Removal and Recycling of Inherent Inorganic Nutrient Species in Mallee Biomass and Derived Biochars by Water Leaching

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Removal and Recycling of Inherent Inorganic Nutrient Species in Mallee Biomass and Derived Biochars by Water Leaching

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ABSTRACT: Biomass growth extracts inorganic nutrients from soil as inherent nutrient species in the biomass. Unless at least some of these inherent inorganic nutrients are eventually recycled to the soil, biomass utilization during its full life cycle may not be sustainable. This study reports the removal and recycling of inherent inorganic species in mallee biomass and its derived biochars by water leaching. A series of biochars were produced from the pyrolysis of various mallee components including wood, leaf, and bark under various conditions. An increasing pyrolysis temperature leads to increases in biochar C content and aromaticity and decreases in biochar H and O contents as well as oxygen functional groups. Most of the alkali and alkaline earth metallic species (Na, K, Mg, and Ca) and P are retained in the biochars, while substantial amounts of S, N, and Cl are released during pyrolysis. For biomass samples, almost all of K, Na, and Cl and large proportions of S, P, and Mg can be recycled by water leaching, but limited Ca and little N can be recycled. However, nutrients recycling via water leaching of biochars results in substantial reductions in the overall recycling of most nutrient species originally present in biomass, due to either substantial release of nutrients (Cl, S, and N) during pyrolysis or the forms of nutrient species (Na, K, Mg, P) in biochars becoming increasingly water insoluble. The results also suggest that heat treatment may be employed to tune the biochars to facilitate the recycling of Ca which is the dominant inherent inorganic nutrient species of the samples investigated. It is noted that water leaching can also remove small amounts of organic matter, generally <2% (quantified as total organic carbon) of the total carbon in these biochars.

1. INTRODUCTION

Energy security and sustainable development are two key challenges facing the world today, due to increasing energy demand, depleting fossil fuels reserves, and the significant environmental impacts associated with fossil fuels use. Biomass is one of the most important renewable energy sources and an alternative to fossil fuels. In Australia, mallee biomass is a byproduct of dryland salinity management with a potential for large-scale production.[1,2] Its production is economic, close to carbon neutral, and exhibits excellent energy performance.[3−6] Biomass pyrolysis is an attractive technology to produce biochar and/or bio-oil fuels from biomass.[7−12] Using biochar as a fuel addresses the key problems hindering the use of raw biomass as a direct fuel due to its bulky nature, high moisture content, poor grindability, and high particulate matter emission.[13−16] Efforts were also made on research into biochar characterization and various applications, e.g. refs 17−26 to name a few.

A distinct and important feature of biomass and its derived biochars is that these materials contain abundant inorganic species and other nutrient elements which were extracted from the soil during biomass growth. The presence of these inorganic species has significant implications to the sustainability of the application processes based on biomass and its derived products such as biochar. For example, returning biochar to the field can potentially achieve both soil amendment through modification of the soil physical, chemical, and biological characteristics[25], and carbon sequestration that boosts the carbon performance toward an anticipated carbon negative system.[26−29] As many of the inorganic species in the biochar are macro- and micro-nutrients indispensable to plant growth, recycling of these

inherent nutrients in biochars to the soil becomes essential to the overall sustainability of biomass utilization. Sustainable recycling of nutrients can be achieved by enhancing both nutrient retention in biochar and the leachability of such elements to promote additional cycles of plant growth and harvesting. The nutrient retention in the biochar and the nutrient leachability may be closely related to the biochar composition and structure, which, in turn, may be greatly affected by the biochar production conditions such as pyrolysis temperature. In other applications such as using biochars for energy production, biochar is known to be a good solid fuel for such applications.[13−16,30] However, the inorganic species in biochar are ash-forming species which may lead to various ash-related operating problems.

Previous efforts were undertaken to study the performance of water leaching to remove inorganic constituents from the raw biomass[27,31−34] for addressing the ash-related problems during biomass combustion/gasification. However, there are few studies[35] on the leaching of inherent inorganic species in the biochar produced from biomass pyrolysis. To date, little data are available on the effect of pyrolysis conditions (e.g., pyrolysis temperature) on the leaching behaviors of biochars. Particularly, the recyclability of the inherent inorganic nutrients in biochars has been scantly discussed in the literature while as aforementioned, such data are important to applications such as returning biochar to the field for nutrients recycling and carbon

Table 1. Proximate and Ultimate Analysis of Raw and Leached Biomass and Biochars, for Wood, Leaf and Bark[a]

