. 2. Biomass yield comparison for different waste nitrogen sources (WNF1, WNF2, and WNF3) and urea for *Picochlorum* sp., *Synechococcus* sp., and *Tetraselmis* sp.

stretching at (3450 cm^{-1}, 1462 cm^{-1}), and C═O acyl bond stretching vibration at 1161 cm^{-1} (Factorovich et al., 2011; Liu et al., 2019). Although urea contains ammonium as an impurity, decomposition of urea fertilizer during the production process could lead to the formation of aromatic compounds such as cyanic acid-keto, biuret, triuret and cyanuric acids (Redemann et al., 1958). High amounts of biuret in urea fertilizer could reduce the urea solubility in water at low to ambient temperature. Compounds like biuret are toxic to specific crops and plants (e.g., apple, grapes, etc.) (Achor and Albrigo, 2005; Hamidipour et al., 2005). For biuret, FTIR peaks could appear at 1405 cm^{-1}, 1330 cm^{-1}, 1075, and 1021 cm^{-1}; for cyanuric acid, the FTIR peak could be found at 1158 cm^{-1}(Factorovich et al., 2011). FTIR spectra of WNF2 and WNF3 samples showed a peak at 1405 cm^{-1}, whereas WNF3 showed a peak at 1405 cm^{-1}, 1330 cm^{-1}, 1075 cm^{-1}, and 1021 cm^{-1}, indicating biuret type compounds could be present. The peak at 1158 cm^{-1} for WNF1 and WNF3 could represent cyanuric acid. The presence of minor peak at 2195 cm^{-1} in all the WNF samples indicated that cyanides and cyanate compounds could be present.

Among the three waste samples, WNF3 had the least contamination than the other two samples (Table 2). Sodium, calcium, and potassium were the major three contaminants for all the waste nitrogen sources. It should be mentioned here that all these waste samples were collected from an open metal carte - kept in an isolated area within the fertilizer company. Hence, it could be possible that some of the metal contamination could come from the carte itself.

3.2. Growth comparison of microalgae using the waste nitrogen sources

The comparison of biomass yields of the three strains for different nitrogen sources is shown in Fig. 2. All the strains were able to utilize all the WNFs. However, the biomass yield and growth rate, for all the three strains, were lower and slower for WNFs-added cultures compared to urea-added culture (growth data not shown here). Among the three strains, the biomass yield of *Synechococcus* sp. was the lowest for all the WNFs as compared to the corresponding biomass yields of the other two strains. Although at a low dosage of WNF3 addition (e.g., 100 mg N/L) almost 50% of the nitrogen was found soluble in the water after 24 h, it was surprising that the biomass yields for WNF3-added cultures were 56, 75, and 93% of control culture for *Synechococcus* sp., *Picochlorum* sp., and *Tetraselmis* sp., respectively. Hence, *Tetraselmis* sp. and *Picochlorum* sp. could have utilized the nitrogen from the non-soluble part of WNF3; it was also possible that the residual non-soluble nitrogen was also solubilized at a slow rate as the microalga consumed the soluble nitrogen fraction.

Table 2
Concentration of various metals (mg/kg) in three waste nitrogen sources.

Element	WNF1	WNF2	WNF3
Ba	0.02	0.00	0.02
Be	0.13	0.09	0.10
Ca	41.75	44.81	37.98
Co	0.00	0.06	0.12
Cu	1.54	0.00	0.00
Cr	0.17	0.00	0.05
Fe	7.96	3.38	0.00
K	10.84	15.21	7.06
Mg	1.55	3.20	1.45
Mn	0.08	0.07	0.00
Mo	0.07	0.00	0.00
Na	116.66	107.98	115.28
Ni	0.26	0.00	0.15
Zn	2.37	0.00	0.00
Pb	0.50	0.00	0.00
V	0.48	0.62	0.65

