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Baltic Sea microalgae transform cement flue gas into valuable biomass

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ABSTRACT

We show high feasibility of using cement industrial flue gas as CO_2 source for microalgal cultivation. The toxicity of cement flue gas (12–15% CO_2) on algal biomass production and composition (lipids, proteins, carbohydrates) was tested using monocultures (*Tetraselmis* sp., green algae, *Skeletonema marinoi*, diatom) and natural brackish communities. The performance of a natural microalgal community dominated by spring diatoms was compared to a highly productive diatom monoculture *S. marinoi* fed with flue gas or air–CO_2 mixture. Flue gas was not toxic to any of the microalgae tested. Instead we show high quality of microalgal biomass (lipids 20–30% DW, proteins 20–28% DW, carbohydrates 15–30% DW) and high production when cultivated with flue gas addition compared to CO_2–air. Brackish Baltic Sea microalgal communities performed equally or better in terms of biomass quality and production than documented monocultures of diatom and green algae, often used in algal research and development. Hence, we conclude that microalgae should be included in biological solutions to transform waste into renewable resources in coastal waters.

1. Introduction

1.1. Flue gas as CO_2 source for microalgae

The cement industry is responsible for approximately 4–5% of global CO_2 emissions [1–3]. Using mass cultivation of microalgae is considered environmentally safe and sustainable for the abatement of CO_2 from industrial flue gas [4–8]. Recent studies questioned the contribution of algae to global CO_2 removal since algae fix CO_2 from flue gas but do not offer permanent storage nor are energy efficient [9,10]. However, microalgae biomass can deliver products (biofuels, industrial material etc.) that may replace an equivalent amount of fossil fuels, hence facilitating the sustainability of microalgae-based product development [9]. By 2030 the EC proposes that emissions from sectors covered by emission trade scheme (ETS) will be 43% lower than in 2005 [11]. This proposal, combined with political climate change targets and market forces can provide economic incentive for future company investments in new technology.

Flue gas generally contains 3–15% CO_2 (v/v) depending on fuel feedstock and type of operation [12] and thus can be used as a source of CO_2 for microalgae cultivation. Microalgae show a good growth potential in CO_2 concentrations up to 10–20% regardless of the source, e.g. pure CO_2 [13,14] and industrial flue gas [15–17,6,18,8]. Industrial flue gas contains over 100 substances, of which several are potentially toxic to microalgae (e.g. SO_x, NO_x, HF, heavy metals) [19]. Numerous studies have weighed opportunities and limitations of microalgal cultivation and based on predictions have showed the potential of a process where industrial waste CO_2 is converted to bioproducts through algae [20–24]. Empirical studies on the tolerance of microalgae to industrial flue gas are increasing steadily but rarely include various taxonomic groups of microalgae, and trials with natural or multispecies communities are noticeably lacking.

1.2. Importance of diversity and production for microalgae cultivation

Outdoor mass cultivation of microalgae has generally focused on highly productive monoclonal cultures for biomass production or targeting specific chemicals. Few studies have been using multispecies cultures or natural assemblages of microalgae to improve production yields. Productivity and stability of natural terrestrial ecosystems have been positively linked to diversity and species richness [25–28] but may be applicable to marine habitats [29]. Productivity of agro systems is considered to benefit from intercropping through the establishment of stable and sustainable ecosystems within crop farmlands [30]. Both observational [31] and experimental studies [32–34] indicate that this applies also for microbial communities, including microalgae. The positive relationship between diversity and productivity may be explained by 1) the complementary effect, where resource utilization is higher in a more diverse community [35,29,36] and 2) the selection effect, where one highly productive species, is favored by certain environmental conditions over other species in a diverse community [37]. The two

Abbreviations: Chla, chlorophyll *a*; DW, dry weight; EC, European Commission; FG, flue gas; KAC, Kalmar Algae Collection; NC, natural community; PBR, photobioreactor; PTFE, polytetrafluoroethylene; Sm, *Skeletonema marinoi*; SYKE, Finnish Environment Institute; TC, total carbohydrates; TL, total lipids; TP, total proteins; v, volume; w, weight.

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mechanisms may not be complete contrasts but should both be accounted for, while estimating the effect of diversity on productivity [26,37]. The complementary effect in diverse microalgae communities could lead to a more stable and resilient system less prone to invasive species and zooplankton grazing pressure [38]. The same mechanism of decreased pest susceptibility was shown for plant crops [39]. Diverse communities seem to be more productive and resilient in natural variable environments where changing abiotic factors affect productivity.

Additionally, the spectrum of valuable chemicals in terms of lipids, proteins, carbohydrates and pigments produced will most likely be more diverse in a diverse community. Smith et al. [40] suggested that multispecies communities of microalgae in open pond cultivation systems could accumulate more solar energy as lipids due to a more efficient utilization of light from different functional groups of microalgae, in contrast to closed systems with monocultures. Positive effects of species richness (level of two, three and four species) were found on both algal biovolume and lipid content compared to monocultures [41]. These effects were attributed to complementarity rather than selection effects. Stockenreiter et al. [42] found the relationship of functional group richness more strongly linked to lipid content than mere species richness, suggesting that a more efficient light utilization within functionally diverse communities contributed to the higher lipid content. Extrapolating these findings from natural and artificial ecosystems to industrial mass cultivation of microalgae leads to a combination of uncertainties. Nonetheless, the use of natural community as inoculum in large-scale production system could increase the stability, resilience and productivity of the system.

