Supplementary Information

Sequential ammonia and carbon dioxide adsorption on pyrolyzed biomass to recover waste stream nutrients

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Supplementary Methods

Conversion of wood chips and human solid waste into biochar

Human solid waste (HSW) was collected from five urine-diversion Fresh Life latrines in the informal settlement of Mukuru in Nairobi, Kenya, in which sawdust was not provided as a cover material. The latrine design allows for separation of urine and feces, which are collected in separate containers. Each latrine is visited by about 50 people daily. About 3 kg of (wet) raw HSW was randomly subsampled from waste barrels the day after removal from latrines in Mukuru. Raw HSW was sun-dried to a gravimetric water content below 30% (Kern PCB 2500, Kern & Sohn GmbH, Balinger, Germany).

Maple wood (*Acer rubrum* L.) chips were obtained from Robinson Lumber sawmill in Owego, New York. Both HSW and wood chip feedstocks were pyrolyzed under argon at 500 °C for 30 min in a modified muffle furnace (Fisher Isotemp Model 126, Thermo Fisher Scientific, Waltham, MA). The resulting materials were ground and sieved to a particle size range of 149-850 µm.

Adsorption experiment with NH$_3$ and CO$_2$

Samples of py-HSW and py-ox wood were exposed to pure NH$_3$ (99% NH$_3$; 10 atom% (AT%) $^{15}$N/$^{14}$N, Sigma Aldrich, St. Louis, Mo) and pure CO$_2$ (99% CO$_2$; 10 AT% $^{13}$C/$^{12}$C, Sigma Aldrich, St. Louis, MO) within a thermogravimetric analyzer (TGA; Q50 EGA furnace, TA instruments) at 30 °C in different sequences described in the main manuscript, and outlined in Table S1. Sample mass and temperature were recorded every 4.6 seconds. Using both elemental stoichiometry and the mass change with adsorption was important for accurately determining N and C uptake, as adsorption of the relatively heavy $^{16}$O from CO$_2$ alters the original weight of the material with respect to the sorbing atom of interest, C or N.

The microbalance used to monitor sample mass was continually flushed with argon (Instrument grade, Airgas, Ithaca, NY). Purge lines for NH$_3$ and CO$_2$ were routed through an external mass flow
controller (MFC; MKS 247D 4-channel, MKS Instruments Andover, MA) directly into the TGA furnace. Flow rates were lowered to 1 L min\(^{-1}\) through the microbalance and 9 mL min\(^{-1}\) through the furnace to minimize static charging of samples. A 100-μL platinum pan was used for all experiments. Before exposure to CO\(_2\) or NH\(_3\), samples were degassed a second time within the TGA under argon at 105 °C for 30 min. The argon purge continued at 30 °C until achieving a stable weight. The weight of adsorption during gas exposure within the TGA (\(g_{\text{adsorption}}\)) was calculated as the difference between the average of the final 10 minutes during the final argon purge (\(g_{\text{final}}\)) and the average of the final 10 minutes of the initial argon purge prior to CO\(_2\) or NH\(_3\) exposure (\(g_{\text{initial}}\)) (Equation S1).

Equation S1

\[ g_{\text{adsorption}} = g_{\text{final}} - g_{\text{initial}} \]

For all samples, between each gas exposure event, the TGA furnace was purged with argon for one hour to prevent residual CO\(_2\) and NH\(_3\) from reacting and precipitating in flow lines.

### Preparation of materials for heat of CO\(_2\) adsorption

To assure clean surfaces for isotherms, samples were degassed twice at 150 °C for 12 hours under vacuum first on the degas port and subsequently on the sample port\(^1\). Sample tubes were immersed in ice water for isotherms at 0 °C while heating jackets were used for isotherms at 25 °C at 35 °C. The ASAP 2020 porosimeter was set in manual mode to control the temperature.

### Fitting Avrami model to adsorption data

Equilibrium CO\(_2\) adsorption at 30 °C (\(q_e\)) was equated to the maximum CO\(_2\) uptake during an adsorption isotherm at 25 °C. For NH\(_3\) sorption on py-ox wood, equilibrium adsorption (\(q_e\)) for the first exposure interval was inferred by fitting a non-linear pseudo second order equation (Equation S2) to sorption (\(q_t\)) using measured NH\(_3\) sorption data (\(q_t\)) over a time scale (t) of 500 minutes; our actual
experiment lasted only one hour and we were unable to reach equilibrium NH$_3$ adsorption. We took the maximal values from the second and third NH$_3$ exposure intervals as the NH$_3$ equilibrium point for py-ox wood.

Equation S2

$$q_t = \frac{k_A q_e^2 t}{1 + k_A q_e t}$$

Model parameters $n_A$ and $k_A$, along with the percent root mean squared error (RMSE (%), Equation S3) of the model fit to the measured percent increase in sample weight with adsorption are presented in Table S2. The RMSE was calculated for each modeled value ($\hat{y}$) and measured value ($y$) of NH$_3$ adsorption, using Equation S3.

Equation S3

$$\text{RMSE} (%) = \sqrt{\frac{\sum_{i=1}^{n} (\hat{y}_i - y_i)^2}{n - 1}} \times 100$$

**FTIR spectral processing**

An atmospheric compensation algorithm was applied to spectra to remove water vapor interference and instrumental drift. Spectra were baseline corrected using the rubber-band method followed by a min-max normalization according to Equation S4, where $x_i$ are unnormalized spectral counts, min($x$) are minimum counts values per spectra, max($x$) are maximum counts per spectra, and $z_i$ are normalized counts.

Equation S4

$$z_i = \frac{x_i - \text{min (x)}}{\text{max (x)} - \text{min (x)}}$$
Processing of NanoSIMS data

Secondary ions $^{12}\text{C}^{12}\text{C}^-$, $^{12}\text{C}^{13}\text{C}^-$, $^{12}\text{C}^{14}\text{N}^-$, and $^{12}\text{C}^{15}\text{N}^-$ were measured, and isotope ratios are reported in standard delta ($\delta$) notation in units of per mille (‰):

Equation S5

$$\delta = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000\%,$$

where $R_{\text{sample}}$ is the measured $^{13}\text{C}^{12}\text{C}^-/^{12}\text{C}^{12}\text{C}^-$ or $^{12}\text{C}^{15}\text{N}^-/^{12}\text{C}^{14}\text{N}^-$ ratio of a sample and $R_{\text{standard}}$ values are ion ratios measured in a yeast standard that has been calibrated for $\delta^{13}\text{C}$ using bulk isotope ratio analysis relative to VPDB\(^2\). Images of 30 µm x 30 µm containing 256 pixels x 256 pixels provided lateral resolution approximately the size of the primary ion beam diameter, ~115 nm. Images were acquired over multiple scan planes, varying in number between 6-12. Hue Saturation Intensity (HSI) images were generated from ion ratios across each pixel and color-scaled across the minimum and maximum delta values measured for all samples.