Microalgae are known to selectively uptake nitrogen from water-soluble organic compounds such as urea (Markou et al., 2014). Several microalgae (e.g., *Chlamydomonas reinhardtii*) could oxidize water-insoluble nitrogenous compounds (e.g., uric acid) to ammonia and urea derivatives, which they could utilize for their growth (Clode et al., 2009; Harris, 2001). The biomass yield of *Picochlorum* sp. for all the WNFs was ≤80% compared to the biomass yield – obtained using urea (i.e., control). On the contrary, the biomass yield of *Tetraselmis* sp. for the WNFs was 90–96% of the biomass yield for the control culture. Hence, the efficiency of utilizing non-soluble nitrogenous by-products of the fertilizer company was strain-dependent. Among the WNFs, WNF1 produced the highest biomass yield for all the strains. Although the solubility of WNF1 and WNF2 were the same as urea, the biomass yield of *Picochlorum* sp. and *Synechococcus* sp. for these two WNFs were lower compared to urea, probably due to the presence of other contaminants in the WNFs. On the contrary, *Tetraselmis* sp. was able to utilize all these WNFs better than the other two strains. Similarly, *Tetraselmis* sp. was able to grow in an industrial facility under stressful conditions; furthermore, toxic compounds and pathogens were also absent in the harvested *Tetraselmis* biomass (Pereira et al., 2019). Therefore, *Tetraselmis* sp. was selected for the large-scale cultivation study and LCIA study of microalgal biomass production using waste nitrogen sources from the industry.

3.3. Large scale growth of the selected microalgae using the waste nitrogen source

Tetraselmis sp. growth curve in 25,000 L and 100,000 L raceway ponds for both WNFs and urea added cultures were shown in Fig. 3. Similar to the PBR experiment, both the biomass yield and growth rate were higher for urea as compared to WNFs in both size raceway ponds. However, the biomass yield of *Tetraselmis* sp. in the raceways

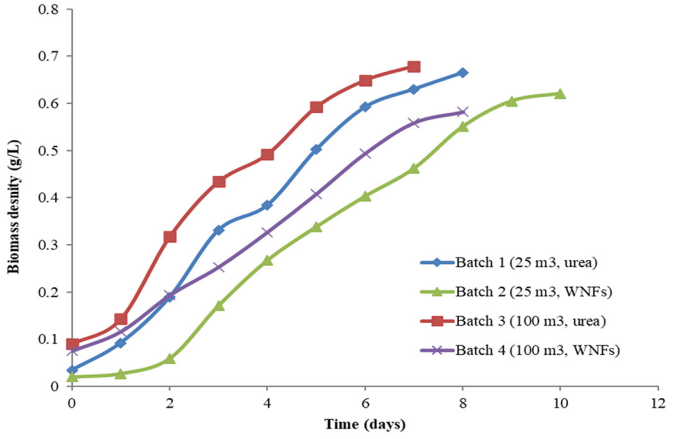

Fig. 3. Growth comparison of *Tetraselmis* sp. using urea and WNFs in 25,000–100,000 L raceway ponds.

pond was lesser compared to those obtained in the PBR experiments. For example, in the 100,000 L raceway pond, the biomass yield of *Tetraselmis* sp. was 0.679 g/L and 0.582 g/L, respectively. In another study, the biomass yield for *Tetraselmis striata* in an open raceway pond (10 m^2; 2000 L) was reported as 0.58 g/L (Boopathy et al., 2020). In our earlier outdoor large-scale batch cultivation studies, the biomass yield of *Tetraselmis* sp. was in the range of 0.5–0.69 g/L (Das et al., 2016, 2019c). Furthermore, the biomass yield of *Tetraselmis* sp. in different WNFs-added cultures was lower than that was obtained in urea-added culture. Therefore, it was expected that the mixture of WNFs would yield lower biomass density compared to the biomass density in the control culture. Nevertheless, the ability to tolerate a wide range of temperature and salinity and the requirement of low nutrients make *Tetraselmis* spp. very promising for commercial cultivation using saline water (Fon-Sing and Borowitzka, 2015).

CO_2 utilization by *Tetraselmis* sp. was better in the larger raceway pond as it had a deeper CO_2 sump compared to a smaller raceway pond. In the 100,000 L pond, CO_2 utilization was 49.6 and 37.3% for urea and WNFs, respectively; the difference in CO_2 utilization was due to the difference in the cultivation period (see Supplementary). The paddlewheel energy utilization for urea and WNFs – added cultures was 5.4 and 6.2 MJ/kg biomass, respectively. The combined biomass harvesting energy was 2.9 and 3.4 MJ/kg of biomass production for urea and WNF added cultures, respectively; the difference in harvesting energy requirement was due to the difference in biomass density in these cultures.

