Supplementary Information (SI) for Environmental Science: Atmospheres.

Wavelength-resolved quantum yields for Phenolic Carbonyls in Acidic Solution: Molecular Structure Effects on Brown Carbon Photochemistry

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Supplemental Material

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Supplemental Figures

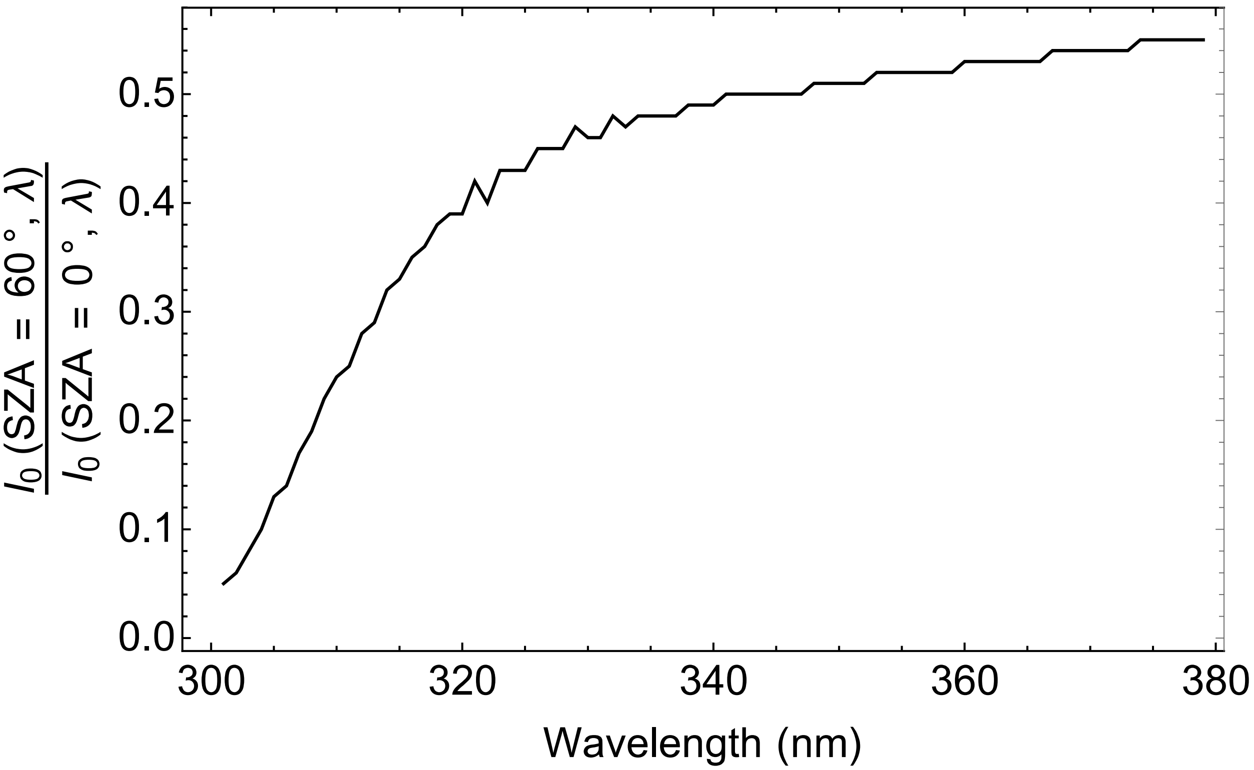
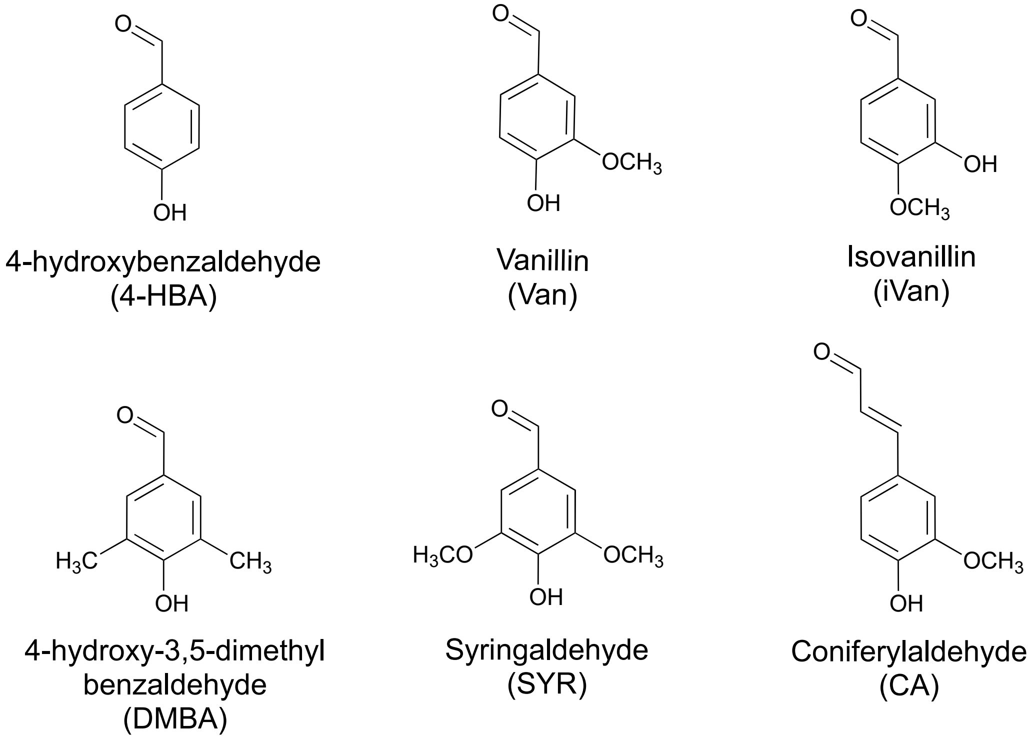