To observe changes in isotopic enrichment with depth, samples were sputtered in a single location with a Cs\(^+\) beam of more than double the current used for image rastering, ~3.6 pA. The sputtering rates of our materials were between maximum and minimum values based on the sputtering rate range reported for biological samples, 1-2.5 (nm mm pA\(^{-1}\) s\(^{-1}\))\(^2,3,4\). The beam area was determined by measuring the sputtering hole in samples using Image J. The average over four beam area measurements was used in this work, 0.3685 µm\(^2\).

Images were processed using OpenMIMS, an Image J software plugin\(^5\). Spatial alignment of images was first adjusted using the ‘Autotrack’ function. A deadtime correction was then applied, and data across multiple scan planes were summed into a single image. We generated average isotope ratios for each image by averaging over twenty circular regions of interest (ROIs) comprised of 12 pixels each. ROIs were chosen on flat, prominent regions within each image (Figure S5 to S9), the ion counts of which best represented surface chemistry. Ions $^{12}\text{C}^{12}\text{C}^-$, $^{12}\text{C}^{14}\text{N}^-$, $^{12}\text{C}^{15}\text{N}^-$, $^{16}\text{O}^-$, and ratios $^{12}\text{C}^{15}\text{N}^-/^{12}\text{C}^{14}\text{N}^-$...
and $^{16}\text{O}^{12}\text{C}^{12}\text{C}^{-}$ were evaluated for py-ox wood and py-ox wood NH$_3$. For py-HSW and py-HSW CO$_2$+NH$_3$ we used ions $^{12}\text{C}^{12}\text{C}^{-}$, $^{12}\text{C}^{13}\text{C}^{-}$, $^{12}\text{C}^{14}\text{N}^{-}$, $^{12}\text{C}^{15}\text{N}^{-}$, $^{31}\text{P}^{-}$, and ratios $^{12}\text{C}^{15}\text{N}^{-}$/$^{12}\text{C}^{14}\text{N}^{-}$ and $^{12}\text{C}^{13}\text{C}^{-}/^{12}\text{C}^{12}\text{C}^{-}$.

**NEXAFS spectral processing**

Water-suspended samples were deposited onto gold-coated silicon wafers that were mounted onto sample holders with carbon tape. Following exposure with $10^{11}$ photons s$^{-1}$, N Kα fluorescence emitted between 350 and 450 eV was acquired in the slew scanning mode of a spherical grating monochromator (SGM) at the Canadian Light Source (CLS) in Saskatoon, Canada. Samples were scanned in 50 different locations for 60 seconds each, which helped minimize the signal to noise ratio and safeguard against beam damage. Partial fluorescence data were collected in four different silicon drift detectors. For each sample, for each detector, partial fluorescence counts from 50 scans were summed and normalized by the beamline incidence flux on a gold mesh.

The energy scale of sample spectra was calibrated from N$_2$ adsorption spectrum for ammonium sulfate (400.807 eV)$^{6,7}$ by right-shifting by 0.15 eV. The pre- and post-edge of calibrated spectra were then background corrected, merged over all four detectors, and normalized to an edge step of one unit (Athena 0.8.056, Bruce Ravel; Ifeffit 1.2.11, Matt Newille, University of Chicago, Chicago). Normalized spectra were deconvoluted into constituent N-species through iterative fitting to curves associated with known N-containing compounds$^{6-9}$ with Fityk software (Fityk 0.9.8)$^{10}$. Although absorbance was observed in both $\pi^*$ and $\sigma^*$ orbitals in N-containing standard compounds, only the $\pi \rightarrow \pi^*$ transition is discussed because of the high degree of peak overlap in $\sigma^*$ regions. Peak assignments for N-bonds from standard compounds$^{6}$ are presented after averaging, normalization, and deconvolution in Table S4.
The fitting of Gaussian curves associated with model N-compounds was carried out with the non-linear least-squares Levenberg-Marquardt algorithm. An arctangent function bounded curve height and the cumulative area of curves in the $\pi \rightarrow \pi^*$ transition region. Arctangent parameters were optimized for the edge-step energy and the height between pre- and post-edge regions across all samples ($a_1=0.33$, $a_2=404.5$, $a_3=1.5$, $a_4=0.5$); the same arctan function was used for each spectrum.

For each sample spectrum, our model first optimized the peak height of fitted Gaussian curves corresponding to N-bonds in standard compounds (Table S4), while keeping peak center and half-width at half-maximum (HWHM) fixed. After each model run, curves with peak areas below 0.1 were removed from the model, and the model was re-fit. This process was reiterated until the area of all remaining curves was greater than 0.1. A new model was then executed on curves with areas greater than 0.1 in which the HWHM and peak height were floated according to a sin function (Equation S6 for $\pi \rightarrow \pi^*$ transition regions).

Equation S6

\[ HWHM = 0.4 + 0.2 \times \sin (\sim 0) \]

The same elimination procedure was applied until remaining curves had areas greater than 0.1. The relative area for each N species in standard compounds was calculated for $\pi \rightarrow \pi^*$ transition regions and is listed in Table S10. The absolute area and full-width at half-maximum (FWHM) values of experimental samples are listed in Table S11.

**XPS instrument settings and data analyses**

The XPS instrument used a focused monochromatic Al Kα X-ray (1486.7 eV) source for excitation and a spherical section analyzer and has a 32-element multichannel detection system. The X-ray beam was incident normal to the sample and the photoelectron detector was at 45 ° off-normal.
High energy resolution (narrow scan) spectra were collected using a pass-energy of 69.0 eV with a step size of 0.125 eV. For the Ag 3d$_{5/2}$ line, these conditions produced a full-width-half-maximum (FWHM) of 0.92 eV ± 0.05 eV. The binding energy (BE) scale is calibrated using the Cu 2p$_{3/2}$ feature at 932.62 ± 0.05 eV and Au 4f$_{7/2}$ at 83.96 ± 0.05 eV. To minimize charging, low energy electrons at ∼1 eV, 20 μA and low energy Ar$^+$ ions were sputtered over the samples.