3.4. Comparison of Tetraselmis sp. biomass samples grown using urea and waste

In addition to the microalgal biomass yield and productivity, the quality of the WNFs produced biomass was further investigated so that an appropriate application of the biomass could be proposed. The composition of different metabolites of *Tetraselmis* sp. biomass samples, produced using urea and WNFs at 100,000 L raceway pond, was presented in Tables 3a–3c; the profiles of these metabolites between these two samples had minor variations. The concentration of galactose was the highest in both urea and WNFs – produced biomass samples. However, the concentration of galactose was lower for the biomass sample produced using WNFs as compared to the biomass sample produced using urea. Unsaturated fatty acids represent 62.3 and 61.8% of the total lipid fraction of urea and WNFs produced *Tetraselmis* sp. biomass samples, respectively. Palmitic acid had the highest concentration for both the biomass samples, whereas eicosenoic acid (C20:1) was the major compound among the unsaturated fatty acids for these biomass

Table 3a
Comparison of fatty acid methyl esters of *Tetraselmis* sp. biomass obtained from urea and WNFs added culture.

Fatty acid methyl esters	Urea as N source (%)	WNFs as N source (%)
C14:0	0.59	0.43
C16:0	28.34	28.85
C18:0	4.45	3.34
C18:1 n9-c	6.34	8.52
C18:1 n9-t	2.69	2.39
C18:2	13.83	14.19
C 18:3	13.11	10.35
C20:0	1.65	1.77
C20:1	21.20	21.09
C20:4	3.53	3.27
C20:5	1.61	1.98
C24:0	2.66	3.81
Total saturated	37.69	38.20
Total unsaturated	62.31	61.80

Table 3b
Comparison of mon/disaccharides of *Tetraselmis* sp. biomass obtained from urea and WNFs added culture.

Mono/disaccharides	Fructose	Glucose	Maltose	Sucrose	Galactose	Lactose
Urea as N source (g/100 g)	<0.5	<0.5	<0.5	<0.5	2.61	<0.5
WNFs as N source (g/100 g)	<0.5	0.64	<0.5	<0.5	1.09	<0.5

samples. Among the different essential amino acids, cysteine was not present for both the biomass samples. The concentration of arginine was much lesser for WNFs-grown culture compared to its concentration in the urea-grown biomass sample; the other protein compounds were similar in concentration. Nevertheless, *Tetraselmis* sp. biomass produced using WNFs could be a feed ingredient.

As per Qatar National Vision 2030, Qatar envisaged to achieve food security and enhance its internal food production (Ben Hassen et al., 2020). Aquaculture and animal feeds are two of the potential applications where the *Tetraselmis* sp. biomass could be utilized as a source of proteins, lipids, and minerals (Sousa et al., 2008; Tulli et al., 2012). Earlier studies have demonstrated that dried microencapsulated beta-carotene rich *Tetraselmis* sp. biomass could be a promising feed ingredient for European sea bass and pacific white leg shrimp (de Jesús Bonilla-Ahumada et al., 2018; Rahman et al., 2017; Tulli et al., 2012). Therefore, instead of landfilling the WNFs, these could potentially be used to cultivate *Tetraselmis* sp. to produce feed for aquaculture and animal.

Table 3c
Comparison of protein profiles of *Tetraselmis* sp. biomass obtained from urea and WNFs added culture.

Amino acid	Urea as N source (%)	WNFs as N source (%)
Alanine	8.09	8.50
Arginine	10.71	4.34
Asparic acid	10.75	10.28
Cystein+custine	N.A.	N.A.
Glutamic acid	13.58	14.36
Glycine	9.85	10.50
Histidine	1.76	1.82
Isoleucine	3.60	3.95
Leucine	7.37	8.11
Lysine	7.07	7.59
Methionine	7.32	8.16
Phenylalanine	4.58	5.08
Proline	5.31	4.99
Serine	4.45	4.95
Threonine	2.44	4.16
Tyrosine	2.36	2.34
Valine	0.77	0.87

Table 4
Potential impacts of landfilling waste nitrogen fertilizers.

