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Release of Cl, S, P, K, and Na during Thermal Conversion of Algal Biomass

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ABSTRACT: The release of volatile inorganic elements during thermal conversion of algal biomass may cause operational problems in industrial reactors such as fouling, deposition, corrosion, and bed agglomeration. The release of Cl, S, P, K, and Na during the thermal conversion of algal biomass has been experimentally investigated in this paper. A freshwater macroalga (*Oedogonium* sp.), a freshwater polyculture of microalgae, and a marine microalga (*Tetraselmis* sp.) were used as feedstocks to assess the influence of different species and culturing environments on the release of the inorganic elements. Char and ash samples were prepared in a laboratory-scale fixed-bed reactor under isothermal conditions ranging from 500 to 1100 °C, under pyrolysis, combustion, and gasification atmospheres. The release of the inorganic elements was quantified by mass balances based on elemental analyses of the char and ash residues. Differences in the release of Cl, S, K, and Na were significant between the marine alga and the freshwater algae but were only minor between the freshwater microalgae and the freshwater macroalga. In the freshwater algae, the majority of the total Cl was released at low temperatures, below 500 °C. The majority of the fuel-S was also released at low temperatures. The remaining S was released with increasing temperature during combustion and gasification but was partially retained in the char during pyrolysis. Retentions of K and Na in the char and ash residues were both relatively high. Only 20–35% of the total K and 35–50% of the total Na in the freshwater algae had been released by 1100 °C. In the marine alga, only around 20% of the total Cl was released below 500 °C with the majority being released above 850 °C. The fraction of S released at low temperatures was also lower when compared to the freshwater algae. Potassium and Na were more or less completely released from the marine alga by 1100 °C under pyrolysis and combustion conditions and by 1000 °C under gasification conditions. The release behavior of P was similar for all of the tested algae. Phosphorus release commenced around 850 °C under pyrolysis, combustion, and gasification atmospheres, and by 1100 °C, 40–70% of the total P had been released from the algae. Select ash residues were analyzed using X-ray diffraction and scanning electron microscopy, coupled with energy-dispersive spectroscopy, in order to gain insights into the release mechanisms. A two-step mechanism has been proposed for S release. The alkali metals and Cl were released proportionally from the marine alga but disproportionately from the freshwater algae. It is expected that K, Na, and Cl were released from the marine alga primarily by sublimation of alkali chlorides. Different mechanisms were responsible for the release of these elements from the freshwater algae. It has been suggested that Cl is dissociated from the alkali metals and then released as HCl vapor, and that K may be released by volatilization of melted K-phosphates. Sodium appeared to be released by similar mechanisms to K above 700 °C. The mechanisms governing the release of P are not entirely clear and require further investigation.

1. INTRODUCTION

Growing concern for future fuel security, brought about by continual depletion of nonrenewable fossil fuel reserves and an ever-increasing world population, has provided motivation for the development of alternate energy technologies. Technologies based on the sustainable use of biomass are playing a growing role in the global energy mix and are projected¹ to meet a significant portion of the total energy demand in the future. Both micro- and macroalgae are currently unexploited biomass which have several advantageous attributes as feedstocks for energy and fuel production. The production of algae has exceptional potential for high areal energy yields² and can be undertaken on nonarable land.³ Algae can be cultivated in a diverse range of aquatic environments including both freshwater⁴ and seawater⁵ as well as various types of contaminated wastewater,⁶ which opens up opportunities to combine the production of energy and fuels with bioremediation. Pyrolysis,

combustion, and gasification are widely used thermal processes which can be used to convert dried algae to energy and fuels. It is also possible to convert algae when it is wet via oxidation or gasification in supercritical water.^{7,8} However, current technologies based on these novel processes are not well-developed due to the extreme pressures required to achieve supercritical conditions.⁹ In contrast, well-established technologies already exist for conventional thermal processes. Nevertheless, these established technologies are not without their limitations. They suffer from ash-related operational problems caused by inorganic impurities in the biomass.¹⁰ The inorganic matter in biomass is responsible for fouling and deposition,¹¹ high temperature corrosion,¹² and, in the case of fluidized bed

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Table 1. Summary of the Algal Samples Used in This Study

abbreviation	species	micro/macroalgae	water	added nutrients	harvest method
OD	<i>Oedogonium</i> sp.	macro	freshwater	desulfurized flue gas, f/2 ^a medium	filtration, followed by centrifugation
TPC	polyculture dominated by <i>Schroederiella apiculata</i> and <i>Scenedesmus dimorphus</i>	micro	freshwater	desulfurized flue gas, f/2 medium	centrifugation
Tet	<i>Tetraselmis</i> sp.	micro	seawater	CO ₂ , NaNO ₃ , H ₂ PO ₄	electroflocculation, followed by centrifugation

^aA standard nutrient medium containing nitrate, phosphate, and various trace metals.

technologies, bed particle agglomeration¹⁰ involving the sticking together of inert bed particles by various components in the ash. Consequences of ash-related problems include, but are not limited to, plugging of channels between boiler tubes,¹³ erosion of gas turbine components,¹⁴ and bed defluidization,¹⁵ all of which can lead to expensive and unscheduled reactor shutdowns. Prior knowledge of the behavior of the inorganic matter is, therefore, essential before any new feedstock is utilized in thermal processes. Previous research on the thermal behavior of algal biomass has focused mainly on the conversion of the organic matter.^{16–18} A number of recent studies have investigated the sintering tendencies and agglomerating behavior of algal ashes;^{19–21} however, the relevance of these studies is mainly limited to fluidized bed technologies. It is clear that the current knowledge which addresses the behavior of the inorganic matter in algae during conventional thermal processes is limited, particularly with respect to ash-related problems.

There is a large body of knowledge dedicated to the behavior of the inorganic matter in terrestrial biomass and coal. Many studies have shown Cl, S, Na, K, and P to play key roles in ash-related problems. The alkali metals, Na and K, are notorious for forming low-temperature melting compounds which cause the formed ash to become sticky and prone to depositing on surfaces inside and downstream of the reactor. Chlorine is highly volatile in biomass.^{22–25} It tends to mobilize the alkali metals²⁶ and accelerate high-temperature corrosion.²⁷ Sulfur is also highly volatile^{23–25} and is capable of forming dense deposits.²⁸ The formation of molten sodium sulfates is known to be the root cause behind bed agglomeration during fluidized bed combustion of Na- and S-rich low-rank coals.^{29,30} Phosphorus can contribute to ash deposition³¹ and, when present in significant concentrations, bed agglomeration.³² Chlorine, S, P, K, and Na are all present in high concentrations in algae and are expected to play important roles in ash-related problems.

The ultimate fate and role of the inorganic elements in ash-related problems is largely determined by the initial split between the solid and gas phase during fuel particle burnout.¹⁰ The extent to which an inorganic element is released to the gas phase or is retained in the solid residue depends on both feedstock composition and on processing parameters such as reaction temperature and gas atmosphere. The importance of feedstock composition on the release of the inorganic elements is evident when comparing the behavior of the inorganic matter in different types of terrestrial fuels. Previous studies have focused on a broad range of terrestrial fuels including coal,^{33–35} wood and wood-derived fuels,^{23,36,37} agricultural residues,^{24,25,38–40} grasses,^{37,41,42} and sewage sludge.^{43,44} There is generally good agreement in the literature for the mechanisms governing the release of Cl.^{23–25,45,46} A useful schematic summarizing the different release pathways is provided by Johansen et al.²⁵ Several authors^{41,47} have inferred that the release of S is affected by its occurrence mode in the fuel.

Organic forms are thought to be released at low temperatures during the pyrolysis process,^{41,47} involving the initial decomposition of the organic matrix. In combustion and gasification processes, pyrolysis is followed by a heterogeneous gas–solid reaction which involves oxidation or reduction of the residual organic matter (char). Inorganic forms of S are thought to be released during this latter phase of fuel particle conversion.^{24,25,41} Literature on the release of P from terrestrial biomass^{38,43,44} is relatively scarce. The release of the alkali metals, K and Na, is extremely complex and seems to be strongly influenced by the relative proportions of other inorganic elements in the fuel. A substantial amount of work has been done to understand the mechanisms governing the release of the alkali metals, and various authors^{23–25} have attempted to summarize these mechanisms for a range of terrestrial fuels. Commonly reported mechanisms include vaporization of alkali salts (e.g., chlorides, sulfates, and phosphates), dissociation of alkali carbonates, alkali sulfates and alkali metals ion-exchanged to oxygen functionalities in the char matrix, and vaporization of alkali silicates. In many cases, the alkali metals are released by a combination of these mechanisms. The importance of a given mechanism is highly sensitive to feedstock composition and varies significantly from fuel to fuel. The composition of the inorganic matter in algae is distinctively different from both coal and terrestrial biomass, and the occurrence of the main inorganic elements in algae varies significantly for micro- and macroalgae species and for different culturing conditions.¹⁹ Despite this, limited work has been done to characterize the release of Cl, S, P, K, and Na from algae or to understand how the release of these elements varies for different algal species and for different culturing environments.