sample	moisture, wt % (after air-dried)	proximate analysis, wt % db			ultimate analysis, wt % daf				
		ash	VM[b]	FC[c]	C	H	N	S	O[d]
wood									
RB	5.3	0.4	80.7	18.9	49.0	6.7	0.19	0.02	44.1
LB	5.9	0.2	85.4	14.5	49.1	5.9	0.38	0.01	44.6
R300	4.9	1.2	65.2	33.6	59.1	5.9	0.28	0.01	34.7
L300	4.1	0.7	65.4	33.9	59.6	5.8	0.27	0.01	34.3
R500	3.3	2.6	21.5	75.9	84.2	3.8	0.46	0.03	11.5
R500	4.2	1.8	20.6	77.6	85.1	3.9	0.44	0.02	10.5
R750	5.6	3.1	10.1	86.8	89.7	1.5	0.51	0.03	8.2
L750	4.0	2.0	8.6	89.4	92.3	2.1	0.42	0.03	5.1
leaf									
RB	8.3	3.8	74.6	21.6	56.0	7.3	1.46	0.12	34.9
LB	4.4	2.2	80.7	16.1	56.7	7.5	1.96	0.09	33.7
R300	3.7	7.3	58.6	34.1	68.6	6.3	2.01	0.12	22.8
L300	5.7	4.8	57.6	37.6	68.5	6.3	2.03	0.10	23.0
R500	5.1	13.2	23.9	62.9	81.6	4.0	2.42	0.10	11.8
L500	4.2	9.5	23.1	67.4	81.3	3.9	2.38	0.10	12.3
R750	6.2	14.2	17.6	68.2	87.3	2.0	2.17	0.12	8.3
L750	3.6	6.7	14.7	78.6	90.7	2.0	2.37	0.08	4.7
bark									
RB	4.9	5.5	67.7	26.8	52.0	6.4	0.39	0.05	40.9
LB	7.1	6.3	80.4	13.3	49.3	7.0	0.80	0.83	42.1
R300	4.9	8.8	51.0	40.2	62.3	4.8	0.91	0.54	31.4
L300	5.7	7.2	49.1	43.7	63.9	5.2	1.07	0.60	29.3
R500	4.2	12.1	25.1	62.8	88.5	3.4	1.45	0.35	6.30
L500	4.2	10.2	19.4	70.4	82.2	3.4	1.29	0.36	12.7
R750	3.6	17.7	17.1	65.1	84.4	1.7	0.79	0.15	12.9
L750	3.6	12.8	14.7	72.5	87.0	2.0	0.88	0.22	9.9

[a] "RB" means raw biomass, "LB" means leached biomass; e.g. "R300" means raw biochar from 300 °C-pyrolysis, "L300" means leached biochar from 300 °C-pyrolysis, and so on. [b] Volatile matter. [c] Fixed carbon. [d] by difference.

sequestration. Therefore, a good understanding of the biochar properties and the leachability of inherent inorganic species from biochars produced at different temperatures is essential to tailoring the pyrolysis process for producing biochars of desirable characteristics for target applications.

The present study reports the removal of inorganic species by water leaching from a Western Australia mallee biomass and its biochars. It is focused on the leaching and recycling of a wide range of nutrient species in biochars that were prepared at various pyrolysis temperatures, including sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg), iron (Fe), silicon (Si), aluminum (Al), chlorine (Cl), sulfur (S), phosphorus (P), and nitrogen (N). FTIR analysis of the biochars, as well as quantification of carbon, hydrogen, and oxygen contents in the biochar were also carried out for biochars produced at various pyrolysis temperatures. The possible transformations of inorganic species during pyrolysis of the biomass and the effects upon the leachability and recyclability of these species during water leaching are discussed.

2. EXPERIMENTAL SECTION

2.1. Biomass, Biochars, and Water Leaching. The three main mallee components of mallee biomass: wood (150−250 μm),

leaf (150−250 μm), and bark (<250 μm) were prepared from the green mallee trees via biomass component separation, drying, cutting, and sieving. The typical proximate and ultimate analyses of the raw mallee samples are shown in Table 1, where "db" refers to "dry basis" and "daf" refers to "dry-ash-free basis".

Biochars were prepared from the pyrolysis of the raw biomass samples in a fixed-bed quartz reactor housed in an electrically heated furnace under controlled conditions. The detailed configurations of the reactor system can be found elsewhere.[30] Briefly, a biomass sample, loaded into the reactor and held on the quartz frit, was heated at 10 K min^{-1} to a desired pyrolysis temperature and held for 15 min, under ultra high purity UHP argon (purity >99.999%). The pyrolysis temperatures employed were 300, 500, and 750 °C.

The raw biomass samples and the biochars produced from pyrolysis at various temperatures were then subjected to water leaching using Milli-Q water (high-purity water with resistivity >16 Ohm) at 35 °C. Approximately 5 g of sample was immersed in about 1 L of water and stirred gently for 24 h. The mixture was then filtered and the sample was recovered. The above leaching procedure was then repeated twice to produce the leached sample.

2.2. Quantification of Inorganic Species in Biomass and Biochars. A series of analysis methods were used to quantify the
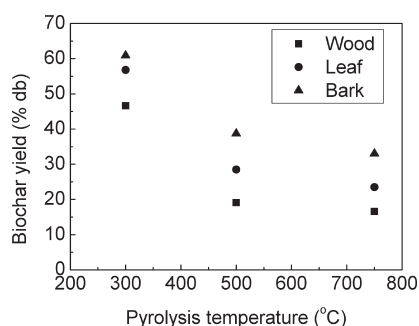
Figure 1. Biochar yield as a function of pyrolysis temperature.

amount of inorganic species in the biomass and biochar samples. Na, K, Mg, Ca, Fe, Al, Si, and P were analyzed by a method detailed elsewhere.[30] Briefly, a biomass or biochar sample was firstly ashed according to a specially designed ashing program that prevents the loss of inorganic species during ashing, followed by borate fusion and then analysis by inductively coupled plasma—atomic emission spectroscopy (ICP-AES) using a Varian Vista Axial CCD Simultaneous ICP-AES instrument. Total S and Cl contents were determined by ICP-AES using a Spectro ARCOS ICP instrument, following combustion of the samples under the Eschka's mixture and acid digestion, based on the method outlined in Australian Standards AS1038.6.3.1[36] and AS1038.8.1.[37] N was determined using a LECO Truspec Analyzer according to Australian Standard AS1038.6.4.[38]

2.3. Quantification of Carbon, Hydrogen, and Oxygen in Biomass and Biochars. The C, H, and O contents of the raw biomass, raw biochar samples, and all washed samples were determined using a series of methods. C, H, and N were analyzed using a LECO Truspec Analyzer according to Australian Standard AS1038.6.4,[38] and O was determined by difference from the C, H, N, S, and Cl contents (daf) of the sample.