Impact categories (CML-2016)	Land spreading of 1-ton municipal sewage sludge (Lombardi et al., 2017)[a]	Landfilling of 1-ton municipal solid waste (Rajcoomar and Ramjeawon, 2017)[b]	Landfilling of 1-ton waste fertilizer (this study)	Unit
Abiotic depletion (ADP elements)	−1.50E-04	4.51E-05	3.45E-06	kg.Sbeq
Abiotic depletion (ADP fossil)	2.22E+03	–	9.78E+02	MJ
Acidification potential (AP)	7.42E+00	1.22E+00	3.59E-02	kgSO2eq
Eutrophication potential (EP)	5.08E+00	2.08E+00	2.46E-02	kgPO4eq
Freshwater aquatic ecotoxicity pot. (FAETP inf.)	3.91E+02	2.92E+00	1.79E-03	kg1,4-DBeq
Global warming potential (GWP 100 years), excl biogenic carbon	1.38E+02	7.67E+02	1.31E-01	kgCO2eq
Human toxicity potential (HTP inf.)	7.72E+02	9.40E+00	1.11E-02	kg1,4-DBeq
Marine aquatic ecotoxicity pot. (MAETP inf.)	–	1.72E+04	1.14E-01	kg1,4-DBeq
Ozone layer depletion potential (ODP, steady state)	1.31E-05	2.78E-06	4.97E-04	kgCFC-11eq
Photochem. ozone creation potential (POCP)	2.35E-02	1.46E-01	1.63E-02	kgC2H4eq
Terrestric ecotoxicity potential (TETP inf.)	5.53E+02	2.55E-01	1.97E-03	kg1,4-DBeq

[a] The landfilling distance was 81 km.
[b] The landfilling distance was 45 km.

3.5. Life cycle impact assessment of waste fertilizer management

3.5.1. LCIA of landfilling waste fertilizers

The impact of landfilling 1-ton WNFs was compared with municipal sewage sludge landfilling and municipal solid waste landfilling in Table 4. The landfilling of WNFs was found to contribute to all the eleven environmental impact categories (Table 4; Supplementary). Among all the categories, the global warming air impact category had the highest impact. As the distance of landfilling site increased, the global warming impact also increased because of its linkage with CO_2 emissions during the transport of WNFs from QAFCO to landfilling sites (see Supplementary). Besides global warming, other impact categories like eutrophication, acidification, smog air, and human health particulate air were some of the major impacts of landfilling WNFs. Environmental impact categories such as human toxicity cancerous, human toxicity non-cancerous, ecotoxicity, and ozone depletion air would have a minimum environmental impact. For the landfilling of municipal sludge, eutrophication would have a major impact, followed by global warming, acidification, and smog formation (Cashman et al., 2014). However, in this study, landfilling WNFs resulted in maximum impact for global warming followed by eutrophication, acidification, and smog formation. In another study, land spreading of sludge showed the highest values for eutrophication and ecotoxicity, whereas other impacts of acidification, global warming, ozone depletion were low (Lombardi et al., 2017).

3.5.2. LCIA of microalgal biomass using the waste nitrogen sources

3.5.2.1. Input parameters for the LCIA study. The mass flow, per ton of *Tetraselmis* sp. biomass production, for all the scenarios were shown in Fig. 4. It should be noted here that the mass flow for scenario III and scenario V are the same as the scenario I and scenario II, respectively; however, the energy flow for these scenarios would vary. The seawater requirement would be 2428 m^3 for batch cultivation without any water recycling; for semi-continuous cultivation with water recycling, the seawater requirement would be 4.29 times lesser. In an earlier study, it was shown that the outdoor growth of *Tetraselmis* sp. was not affected within the salinity range of 4–8% NaCl (Das et al., 2019b). Per ton of microalgal biomass production, the required WNFs and urea were 166 kg (i.e., 71.4 kg N), and 147 kg (i.e., 68.7 kg N), respectively. From this study, the CO_2 requirement was calculated as 25.2 ton/