The aim of this study was to characterize the release of Cl, S, P, K, and Na from a range of different types of algal biomass during thermal conversion. The first objective of this work was to determine the influence of algal properties, in terms of freshwater vs marine and macro vs micro, on the release of the inorganic elements under gas atmospheres relevant to pyrolysis, combustion, and gasification processes. The second objective was to provide insights into the mechanisms governing the release of the inorganic elements.

2. EXPERIMENTAL SECTION

2.1. Algal Samples. A diverse range of algae were selected for this work in order to assess the variability in the thermal behavior of the inorganic elements for different species and different culture environments. The selected samples (Table 1) are all grown for industrial applications. The freshwater macroalga, *Oedogonium* sp. (hereafter referred to as “OD”), and the freshwater polyculture of microalgae (hereafter referred to as “TPC”) are key targets for broad spectrum bioremediation of waste waters.^{48,49} The marine microalga, *Tetraselmis* sp. (hereafter referred to as “Tet”) is a key species for biofuel production.⁵ OD and TPC were grown in ash dam water at the Tarong coal-fired power station in Tarong, Queensland, and Tet was

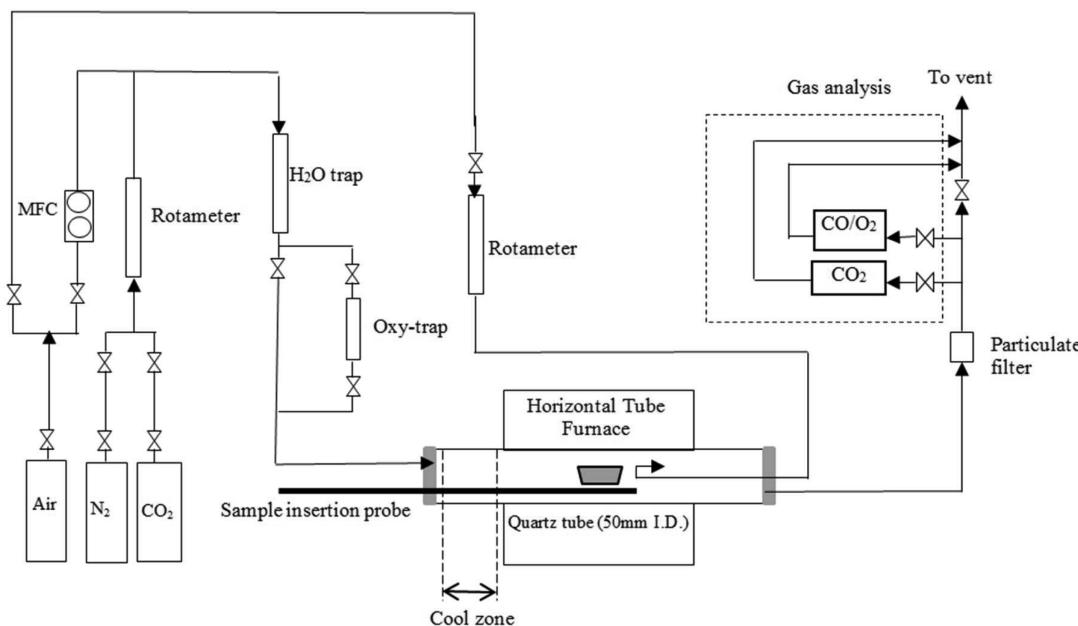


Figure 1. Schematic of the fixed-bed reactor setup used in the release experiments.

grown by Muradel Pty. Ltd. at their pilot plant in Karratha, Western Australia.

OD (genus *Oedogonium*, Genbank KF606974)⁴⁸ was isolated from the Tarong Ash Dam in October 2012 and then scaled up from small-scale cultures to large-scale cultures at James Cook University, Townsville. The scaled biomass was transported to Tarong in May 2013 and cultured directly in ash dam water which was pumped from the ash dam into a series of four 10 000 L culture tanks. The ash dam water was passed through a 10 μm filtration unit before being added to the culture tanks. Flue gas was piped directly from the power stations flue, through a desulfurization unit and into the bottom of the cultivation tanks to supply CO₂. The flue gas supply was linked to an in-line pH probe and set to maintain pH between 8.4–8.6 in the tanks. Nutrients were added as f/2 media,⁵⁰ a standard nutrient mix containing nitrate, phosphate, and various trace elements. Algae were grown under batch conditions, with 100% of the tank volume being harvested every 3–4 days. Harvests were carried out by draining the tanks through a hose into fabric bags which were then spun in a domestic washing machine for 7 min to remove excess water. TPC consists of a range of freshwater microalgae that were originally isolated from water samples collected from the Tarong power station. The polyculture is dominated by the green microalgae *Schroederiella apiculata* and *Scenedesmus dimorphus*. TPC was cultivated in covered, outdoor raceway ponds under ambient conditions. The raceway ponds received desulfurized flue gas, containing 20% CO₂, to maintain pH between 8.0 and 8.5, and the ash dam water was prefiltered as previously described for OD. Raceway ponds were harvested using a commercial centrifuge. Tet was cultivated in an outdoor, raceway pond and was harvested using an in-house electroflocculation process, followed by centrifugation. Detailed descriptions of the growth and harvesting methods used to produce OD and Tet can be found elsewhere.^{16,49}

Harvested algal samples were air-dried (OD and TPC) or oven-dried at 45 °C (Tet) to a moisture content of less than 12 wt %. The microalgae (Tet and TPC) formed brittle aggregates when dried and the macroalgae (OD) coarse tufts of intertwined filaments. Samples were milled in a centrifugal knife mill and then sieved to obtain the 1.6–6.4 mm size fraction. This fraction was used in the release experiments. Samples of each alga were also milled to pass through a 250 μm screen. This size fraction was used for fuel analyses.

2.2. Reactor Setup. A laboratory-scale, fixed-bed, batch reactor was used to prepare char and ash samples from the algae. A schematic of the reactor setup is shown in Figure 1. The setup involved a 1.4 m

long, 50 mm I.D., quartz tube which was positioned horizontally inside a 3-zone, electrically heated furnace so that the tube ends extended 40 and 50 cm from the front and back end of the furnace, respectively. Tapered silicone plugs were used to seal both ends of the quartz tube. A 1.0 m long alumina tube (I.D. 5 mm and O.D. 9 mm), featuring a flat platform cut-out at one end, was used as a sample insertion probe. Samples (1–4 g) were loaded into 20 mL alumina boats without compressing the fuel bed. The alumina boat was then secured to the insertion probe platform using molybdenum-based, temperature-resistant wire (diameter: 0.4 mm). A K-type thermocouple, which ran through the inside of the insertion probe tube, was used to monitor the temperature just under the sample boat. The reactor was designed so that the sample remained cool (<60 °C) and in an inert gas atmosphere while heating up the furnace. Preheated secondary air, introduced at a position just downstream of the sample, was used to oxidize volatiles released during pyrolysis so as to limit tar deposition at the outlet of the quartz tube.

High purity N₂, CO₂, and instrument grade air were used in the release experiments. All gases were fed from cylinders to the reactor via 1/4" nylon tubing. Reactant gases were first passed through a column packed with silica gel to remove any moisture. Nitrogen and CO₂ feed streams were also scrubbed of oxygen impurities using a commercially available oxy-trap. Rotameters were used to control the flow of N₂, CO₂, and secondary air. Gas phase residence times inside the reactor were around 30 s. A mass flow controller was used to control the flow of primary air. Product gases were passed through a quartz wool filter and monitored for O₂, CO, and CO₂ concentrations before being vented to exhaust. Two separate nondispersive infrared gas analysers were used to measure CO and CO₂ and a galvanic cell type analyzer to measure O₂.

2.3. Release Experiments. Release experiments were carried out under pyrolysis, combustion, and gasification conditions at various temperatures between 500 and 1100 °C. The residues were weighed at the end of each test and analyzed to determine the concentrations of Cl, S, K, Na, and P in the residues. Release of the inorganic elements from the algal samples was then calculated by mass balance according to eq 1

$$R_i (\%) = \left[1 - \frac{1}{(1-M)} \left(\frac{W_r}{W_A} \right) \left(\frac{C_{r,i}}{C_{A,i}} \right) \right] \times 100 \quad (1)$$

where R_i is the release of element i in weight percent, M is the moisture fraction of the algal feedstock (w/w), W_r and W_A are the

weights (mg) of the residue and corresponding algal feedstock respectively, and $C_{r,i}$ and $C_{A,i}$ are the concentrations (w/w, dry basis) of element i in the residue and feedstock, respectively.