Figure S1. The ratio of solar intensity at 60º SZA to 0º SZA. While this ratio approaches a constant at longer wavelengths, the sharp decline in the most photochemically active range, 300 -340 nm, shows a steep decline towards shorter wavelengths, highlighting the importance of accounting for the wavelength dependence of Φ_{loss}.



4-hydroxybenzaldehyde (4-HBA)

Vanillin (Van)

Isovanillin (iVan)

4-hydroxy-3,5-dimethyl benzaldehyde (DMBA)

Syringaldehyde (SYR)

Coniferylaldehyde (CA)

Fig S2: The structures and abbreviations of the phenolic carbonyl molecules investigated in this study

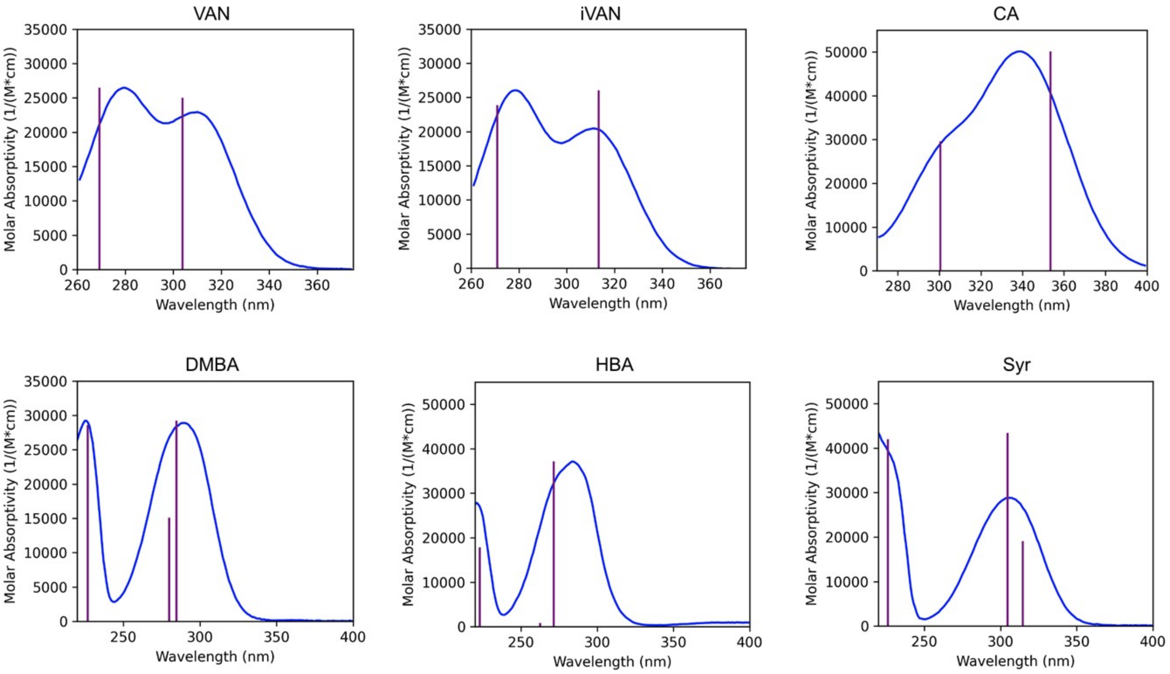


Figure S3. Experimental UV-Vis absorption spectra with ground state geometry optimizations (B3LYP/6-311+G(2d,p)/PCM (ε=78.39)) followed by TD-DFT predictions (B3LYP/6-311+G(2d,p)/PCM (ε_{inf}=1.778)).

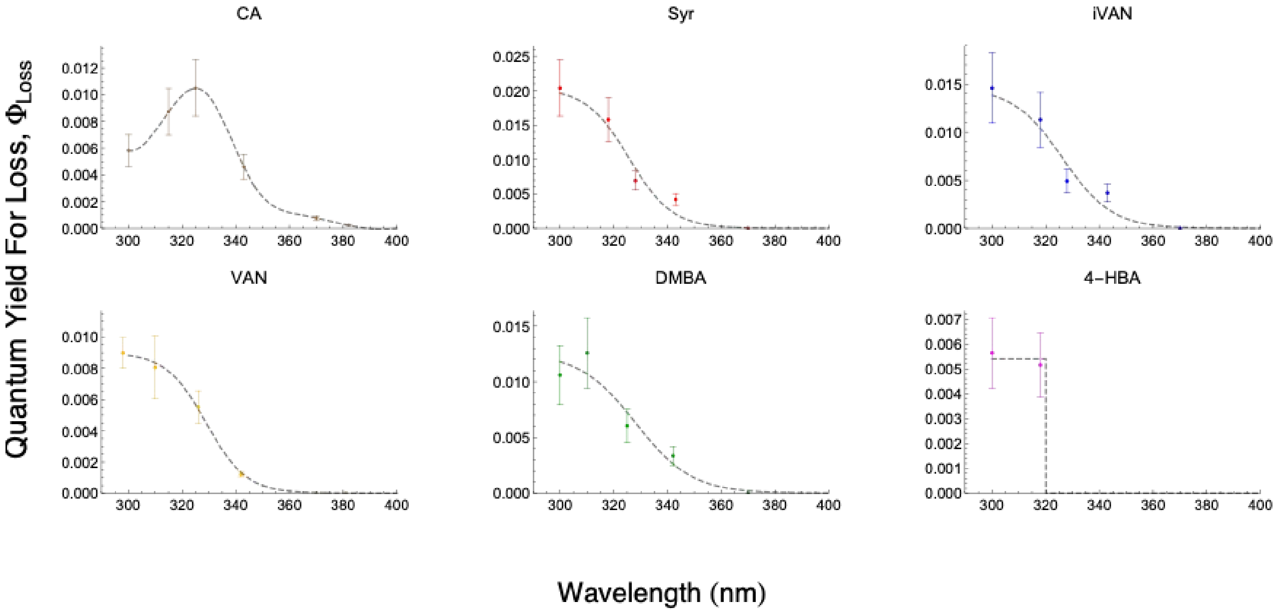


Figure S4. Wavelength dependent quantum yields for loss for all PhC studied. Abbreviations defined in Fig. S1. Dashed lines show interpolation functions used to calculate $j_{eff}(SZA)$