2.4. Fourier Transform Infrared Spectroscopy (FTIR) Analysis. The raw biomass and raw biochars were analyzed using a Perkin-Elmer Spectrum 100 ATR-FTIR spectrometer. Briefly, a sample was ground into powder using an agate mortar and then air-dried overnight in an oven at 40 °C before each analysis. Scanning of each sample was conducted at a resolution of 2 cm^{-1}. The relative intensities of the spectra allow semiquantitative analysis on the functional groups, as each run was conducted with a comparable amount of sample in contact with the diamond, coupled with a constant force of 80 N being applied on the sample. Basic data processing included ATR correction, biomass correction, and automatic data smoothing.

2.5. Quantification of Total Organic Carbon in Solutions of Biomass or Biochar Water Leaching. Efforts were taken to examine the possible removal of organic matter from biomass and biochar leaching using water. The leaching of organics was quantified as total organic carbon (TOC), as percentage of the total carbon in biomass or biochar. The TOC contents of the solutions from water leaching were analyzed using a TOC analyzer (Shimadzu TOC-V$_{CPH}$). The total carbon contents of biomass and biochar were determined following the procedure in Section 2.3.

3. RESULTS AND DISCUSSION

3.1. Pyrolysis Biochar Yield, and C, H, O Contents in Biochars. From Figure 1, the biochar yield decreases with an
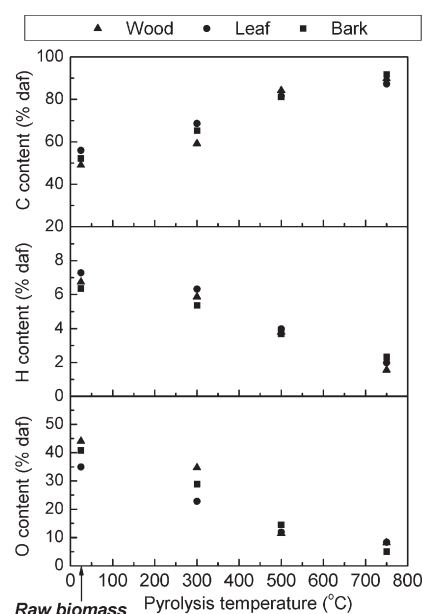

Figure 2. Carbon (C), hydrogen (H), and oxygen (O) contents (% daf) in the raw biomass and raw biochars from different pyrolysis temperatures. Data at 25 °C, as labeled in the figure, represent results for the raw biomass.

Table 2. Inorganic Species Contents (wt % db for Na, K, Mg, Ca, Fe, Si, Al, and P; wt % daf for S, Cl, and N) in the Raw Biomass Samples

element (wt %)	raw wood	raw leaf	raw bark
Na	0.0212	0.5537	0.2094
K	0.0744	0.3797	0.1105
Mg	0.0364	0.1447	0.0796
Ca	0.1236	0.7652	2.6591
Si	0.0026	0.0550	0.0099
Al	0.0025	0.0192	0.0028
Fe	0.0001	0.0142	0.0019
P	0.0182	0.1075	0.0235
S	0.0183	0.1181	0.0509
N	0.1910	1.4574	0.3918
Cl	0.0323	0.1839	0.2601

increase in the pyrolysis temperature, as expected, due to increasing volatile release with pyrolysis temperature. The biochar yield (dry basis) appears to start leveling off at temperature above 500 °C. The char yields of different mallee biomass components are in the order of bark > leaf > wood, which is consistent with the reverse order of volatile matter contents and the order of ash contents of these samples (see Table 1). Figure 2 presents the carbon, hydrogen and oxygen contents in the biochars produced from pyrolysis of the various raw biomass components. Biomass is a low-rank fuel with high oxygen content (at least ~35% in each of the mallee biomass components). It is clear in Figure 2 that the carbon content increases with pyrolysis temperature, whereas the hydrogen and oxygen contents decrease with pyrolysis temperature. This is consistent with the fact that various oxygen functional groups are released as volatiles
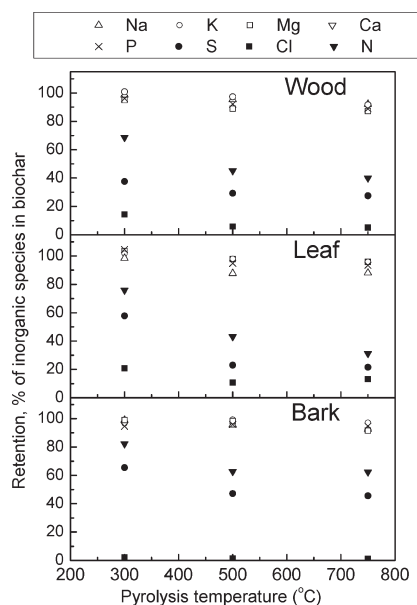
Figure 3. Retention of inorganic species (Na, K, Mg, Ca, P, S, Cl, and N) in the raw biochars at different pyrolysis temperatures. For Cl in wood and bark samples, the retention shown is the maximum possible retention.

during pyrolysis. The evolution of functional groups with pyrolysis temperature will be investigated using FTIR analysis later.

