Phosphorus Speciation and Release in Biochar

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Abstract

Pyrolysis exerts a significant alteration on the element. Compared to the understanding of carbon and nitrogen, less is known about the change of phosphorus speciation during the pyrolytic process. In this study, wood chips, rice husks, and leguminous biomass was pyrolyzed at 300 and 500 °C and their elemental alterations were determined. Using chemical fractionation (Hedley sequential extraction) and spectroscopic techniques (solid-state ^{31}P NMR and synchrotron-based X-ray absorption spectrometry), we found that phosphorus speciation in raw material was changed into (1) inorganic phosphorus through pyro-mineralization, (2) aromatic carbon ring linked phosphate during pyrolysis. Such change played a significant role in affecting phosphorus release. For biomass with a high carbon-to-phosphorus ratio, converting it into biochar enhanced phosphorus release. In contrast, converting biomass with a low carbon-to-phosphorus ratio into biochar reduced phosphorus release.

Introduction

During charring process, elemental composition and availability in biochar can be considerably altered from its raw feedstocks. In this study, the changes of phosphorus (P) during pyrolysis were examined. We applied the Hedley P extraction, solid-state ^{31}P nuclear magnetic resonance (NMR) and synchrotron-base X-ray P absorption spectra to investigate the change of P speciation during charring process.

Materials & Methods

Four plant biomass feedstocks including rice husk (denoted as RH), Japanese cedar (*Cryptomeria japonica*) wood chips (CJ), young and mature *Sesbania roxburghil* (YS and MS) were collected. The feedstocks were charred at 300 and 500 °C, respectively. The biochar samples were denoted as the feedstocks and the charring temperature. The unconverted feedstocks were also used as the comparison in this study.

Table 1. Yield, pH, and elemental concentration of four feedstocks and biochars

	Yield	pH	C	N	H	P	Ca	K	Ash	P recovery
	%			g/kg			mg/kg			%
RH-raw[a]	-	5.6	397	4	50	307	818	1846	128	-
RH300	65	6.4	490	4	39	443	999	2364	186	90
RH500	39	10.0	536	5	23	782	1545	3898	317	71
CJ-Raw	-	5.8	475	1	66	60	986	1244	6	-
CJ300	66	6.7	601	1	49	78	1127	1621	10	86
CJ500	29	9.7	811	1	23	141	2458	2514	19	69
MS-Raw	-	5.4	508	21	73	2218	7965	12983	61	-
MS300	52	8.0	566	21	43	3301	12011	21723	125	82
MS500	32	10.2	629	21	18	4603	20202	30730	211	71
YS-Raw	-	5.2	487	48	53	4173	10783	31091	100	-
YS200	96	5.5	477	43	44	4125	11492	32308	110	95
YS300	60	7.1	587	41	28	6185	17892	49457	150	82
YS400	41	9.0	577	35	16	8008	19665	61626	190	79
YS500	35	10.7	595	34	8	9277	23526	68422	250	78

Table 2. Concentration of P fractions (mg kg^{-1}) of four feedstocks and biochars

	Water		$NaHCO_3$		NaOH		HCl	Residue	TP
	Pi	Po	Pi	Po	Pi	Po			
RH-Raw	216	33	13	6	15	6	8	11	307
RH300	121	68	24	71	66	59	15	19	443
RH500	210	11	60	76	43	9	154	220	782
CJ-Raw	19	7	8	6	2	6	7	5	60
CJ200	18	7	16	9	10	6	8	5	78
CJ300	15	1	20	3	1	6	37	58	141
MS-Raw	1745	111	54	81	18	122	15	72	2218
MS300	1794	382	133	120	328	200	242	103	3301
MS500	526	34	877	64	128	44	1903	1028	4603
YS-Raw	3180	230	290	103	12	115	3	240	4173
YS200	2664	686	168	123	23	158	12	292	4125
YS300	2535	375	684	318	395	584	796	496	6185
YS400	1937	111	1350	85	286	97	3177	965	8008
YS500	938	159	1689	94	138	43	3553	2662	9277