Narrow scan spectra for the C1s, N1s, and O1s core-level regions were deconvoluted with Gaussian and Lorentzian functions after Shirley background subtraction (CasaXPS, version 2.3.19PR1.0). Narrow scan spectra was also used for quantifying C, N, and O surface atomic concentrations of py-ox wood samples while wide scan spectra was used for py-HSW. Potassium (K) surface concentration in py-HSW was quantified using wide-scan data. Atomic concentrations were corrected with relative sensitivity factors (RSFs) for each element derived under extant XPS operating conditions pertaining to the instrument transmission function and source angle corrections.

Spectra and associated functional group chemistry of five standard compounds, ammonium carbonate ((NH$_4$)$_2$CO$_3$)$^{2+}$), ammonium bicarbonate (NH$_4$$^+$HCO$_3^-$), urea, proline, and valine helped inform BE ranges for C, N and O bonds during deconvolution and peak-fitting of experimental samples (Figure S2, Tables S5 and S6), along with online and published literature$^{11-15}$. For deconvolution, the FWHM of curves within each spectrum were constrained to be equal. Spectra for standards and experimental samples were calibrated through charge-referencing of the C1s carbon (C-C, C=C) peak at 294.6 eV.
Table S1. Experimental treatment structure.

| Treatment name      | Pyrolysis feedstock | Oxidation | Gas              | Exposure time  |
|---------------------|---------------------|-----------|------------------|----------------|
| py-ox wood          | wood                | yes       | none             | none           |
| py-ox wood NH\(_3\) | wood                | yes       | \(^{15}\)NH\(_3\) | 1 hour         |
| py-ox wood NH\(_3\)+CO\(_2\) | wood        | yes       | \(^{15}\)NH\(_3\)→\(^{13}\)CO\(_2\)→\(^{14}\)NH\(_3\)→\(^{12}\)CO\(_2\)→\(^{15}\)NH\(_3\)→\(^{13}\)CO\(_2\) | 1 hour (each) |
| py-HSW              | HSW                 | none      | none             | none           |
| py-HSW CO\(_2\)+NH\(_3\) | HSW          | none      | \(^{13}\)CO\(_2\)→\(^{15}\)NH\(_3\) | 1 hour (each) |
Figure S1. Adsorption isotherms of CO\textsubscript{2} on py-HSW and py- ox wood before and after exposure to NH\textsubscript{3} at three temperatures 0 °C, 25 °C, 35 °C. Samples were exposed to unlabeled NH\textsubscript{3} for one hour within a TGA at 30 °C. Prior to isotherms, samples were degassed twice at 150 °C for 12 hours under vacuum first on the degas port and subsequently on the sample port.
Table S2. Avrami model parameters describing CO$_2$ and NH$_3$ adsorption kinetics (n = 3) and the root mean squared error (RMSE) of the model fit to measurements of the percent weight change with adsorption.

| Count | Material                  | Gas     | Exposure interval | $k_A$         | $n_A$  | RMSE (%) |
|-------|---------------------------|---------|-------------------|---------------|--------|----------|
| 1     | py-ox wood NH$_3$+CO$_2$  | CO$_2$  | 1                 | 0.03 ± 0.01   | 0.70 ± 0.10 | 8.77     |
| 2     | py-ox wood NH$_3$+CO$_2$  | CO$_2$  | 2                 | 0.03 ± 0.01   | 0.77 ± 0.05 | 12.37    |
| 3     | py-ox wood NH$_3$+CO$_2$  | CO$_2$  | 3                 | 0.03 ± 0.01   | 0.85 ± 0.05 | 12.91    |
| 4     | py-ox wood NH$_3$+CO$_2$  | NH$_3$  | 1                 | 0.30 ± 0.01   | 0.54 ± 0.01 | 50.84    |
| 5     | py-ox wood NH$_3$+CO$_2$  | NH$_3$  | 2                 | 0.41 ± 0.10   | 1.84 ± 1.04 | 68.74    |
| 6     | py-ox wood NH$_3$+CO$_2$  | NH$_3$  | 3                 | 0.40 ± 0.19   | 0.58 ± 0.32 | 28.71    |
| 7     | py-HSW CO$_2$+NH$_3$      | CO$_2$  | 1                 | 0.04 ± 0.03   | 0.54 ± 0.12 | 11.42    |
| 8     | py-HSW CO$_2$+NH$_3$      | NH$_3$  | 1                 | 0.03 ± 0.00   | 0.79 ± 0.02 | 33.70    |
Table S3. The FTIR wavenumber range assignments depicted in Figure 3A in the main manuscript and associated functional groups\(^6\).

| Peak number | Highlighted frequency \((\text{cm}^{-1})\) | Frequency range \((\text{cm}^{-1})\) | Functional group |
|-------------|------------------------------------------|---------------------------------|-----------------|
| 1           | 2154                                    | 2200-2100                       | Alkynes C≡C     |
|             |                                         | 2600-2200                       | Nitriles C≡N    |
|             |                                         | 2240-2220                       | Aromatic cyanide|
|             |                                         | 2150-1990                       | Isothiocyanate -NCS|
| 2           | 1709                                    | 1725-1700                       | Carboxylic acid |
|             |                                         | 1725-1705                       | Ketone          |
| 3           | 1570                                    | 1630-1575                       | Open chain azo -N=N-|
|             |                                         | 1615-1580                       | C=C-C aromatic ring stretch |
|             |                                         | 1650-1550                       | Primary or secondary amine NH bend |
| 4           | 1435                                    | 1435-1460                       | Ammonium ion NH\(_4^+\) |
| 5           | 1362                                    | 1350-1280                       | Aromatic secondary amine, CN stretch |
|             |                                         | 1360-1310                       | Aromatic tertiary amine CN stretch |
| 6           | 1215                                    | 1200                            | Phenol C-OH stretch |
| 7           | 1034                                    | 1055–1020                       | Silicone Si-O-Si |
|             |                                         | 1050-990                        | Aliphatic phosphates |
|             |                                         | **1090-1020**                   | Primary amine C-N stretch |
Table S4. Nitrogen forms and responding Gaussian peak center assignments used to deconvolute N K-edge NEXAFS spectra.