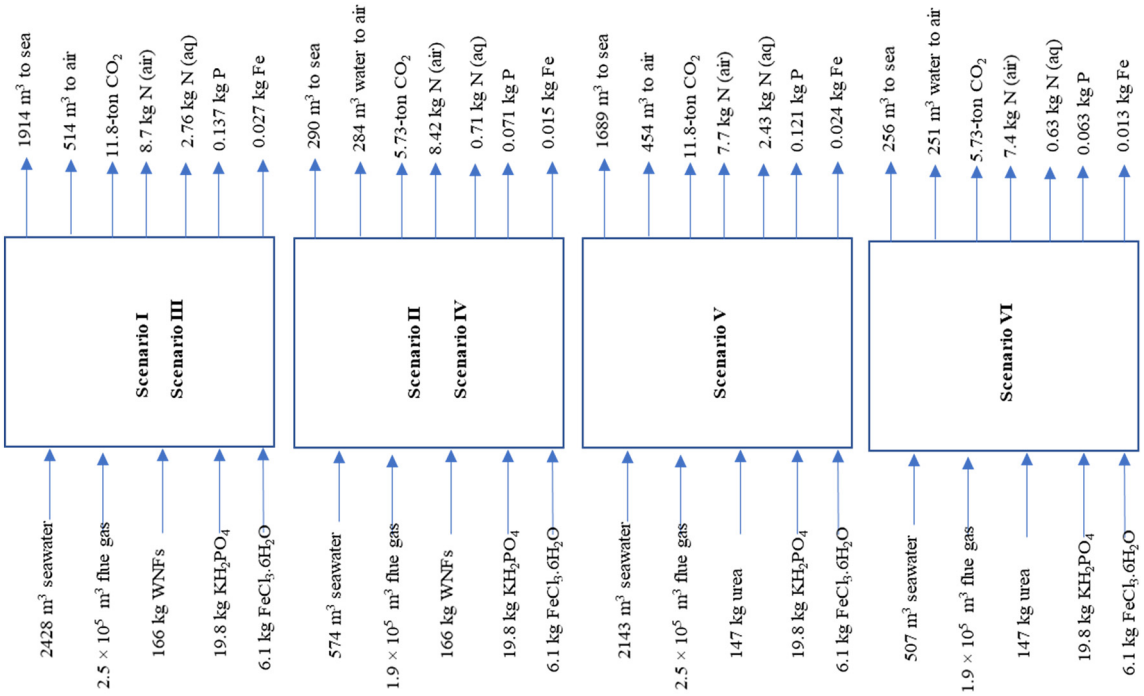

Fig. 4. Mass-flow for the six scenarios – based on 1 ton of microalgal biomass production.

biomass for the scenario I, III, and V; however, for the improved scenarios (i.e., II, IV, and VI), the CO_2 requirement was assumed as 19.1 ton/biomass. The flue gas requirement was 2.5×10^5 and 1.91×10^5 m^3 (assuming the density of flue gas at 1 kg/m^3, and CO_2 content in the flue gas is 10%) for batch and semi-continuous cultivations, respectively. For the scenario I – IV, the required amount of potassium phosphate and ferric chloride were 19.8 and 6.1 kg/ton of biomass, respectively. For scenario V and VI, 19.8 kg potassium phosphate and 6.1 kg ferric chloride were used per ton biomass.

The loss of nitrogen for the batch cultivation was calculated as 8.03–11.46 kg N/ton of biomass. The loss of nitrogen was lowest for scenario VI, whereas the highest loss was observed for scenarios I and III. For all the scenarios, the loss of nitrogen to air was 3 times or more compared to the loss of nitrogen in the discharge water. The loss of phosphorus was in the range of 0.063–0.137 kg/ton biomass. The iron requirement for *Tetraselmis* sp. was previously optimized (Das et al., 2019d); therefore, the loss of iron was in the range of 0.013–0.027 kg Fe/ton biomass. When the concentration of any element in the culture exceeds the requirement, several microalgae could exhibit the luxury uptake phenomenon (Powell et al., 2009; Solovchenko et al., 2019). Therefore, in the semi-continuous cultivation, the loss of N, P, Fe, and the other trace metals could be lower than the corresponding losses in the batch cultivation.

3.5.2.2. Energy analysis for microalgal cultivation for different scenarios. The energy requirement for supplying seawater (E_{sw}) was proportional to the seawater transportation distance and the water requirement per unit of biomass production. While the E_{sw} was the highest for Scenario III and Scenario V (0.28 GJ/ton biomass), it was minimum (0.047 GJ/ton biomass) for Scenario II. The energy requirement for pumping seawater/brackish water was reported as 0.59–1.18 GJ/ton biomass (Rogers et al., 2014). The semi-cultivation of a halotolerant microalga could allow recycling the growth media, and it could consequently reduce the energy requirement per unit of biomass production (Scenario II, IV, and VI). Since Qatar is a flat peninsula country with a low mean seawater level, transportation of seawater would require less energy.

The energy requirement for CO_2 supply (E_{CO2}) would be proportional to CO_2 transportation distance and the CO_2 utilization efficiency. The minimum and maximum values of E_{CO2} was found for Scenario II (0.27 GJ/ton biomass), and Scenario III and V (0.79 GJ/ton biomass).