At the start of each experiment, gas flow rates were preset to their target values. The reactor was then purged with N_2 (4.0 L/min @ STP) while heating the furnace. Once the target furnace temperature had been reached, the sample was moved from the reactor inlet (cool zone) to the middle of the furnace. In the pyrolysis experiments, N_2 was fed to the reactor inlet at a flow rate of 4.0 L/min @ STP and secondary air was supplied at a flow rate of 2.0 L/min @ STP. Once pyrolysis had reached completion, the supply of secondary air was switched off. In combustion and gasification experiments, samples were first pyrolyzed as described for the pyrolysis experiments. This was done to prevent temperature overshoot caused by ignition of evolved volatiles. The residual organic matter was then oxidized or reduced by switching the gas atmosphere to 2% O_2 /balance N_2 (combustion) or to CO_2 (gasification). Air was mixed with N_2 upstream of the reactor to create the target gas atmosphere for combustion experiments. Pyrolysis and combustion progress was tracked by monitoring the concentrations of CO and CO_2 in the product gases. Reactions were allowed to proceed until the concentrations of CO and CO_2 dropped below 50 and 200 ppmv, respectively. Only CO was monitored during gasification. Gasification times were constant for each algal sample and were selected based on the time taken for complete gasification of the sample at 850 °C, which was defined as the time taken for the concentration of CO in the product gases to drop below 50 ppmv. Complete gasification took between 1.5 and 5 h for the different algal samples at 850 °C. Complete pyrolysis and complete combustion at 850 °C took between 15 min and 1 h and between 45 min and 2 h, respectively. At the end of each test, the gas atmosphere was switched back to N_2 , the furnace heating elements switched off, and the sample retracted from the furnace to the cool zone of the reactor. Once the temperature of the sample boat dropped below 50 °C, the sample was removed from the furnace and the residue was weighed immediately. The residue was then crushed to a fine powder using a mortar and pestle and then stored in an airtight, plastic container for analysis. In order to avoid contamination between tests, the reactor was removed from the furnace and its interior was scrubbed in warm water at the end of each test. The reactor outlet was then heated in air (1000 °C) to burn off any tars which may have deposited on the tube walls during the previous test.

2.4. Analysis. Proximate and elemental compositions of the algal samples are presented in Table 2. Proximate composition was determined by thermogravimetric analysis (TGA). Samples were loosely packed into a cylindrical alumina crucible (I.D. 7 mm and height 1.2 mm) to approximately half-full. The crucible was then loaded into a TGA (Setaram Labsys). Samples were heated to 105 °C in N_2 (80 mL·min⁻¹ @ STP) at a rate of 10 °C·min⁻¹ and held at 105 °C for 30 min in order to remove residual moisture. Samples were then heated to 550 °C at a rate of 10 °C·min⁻¹ and held at 550 °C for 1 h in order to determine the volatile matter content. The gas atmosphere was then switched to air in order to oxidize the remaining organic matter and determine the ash content. Fixed carbon content was calculated by difference.

Elemental composition was determined using a range of different methods. Carbon, H, and N were measured in triplicate using an elemental analyzer (LECO Truspec). Chlorine was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using an Ar-filled, Spectro Ciro CCD (charged coupled device) in axial plasma viewing mode, following extraction in 4% v/v HNO_3 . Details of this method can be found elsewhere.⁵¹ Silicon was determined by ICP-OES, following borate fusion and acid dissolution. This method is based on Australian Standard AS 1038.14.1. Sulfur and all other inorganic elements, including K, Na, and P, were determined by ICP-OES, using a radial plasma viewing mode, following digestion in H_2O_2 (30% v/v)/ HNO_3 (68% v/v)/HF (48% v/v). Samples (100 mg) were digested in 15 mL, flat-bottom, Teflon containers for a period of 12 h at a temperature of 140 °C using 0.6, 1.6, and 0.2 mL of H_2O_2 , HNO_3 , and HF, respectively. After 12 h of digestion, samples

Table 2. Proximate and Elemental Compositions of the Tested Algae

algae	OD	TPC	Tet
proximate composition (wt %)			
moisture ^a	7.3	10.8	6.4
volatile matter ^b	58.7	57.7	35.5
fixed carbon ^b	20.4	19.0	5.9
ash ^b	20.9	23.3	58.6
elemental composition (wt %) ^b			
C	34.8	41.3	17.0
H	5.0	5.8	3.3
N	5.4	6.9	2.5
S	0.53	1.01	2.10
Cl	0.25	0.50	17.62
P	1.37	1.36	0.25
Na	0.23	0.51	10.86
K	1.08	0.59	1.03
Ca	1.00	1.67	2.50
Mg	0.26	0.34	1.86
Si	7.55	6.99	0.68
Fe	1.60	0.44	0.30
Al	0.35	0.21	6.17
Ti	0.0102	0.0062	0.0170

^aAfter drying. ^bDry basis.

were evaporated to incipient dryness and the digestion was repeated. Digested samples were diluted in 5% v/v HNO_3 using plasticware so that the concentrations of the inorganic elements in the diluted samples were within the linear calibration range of the ICP-OES instrument. All plasticware was cleaned before use by soaking in a 3 M solution of HCl for a period of at least 12 h. Solution ICP-OES measurements were performed externally by HRL Technology Pty. Ltd. and Waite Analytical Services. For each batch of analysis, one blank and a certified plant reference material (U.S. National Institute of Standards and Technology, Gaithersburg, MD, USA) were analyzed in addition to the unknown samples. The concentrations of Cl, S, P, K, and Na in the algal sample OD were analyzed in quadruplicate in order to estimate the error in the measurement of these elements. Errors (95% confidence interval) were 5.4, 6.2, 6.2, 5.8, and 2.6% for Cl, S, P, K, and Na, respectively.

Scanning electron microscopy, coupled with energy-dispersive spectroscopy (SEM/EDS), and powder X-ray diffraction (XRD) were used to aid interpretation of the results. The morphology and composition of combustion ashes prepared at a low (700 °C) and a high temperature (1100 °C) were studied using a Philips XL30 SEM equipped with EDS. Sample preparation involved mounting intact ash particles on stubs, followed by carbon coating. Mineralogical analyses were performed on each alga and on high-temperature (1100 °C) combustion ashes. Samples were oven-dried (80 °C) and then milled using a mortar and pestle before being pressed into stainless steel sample holders. XRD patterns were recorded using a PANalytical XPert Pro Multipurpose Diffractometer using Fe-filtered Co $K\alpha$ radiation, an automatic divergence slit, 2° antiscatter slit, and fast X'Celerator Si strip detector. The diffraction patterns were recorded from 3° to 80° in steps of 0.017° 2θ with a 0.5 s counting time per step for an overall counting time of approximately 35 min. The XRD patterns were recorded and interpreted externally, by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Division of Land and Water.

3. RESULTS AND DISCUSSION

The Results and Discussion section consists of three parts: (1) release profiles for Cl, S, P, K, and Na, (2) SEM/EDS and XRD analyses of algal ashes, and (3) a discussion on the release mechanisms.

3.1. Release Profiles. The release profiles are based on elemental analyses of char and ash samples prepared under pyrolysis, combustion, and gasification conditions at various temperatures between 500 and 1100 °C. The profiles are presented in Figures 2–6 and were used to determine the influence of algal type, in terms of micro vs macro and freshwater vs marine, on the release of the inorganic elements. Note that data is not presented for gasification of OD and TPC at 500 °C or for gasification of Tet at 500 and 700 °C since the algal chars were barely reactive under these conditions. Errors in the calculated release values are presented for OD under pyrolysis conditions in Figures 2–6 and were found to diminish with increasing release. It is expected that the errors would have followed a similar trend for the different gas atmospheres and for each of the tested alga. The errors were estimated by propagation of the errors in the elemental concentration measurements and the algal moisture content measurements which were based on two standard deviations of the measured quantities.

Chlorine. The freshwater algae (OD and TPC) both display similar Cl-release behavior (see Figure 2). Over half of the Cl in OD and TPC is released by 500 °C and virtually all of the Cl is released by 1000 °C under pyrolysis conditions. Under combustion and gasification conditions, complete release of chlorine is shifted toward lower temperatures (700 °C). Differences in the behavior of Cl under combustion and gasification conditions are minor. Interestingly, the release profiles for OD and TPC closely resemble that of corn stover,²⁵ which has a similar Cl content to the two freshwater algae (0.25 and 0.50 wt %, dry basis). The behavior of Cl in the marine alga, Tet, is significantly different to that of the freshwater algae, which is not surprising, given that there is over an order of magnitude more Cl in Tet. In Tet, a lower proportion of the total Cl is released below 500 °C (around 20%) and complete release of Cl occurs between 1000 and 1100 °C under pyrolysis, combustion, and gasification conditions.