| N Form                                         | Peak Energy (eV) 1s→π* | Peak Energy (eV) 1s→σ* | Reference |
|------------------------------------------------|------------------------|------------------------|-----------|
| NH$_3^+$ (putative)                            | 397.88                 |                        | 17-19     |
| C=N pyridine, pyrimidine (putative)            | 398.1                  |                        | 17-19     |
| C=N pyridine, pyrimidine                       | 398.76                 | 408.01, 412.28         | 6-9       |
| C=N pyrimidine with keto group                 | 399.2                  | 405.00, 408.40         | 6-9       |
| C=N pyrimidine bonded to furan with keto groups| 399.44                 | 407.6                  | 6-9       |
| C=N imidazole and C=N nitrile                  | 400.05                 | 406.43, 410.87, 413.75 | 6-9       |
| Quaternary C-N in pyridine                     | 400.46                 | 408.86                 | 6-9       |
| C=N pyridine with keto or phenol group          | 400.64                 | 406.92                 | 6-9       |
| cyclic amide                                    |                        | 401.15, 406.1          | 6-9       |
| C=N imidazole                                  | 401.43                 |                        | 6-9       |
| C=N imidazole                                  | 401.85                 |                        | 6-9       |
| C=N pyrrole                                    | 402.4                  | 407                    | 6-9       |
| C-NH$_2$ amine-substituted pyridine            |                        | 403                    | 19,6,8,9  |
| C-NO$_2$ nitro bonded to pyridine or pyrimidine| 403.65                 | 412.79, 413.65         | 6-9       |
| C=N in pyridine or pyrimidine                  | 404.11                 |                        | 6-9       |
| N-H                                            |                        | 405                    | 6-9       |
| C-NH$_2$: aliphatic amine                      |                        | 406.58                 | 6-9       |
Figure S2. Normalized XPS spectra for C1s, N1s, and O1s core-level electron excitations of five standard compounds. Spectral deconvolution is also displayed in the fitting of multiple Lorentzian-Gaussian curves to each spectrum. Assigned peak positions of C, N, and O bonds and the relative peak areas associated with those bonds are outlined in Tables S5 and S6.
Table S5. The proportion of C, N, and O bonds in five standard compounds, based on the binding energies (BE) and full-width at half-maximum values (FWHM) of deconvoluted curves and relative areas, as measured with XPS.

| Bond level | Bond form | BE range (eV) | Ammonium carbonate | Urea | Ammonium bicarbonate | Proline | Valine |
|------------|-----------|--------------|---------------------|------|----------------------|---------|--------|
|            |           | BE (eV)      | FWHM area (%)       | BE (eV) | FWHM area (%)       | BE (eV) | FWHM area (%) | BE (eV) | FWHM area (%) |
| C1s        | C-C, C≡C  | 284.0-285.0  | 284.5 1.28 57.37    | 248.4 1.89 | 284.5 1.31 57.34 284.1 1.69 | 37.21 284.3 1.65 | 45.77 |
| C1s        | C-N       | 285.0-286.0  | 285.3 1.28 21.99    | 285.0 1.89 4.09 | 285.1 1.31 20.29 285.0 1.69 | 36.19 285.1 1.65 | 25.92 |
| C1s        | C-O       | 286.0-287.0  | 286.3 1.28 13.01    | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 |
| C1s        | C-OH      | 286.0-287.0  | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 |
| C1s        | R-C≡O     | 287.0-287.5  | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 |
| C1s        | R-C=O     | 287.5-288.0  | 288.6 1.28 7.62    | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 |
| C1s        | (C=O)O    | 288.3-288.8  | -- -- 0.00 | -- -- 0.00 | 288.7 1.31 8.74 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 |
| C1s        | N-C=O     | 288.8-290.0  | -- -- 0.00 | -- -- 0.00 | 289.0 1.89 89.37 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 |

| N1s        | Pyridinic N | 398.0-398.9 | 398.3 1.09 7.68 | 398.7 1.31 21.98 | 398.0 1.41 2.27 | -- -- 0.00 | -- -- 0.00 |
| N1s        | C-NH₂      | 399.0-399.5 | 399.1 1.09 59.02 | 399.5 1.31 45.4 | 399.2 1.41 45.32 | 399.6 1.84 | 47.9 | 399.5 1.99 | 6.78 |
| N1s        | C-O-NH₂⁺   | 399.5-400.0 | 399.9 1.09 20.57 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 |
| N1s        | N-C≡N      | 400.0-400.5 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | 400.1 1.84 | 52.1 | -- -- 0.00 |
| N1s        | N-(C=O)    | 400.0-400.9 | -- -- 0.00 | 400.6 1.31 26.6 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 |
| N1s        | N-(C=O)    | 400.5-400.9 | 400.8 1.09 7.39 | -- -- 0.00 | 400.9 1.41 34.02 | -- -- 0.00 | 400.7 1.99 | 93.22 |
| N1s        | NH₂⁺       | 401.0-403.0 | 401.7 1.09 5.34 | 401.2 1.31 6.02 | 401.8 1.41 18.39 | -- -- 0.00 | -- -- 0.00 |

| O1s        | 529.5-530.0 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | 529.8 1.74 | 73.69 | -- -- 0.00 |
| O1s        | 530.5-530.5 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | 530.4 1.69 | 71.51 |
| O1s        | 530.5-531   | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | 530.7 1.74 | 26.31 | -- -- 0.00 |
| O1s        | 531.0-531.3 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 | 531.2 1.69 | 28.49 |
| O1s        | C=O        | 531.3-532.0 | 531.7 1.61 52.39 | 531.5 2.09 100 531.6 1.63 60.25 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 |
| O1s        | C-O        | 532.0-533.3 | 533.1 1.61 47.61 | -- -- 0.0 | 533.0 1.63 39.75 | -- -- 0.00 | -- -- 0.00 | -- -- 0.00 |
Table S6. The binding energy (BE) peak range assignments for the XPS C1s, N1s, and O1s core levels used for our deconvolution model\textsuperscript{11,12,20}.