3.2. Inorganic Species in Raw Biomass and Their Retentions in Biochars. The contents of inorganic species in the biomass samples are presented in Table 2. Consistent with proximate analysis, the data in Table 2 show that bark has the highest inorganic content, followed by leaf and wood. The alkali and alkaline earth metallic (AAEM) species (particularly, Na, K, Mg, and Ca) are dominant metallic species in all the biomass samples, with Ca being the most abundant. The transition metal Fe is of very low level in the biomass samples. The contents of Si and Al are also low. The biomass samples contain various amount of other inherent species, namely S, Cl, P, and N, which are important nutrients in biomass. Therefore, the results and discussion that follow will hence focus on Na, K, Mg, Ca, S, Cl, P, and N.

From the biochar yield (see Figure 1), as well as the inorganic species content in the biomass and biochars, the retention of inorganic species in the biochars was calculated. Figure 3 shows the retention of the various inorganic species in the biochars after pyrolysis. It is clear that under the current conditions for biochar preparation at low pyrolysis temperatures and slow-heating rates, the majorities of the AAEM species are retained in the biochars. Under such pyrolysis conditions, the interactions between volatiles and pyrolysis biomass particles are minimal, therefore the effect of volatile—biochar interactions[39] is small. The marginal loss/volatilization of AAEM observed here is most probably due to the release of AAEM as carboxylates during pyrolysis.[40] In contrast, P is likely to exist in some phosphate forms or some complex mineral compounds[41,42] therefore it is not easily released during pyrolysis under such conditions. On the other hand, N and S are released to a relatively greater extent. Their volatilization increases with pyrolysis temperature. Via pyrolysis, N in solid fuels may be released as HCN, NH_3, and/or other gaseous products (e.g., N_2)[43] whereas S is probably volatilized as
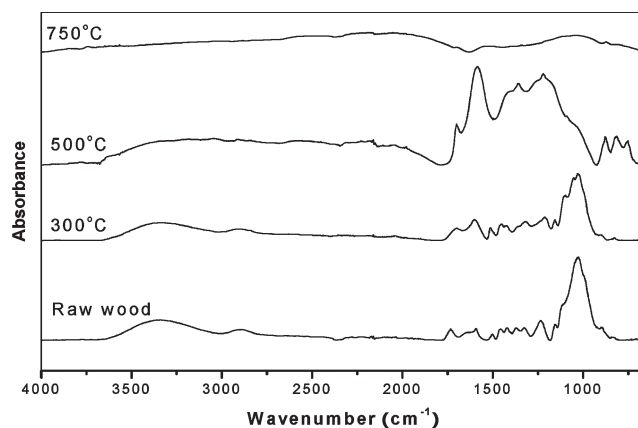
(a)
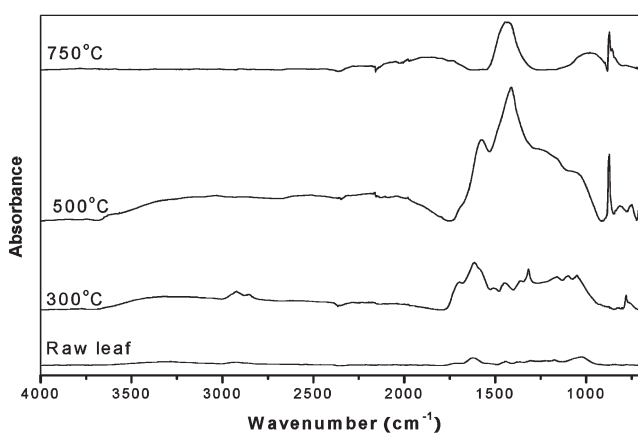
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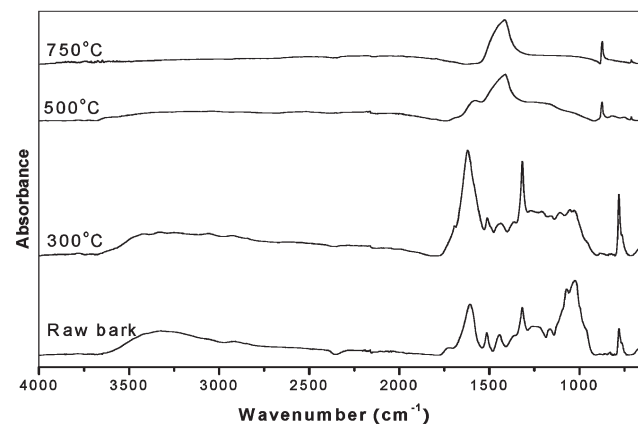
(c)

Figure 4. FTIR spectra for raw biomass and raw biochars from different pyrolysis temperatures (300, 500, and 750 °C): (a) wood, (b) leaf, and (c) bark.

H_2S.[44] Cl is generally known to be released significantly during solid fuels pyrolysis,[45] particularly volatilized as organic chloride and HCl during low-rank fuel pyrolysis.[40] Note that in Figure 3, for wood and bark bio chars, due to the low Cl contents and the detection limit of the method used for Cl analysis, the retention shown is only the maximum possible retention.