Composition of the flue gas from the cement industry varies with the origin of the raw substrate and the combustion process. For the first time the potential use of flue gas from Cementa AB, Degerhamn, Öland, SE for microalgal biomass production was evaluated using monocultures and natural communities from the Baltic Sea.

This study aims to test the toxicity of cement flue gas on biomass production of a monoculture (*Tetraselmis* sp., green algae), and to compare biomass composition (lipids, proteins, carbohydrates) and production of a natural microalgal community dominated by spring diatoms to one highly productive diatom monoculture during treatments of flue gas or air–CO_2 mixture. The reference monoculture was *Skeletonema marinoi* (strain SMTV1), a rapidly growing diatom common in the spring bloom community in the Baltic Sea.

2. Material and methods

2.1. Study site

Cementa AB Degerhamn, Öland, southeast Sweden, manufactures 300,000 tons of cement annually and releases approximately 260,000 tons of CO_2 through their flue gas. The major components of the flue gas emissions, besides CO_2, are SO_2, NO_x and dust (Table 1). The Cementa HeidelbergCement group is working to reduce the CO_2 emissions by 10% by the year 2020 at the plant in Degerhamn, and will strive to achieve 0% by 2050. The possibility of lowering their carbon footprint by using mass cultivation of microalgae to capture the CO_2 rich flue gas is currently being evaluated in an academia–industry collaboration. The valorization of the produced algal biomass to generate bulk chemicals, such as lipids, carbohydrates and proteins for conversion to bioenergy or high value products is also assessed.

2.2. Flue gas and CO_2

The cement flue gas was collected from the monitoring sampling point in one of the flue stacks at the Cementa AB Degerhamn factory by using a high-pressure compressor and filling the flue gas into gas cylinders at 150–200 bar. The composition of the flue gas varied 12–15% during the experiments (Table 1). Industrial grade CO_2–air mixture (13.5% CO_2) was obtained from AGA Gas AB.

Table 1
Composition of the conditioned flue gas collected from Cementa AB, Degerhamn, Sweden for this study. Values are valid from April 2013 to May 2014, metal levels were measured in September 2012.
Source: environmental report HeidelbergCement, Degerhamn 2013.

Temperature	150–200 °C
CO_2	12–15%
O_2	0–21%
H_2O	0–15%
NO_x	<800 mg/Nm^3
SO_2	<50 mg/Nm^3
CO	0–1000 mg/Nm^3
NH_3	<50 mg/Nm^3
HCl	<10 mg/Nm^3
HF	0–0.01 mg Nm^{-3}
Dust particles	<10 mg/Nm^3
Metals[a]	<0.5 mg/Nm^3
Mercury (Hg)	<0.03 mg/Nm^3
Cadmium (Cd) + titanium (Ti)	<0.05 mg/Nm^3

[a] Metals: Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V.

2.3. Microalgal stock cultures

The green algae *Tetraselmis* (strain KAC21) and the diatom *S. marinoi* (strain SMTV1) were grown in filtered Baltic seawater (salinity 7, filtered 0.2 μm) enriched with original Guillard's f/2 medium and f/2 + Si respectively [43]. Strains were obtained from the Kalmar Algal Collection (KAC) and the Finnish Environment Institute (SYKE). Cultures were grown in 10 L glass flasks, gently bubbled with air at temperature 18 °C (*Tetraselmis*) and 15 °C (*S. marinoi*), and at irradiance 300–500 μmol photons s^{-1} m^{-2}. Irradiance was measured with a digital scalar irradiance meter (Biospherical Instruments Inc.). A natural microalgal community was sampled during the spring bloom of 2013 in the SW Baltic Sea (PRODIVERSA cruise, station 8, 18 April, longitude 17.33342 latitude 56.2559). Diatoms dominated the community, primarily of the genus *Chaetoceros* spp. dinoflagellates, cryptophytes, euglenophytes and chlorophytes (green algae) were also present in lower abundance.

2.4. Experimental design

2.4.1. Can microalgae use the CO_2 in flue gas and how is the quality of the biomass affected?

Tetraselmis was inoculated (5000 cells mL^{-1}) in six cylinders in photobioreactor 1 (PBR1, Fig. 1, Table 2) filled with f/2 Baltic seawater medium. Three replicates were supplied with air (control) and three with cement flue gas daily for 40–120 s at a flow rate of 5 L min^{-1}. Growth performance of *Tetraselmis* was monitored over 10 days. Samples were taken daily in each replicate cylinder for cell density and pH (days 1–10), and dry weight (DW) from day 3 to 10. Endpoint lipids and inorganic nutrient levels were also measured at day 10. Cells were fixed with Lugol's solution prior to counting. pH was measured with a

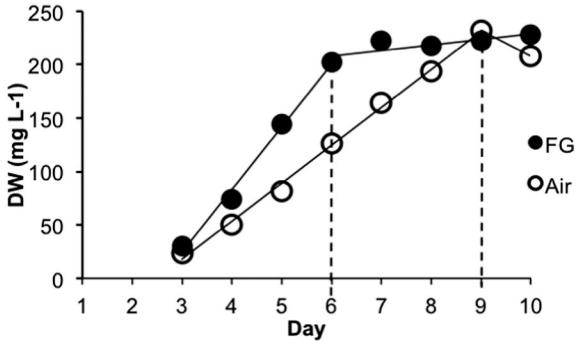

Fig. 1. Dry weight (DW) of *Tetraselmis* sp. during the experiment excluding the initial two-day lag-phase ($n = 2$).