| Core level | Bond form | BE (eV) |
|------------|-----------|---------|
| C1s        | C-C, C=C (low) | 283.0-284.0 |
| C1s        | C-C, C=C      | 284.0-285.0 |
| C1s        | C-N          | 285.0-286.0 |
| C1s        | C-O          | 286.0-287.0 |
| C1s        | C-OH         | 286.0-287.0 |
| C1s        | R-C=O (R aromatic) | 287.0-287.5 |
| C1s        | R-C=O        | 287.5-288.0 |
| C1s        | (C=O)-O      | 288.3-288.5 |
| C1s        | (C=O)-OH     | 288.5-288.8 |
| C1s        | N-C=O        | 288.8-290.5 |
| N1s        | N pyridine   | 398.0-398.9 |
| N1s        | C-NH\textsubscript{2} | 399.0-399.5 |
| N1s        | C-O--NH\textsubscript{4} \textsuperscript{+} | 399.5-400.0 |
| N1s        | N=C-(C=O)-   | 400.0-400.5 |
| N1s        | N-(C=O)-     | 400.5-400.9 |
| N1s        | NH\textsubscript{3} \textsuperscript{+} | 401.0-403.0 |
| O1s        | R-C=O (R aromatic) | 529.5-530.0 |
| O1s        | R-C=O        | 530.5-530.5 |
| O1s        | R-C-OH (R aromatic) | 530.5-531.0 |
| O1s        | R-C-OH       | 531.0-531.3 |
| O1s        | C=O          | 531.3-532.0 |
| O1s        | C-O          | 532.0-533.3 |
| O1s        | H\textsubscript{2}O, OH | 533.5-536.0 |
Table S7. R software packages used for data organization, analysis, and presentation.

| Count | R package     | Reference |
|-------|---------------|-----------|
| 1     | broom         | 21        |
| 2     | cowplot       | 22        |
| 3     | data.table    | 23        |
| 4     | devtools      | 24        |
| 5     | dplyr         | 25        |
| 6     | GGally        | 26        |
| 7     | ggplot2       | 27        |
| 8     | ggpmisc       | 28        |
| 9     | grid          | 29        |
| 10    | lattice       | 30        |
| 11    | lsmeans       | 31        |
| 12    | multcomp      | 32        |
| 13    | plotly        | 33        |
| 14    | plyr          | 34        |
| 15    | reshape2      | 35        |
| 16    | stringr       | 36        |
| 17    | stats         | 30        |
| 18    | tidyverse     | 37        |
| 19    | xlsx          | 38        |
| 20    | xlsxjars      | 39        |
Figure S3. (A) Three replicate thermograms depicting the weight change with exposure to CO₂ (orange) followed by NH₃ (blue), separated an argon purge (gray). (B) Three replicates of gravimetrically-measured CO₂ and NH₃ adsorption onto py-HSW (blue) overlaid with modeled adsorption curves using Avrami’s fractional order model (black line). (C) Three replicates of gravimetrically-measured CO₂ and NH₃ adsorption at three sequential exposure intervals (1,2,3) onto py-ox wood (colors) overlaid with modeled adsorption curves using Avrami’s fractional order model. CO₂ adsorption does not differ between each consecutive exposure, even though NH₃ adsorption decreases from the first to the consecutive exposure and remains significant.
Table S8. Nanoscale secondary ion mass spectrometry ion ratios detected on sample surfaces averaged over 20 regions of interest per image, for replicate images shown in Figures S5-S9.

| Treatment          | Replicate images | $\delta^{12}{C^{13}}{C^{12}}{C^{12}}$ | $\delta^{12}{C^{15}}{N^{12}}{C^{14}}{N^{14}}$ |
|--------------------|------------------|--------------------------------------|-----------------------------------------------|
| py-ox wood         | n = 2            | 34.11 ± 29.77                        | -6.49 ± 86.56                                 |
| py-ox wood NH$_3$  | n = 3            | 25.31 ± 57.44                        | 15145.84 ± 619.20                             |
| py-ox wood NH$_3$ + CO$_2$ | n = 3          | 6.03 ± 21.77                         | 19094.43 ± 1349.11                            |
| py-HSW             | n = 4            | 51.52 ± 15.92                        | -30.33 ± 62.33                                |
| py-HSW CO$_2$ + NH$_3$ | n = 4            | 135.67 ± 75.27                      | 2635.02 ± 159.34                             |
Figure S4. Isotopic enrichment at the minimum and maximum depths for (A-C) three replicates of py-ox wood NH$_3$+CO$_2$, py-ox wood NH$_3$, and py-ox wood control (D-F) three replicates of py-HSW CO$_2$+NH$_3$ and py-HSW control, calculated using a sputtering rate range for biological materials$^{2,3,4}$.
Figure S5. Two replicate NanoSIMS images of $^{12}$C$^{12}$C$^-$ ions (A,B) $^{13}$C$^{12}$C$^-$ (C,D) and $^{12}$C$^{15}$N$^-$/12C$^{14}$N$^-$ (E,F) ion ratios in py-ox wood. Images A and B display 20 ROIs used to calculate sample isotope ratios presented in Table S9.
Figure S6. Three replicate NanoSIMS images of $^{12}\text{C}^{12}\text{C}^-$ (A-C), $^{13}\text{C}^{12}\text{C}^-$ (D-F) and $^{12}\text{C}^{15}\text{N}^-/^{12}\text{C}^{14}\text{N}^-$ (G-I) ion ratios in py-ox NH$_3$. Images A, B, and C display 20 ROIs used to calculate sample isotope ratios presented in Table S9.
Figure S7. Three replicate NanoSIMS images of $^{12}$C$^{12}$C$^-$ ions (A-C), $^{13}$C$^{12}$C$^-$ (D-F) and $^{12}$C$^{15}$N$^-$/$^{12}$C$^{14}$N$^-$ (G-I) ion ratios in py-ox wood NH$_3$+CO$_2$. Images A, B, and C display 20 ROIs used to calculate sample isotope ratios presented in Table S9.
Figure S8. Four replicate NanoSIMS images of $^{12}\text{C}^{12}\text{C}^-$ ions (A-D) $^{13}\text{C}^{12}\text{C}^-$ (E-H) and $^{12}\text{C}^{15}\text{N}^-/^{12}\text{C}^{14}\text{N}^-$ (I-L) ion ratios in py-HSW controls, unexposed to NH$_3$ or CO$_2$. Images A, B, C, and D display 20 ROIs used to calculate sample isotope ratios presented in Table S9.
Table S9. Four replicate NanoSIMS images of $^{12}\text{C}^{12}\text{C}^-$ ions (A-D), $^{13}\text{C}^{12}\text{C}^-$ (E-H) and $^{12}\text{C}^{15}\text{N}^-/^{12}\text{C}^{14}\text{N}^-$ (I-L) ion ratios in py-HSW CO$_2$+NH$_3$. Images A, B, C and D display 20 ROIs used to calculate sample isotope ratios presented in Table S9.