3.3. Fourier Transform Infrared Spectroscopy (FTIR) Analysis. Figure 4 shows the FT-IR spectra of raw wood, leaf, and bark and their respective biochars prepared at low (300 °C), intermediate (500 °C), and high (750 °C) temperatures. Generally, for all cases, in the raw biomass and biochars at the low temperature, oxygen functional groups are abundant. OH groups are apparent in the broad absorption range within $3600-3200$ cm^{-1}, possibly due to overlapping hydroxyl bands. This indicates the possible presence of phenols and carboxylic acids, where the significant band broadening effect and shift toward lower wavenumbers is characteristic of the strong hydrogen bonding of carboxylic acids.[46] The $1800-1700$ cm^{-1} region can be attributed to carbonyl structures such as carboxylic acids, lactones, anhydrides, esters, and other acetyl derivative groups.[46-48] Possible olefinic C=C stretching bands are found in the region of $1680-1620$ cm^{-1}, whereas a peak at 1600 cm^{-1} is likely to be due to the presence of conjugated C=C bonds. A general trend toward the intermediate temperature is the increasingly conjugated nature of the C=O functional groups, as explained by the shift of the bands toward lower wavenumbers, which overlaps the region of olefinic C=C stretching absorptions mentioned above.[46] This is also a spectral feature of aromatization, which leads to more conjugated bonds of the C=O with an aromatic nucleus or another C=C bond.[10,48,49] The 1600 cm^{-1} peak assigned to conjugated C=C bonds[46] increases from the low to intermediate temperature and diminishes approaching the high temperature, for all biochars. The initial increase is most probably due to the increasingly conjugated nature of C=O bonds at the intermediate temperature as aforementioned. At a high temperature, this peak is no longer observable, due to loss of oxygen and the increasing dominance of aromatic rings structures in the high-temperature biochar spectra.

Progressive aromatization is obvious for biochars starting from the intermediate temperature, as evidenced from the general trend of increasing bands in the $1615-1450$ cm^{-1} region[46-48] attributed to aromatic C=C—C stretching. The ratios between the C=O and aromatic C=C—C stretching bands noticeably decreases with increasing pyrolysis temperature. Approaching the high temperature, the clearly visible bands that remain for the bark and leaf chars are those attributed to C=C—C aromatic ring stretching ($1615-1450$ cm^{-1}) and aromatic C—H out-of-plane bending ($900-760$ cm^{-1}).[46,49,50] This indicates that the remaining biochar structure at high temperatures is predominantly aromatic rings with a certain degree of substitution.[49,51] The absence of obvious bands for the high temperature wood char is probably due to the higher extent of turbostratic crystallinity in wood biochars,[52,53] which induces a negligible change in dipole moment hence rendering IR inactive behavior.[48,54] Approaching a high temperature, much of the oxygen has been removed, and the remaining oxygen is expected to exist as aromatic ether.[49] Overall, common to all biochars, with increasing temperature, a reduction of all the assigned oxygen functional groups as well as an increase of aromaticity can be observed. These results from FTIR are also in accordance with the decreasing O and H contents observed earlier (Figure 2).

3.4. Removal of Organic Matter from Biomass and Biochars by Water Leaching. Water leaching of biomass or biochar may result in the removal of organic matter that may have important implications. For example, for biochar application in soils, leaching of organic matter may be undesired as it leads to reduction in carbon sequestration benefits and potential soil contamination. Figure 5 presents the data on the removal of
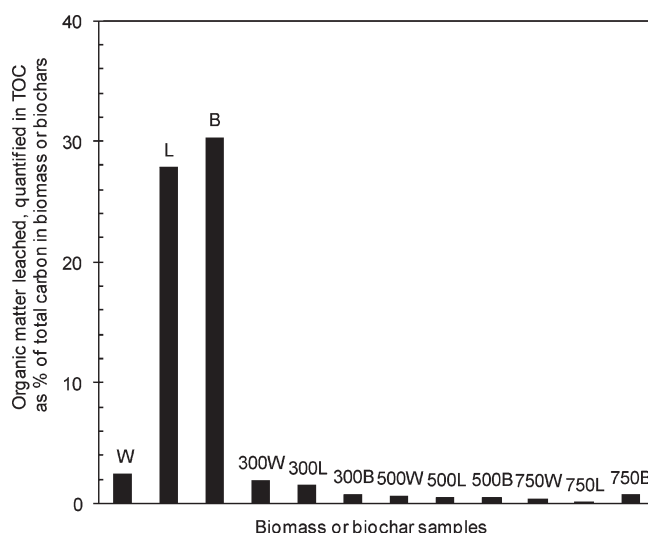

Figure 5. Removal of organic matter during water washing of biomass or biochars, quantified in total organic carbon (TOC) as percentage of total carbon in the samples. Biomass samples are labeled as W (wood), L (leaf), and B (bark). Biochar samples use the same notation but are prefixed by their pyrolysis temperature (°C), e.g., 300W refers to biochar produced from the pyrolysis of wood at 300 °C.

organic matter during water leaching of various biomass and biochar samples, quantified as total organic carbon as the percentage of total carbon in each sample. It can be seen that removal of organic matter in biomass via water leaching can be substantial and is strongly dependent on the biomass component. For example, ~28% and 30% of the total carbon in leaf and bark biomass were removed via water leaching while only ~2.5% in wood was removed. Although the exact reasons are unknown at present, such different leaching behavior must be due to the differences in the chemical structures of wood, leaf, and bark. Future work is required to clarify this point. Figure 5 also shows that the leaching of organic matter (quantified as total organic carbon) from all biochar samples is low, generally <2% of the total carbon in biochar, considerably less than that from biomass. The results suggest that pyrolysis has transformed the organic structure of the raw biomass into recalcitrant forms which are unresponsive toward water leaching.