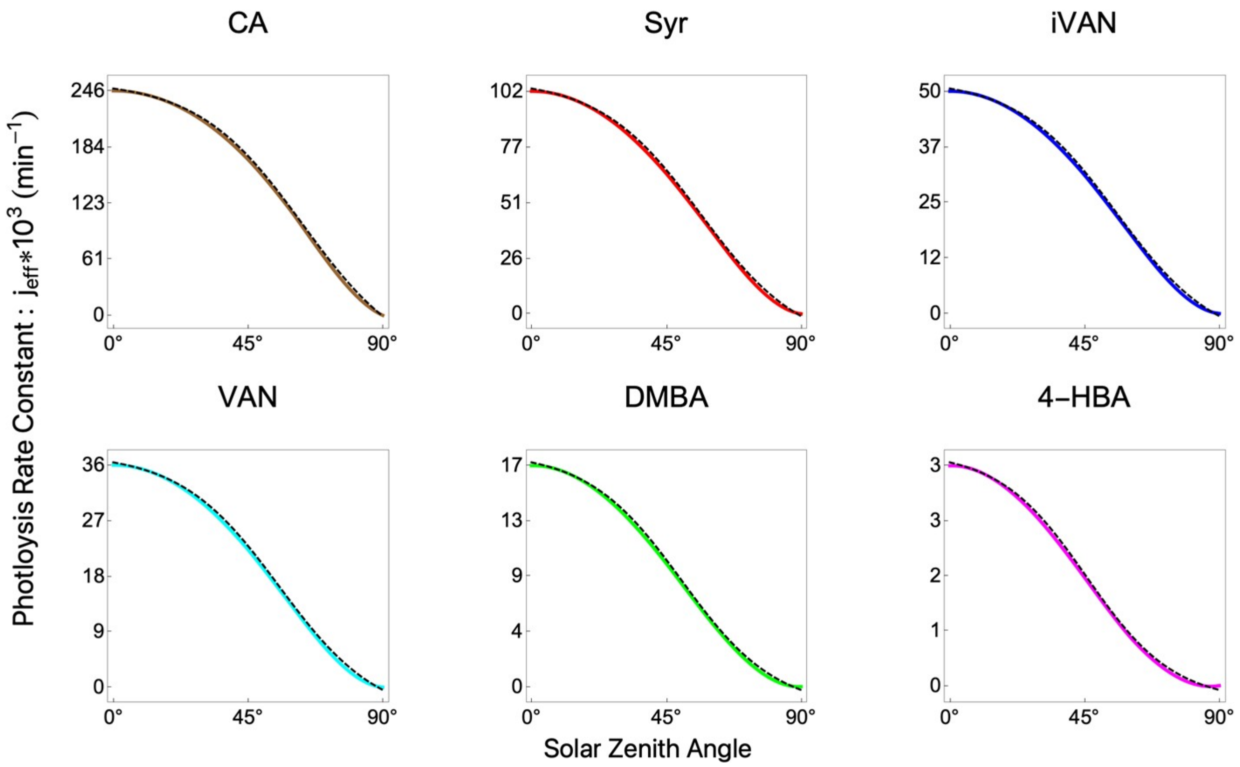


Figure S5. Agreement between analytical fits (dashed, black lines) and the calculated (multi-colored lines) solar zenith angle photolysis rate constants for all six PhC at $[PhC] = 10\ \mu M$ and pH = 2. Note that j values have been multiplied by 1000. Analytical fits have the functional form :

$$j(SZA;10\ \mu M\ PhC;pH=2)=\Phi_{Max}+\beta\frac{1}{1+e^{\left(-\frac{SZA\ -\ SZA_{C}}{\omega}\right)}}$$