The energy requirement for nutrient supply (E_{NS}) would mainly depend on the nitrogen requirement as the requirements for phosphorus, iron, and other elements are rather low. E_{NS} value would be minimum (0.25 GJ/ton biomass) for Scenario I, II, III, and IV, where WNF would be used. On the contrary, in Scenario V, and VI, the E_{NS} value would be maximum (3.5 GJ/ton biomass); the higher values of E_{NS} was due to the energy associated with nitrogen fertilizer supply.

The energy requirement by paddlewheel for cultivation (E_{PW}) would mainly vary based on the biomass productivity and efficiency of the paddlewheel-motor assembly. The E_{PW} value for the existing motor and paddlewheel assembly would be 7.2 GJ/ton biomass, whereas E_{PW} value could be reduced to 0.5 GJ/ton by using an optimized motor and paddlewheel assembly. Typical paddlewheel energy requirement was estimated as 0.5–20 GJ/ton biomass (Huang et al., 2016; Jorquera et al., 2010; Lundquist et al., 2010).

Recently, a pilot-scale membrane module was developed at the ATP demo facility consisting of 100 m^2 effective surface area; the energy requirement for harvesting *Tetraselmis* sp. biomass (culture salinity 4.6% NaCl) was estimated as 1.6 MJ/m^3 of biomass (unpublished). Hence, for Scenario I, III, and V, the cross-flow energy requirement would be 2.76 GJ/ton of biomass production. However, harvesting *Tetraselmis* sp. from a 6% NaCl salinity culture (average of 4–8% NaCl), the cross-flow energy requirement was found to be 80% higher than the energy required for 4.2% NaCl culture (Das et al., 2019c). Therefore, for Scenario II, IV, and VI, the culture would have incremental salinity, and the corresponding energy requirement for the cross-flow membrane was estimated as 4.95 GJ/ton. The energy requirement for the centrifugation would remain the same (0.62 GJ/ton biomass) for all the scenarios, as the same industrial centrifuge will be used (see Supplementary). Further reduction in harvesting energy could be possible by growing a self-settling or flocforming microalgae or cyanobacteria strains (Das et al., 2018a, 2018b).

For the scenario I, III, and V, wet biomass drying would cost 9.5 GJ/ton biomass, which included the heating energy and the energy for the rotary drum dryer. For scenario II, IV, and VI, the waste heat of QAFCO would be used; therefore, only the rotary drum energy (0.26 GJ/ton biomass) would be required. For scenarios IV and VI, since the cultivation of microalgae would take place at 10 km away from QAFCO, there would be an additional energy requirement of 0.063 GJ/ton biomass for truck transportation of the wet biomass to QAFCO.

The total energy requirement per ton of *Tetraselmis* sp. biomass production in different scenarios was shown in Fig. 5. Among these six scenarios, the energy required to produce microalgal biomass was the lowest (i.e., 6.9 GJ/ton) in scenario II and the highest (i.e., 24.6 GJ/ton) in scenario V. The energy requirement for biomass production for other strains in different locations could vary from 0.72 to 45.72 GJ/ton biomass (Jorquera et al., 2010; Marsullo et al., 2015; Medeiros et al., 2015); pumping and dewatering of microalgae were reported as two of the

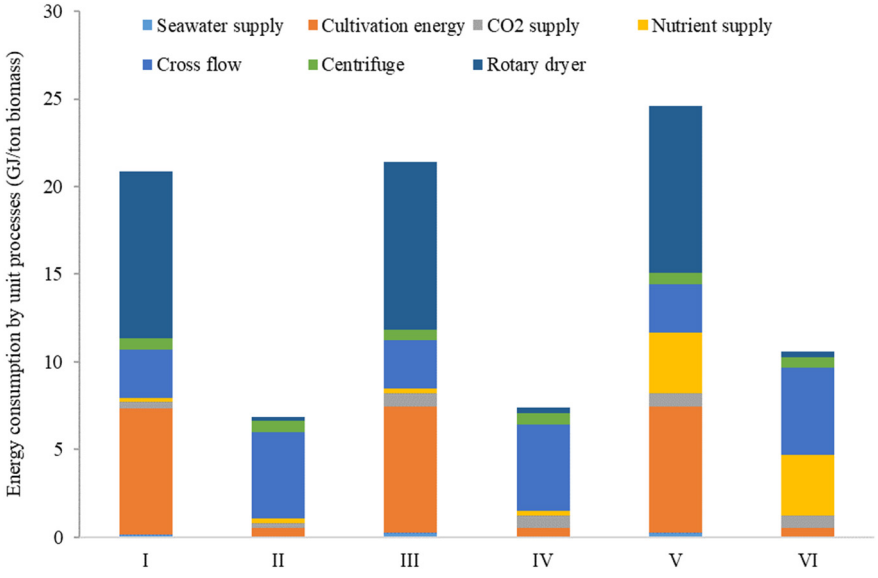

Fig. 5. Energy requirement for different unit processes per ton of nitrogen fertilizers (waste nitrogen sources, urea) for six different scenarios.