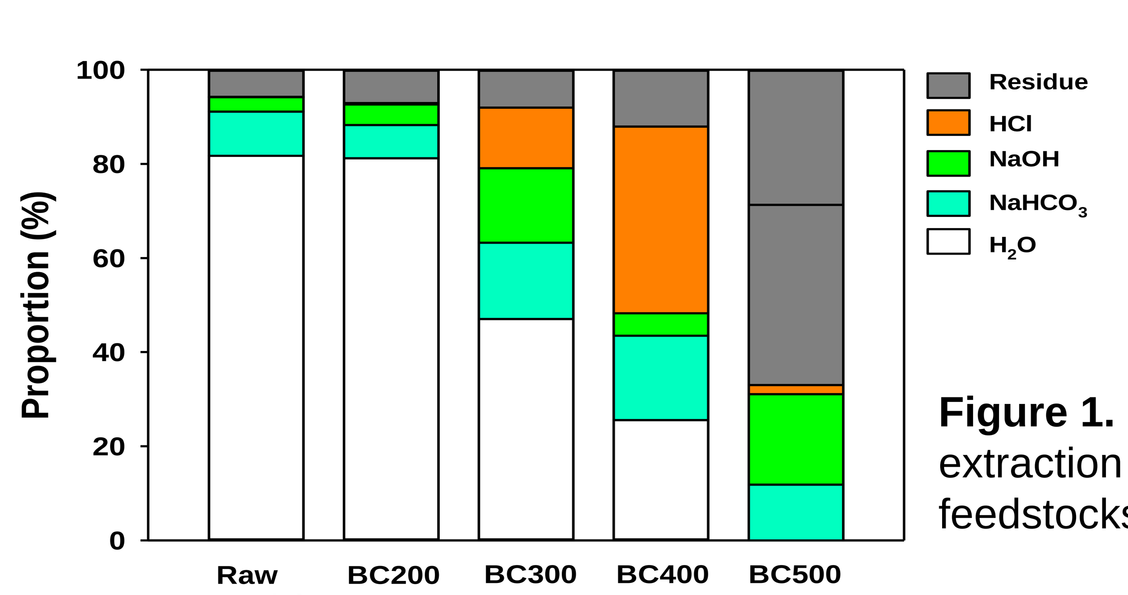

Figure 1. Proportion of Hedley P extraction for young *Sesbania* feedstocks and biochars.

Results & Discussion

- Total P content varied widely among feedstocks and biochars and increased with charring temperature **(Table 1)**. Phosphorus recovery during charring process were 69-90%.
- Charring process led to the loss in water extracted P, while became dominated by a larger amount in HCl P and residual P in biochars **(Table 2; Figure 1)**.
- The charring process shifted the ^{31}P NMR peaks downfield to 1.8 ppm for BC300 and 2.3 ppm for BC500 due to the formation of Ca-P structure. A small shoulder located between -3 and -10 ppm which was assigned as pyrophosphates and aromatic phosphates was developed **(Figure 2)**.
- The P NEXAS spectra also indicated the formation of Ca-P during charring process **(Figure 3)**.
- Total P release was high in Raw and 300°C biochar, but a net P immobilization was found in Raw feedstock compared to net P mineralization in both 300 and 500°C biochars **(Figure 4)**.

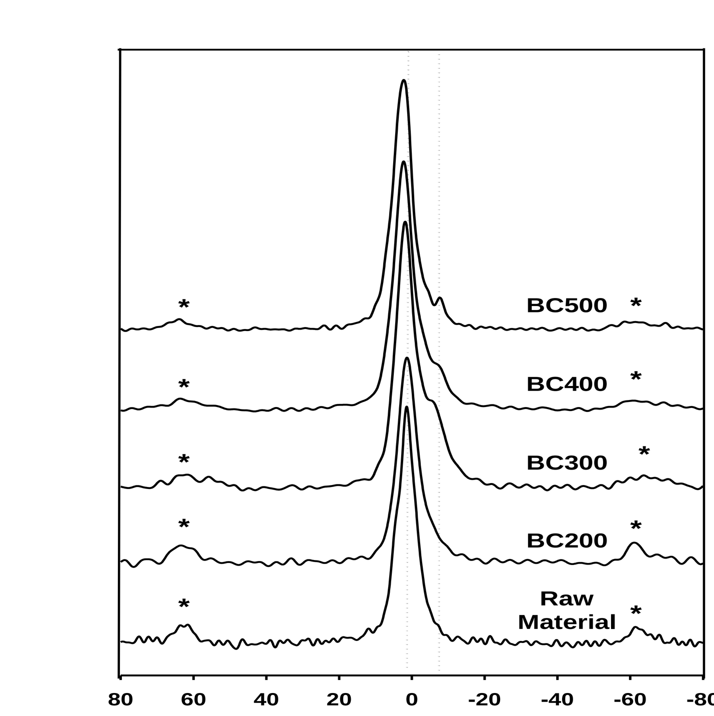

Figure 2. Solid-state single-pulse ^{31}P NMR spectra for young *Sesbania* feedstock and biochars. Asterisk refers to spinning sidebands.