| Image 1 | Image 2 | Image 3 | Image 4 |
|---------|---------|---------|---------|
| ![Image 1](image1.png) | ![Image 2](image2.png) | ![Image 3](image3.png) | ![Image 4](image4.png) |
| 30x30 microns (256x256), 32-bit, 256k | 30x30 microns (256x256), 32-bit, 256k | 30x30 microns (256x256), 32-bit, 256k | 30x30 microns (256x256), 32-bit, 256k |

Figure S9. Four replicate NanoSIMS images of $^{12}\text{C}^{12}\text{C}^-$ ions (A-D), $^{13}\text{C}^{12}\text{C}^-$ (E-H) and $^{12}\text{C}^{15}\text{N}^-/^{12}\text{C}^{14}\text{N}^-$ (I-L) ion ratios in py-HSW CO$_2$+NH$_3$. Images A, B, C and D display 20 ROIs used to calculate sample isotope ratios presented in Table S9.
Table S9. Chemical and physical properties of py-ox wood and py-HSW.

|                     | py-ox wood | py-HSW  |
|---------------------|------------|---------|
| pH in water         | 5.2        | 10.3    |
| SSA (m$^2$ g$^{-1}$)| 275.7      | 74.0    |
| Total N (%w w$^{-1}$)| 0.91      | 4.8     |
| Fixed C (%w w$^{-1}$)| 63.9      | 46.2    |
| Ash (%w w$^{-1}$)   | 0.7        | 39.0    |
Figure S10. Wide-scan XPS spectra for unexposed py-HSW depicting a prominent peak for nitrogen (N1s) and no peak features for silicon (Si 2s, Si 2p, Si 2p1/2, Si 2p3/2).
Table S10. Percent of nitrogen forms in experimental samples associated with Gaussian curve centers and relative areas in the $\pi \rightarrow \pi^*$ transition region, measured with N K-edge NEXAFS, and derived from a deconvolution procedure relying on standard compounds$^6$ and shown in Table S4.

| N form                                    | Center         | Peak number | py-HSW area % | py-HSW CO$_2$+NH$_3$ area (%) | py-ox wood NH$_3$ area (%) | py-ox wood NH$_3$+CO$_2$ area (%) |
|-------------------------------------------|----------------|-------------|---------------|-------------------------------|----------------------------|----------------------------------|
| NH$_3^+$ (putative)                       | 397.27-397.28  | 1           | 0.00          | 0.00                          | 0.00                       | 5.87                             |
| C=N pyridine, pyrimidine (putative)       | 398.08-398.36  | 2           | 17.75         | 15.87                         | 21.69                      | 6.36                             |
| C=N pyridine, pyrimidine                  | 398.76         | 3           | 10.00         | 13.94                         | 0.00                       | 7.90                             |
| C=N pyrimidine with keto group            | 399.2          | 4           | 0.00          | 0.00                          | 18.65                      | 0.00                             |
| C=N pyrimidine                           | 399.54-399.81  | 5           | 8.00          | 6.10                          | 0.00                       | 12.51                            |
| C=N imidazole, nitrile C=N                | 400.05         | 6           | 6.83          | 4.66                          | 0.00                       | 0.00                             |
| C=N pyridine, pyrimidine, keto-or alcohol-substituted | 400.64         | 7           | 8.06          | 11.76                         | 22.27                      | 13.66                            |
| C=N imidazole                             | 401.43         | 8           | 19.20         | 15.51                         | 20.84                      | 15.57                            |
| C=N pyrrole                               | 402.4          | 9           | 11.82         | 15.77                         | 0.00                       | 14.98                            |
| C-NH$_3$ primary amine bonded to pyridine  | 403.24-403.49  | 10          | 10.71         | 8.66                          | 16.55                      | 12.41                            |
| C=N pyridine, pyrimidine                  | 404.11         | 11          | 7.64          | 7.75                          | 0.00                       | 10.74                            |

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Table S11. Nitrogen chemistry measured with N K-edge NEXAFS in py-ox wood and py-HSW before and after exposure to NH$_3$ and NH$_3$+CO$_2$ based on curve center energies and full-width-half-max (FWHM) values, relying on standard compounds$^6$ and shown in Table S4.