Further proximate and ultimate analyses were also conducted to investigate the properties of the biomass and biochar samples before and after water leaching. Such data are listed in Table 1, allowing quantitative comparison of biomass/biochar chemical compositions to understand variations resulting from water leaching. It is known that inorganic species are leached out during water leaching of biomass and biochar so that ash contents decrease following water leaching. This is generally reflected in the proximate analysis data (see Table 1) of biomass and biochars before and after water leaching. However, it is interesting to see that the ash contents of bark after water leaching are actually increased, suggesting that, relatively, more organic matter is removed than inorganic species in bark during water leaching. Furthermore, the ultimate analysis data in Table 1 also indicate that there are no significant changes in the elemental compositions of biomass and biochar samples before and after water leaching. This suggests that while there may be substantial organic matter leaching out (e.g., leaf and bark), the leaching of individual elements is proportional.

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Table 3. Inorganic Species Contents (wt % db for Na, K, Mg, Ca, and P; wt % daf for S, Cl and N) in Raw and Leached Biomass and Biochars, for Wood, Leaf and Bark[a]

	wood							
element (wt %)	RB	LB	R300	L300	R500	L500	R750	L750
Na	0.021	<0.01	0.045	<0.01	0.106	0.025	0.118	0.052
K	0.074	0.002	0.161	0.010	0.379	0.120	0.411	0.047
Mg	0.036	0.020	0.074	0.048	0.169	0.151	0.191	0.183
Ca	0.124	0.084	0.267	0.222	0.583	0.485	0.669	0.556
Cl	0.032	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
S	0.018	0.010	0.015	0.009	0.029	0.020	0.031	0.031
P	0.018	0.003	0.037	0.014	0.088	0.067	0.097	0.086
N	0.191	0.203	0.283	0.272	0.462	0.437	0.515	0.418

	leaf							
element (wt %)	RB	LB	R300	L300	R500	L500	R750	L750
Na	0.554	0.019	1.009	0.192	1.902	0.895	2.258	0.774
K	0.380	0.021	0.679	0.336	1.306	0.773	1.550	0.057
Mg	0.145	0.077	0.251	0.248	0.445	0.452	0.543	0.543
Ca	0.765	1.142	1.333	1.395	2.556	2.388	3.022	1.403
Cl	0.184	0.026	0.069	0.028	0.075	0.038	0.116	0.066
S	0.118	0.088	0.124	0.100	0.104	0.097	0.121	0.081
P	0.108	0.054	0.198	0.150	0.357	0.354	0.428	0.442
N	1.457	1.800	2.005	2.027	2.415	2.383	2.173	2.367

	bark							
element (wt %)	RB	LB	R300	L300	R500	L500	R750	L750
Na	0.209	0.006	0.340	0.075	0.517	0.110	0.587	0.139
K	0.111	0.007	0.175	0.080	0.284	0.054	0.326	0.020
Mg	0.080	0.026	0.129	0.113	0.202	0.195	0.221	0.215
Ca	2.659	3.162	3.977	4.182	6.356	6.198	6.967	3.518
Cl	0.260	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
S	0.051	0.051	0.056	0.051	0.068	0.058	0.077	0.051
P	0.023	0.014	0.037	0.031	0.058	0.061	0.067	0.068
N	0.392	0.533	0.547	0.539	0.692	0.684	0.817	0.704

[a] "RB" means raw biomass, "LB" means leached biomass, e.g., "R300" means raw biochar from 300 °C-pyrolysis, "L300" means leached biochar from 300 °C-pyrolysis, and so on.

3.5. Removal of Inorganic Nutrient Species in Biomass and Biochars via Water Leaching. The proximate analysis data in Table 1 indicate that generally the ash yield of the various samples is reduced by water leaching. Quantification of individual inorganic nutrient species in the biomass and biochar samples before and after water leaching were also carried out and the data are presented in Table 3. It is clear that various extents of removal of inherent inorganic nutrient species from biomass and biochar samples were achieved via water leaching, depending on biomass components, inorganic species, and pyrolysis conditions. It is noted in Table 3 that in some cases for the biomass, the contents of some inorganic species (such as Ca) (from Table 3) in the water leached biomass sample are slightly higher than that of the raw biomass sample, due to the substantial removal of organic matter (see Figure 5) during the water leaching process.