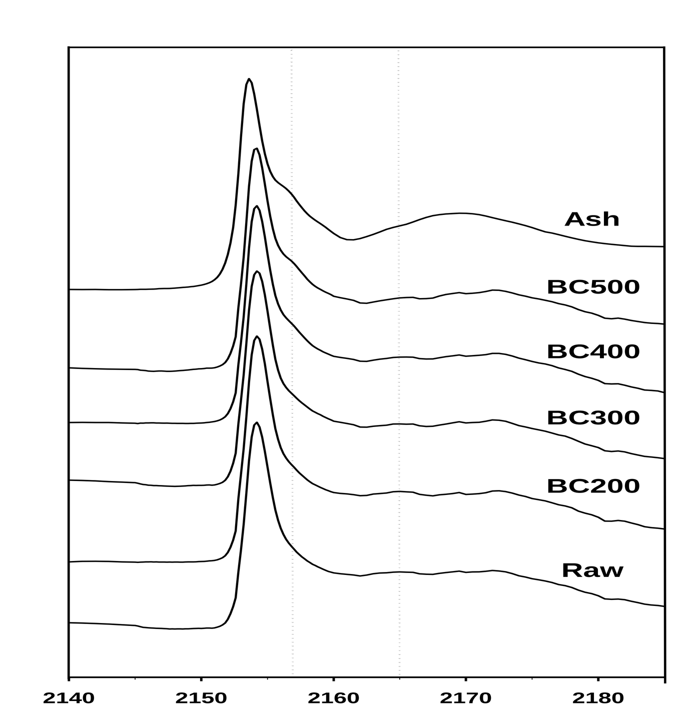

Figure 3. P XANES spectra for young *Sesbania* feedstock and biochars.

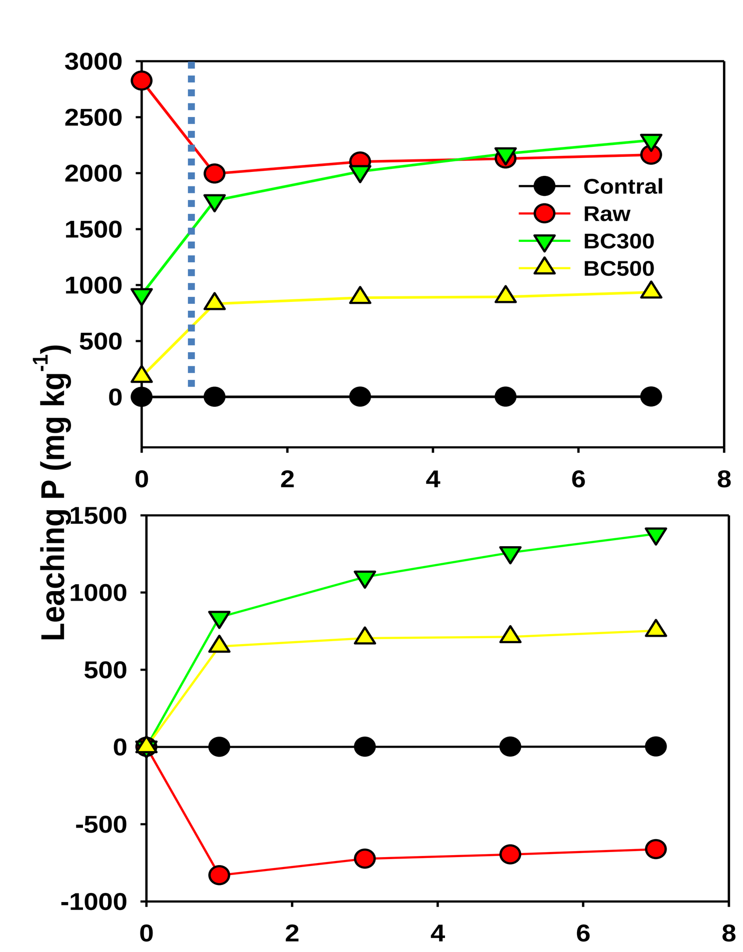

Figure 4. P leaching release and net P immobilization/mineralization for young *Sesbania* feedstock and biochars.

Summary

The results of Hedley extraction and solid-state ^{31}P NMR allowed us for investigating change of P structure during charring process. Compared with raw feedstocks, biochars have a much more complex chemical composition. Major changes during charring process included: (1) decrease in water extractable P, (2) developments of pyrophosphates and Ca-P compounds, and (3) formation of aromatic phosphates.

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