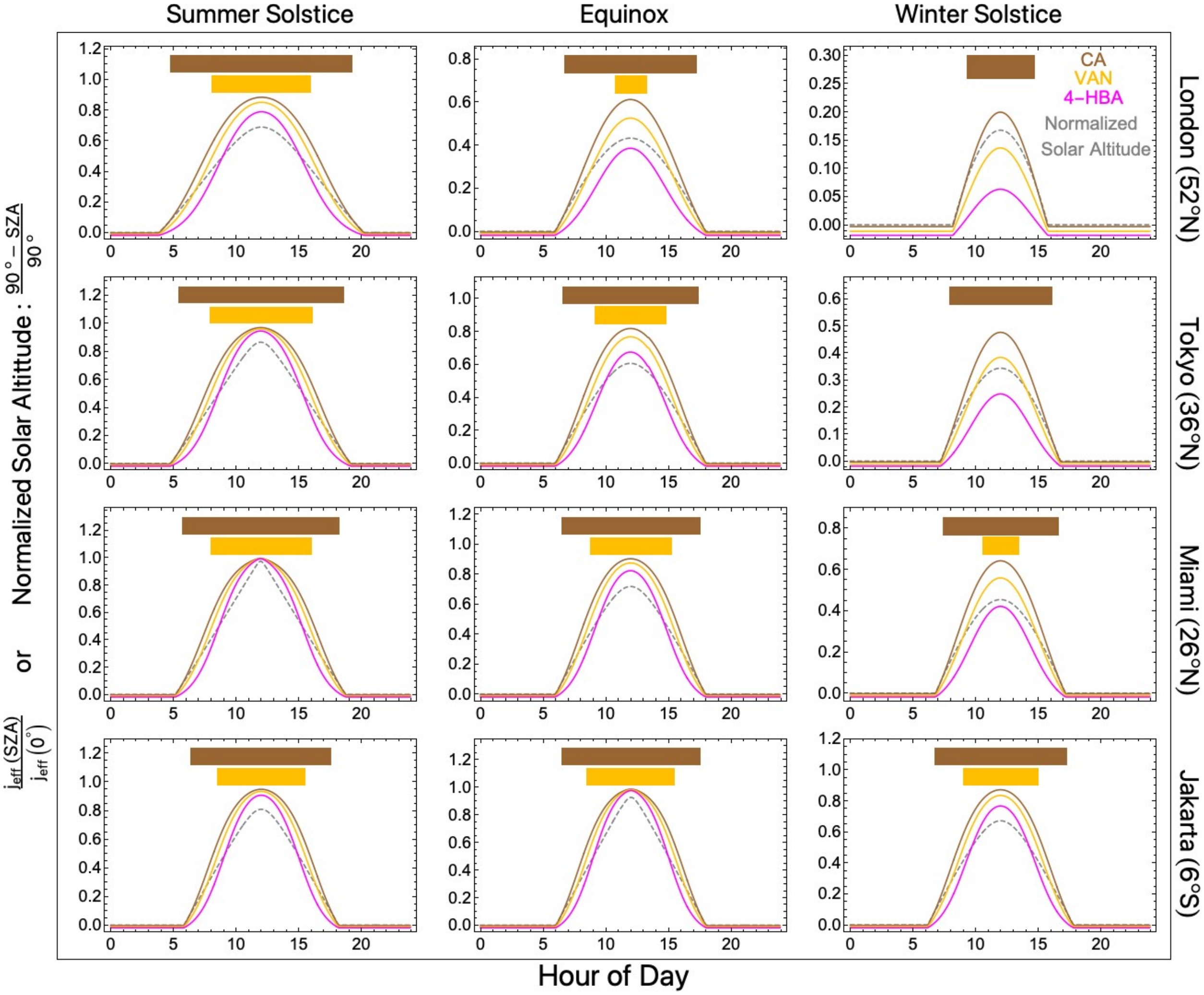


Figure S6. Seasonal differences in the effective 1st order rate constant for loss (j_{eff}) of 3 PhC compounds: CA (brown), SYR (red), and VAN (yellow). j_{eff} values are normalized to the maximum value at $0°$ SZA.Trends are shown for locations spanning latitudes from nearly equatorial (Jakarta, $6°S$) to a high mid-latitude (London $52°N$). In addition, the solar altitude ($90° - SZA$) is plotted (gray), normalized to the maximum value of $90°$. The brown and yellow bars indicate periods when the PhC lifetime is an hour or less for CA and VAN, respectively. 4-HBA has a minimum atmospheric photochemical lifetime of ~17 hours in acidic atmospheric water.

Table S1. Geometry optimized structures of the ground single state at the B3LYP/6-311+G(2d,p)/PCM (ε=78.39) level of theory

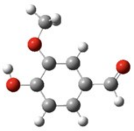
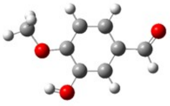
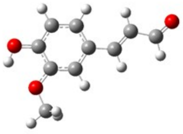
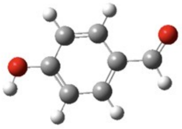
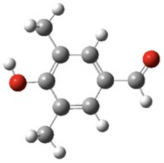
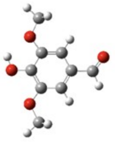
Van	iVan	CA	HBA	DMBA	Syr
					

Table S2. TDDFT excitation wavelengths computed with ground state geometry optimizations (B3LYP/6-311+G(2d,p)/PCM (ε=78.39)) followed by TD-DFT predictions (B3LYP/6-311+G(2d,p)/PCM (ε_{inf}=1.778)).

PhC	λ_1	λ_2	λ_3	n-pi*
Van (Vacuum)	260.75	287.94		327.04
Van (PCM Solvent)	269.24	303.79		317.77
iVan (Vacuum)	299.06			329.04