most energy-intensive unit processes for the production of microalgae biomass in open raceway ponds. For scenario II, the energy requirements for all the unit processes were the lowest compared to the corresponding values for other scenarios. For scenario IV, the total energy requirement was 9.3% higher than that of scenario II – which was mainly attributed to the difference in energy requirements for transferring CO_2 and seawater among these scenarios. For scenario VI, the total energy requirement was 54% higher compared to the energy requirement for scenario II, which was mainly dominated by the energy requirement for urea fertilizer production. For scenarios I, III, and V, the energy requirement by paddlewheel and the drying energy were the two main contributors to the total energy requirement. Overall, the production of microalgal biomass using QAFCO waste streams, inside the company premises or 10 km outside the company, could be very promising, which could contribute to national food security. While landfilling of the WNFs could have negative environmental impacts, the energy involved in the production of WNFs would also be wasted. Furthermore, microalgal biomass production would also allow capturing CO_2 and waste heat from the industry, which could improve the environmental sustainability of QAFCO.

3.5.2.3. LCIA of microalgal biomass production using waste nitrogen sources. Fig. 6 shows the relative contribution of various inputs of microalgal cultivation in each of the 11 environment impact categories. The actual values of these impacts were compared in the Supplementary file. According to CML 2001, if a microalga could be cultivated using WNFs from QAFCO, regardless of inside or outside QAFCO premises (i.e., Scenario I – IV), there would be no impact for the five environmental categories, such as terrestrial ecotoxicity potential, photochemical ozone creation potential, ozone layer depletion, marine aquatic ecotoxicity, and human toxicity potential. The environmental impact values obtained for landfilling WNF were much higher compared to impact results obtained for the four scenarios, where WNF would be used to produce microalgae biomass. On the contrary, if urea is used as the source of nitrogen for cultivating microalgae, it would contribute to all the environmental impact categories.

Normalized global warming potential for landfilling 1-ton waste nitrogen fertilizer was 1.29E-01 whereas, the global warming impact values for microalgae cultivation using waste nitrogen fertilizer ranged from −2.80E+00 to −3.69E+00. In another LCA study, microalgae biomass production for biofuel synthesis had lower GWP impact values similar to low GWP values for six scenarios found in this study (Lardon et al., 2009). Grierson et al. (2013) have also reported negative global warming impact values for the microalgae cultivation process, whereas harvesting and drying processes had positive impact values for acidification, eutrophication, water use, photochemical smog, and fossil fuel depletion. Nevertheless, in this study, the utilization of waste nitrogen fertilizer for microalgae biomass production could effectively lower the environmental impacts caused by landfilling of waste nitrogenous fertilizer.

4. Conclusion

Landfilling of waste nitrogen fertilizers could be detrimental to the environment. Instead of landfilling the waste nitrogen fertilizers (WNFs), these could be used as sources of nitrogen to cultivate specific microalgae (e.g., *Tetraselmis* sp.), which would eliminate the need for