Sulfur. The majority of S (>70%) in OD and TPC is released by 500 °C during pyrolysis (see Figure 3). The low-temperature release from Tet on the other hand is much lower (around 30%). There is only a gradual increase in the release of S from all of the tested algae under pyrolysis conditions with increasing temperature above 500 °C. Combustion and gasification atmospheres on the other hand result in an additional release of S above 500 °C. In the case of OD and TPC, complete desulfurization occurs by 850 °C under both combustion and gasification conditions. Complete desulfurization of Tet occurs around 1100 °C during combustion and 850 °C during CO₂ gasification.

Phosphorus. The release profiles for P (Figure 4) are similar for all of the tested algae. Very little of the total P (<10%) is released below 850 °C, indicating that the onset of P release occurs above 850 °C. The slightly negative release values reported for TPC and Tet are likely due to inhomogeneities in fuel composition but may also be due to errors in the measurement of P. Increasing temperature above 850 °C causes an increase in the release of P. By 1100 °C, between 40% and 70% of the total P is released to the gas phase. These values are similar to P-release data reported by Wu et al.³⁸ during bran combustion in a fixed-bed reactor at 1100 °C. The different gas atmospheres were found to have only a minor effect on the release of P from the algae.

Potassium. Low levels of K (2–12%) are released below 700 °C from each of the tested algae (see Figure 5). Above 700 °C,

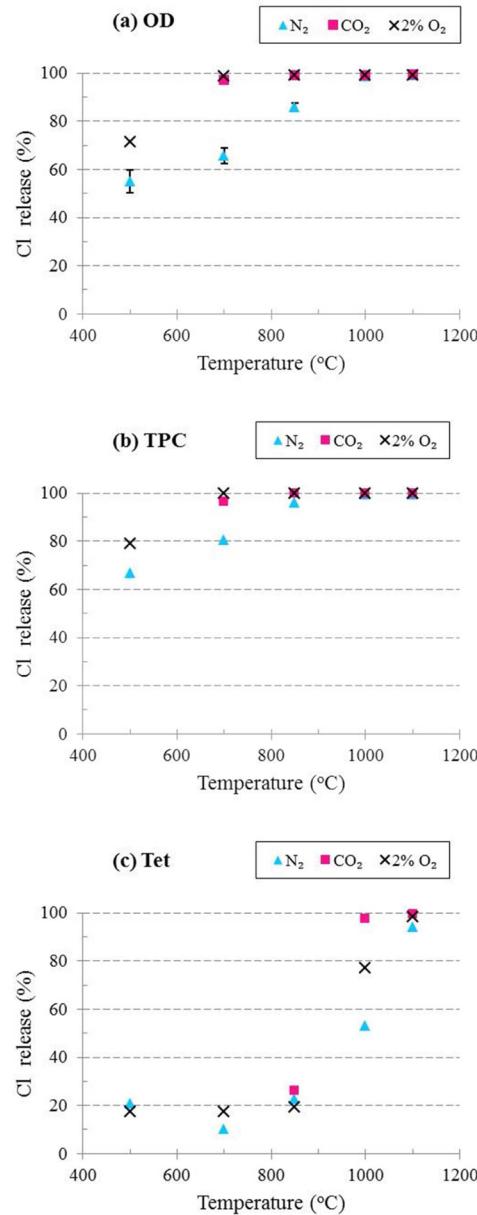


Figure 2. Release to the gas phase of Cl from OD (a), TPC (b), and Tet (c) as a function of reactor temperature. Release data are presented for pyrolysis (N₂), combustion (2% O₂/balance N₂), and gasification (CO₂) gas atmospheres. Note that data is not shown for CO₂ at 500 °C in (a) and (b), and at 500 and 700 °C in (c).

K is released gradually from OD and TPC and seems to be unaffected by differences in gas atmosphere. Only 20–35% of the total K in OD and TPC is released by 1100 °C. These values are relatively low when compared to K-release data reported in the literature for different types of terrestrial biomass.^{25,38,39} The high-temperature release (>700 °C) of K is much greater from Tet. Over 60% of the total K in Tet is released by 1000 °C and virtually all K is released by 1100 °C under pyrolysis and combustion conditions. Complete release of K is shifted toward slightly lower temperatures (1000 °C) under gasification conditions. The more pronounced release of K under gasification conditions may be due to differences in the reactivity of Tet char particles under reducing and oxidizing gas atmospheres. The rate of char conversion under combustion

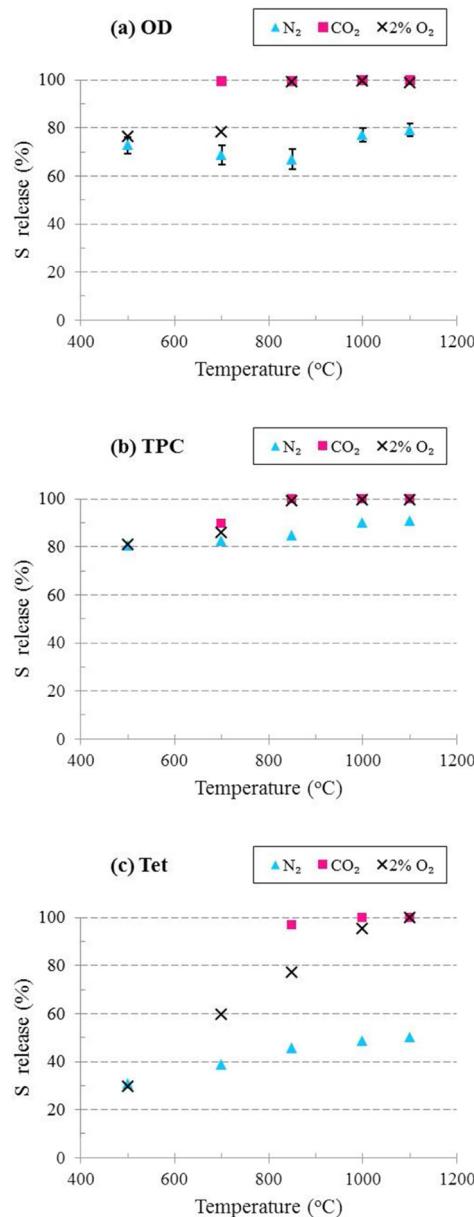


Figure 3. Release to the gas phase of S from OD (a), TPC (b), and Tet (c) as a function of reactor temperature. Release data are presented for pyrolysis (N₂), combustion (2% O₂/balance N₂), and gasification (CO₂) gas atmospheres. Note that data is not shown for CO₂ at 500 °C in (a) and (b), and at 500 and 700 °C in (c).

conditions is likely mass-transport limited for temperatures above 850 °C and for char particles of the order of 1 mm in size.⁵² Combustion reactions are, therefore, likely to be concentrated at the surface of the char particles, which hinders pore development.⁵³ Chemical reactions are much slower in CO₂ (gasification)⁵³ and presumably take place deeper within the internal pores of the char particle. This promotes pore enlargement through product gas evolution inside the particle itself. The formation of larger pores during gasification could lead to lower K vapor pressure within the pores and consequently enhance the rate of K volatilization from the char. A similar rationale has been suggested⁵⁴ for the high release of Na during gasification of brown coal.

Sodium. Release of Na (Figure 6) below 700 °C ranges between 10% and 25% and seems to be unaffected by

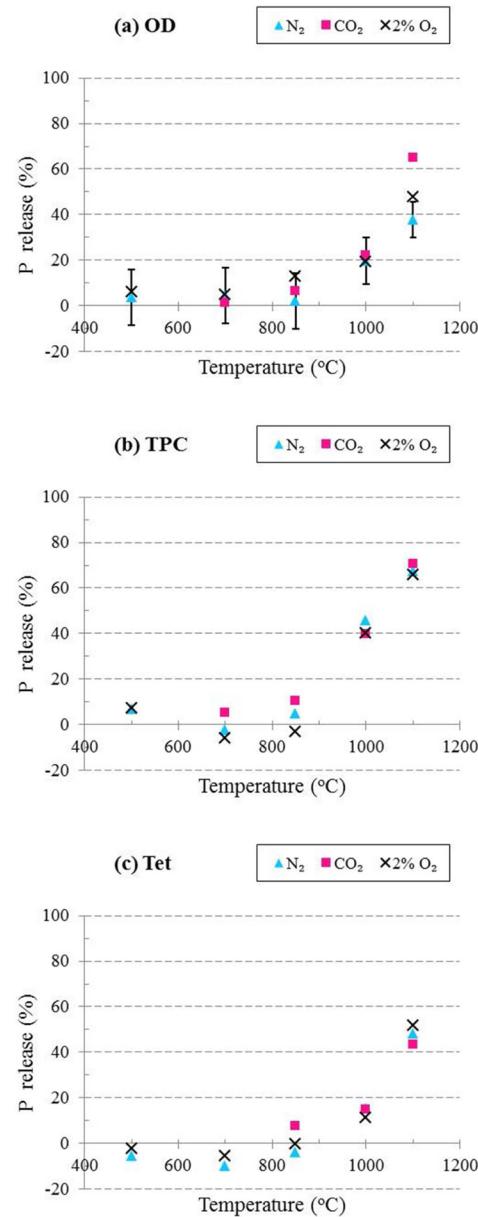


Figure 4. Release to the gas phase of P from OD (a), TPC (b), and Tet (c) as a function of reactor temperature. Release data are presented for pyrolysis (N₂), combustion (2% O₂/balance N₂), and gasification (CO₂) gas atmospheres. Note that data is not shown for CO₂ at 500 °C in (a) and (b), and at 500 and 700 °C in (c).

differences in gas atmosphere. The low-temperature release of Na (<700 °C) is on average greater than that of K. Interestingly, van Lith et al.²³ also reported a greater low-temperature release of Na than K during combustion of wood-derived fuels in a reactor setup similar to the one used in this study. The behavior of Na closely resembles that of K within the temperature interval of 700–1100 °C for all of the tested algae.