Considering part of the inherent nutrients may be released during pyrolysis, the actual amount of an inherent nutrient species in a biochar available for removal and recycling via water
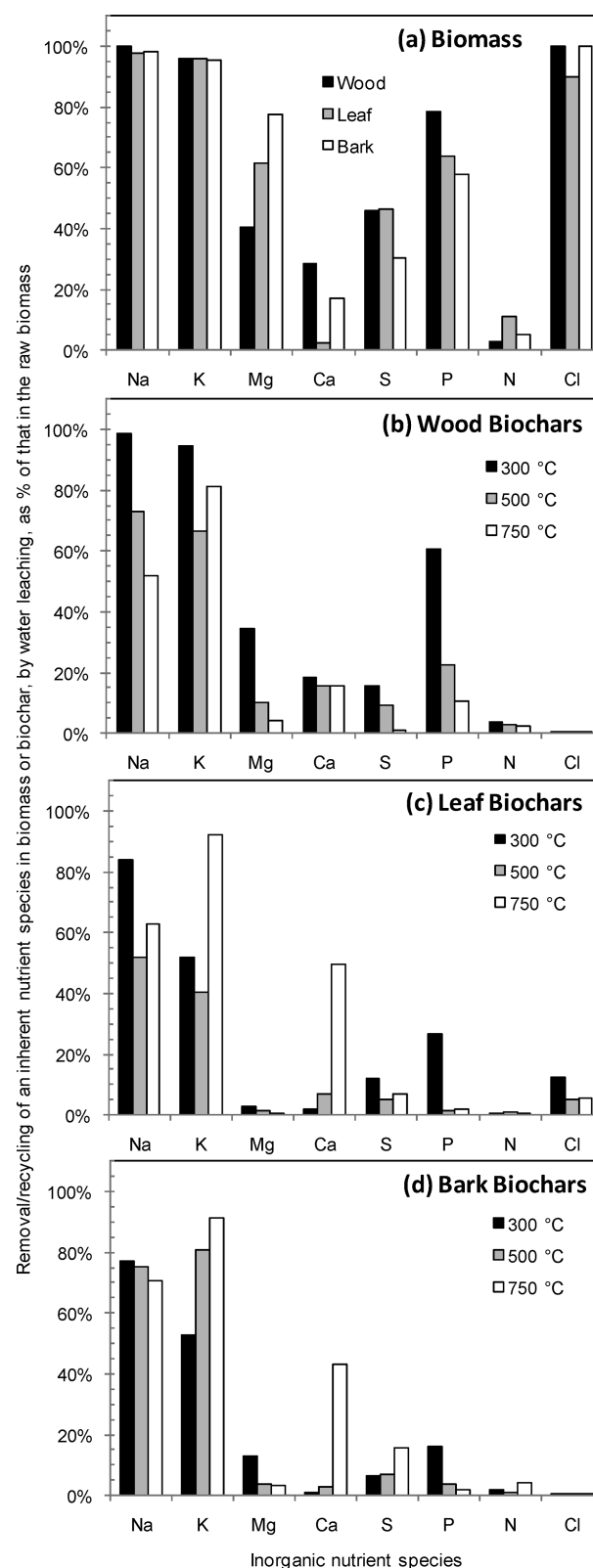
Figure 6. Overall removal (or recycling) of various inherent nutrients in biomass and biochar samples via water leaching, normalized to the total nutrients originally present in biomass.

leaching may be less than that originally in the biomass. Therefore, the removal/recycling of each nutrient species in a biomass

or biochar is then normalized as % of total amount of that nutrient species originally available in the biomass. The data are presented in Figure 6, and directly shows the proportions of inorganic nutrient species originally present in biomass (i.e., extracted from the soil during biomass growth) which can be ultimately recycled by biochar production from biomass pyrolysis followed by biochar water leaching. The inherent inorganic matter in the biomass or biochars can be present in one or more of the following forms: (1) salts that are ionically bound, (2) inorganic materials bound organically to the carbonaceous material, and/or (3) included and excluded mineral matter.[55] The extent of leaching of various inorganic species by water depends dominantly on the forms/mode of occurrence of the inorganic species in the biomass or biochar.

As shown in Table 3 and Figure 6a, water leaching of biomass can remove and recycle almost all Na, K, and Cl in all biomass components (wood, leaf, and bark). Figure 6a also indicates that 40−80% of Mg, 30−50% of S, and 60−80% of P can be leached out by water from the raw biomass, depending on the biomass component. However, only 5−30% Ca, which is the most abundant species in these biomass samples, can be leached. Therefore, in the biomass samples, at least part of these water-soluble alkali and alkaline earth metallic species (Na, K, Mg, and Ca) are likely to exist in the form of water-soluble salts including chlorides, sulfates, and phosphates. The molar ratios of (Na + K + 2Mg + 2Ca)/(Cl + 2S + 3P) in the leached solutions obtained from water leaching of wood, leaf, and bark are 2.1, 2.8, and 3.3, respectively. The ratios well exceed 1, suggesting that at least some of these inorganic species may also exist in other water-soluble forms besides water-soluble salts. The most likely forms are alkali (Na and K) ion-exchangeable carboxylates (an acidic/oxygen functional group and humic acid material) because the alkaline earth metal (Mg and Ca) carboxylates are hardly water-soluble. Additionally, the limited leaching of Ca that is the dominant inorganic species in these biomass samples especially bark and leaf also suggests that Ca is largely in water-insoluble forms such as carboxylates. This is consistent with the apparent carbonyl bands observed from FT-IR (Figure 4) for the raw biomass which indicates the presence of functional groups providing capacity for ion-exchange of metal cations. Figure 6a also indicates that N removal and recycling of N from water leaching of biomass is little. This is consistent with the fact that N occurs largely as organically bound nutrients in biomass and is generally unavailable to plants as suggested previously.[52,56−58]

For water leaching of biochars, the results are presented in Figure 6b−d for the overall recycling of inherent nutrient species in biochars. The data indicate that via biochar production from pyrolysis followed by biochar water leaching, the overall removal and recycling of most nutrients species are substantially reduced. Approximately 40−90% of Na and K in the biochars can be removed via water leaching (less than those in biomass water leaching), depending on biomass component, nutrients species, and pyrolysis conditions. The majority of Na and K are retained as nutrients in biochars (see Figure 3), whereas most of Cl in biomass is released during pyrolysis. Therefore, the overall recycling of Cl is close to zero via biochar applications. Clearly, Cl is released separately from the Na or K, instead of as Na or K chloride molecules, consistent with previous data on brown coal pyrolysis.[40] The reductions in Na and K recycling in the case of biochars are most likely due to the change in the chemical forms of Na and K in the biochars after pyrolysis. Na or K originally associated to Cl may be transformed into the organically bound

forms in biochar following the release of Cl during pyrolysis, either ion-exchanged to the oxygen functional groups (likely for the low- and intermediate-temperature biochars) or directly bonded to the biochar matrix (especially for the high-temperature biochars). This is supported by, as seen from FT-IR (Figure 4), the presence of possible carboxylic acid bands for the low- and intermediate-temperature biochars. Yet, as pyrolysis temperature increases, the progressively decreasing oxygen functional groups (Figure 4), hence the decreasing O and H contents (see Figure 2), dictate a higher susceptibility of direct bonding of the species to the biochar matrix. Excess metallic species may also be transformed into other forms such as carbonates or oxides.[59] The above could account for the variation of leaching extent of Na and K with respect to pyrolysis temperature: part of the Na and K that exists in chlorides, carboxylates, or carbonates in the biochars can still be leached out by water, while Na and K that have been directly bound to the biochar matrix or that have been transformed into oxides thus cannot be leached out.