| Center (eV) | Peak number | py-HSW | py-HSW CO$_2$+NH$_3$ | py-ox wood | py-ox wood NH$_3$ | py-ox wood NH$_3$+CO$_2$ |
|------------|-------------|--------|----------------------|------------|------------------|------------------------|
| NH$_3^+$ (putative) | 397.27-397.28 | 0.00 | 0.00 | 0.00 | 0.00 | 1.20 | 0.17 | 0.79 | 0.13 |
| C=N pyridine, pyrimidine (putative) | 398.08-398.36 | 1.20 | 0.62 | 1.20 | 0.61 | 0.57 | 0.39 | 0.95 | 0.19 | 0.82 | 0.21 |
| C=N pyridine, pyrimidine | 398.76 | 0.95 | 0.35 | 1.10 | 0.54 | 0.00 | 0.00 | 0.90 | 0.23 | 0.78 | 0.17 |
| C=N pyrimidine with keto group | 399.20 | 0.00 | 0.00 | 0.00 | 0.00 | 0.62 | 0.34 | 0.00 | 0.00 | 0.81 | 0.14 |
| C=N pyrimidine | 399.54-399.81 | 0.86 | 0.28 | 0.62 | 0.24 | 0.00 | 0.00 | 0.99 | 0.37 | 0.78 | 0.27 |
| C=N imidazole, nitrile C≡N | 400.05 | 0.96 | 0.24 | 0.65 | 0.18 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| C=N pyridine, pyrimidine, keto-or alcohol-substituted | 400.64 | 0.91 | 0.28 | 1.03 | 0.45 | 0.96 | 0.40 | 1.11 | 0.40 | 1.03 | 0.45 |
| C=N imidazole | 401.43 | 1.13 | 0.67 | 1.11 | 0.60 | 1.20 | 0.38 | 1.20 | 0.46 | 1.06 | 0.44 |
| C=N pyrole | 402.40 | 0.98 | 0.41 | 1.20 | 0.61 | 0.00 | 0.00 | 1.10 | 0.44 | 1.20 | 0.64 |
| C-NH$_2$ primary amine bonded to pyridine | 403.24-403.49 | 0.98 | 0.37 | 1.04 | 0.33 | 0.63 | 0.30 | 0.96 | 0.37 | 0.94 | 0.48 |
| C=N pyridine, pyrimidine | 404.11 | 0.94 | 0.27 | 1.12 | 0.30 | 0.00 | 0.00 | 1.08 | 0.32 | 0.90 | 0.35 |
| N-H amine | 405.00 | 1.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 4.42 | 1.13 | 2.66 | 0.72 |
| C-N amide (secondary peak) | 406.43 | -- | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 3.07 | 0.54 |
| C=N pyrole (secondary peak) | 406.92 | -- | 0.00 | 0.00 | 2.74 | 0.83 | 3.01 | 1.81 | 0.00 | 0.00 | 0.00 |
| C=N pyrole (secondary peak) | 407.00 | -- | 3.22 | 0.99 | 4.53 | 1.25 | 3.87 | 1.70 | 0.00 | 0.00 | 0.00 |
| C=N pyridine, pyrimidine (secondary peak) | 408.01 | -- | 3.94 | 0.35 | 2.34 | 0.25 | 4.96 | 2.14 | 3.73 | 0.73 | 3.53 | 0.93 |
| C=N pyrole (secondary peak) | 410.87 | -- | 3.31 | 0.56 | 3.35 | 0.91 | 3.56 | 1.20 | 2.53 | 0.30 | 2.88 | 0.59 |
| C=N pyrole (secondary peak) | 412.28 | -- | 0.00 | 0.00 | 0.00 | 0.00 | 3.81 | 1.33 | 2.49 | 0.19 | 2.00 | 0.15 |
| C=N pyrole (secondary peak) | 413.75 | -- | 3.49 | 0.39 | 3.77 | 0.74 | 4.93 | 1.51 | 2.59 | 0.26 | 2.29 | 0.20 |
Table S12. The relative proportion of bond forms containing C, N, and O associated with the BE range of curve centers as measured with XPS. Deconvolution relied on standard compounds as well as online and published literature\textsuperscript{11-15} shown in Tables S5 and S6.

\[
\begin{array}{|c|c|c|c|c|c|c|c|c|}
\hline
\text{Core level} & \text{Bond} & \text{BE range (eV)} & \text{Peak} & \text{py-HSW CO}_2=\text{NH}_3 & \text{py-HSW CO}_2=\text{NH}_3 & \text{py-ox wood CO}_2=\text{NH}_3 & \text{py-ox wood NH}_3 & \text{py-ox wood NH}_3 \\
\hline
\text{C1s} & \text{C-C, C=C (i)} & 283.0-284.0 & 7 & 0.00 & 0.00 & 0.00 & 0.00 & 30.02 \\
\text{C1s} & \text{C-C, C=C} & 284.0-285.0 & 6 & 48.31 & 53.29 & 56.48 & 40.39 & 38.17 \\
\text{C1s} & \text{C-N} & 285.0-286.0 & 5 & 31.15 & 29.77 & 21.49 & 34.01 & 0.00 \\
\text{C1s} & \text{C-OH} & 286.0-287.0 & 4 & 9.35 & 9.74 & 10.11 & 10.62 & 14.00 \\
\text{C1s} & \text{R-C=O (R aromatic)} & 287.0-287.5 & \_ & 0.00 & 0.00 & 0.00 & 0.00 & 8.79 \\
\text{C1s} & \text{R-C=O} & 287.5-288.0 & 3 & 2.81 & 4.28 & 5.29 & 6.85 & 0.00 \\
\text{C1s} & \text{(C=O)-OH} & 288.5-288.8 & 2 & 0.00 & 0.00 & 5.01 & 6.76 & 6.68 \\
\text{C1s} & \text{N-C=O} & 289.0-290.5 & 1 & 8.37 & 2.92 & 1.63 & 1.36 & 2.33 \\
\hline
\text{N1s} & \text{pyridinic N} & 398.0-398.9 & 15,14 & 26.4 & 44.14 & 27.32 & 23.33 & 0.00 \\
\text{N1s} & \text{C-NH}_2 & 399.0-399.5 & 13 & 28.02 & 0.00 & 0.00 & 4.23 & 0.00 \\
\text{N1s} & \text{C-O=NH}_2^+ & 399.5-400.0 & 12 & 28.96 & 0.00 & 55.89 & 60.32 & 0.00 \\
\text{N1s} & \text{N=C-(C=O)} & 400.0-400.5 & 11 & 0.00 & 48.27 & 0.00 & 0.00 & 0.00 \\
\text{N1s} & \text{N-C-(C=O)} & 400.5-400.9 & 10 & 14.87 & 0.00 & 0.00 & 0.00 & 100 \\
\text{N1s} & \text{NH}_4^+ & 401.9-403.0 & 9.8 & 1.75 & 7.59 & 16.79 & 12.12 & 0.00 \\
\hline
\text{O1s} & \text{R-C=OH} & 531.0-531.3 & 20 & 75.42 & 69.8 & 0.00 & 0.00 & 0.00 \\
\text{O1s} & \text{C=O} & 531.3-532.0 & 19 & 0.00 & 0.00 & 55.74 & 59.38 & 51.98 \\
\text{O1s} & \text{C-O} & 532.0-533.3 & 18 & 19.7 & 26.49 & 44.26 & 40.62 & 48.02 \\
\text{O1s} & \text{H}_2\text{O, OH} & 533.5-536.0 & 16,17 & 4.88 & 3.71 & 0.00 & 0.00 & 0.00 \\
\hline
\end{array}
\]
Table S13. The binding energies (BE) and full-width at half-maximum values (FWHM) of deconvoluted curves of py-ox wood and py-HSW samples before and after exposure to NH\(_3\) and CO\(_2\), measured with XPS. Deconvolution relied on standard compounds as well as online and published literature\(^{11-15}\) shown in Tables S5 and S6.