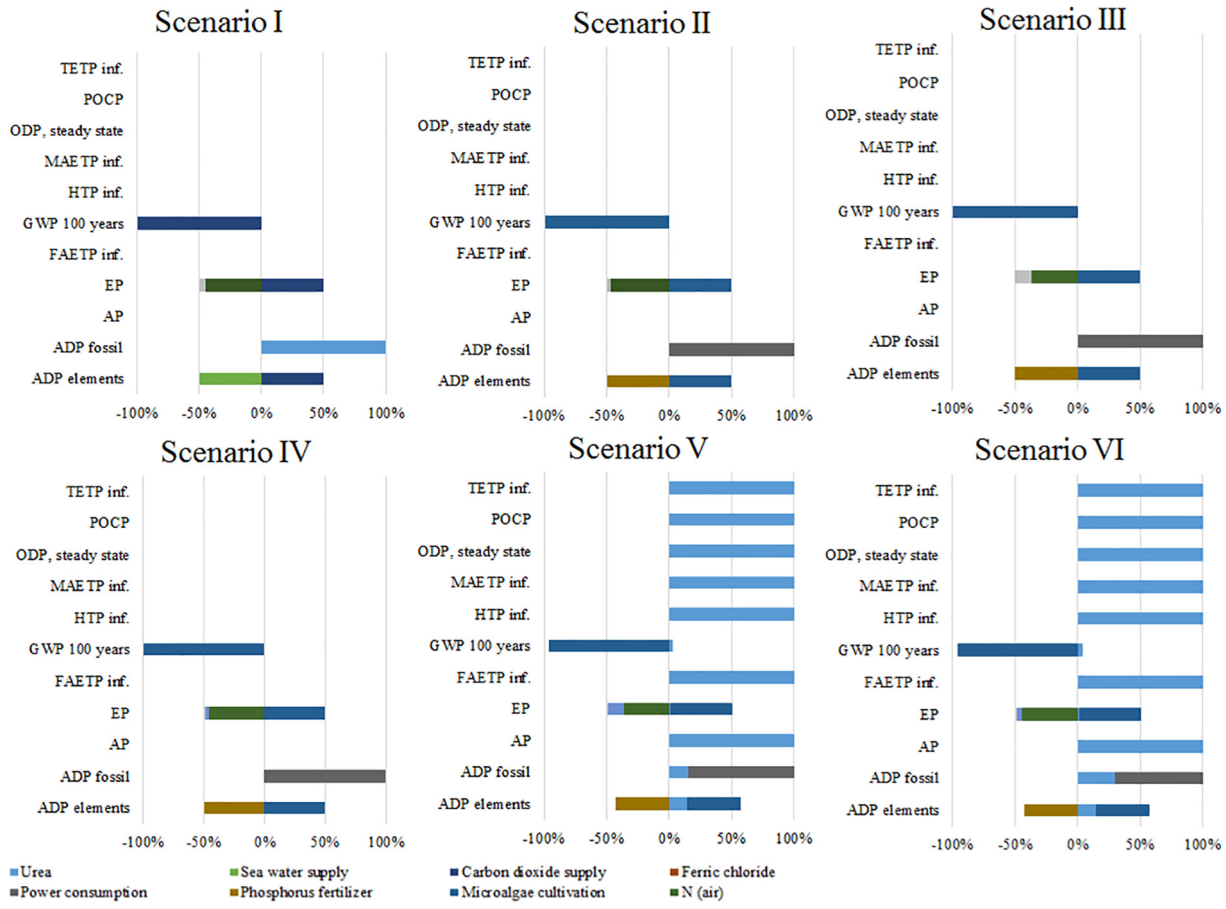

Fig. 6. The relative distribution of relevant environmental impacts, due to various input in microalgal cultivation, for six potential scenarios. (Abiotic depletion: ADP elements; abiotic depletion: ADP fossil; acidification potential: AP; eutrophication potential: EP; freshwater aquatic ecotoxicity pot.: FAETP. inf.; global warming potential: GWP 100 years; human toxicity potential: HTP inf.; marine aquatic ecotoxicity pot.: MAETP inf.; ozone layer depletion potential: ODP, steady-state; photochem. ozone creation potential: POCP; terrestric ecotoxicity potential: TETP inf.)

landfilling these wastes. Per unit of biomass production, the selection of microalgal cultivation site could highly influence the overall energy requirement and environmental impacts. Integration of other waste streams (i.e., flue gas, waste heat), from the fertilizer company, in the production of microalgae biomass could enhance the environmental sustainability of the fertilizer company while reducing the cost and energy requirement of microalgal biomass production. However, as compared to urea, WNFs resulted in lower biomass yield and productivity of *Tetraselmis* sp. Nevertheless, WNFs had little or no effect on different metabolites profiles of *Tetraselmis* sp. The viability and techno-economic feasibility of using waste nitrogen fertilizers – produced microalgae biomass as ingredients for fish feed would be studied in the future.

CRediT authorship contribution statement

Hareb Al-Jabri: Methodology, Writing - original draft, Writing - review & editing. **Probir Das:** Conceptualization, Methodology, Funding acquisition, Writing - review & editing. **Mahmoud Thaher:** Data curation, Writing - original draft. **Shoyeb Khan:** Data curation, Writing - original draft. **Mohammad AbdulQuadir:** Data curation, Writing - original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.142532.

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