The data further indicate that S is only marginally removed from biochars through water leaching. Considering also the substantial release of S during biomass pyrolysis (see Figure 3), the overall recycling of S is small, as shown in Figures 6b−d. The dependence of leaching and recycling of S in biochars on different pyrolysis temperatures may be attributed to two reasons. One is the different retentions of S in biochars during biomass pyrolysis (see Figure 3). The other is the transformations of sulfur between water-soluble (such as alkali sulfates) and water-insoluble (such as organic sulfur) forms during pyrolysis.[60] For P, it is mostly retained in biochars during biomass pyrolysis at various pyrolysis temperatures (see Figure 3). It is noted that P can still be leached from the biochars prepared at 300 °C, suggesting this fraction possibly still exists as some water-soluble phosphates. As the pyrolysis temperature increases, these water-soluble P appear to be transformed into some water-insoluble minerals, e.g., apatite and/or other complex phosphorus-containing compounds.[41,42] The data in Table 3 show that little N can be leached from the biochars for all cases, suggesting that the N retained in biochars still exist as organically bound form and hence are not leachable by water. As the retention of N following pyrolysis is also comparatively low (see Figure 3), the overall recycling of N via the leaching of the remaining N in the biochar is low, further reducing the prospect of directly supplying N to soils via biochars. The relative unavailability of macronutrients N and P may be a downfall in terms of direct nutrient benefits of these biochars. Therefore, mitigation strategy such as the application of biochar in conjunction with conventional N, S, and P fertilization can potentially increase the efficiency and plant response of such supplements, as shown in previous studies[28,61] because of enhanced ammonium and phosphate retention due to reversible adsorption effects.[52] The findings on different leachability that can be achieved with different biomass components at different pyrolysis temperatures may also provide guidelines for developing optimum strategy for such applications. Particularly, because Ca is the dominant inorganic nutrient species in biomass and biochar samples, the substantial leaching of Ca in biochar prepared at 750 °C suggests that simple heat treatment may be employed to tune biochars to facilitate the recycling of Ca in these biochars.

Following pyrolysis, it is important to note that the leaching and recycling of Mg becomes almost zero, suggesting that the originally water-soluble Mg has been transformed into organically bound forms or compounds such as carbonate and/or

oxide[59] which are hardly water-soluble. These transformations stem from the decreasing oxygen functional groups and the increasing aromaticity as pyrolysis progresses to higher temperatures, as evidenced from FTIR (Figure 4). As alkaline earth metal (Mg and Ca) carboxylates and carbonates are hardly water-soluble, partly explaining the lower leachability of Mg and Ca compared to Na and K from the biochars. It is also interesting to note that a somewhat reverse trend, compared to that of Mg, is observed for the leaching of Ca with pyrolysis temperature. The leaching of Ca increases substantially at 750 °C. The data suggest that following pyrolysis, Ca most probably still exists in organically bound forms or exists as carbonate and oxide,[59] which are not soluble or only sparingly soluble in water. Hence, the high leaching of Ca at the high pyrolysis temperature is most likely to be due to emergence of calcium bicarbonate ($Ca(HCO_3)_2$), a salt existing in aqueous solution which has much higher solubility than $CaCO_3$ during water leaching.

4. CONCLUSION

This study investigated the removal of a broad range of inherent inorganic species from mallee biomass and biochars by water leaching. With increasing pyrolysis temperature, the biochar yield decreases, the biochar C content increases, while the biochar H and O contents decrease. The AAEM species and P are mostly retained in the biochars following pyrolysis. During pyrolysis, substantial amounts of N and S are volatilized, while Cl is almost all released during pyrolysis under the experimental conditions. FTIR analysis has provided evidence that the oxygen functional groups in the biochars diminish and the biochar aromaticity increases with increasing pyrolysis temperature. Water leaching can recycle almost all of K, Na, and Cl, large proportions of S, P, and Mg, but limited Ca and little N in all biomass samples. The data further show that via biomass pyrolysis followed by biochar water leaching, the overall recycling of most of the nutrient species originally present in biomass (as results of leaching of inherent nutrients in biochars) is substantially reduced. Such reductions are due to either substantial release of nutrients (Cl, S, and N) during pyrolysis or most nutrient species (Na, K, Mg, P) in biochars being transformed into increasingly stable forms that are difficult to be leached by water. For Ca that is the dominant inorganic nutrient species in these biomass and biochar samples, the data suggest that heat treatment may be employed to tune these biochars to facilitate their recycling. Furthermore, water leaching also leads to the removal of small amounts of organic matter from biochars, generally <2% (quantified as total organic carbon) of the total carbon in the biochars.

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■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on October 6, 2011, with a minor text error on the first page and minor errors in the first column of Table 1. The corrected version was reposted on October 10, 2011.