iVan (PCM Solvent)	270.92	313.33		319.43
HBA	255.75	260.62		328.97
HBA (PCM Solvent)	271.58			318.30
DMBA (Vacuum)	268.77			331.03
DMBA (PCM Solvent)	279.86	284.71		318.93
Syr (Vacuum)	290.11	302.08		326.21
Syr (PCM Solvent)	304.67	314.64		317.92
CA (Vacuum)	249.55	287.94	334.88	361.73
CA (PCM Solvent)	249.60	300.48	353.58	340.55

Table S3. Singlet (S0) and triplet (T1) geometry optimized energies (B3LYP/6-311+G(2d,p)/PCM (ε=78.39)).

	S0 (Hartree)	T1 (Hartree)	ΔE (E_{T1}-E_{S0}) (kJ/mol)
VAN	-535.503	-535.246	676
iVAN	-535.502	-535.247	668
CA	-612.930	-612.673	673
HBA	-420.942	-420.708	612
DMBA	-499.460	-499.354	278
Syr	-650.060	-649.775	748

Supplemental Information

S1 Concentration Dependence

It was previously shown that the Φ_{loss} for vanillin is concentration dependent, indicating that the rate of loss for PhC occurred via primarily second order kinetics. To determine the generalizability of this finding for PhC, all experiments were repeated with either 5 or 20 μM concentrations and compared with Φ_{loss} at 10 μM. Our analysis revealed a near linear concentration dependence in Φ_{loss} for all the PhC molecules studied, with an average increase by a factor of 1.85 when doubling concentration. Second order kinetics indicate a mechanism involving an excited triplet (^{3*}PhC) reacting with a ground state PhC molecule to produce two radicals, one with an added hydrogen atom and another with one hydrogen atom lost.