3.2. SEM/EDS and XRD Analyses. SEM images of algal combustion ashes prepared at both low (700 °C) and high (1100 °C) temperatures are presented in Figures 7–9 for OD, TPC, and Tet. Also presented in Figures 7–9 are the bulk compositions of the ashes determined using EDS. The low-temperature ashes of OD (see Figure 7a) and TPC (see Figure 8a) contain separate seed-like particles, 10–30 μm in size.

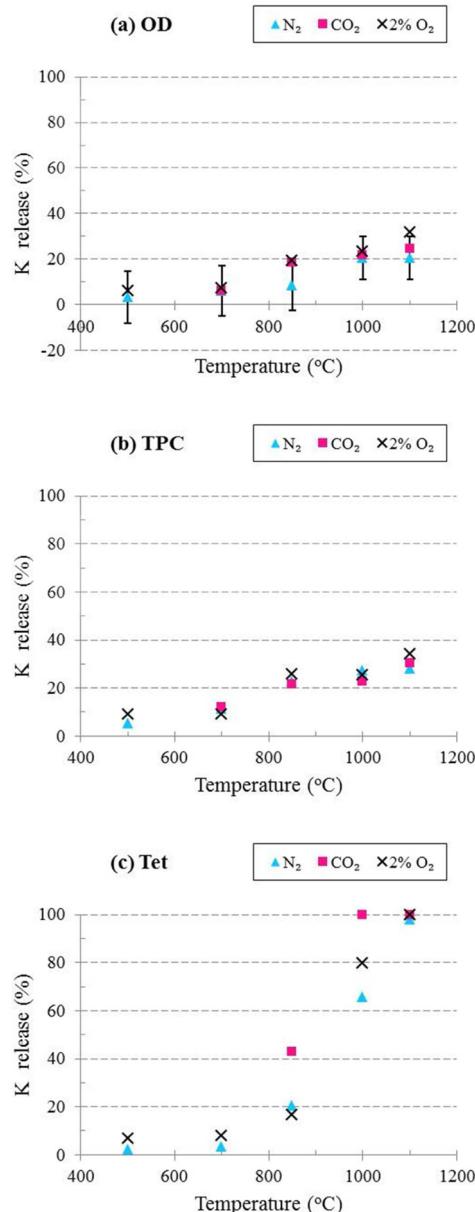


Figure 5. Release to the gas phase of K from OD (a), TPC (b), and Tet (c) as a function of reactor temperature. Release data are presented for pyrolysis (N₂), combustion (2% O₂/balance N₂), and gasification (CO₂) gas atmospheres. Note that data is not shown for CO₂ at 500 °C in (a) and (b), and at 500 and 700 °C in (c).

Their high-temperature ashes (see Figures 7b and 8b), on the other hand, consist of large, smooth blocks, which suggest that the ash particles fuse together above 700 °C, possibly via the formation of molten ash. The ashes of OD and TPC are dominated by Si (see Figures 7c and 8c), which could be expected given the substantial Si contents (7–8 wt %, dry basis) in these algae and the refractory nature of Si at temperatures below 1100 °C.⁵⁵ Phosphorus concentrations in the ashes of OD and TPC were much lower, but still significant, particularly in the ashes of TPC. The low-temperature ashes of Tet are dominated by Al, Na, and Cl (see Figure 9c) and contain discrete cubic particles 2–8 μm in size (see Figure 9a). EDS point analyses were performed on several of these particles in order to determine their identity. The results are presented in Figure 9c. The particles consist almost exclusively of Na and

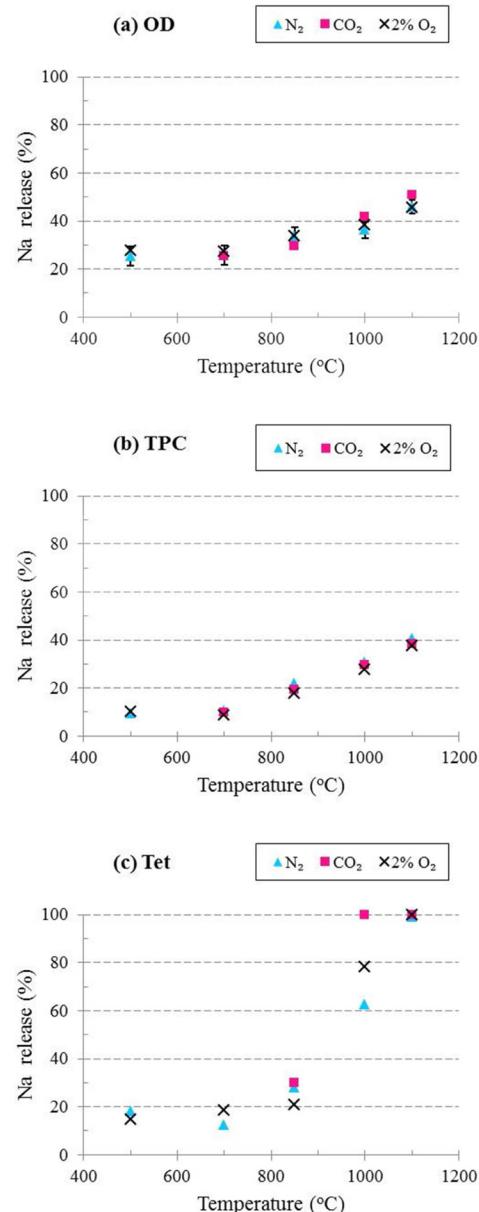


Figure 6. Release to the gas phase of Na from OD (a), TPC (b), and Tet (c) as a function of reactor temperature. Release data are presented for pyrolysis (N₂), combustion (2% O₂/balance N₂), and gasification (CO₂) gas atmospheres. Note that data is not shown for CO₂ at 500 °C in (a) and (b), and at 500 and 700 °C in (c).

Cl and are probably unreacted NaCl crystals which had precipitated from the algae during biomass drying. The cubic particles were not observed in the high-temperature ashes of Tet (see Figure 9b), and negligible levels of Na and much lower levels of Cl were detected in the ashes (see Figure 9c). This finding is consistent with the Na and Cl release profiles for Tet, which show these elements to be more or less completely released from Tet by 1100 °C. The high-temperature ashes of Tet consist mainly of Al but also contain significant levels of Ca and Mg (see Figure 9c). The Al in Tet is introduced to the alga as aluminum hydroxide⁵⁶ during the harvesting process, which involves flocculating algae from the growth medium by applying an electric current to sacrificial aluminum electrodes, which provide ions for flocculation.¹⁶

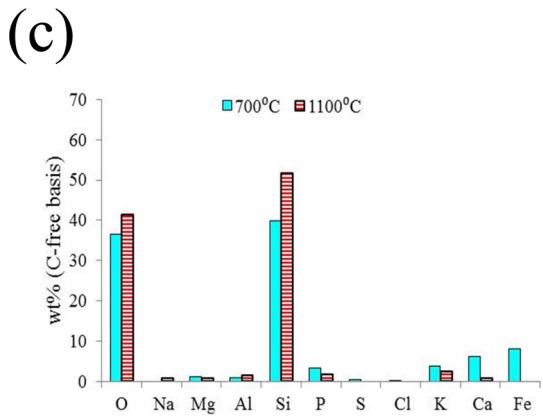
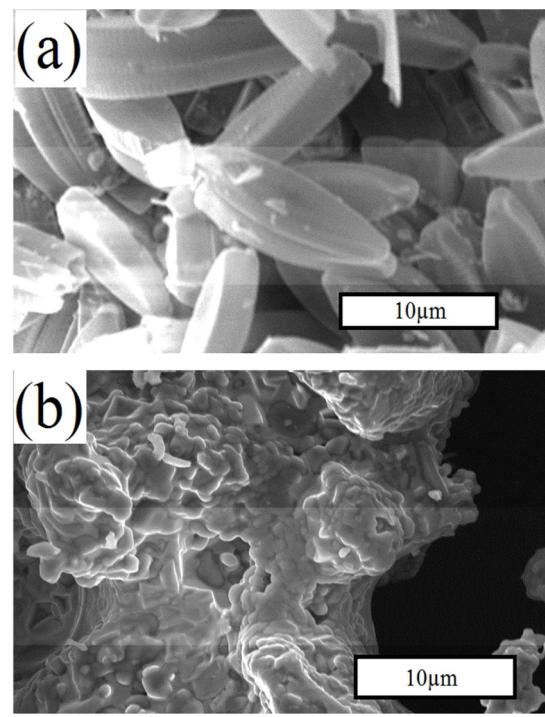


Figure 7. SEM images of OD combustion ashes prepared at 700 °C (a) and 1100 °C (b). (c) Elemental composition of the ashes determined using EDS.