| Core level | Bond                        | BE range (eV) | Peak | py-HSW CO\(_2\)+NH\(_3\) | py-HSW | py-ox wood CO\(_2\)+NH\(_3\) | py-ox wood NH\(_3\) | py-ox wood |
|------------|-----------------------------|---------------|------|---------------------------|--------|-----------------------------|---------------------|------------|
|            |                             |               |      | BE (eV)                   | FWHM   | BE (eV)                      | FWHM                | BE (eV)    |
| Cls        | C-C, C=C                    | 283.0-284.0   | 7    | --                        | --     | --                          | --                  | 283.76     |
| Cls        | C-C, C=O                    | 284.0-285.0   | 6    | 284.31                    | 1.36   | 284.34                      | 1.46                | 284.19     |
| Cls        | C-N                         | 285.0-286.0   | 5    | 285.07                    | 1.36   | 285.39                      | 1.46                | 285.00     |
| Cls        | C-OH                        | 286.0-287.0   | 4    | 286.12                    | 1.36   | 286.55                      | 1.46                | 286.35     |
| Cls        | R-C=O (R aromatic)           | 287.0-287.5   | --   | --                        | --     | --                          | --                  | 287.46     |
| Cls        | R-C=O                       | 287.5-288.0   | 3    | 287.73                    | 1.36   | 287.93                      | 1.46                | 287.66     |
| Cls        | (C=O)-OH                    | 288.5-288.8   | 2    | --                        | --     | --                          | --                  | 288.80     |
| Cls        | N-C=O                       | 289.0-290.5   | 1    | 289.37                    | 1.36   | 289.47                      | 1.46                | 290.02     |
| Nls        | pyridinic N                  | 398.0-389.9   | 15,14| 398.00                    | 1.20   | 398.35                      | 1.85                | 398.63     |
| Nls        | C-NH\(_2\)                   | 399.0-399.5   | 13   | 399.94                    | 1.20   | --                          | --                  | 399.29     |
| Nls        | C-O--NH\(_2\)               | 399.5-400.0   | 12   | 399.9                      | 1.20   | --                          | --                  | 399.71     |
| Nls        | N=C=O (C=O)                 | 400.0-400.5   | 11   | --                        | --     | 400.08                      | 1.85                | --         |
| Nls        | N=C=O (C=O)                 | 400.5-400.9   | 10   | 400.67                    | 1.20   | --                          | --                  | 400.77     |
| Nls        | NH\(_4^+\)                  | 401.0-403.0   | 9,8  | 401.89                    | 1.20   | 401.88                      | 1.85                | 401.32     |
| Ols        | R-C-OH                      | 531.0-531.3   | 20   | 531.23                    | 1.87   | 531.15                      | 1.99                | --         |
| Ols        | C=O                         | 531.3-532.0   | 19   | --                        | --     | --                          | --                  | 531.58     |
| Ols        | C-O                         | 532.0-533.3   | 18   | 532.54                    | 1.87   | 532.61                      | 1.99                | 533.23     |
| Ols        | H\(_2\)O, OH                | 533.5-536.0   | 16,17| 535.70                    | 1.87   | 534.86                      | 1.99                | --         |
Table S14. Carbon (C), nitrogen (N), and oxygen (O) weight percent and the molar O to C ratio of milled samples by determined by IRMS with correction for sample mass change shown in Figure S3A (IRMS w/TGA) and IRMS with no mass correction (IRMS). The surface atomic percent of C, N, and O was also determined using XPS of whole particles. Total potassium (K) concentration was also determined for py-HSW.

| Treatment     | C (AT%) | C (%w w$^{-1}$) | N (AT%) | N (%w w$^{-1}$) | O (AT%) | O (%w w$^{-1}$) | O/C (mol mol$^{-1}$) | K (AT%) |
|---------------|---------|-----------------|---------|-----------------|---------|-----------------|----------------------|---------|
|               | XPS$^a$ | IRMS$^b$ w/TGA | IRMS    | XPS IRMS w/TGA  | IRMS    | IRMS XPS        | IRMS w/TGA IRMS XPS  |         |
| py-HSW CO$_2$+NH$_3$ | 33.25   | 46.96 ± 0.61    | 45.88 ± 0.73 | 3.75 | 5.33 ± 0.13 | 5.20 ± 0.15 | 40.65 | 20.25 ± 0.99 | 19.78 ± 0.85   | 0.43 | 0.43 | 8.15  |
| py-HSW        | 47.49   | 44.04 ± 0.66    | 44.04 ± 0.66 | 3.76 | 4.57 ± 0.04 | 4.57 ± 0.04 | 33.1  | 19.90 ± 0.48 | 19.90 ± 0.48   | 0.45 | 0.45 | 3.68  |
| py-ox wood NH$_3$+CO$_2$ | 81.66 ± 0.59 | 77.25 ± 5.85    | 67.25 ± 5.02 | 3.65 | 4.05 ± 0.13 | 4.05 ± 0.13 | 14.69 | 20.61 ± 1.76 | 19.39 ± 1.43   | 0.27 | 0.29 | n/a   |
| py-ox wood NH$_3$ | 78.55 ± 1.85 | 74.54 ± 0.27    | 71.48 ± 0.24 | 4.40 | 3.74 ± 0.17 | 3.59 ± 0.70 | 17.05 | 19.90 ± 0.58 | 19.90 ± 0.48   | 0.27 | 0.27 | n/a   |
| py-ox wood NH$_3$ | 79.85 ± 1.05 | 74.13 ± 1.73    | 74.13 ± 1.73 | 0.22 | 0.21 ± 0.08 | 0.21 ± 0.08 | 19.93 | 22.04 ± 0.66 | 22.04 ± 0.66   | 0.3  | 0.3  | n/a   |
| XPS RSF$^c$   | 21.12   | 33.71           | 49.75    |                 |         |                 | 1.55               |         |

$^a$ XPS quantification shows the average of n = 2 narrow scans for py-ox wood samples. Wide scan data was used for py-HSW.

$^b$ IRMS data shows the average of n = 2 experimental replicates.

$^c$ Atomic concentrations of C, N, O, and K were corrected using instrument-specific relative sensitivity factors (RSF).
Figure S11. Narrow scan XPS spectra in the C1s region showing peaks for the K2p region for potassium between 296-290 eV, highlighted with black arrows. The K2p 1 peak between 293-290 eV increases in area by 2.7-fold in py-HSW CO₂+NH₃ compared to py-HSW.
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