Mineralogical analyses were conducted using XRD. The analyses are presented in Table 3 for combustion ashes prepared at 1100 °C and for the corresponding algal feedstocks. Cristobalite (SiO_2) was identified as a dominant phase in the ashes of OD and TPC and spinel (MgAl_2O_4) as a dominant phase in the ashes of Tet. These findings are in agreement with the SEM/EDS analyses, which show Si to be a main component of the high-temperature ashes of OD and TPC, and Al and Mg to be major components in the high-temperature ashes of Tet. Halite (NaCl) was identified as dominant in Tet but was not identified in the combustion ashes of Tet. This finding provides further evidence that Na and Cl are more or less completely released from Tet at high temperatures.

3.3. Release Mechanisms. An interpretation of the release profiles is presented in this section in terms of the governing release mechanisms. The interpretation was supported by (1) the SEM/EDS and XRD analyses presented in section 3.2, (2) a review of the literature on the mechanisms responsible for the

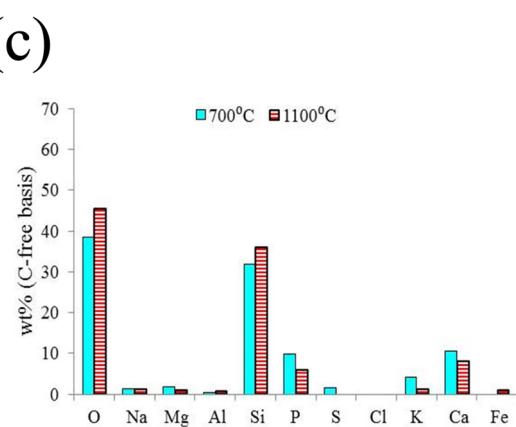
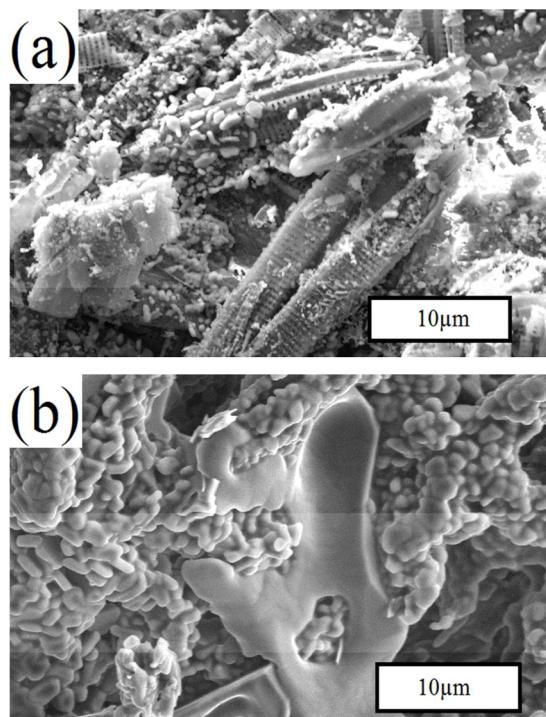


Figure 8. SEM images of TPC combustion ashes prepared at 700 °C (a) and 1100 °C (b). (c) Elemental composition of the ashes determined using EDS.

release of inorganic elements from terrestrial biomass, and (3) consideration of the occurrence modes of the main inorganic elements in algae.

Chlorine is almost certainly present in dried algal biomass as precipitated alkali chlorides.¹⁹ Release of Cl from alkali chlorides is understood to take place via two separate mechanisms during thermal conversion of terrestrial fuels.^{22,24,25} Mechanism (1) probably commences at around 300 °C²² and involves incorporation of the alkali metal into proton donor sites in the char matrix (e.g., carboxylic groups)^{46,57} and the simultaneous release of Cl to the gas phase as HCl. Mechanism (2) involves the sublimation of alkali chlorides and becomes significant at temperatures above 700 °C. The principal mechanism of release seems to depend on the absolute Cl content of the fuel. For Cl-lean fuels (<0.6 wt % Cl) such as wood,²³ mechanism (1) tends to dominate. For Cl-rich fuels (>0.6 wt % Cl) such as barley,²⁴ mechanism (2) tends to dominate since release by mechanism (1) is limited by the availability of proton donor sites in the char matrix for alkali

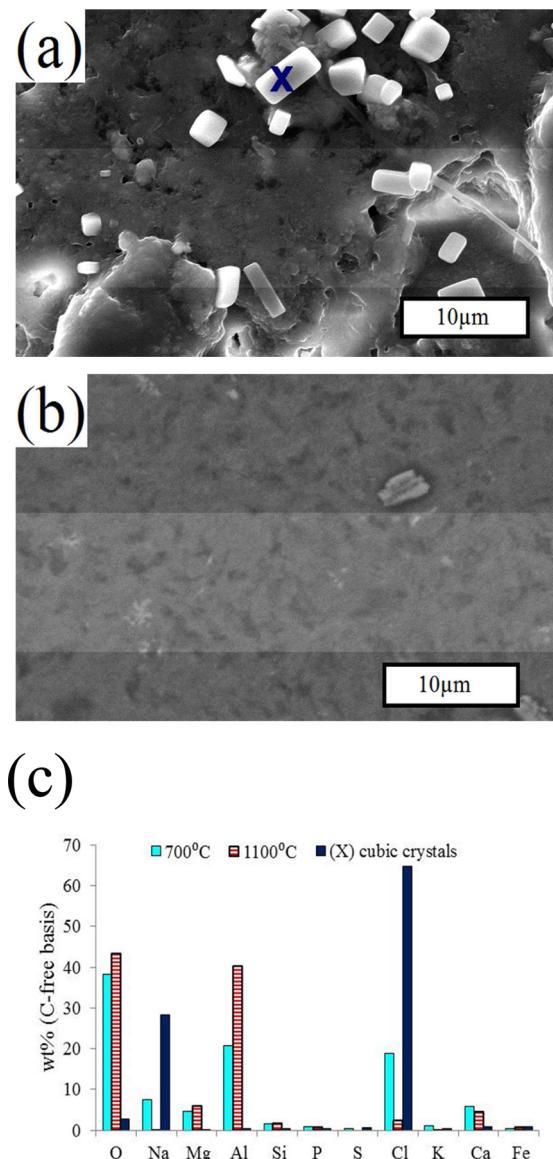


Figure 9. SEM images of Tet combustion ashes prepared at 700 °C (a) and 1100 °C (b). (c) Elemental composition of the ashes determined using EDS. Also shown in (c) is the average composition of the cubic crystals in (a), which was determined by performing EDS point analyses on 8 different crystals. An example of a cubic crystal in (a) is identified with an (X).

capture. A comparison of the absolute release of the alkali metals and Cl from the tested algae during combustion is

presented in Figure 10. Results are expressed as mmol per gram of dry algae. The majority of the Cl in the freshwater algae, OD, and TPC, is released by 500 °C, and the release of Cl is disproportionate to the release of the alkali metals. It is, therefore, expected that mechanism (1) is the principal mechanism governing the release of Cl from these algae. The marine alga, Tet, contains extremely high levels of NaCl (around one-quarter of the biomass by weight) and low levels of fixed carbon (5.9 wt %, dry basis), which indicates that the number of sites in the char for Na capture, required for release by mechanism (1), would be extremely limited. There is substantial evidence that mechanism (2) dominates in the case of Tet. The release of Cl is relatively low from Tet below 700 °C (<20%), and there is a striking correlation between the release of the alkali metals and Cl with increasing temperature (see Figure 10c). On top of this, NaCl crystals were identified in Tet combustion ashes prepared at 700 °C.

The high release of S from OD and TPC (65–90% of the total fuel-S) during pyrolysis indicates that a large portion of the S in these algae is released during initial decomposition of the organic matrix. Lower levels (30–50%) of S are released from Tet during pyrolysis. Sulfur occurs in algae in both organic and inorganic forms.⁵⁸ It is possible that differences in the proportions of these two forms in the freshwater algae and Tet could account for the different fractions of S released during pyrolysis. Inorganic CaSO₄ was identified as trace in the XRD spectrum for Tet but not in the spectra for OD and TPC (see Table 3). Furthermore, in previous work,¹⁹ we compared the leaching behavior of S in Tet to that in freshwater algae. The water-soluble fraction was found to be greater in Tet than in the freshwater samples. This could imply that there is less organically associated S in Tet and, therefore, explain the lower release of S from Tet during pyrolysis. An additional release of S takes place after pyrolysis, during the char oxidation/reduction phase of fuel particle conversion. Note that this additional release is relevant to combustion and gasification processes only. In the case of OD and TPC, it is unlikely that alkali sulfate vaporization accounts for the additional release of S given the high melting points of Na₂SO₄ and K₂SO₄ (884 and 1069 °C, respectively⁵⁹) and that desulfurization is more or less complete by 850 °C under combustion and gasification conditions. Instead, decomposition of metal sulfates involving the release of SO₂ (combustion^{33,41,47}) or H₂S and COS (gasification^{33,37}) to the gas phase, is expected.

The extent of S retention in the char/ash residues is closely linked to the availability of base cations, particularly the alkali and alkaline earth metals.^{24,47} Sulfur that has been released to the gas phase may even be recaptured in the fuel bed by base cations.²⁴ The availability of the base cations in terrestrial

Table 3. XRD Analyses for the Tested Algae and Their Combustion Ashes (1100 °C)^a

sample	dominant	minor	trace
OD	amorphous material		halite (NaCl) and possible quartz (SiO ₂)
TPC	amorphous material		anorthite (CaAl ₂ Si ₂ O ₈) and quartz (SiO ₂)
Tet	halite (NaCl)	amorphous material	quartz (SiO ₂), gypsum (CaSO ₄ ·2H ₂ O), and basanite (CaSO ₄ ·0.5H ₂ O)
OD ashes	cristobalite (SiO ₂)	powellite (CaMoO ₄)	quartz (SiO ₂), halite (NaCl), and hematite (Fe ₂ O ₃)
TPC ashes	cristobalite (SiO ₂) and powellite (CaMoO ₄)	augite [Ca(Mg,Fe)Si ₂ O ₆] and apatite [Ca ₅ (PO ₄) ₃ (Cl,F)]	hematite (Fe ₂ O ₃) and quartz (SiO ₂)
Tet ashes	spinel (MgAl ₂ O ₄) and powellite (CaMoO ₄)		corundum (Al ₂ O ₃), anorthite [(Ca ₂ Na)(Al,Si) ₂ Si ₂ O ₈], quartz (SiO ₂), and cristobalite (SiO ₂)

^aThe approximate abundance of each phase is indicated by the following ranges: dominant (>60%), co-dominant (sum >60%), minor (5–20%), and trace (<5%).

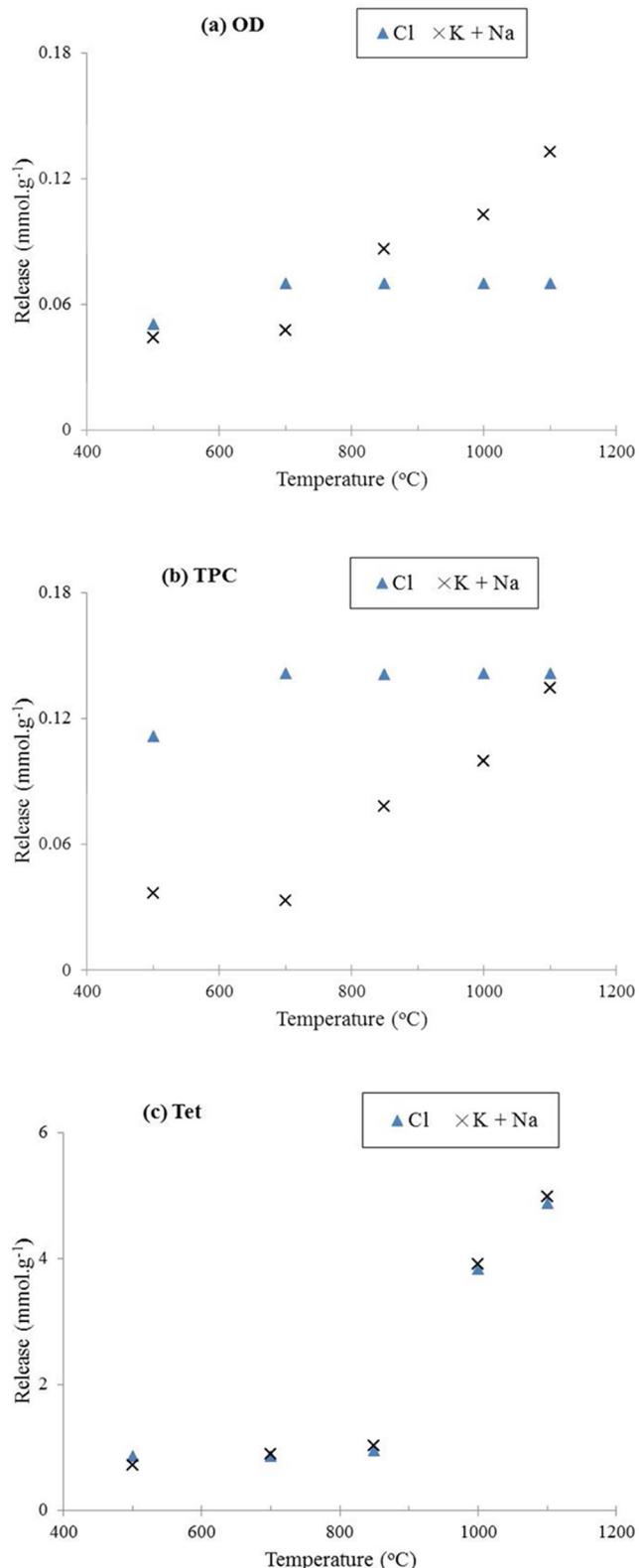


Figure 10. Absolute release of the alkali metals and Cl from OD (a), TPC (b), and Tet (c) during combustion in 2% O₂/balance N₂. Results are expressed in mmol·g⁻¹ of dry algae. The scale on the y-axis for Tet is higher to account for the greater levels of Na and Cl in Tet.

biomass for S retention is limited by the formation of alkali and alkaline earth metal silicates.²⁴ Phosphorus has a greater affinity for the base cations than does S⁶⁰ and, therefore, might also

limit the potential for S retention. In algae, P and Si are present in significant concentrations and are both expected to affect the potential for S retention. Sulfur is completely released to the gas phase during combustion of OD and TPC at 850 °C, whereas S is partially retained in the ashes of Tet during combustion under the same conditions. It is expected that differences in the proportions of the inorganic elements in the freshwater algae and Tet account for the differences in S-release behavior during combustion. The two freshwater algae (OD and TPC) contain relatively high proportions of P and Si compared to the base cations. The converse is the case for Tet. These differences in chemical composition are shown schematically in Figure 11. Terrestrial biomass fuels studied by Knudsen et al.,²⁴ which have proportions more similar to Tet than the freshwater algae, are also included in Figure 11 for comparison.

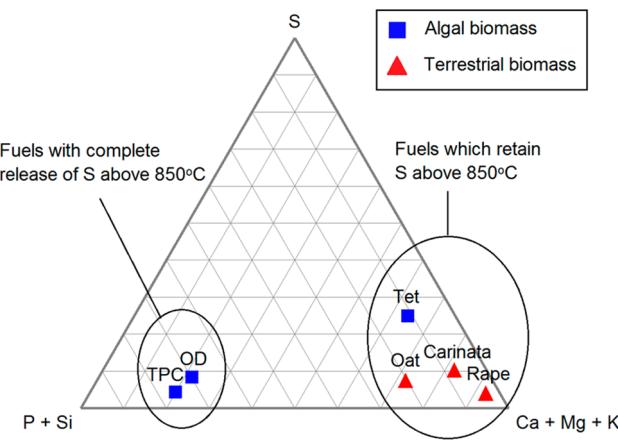


Figure 11. Compositional triangle (weight percent) of the system (P + Si) – S – (Ca + Mg + K). The algal samples are compared to terrestrial biomass fuels studied by Knudsen et al.²⁴ in terms of their S-release behavior.

The mechanisms governing the release of P from biomass are not well-understood. Wu et al.³⁸ proposed that P is released during bran combustion via the formation of molten phase phosphate compounds, followed by vaporization of KPO₃. It is possible that a similar mechanism, involving the formation of a phosphate melt, is responsible for the release of P from algae. In a previous study on the agglomerating behavior of algal ashes,¹⁹ P was found concentrated in smooth globules inside the ashes (850 °C) of *Oedogonium*, which indicates the formation of molten phase phosphate compounds during combustion. According to the mechanism proposed by Wu et al.,³⁸ the release of P is dependent on the melting behavior of phosphate species in the ashes, which is largely controlled by the amount of alkaline earth metals, Ca and Mg, in the ashes.^{31,61,62} In general, the melting behavior of phosphate compounds is shifted toward higher temperatures, the greater the alkaline earth metal content. The tested algae all contain relatively high levels of Ca and Mg (1.3–3.5 wt %, dry basis), which may explain why P is partially retained in the char/ash residues at temperatures below 1100 °C. Interestingly, the P-containing mineral, apatite [Ca₅(PO₄)₃], was identified in the high-temperature ashes (1100 °C) of TPC but not in the ashes of OD and Tet. There is no clear correlation between the release of P and the release of the alkali metals, K and Na, from the tested algae. Phosphorus release from OD and TPC is much more sensitive to increases in temperature within the

temperature interval of 850–1100 °C than the release of the alkali metals. It is, therefore, difficult to infer from the release profiles what species P is being released as from the algae. The measurement of P-containing species in the gas phase may help to make this clear and is recommended for future work.

In terrestrial biomass, the low-temperature release of K (<700 °C) is thought to be due to decomposition of organically associated K during pyrolysis.^{39,63,64} It is likely that this is also the case for algae, given that only a small amount of the total K (<10%) is released below 700 °C (see Figure 5) and that only a minor portion of the total K in algae is organically associated (estimated to be around 10% based on chemical fractionation analyses of various algal samples¹⁹). In the case of Tet, there is a striking correlation between the release of Cl and the release of K above 700 °C, as can be seen by comparison of Figures 2c and 5c. It is, therefore, expected that sublimation of KCl is the main mechanism governing the high-temperature release of K from Tet. The mechanisms responsible for the release of K from OD and TPC above 700 °C are less clear. Sublimation of KCl is unlikely to be significant, given that K is present in stoichiometric excess to Cl in the algae and that the vast majority of Cl is released from these algae below 700 °C. Vaporization of K₂SO₄ is not significant below 1000 °C, according to Knudsen et al.,²⁴ and is, therefore, also considered unlikely given that desulfurization of OD and TPC is complete by 850 °C under combustion and gasification conditions. Vaporization of melted K-phosphates, particularly KPO₃ and CaK(PO₃)₃, which have melting points of 810 and 846 °C, respectively,⁶² could be expected, given the high affinity of K for P in thermal processes⁶⁰ and the significant release of P from algae above 850 °C. It is well-known that the alkali metals can undergo various transformations during thermal processes. Potassium may also be partially released from OD and TPC by decomposition of potassium carbonates and sulfates even if these compounds are not initially present in the algae.

The behavior of Na during thermal conversion has been studied in depth in brown coal^{34,35,57,65,66} and to a much lesser extent in terrestrial biomass.^{23,39,55} Most authors report only a minor release of Na at low-temperatures (<700 °C); however, a few studies^{23,39} have reported significant release at temperatures as low as 500 °C. In algae, a significant fraction (10–25%) of the total Na is released below 500 °C. It has been suggested in the literature,^{39,67} but not definitively proven, that the low-temperature release of Na is a result of detachment of sodium carboxylate from the organic matrix during pyrolysis. Sodium is almost exclusively water-soluble in algae¹⁹ and presumably occurs as NaCl. On heating, NaCl partly dissociates^{65,68} and some Na may be converted into organic forms.⁶⁵ It is, therefore, possible that volatilization of carboxylate sodium could cause Na to be released from algae at low temperatures. However, in the case of Tet, it is considered highly unlikely that this mechanism accounts for all of the Na released at low temperatures, given the substantial level of Na (10.9 wt %, dry basis) and the relatively low level of fixed carbon (5.9 wt %, dry basis) in Tet. Chlorine and the alkali metals, Na and K, are released proportionally from Tet below 700 °C (see Figure 10c); however, the exact mechanisms governing the low-temperature release of Na are not entirely clear. Many of the mechanisms reported in the literature for Na release above 700 °C are similar to those reported for K release. NaCl sublimation^{42,66} and sodium carbonate decomposition^{23,66} have been suggested by a number of authors. In many brown coals, Na is released disproportionately to Cl.^{34,68}

Kosminski et al.⁶⁶ identified sodium carbonate in the residual char after pyrolysis of a Victorian brown coal and proposed that Na is released in elemental form from the char as a result of carbonate decomposition. Dayton et al.⁴² measured alkali vapor species released during combustion of Cl-rich switchgrass using molecular beam sampling/mass spectrometry and found NaCl to be the primary Na-containing species. In algae, the release profiles for Na closely resemble that of K within the temperature interval of 700–1100 °C. It is, therefore, expected that Na is released by mechanisms similar to those described for K above 700 °C.

Around 65–80% of the total K and around 50–65% of the total Na in OD and TPC are retained in the char and ash residues (see Figures 5a,b and 6a,b) at temperatures as high as 1100 °C. The alkali metals in Tet, on the other hand, are almost completely released to the gas phase at such high temperatures (see Figures 5c and 6c). The extent of release of the alkali metals during thermal conversion has been found to vary significantly in different types of terrestrial biomass.^{23–25,39} Knudsen et al.²⁴ compared the release of K from annual biomass with different chemical compositions and concluded that the compositional parameters K/Cl and K/Si have significant influence on the retention of K. It is understood that K is preferentially released in the form of KCl until Cl becomes limiting. The release of the remaining K depends on the availability of Si to form nonvolatile silicates in the char and ash residues. Both potassium and sodium silicates have been identified in the ashes of biomass^{24,69} and coal.⁷⁰ In Tet, the molar ratio Cl/(Na + K) is almost exactly 1:1 and it is, therefore, likely that there is sufficient Cl to enable complete release of the alkali metals as alkali chlorides. During thermal conversion of OD and TPC, on the other hand, Cl becomes deficient and no doubt limits the release of the alkali metals as alkali chlorides. It is possible that a significant portion of the total K and Na is incorporated into nonvolatile silicates, given the high concentrations of Si found in the combustion ashes of OD and TPC. Formation of nonvolatile alkali phosphates may also play a role in inhibiting the release of the alkali metals.

4. CONCLUSIONS

Differences in the release of Cl, S, K, and Na between the freshwater microalgae and the freshwater macroalga were found to be minor. The majority of Cl is released from the freshwater algae below 500 °C, and dechlorination is complete by 1000 °C under pyrolysis conditions and by 850 °C under combustion and gasification conditions. The majority of the S in the freshwater algae is released during pyrolysis at low temperatures. The remaining S is released with increasing temperature under combustion and gasification conditions but is partially retained in the char residue under pyrolysis conditions. The release of K is low (<10%) below 700 °C. The proportion of total Na released at low temperatures is slightly higher (10–25%). Potassium and Na are released gradually from the freshwater algae with increasing temperature above 700 °C. At least half of the initial Na and K are retained in the char and ash residues at 1100 °C. The release of K and Na from the freshwater algae is similar under pyrolysis, combustion, and gasification conditions. Substantial differences in the release of Cl, S, K, and Na were found when comparing the marine alga to the freshwater algae. A much lower proportion of the fuel-Cl is released from the marine alga at low temperatures (<500 °C) with the majority being released above 850 °C. There is a strong correlation between the release of Cl and the release of

the alkali metals, Na and K, from the marine alga. Chlorine, K, and Na are substantially released by 1100 °C under pyrolysis and combustion conditions and by 1000 °C under gasification conditions. The release of P is similar for all of the tested algae under pyrolysis, combustion, and gasification conditions. The onset of P release occurs at around 850 °C, and between 40% and 70% of the fuel-P is released by 1100 °C.

Possible release mechanisms for each of the main inorganic elements are proposed. Chlorine appears to be released together with the alkali metals from the marine alga, primarily by sublimation of NaCl. In the freshwater algae, Cl is present in much lower proportions and is mainly released separately from the alkali metals, presumably in the form of HCl. Sulfur is released in two stages. It is proposed that organic forms are released first as part of the pyrolysis process and inorganic forms are released later during oxidation or reduction of the residual char. Sulfur is released from the freshwater algae at lower temperatures than K and Na. Vaporization of alkali sulfates is considered unlikely. The mechanisms governing P release are not clear. It is suggested that molten phase phosphates are formed in the char and ash residues and are then evaporated. Sublimation of KCl appears to be the primary release mechanism for K in the marine alga. Potassium is released from the freshwater algae by different mechanisms. Volatilization of melted K-phosphates is suggested. It is expected that Si plays a key role in inhibiting the complete release of K from the freshwater algae. Sodium appears to be released by similar mechanisms to K at temperatures above 700 °C. An additional low-temperature mechanism is also responsible for the release of Na.

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Notes

The authors declare no competing financial interest.

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