Singlet oxygen is produced from brown carbon-containing cooking organic aerosols (BrCOA) under indoor lighting

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1. Experimental setup

1.1 Ingredients and recipes

1.1.1 Pancakes

For preparing the pancakes mix, the following ingredients were used:

- 400g flour
- 100g sugar
- 1/4 tsp salt
- 1 tsp vanilla extract
- 4 eggs
- 400ml 2% milk
- 100ml sunflower oil
- butter

The ingredient were combined using the following recipe:

- 1. In a large bowl, whisk together flour, sugar and salt;
- 2. In a separate bowl, whisk milk, vanilla extract and the eggs;
- 3. Pour the wet ingredients into the bowl with the dry ingredients. Stir until just combined everithing;
- 4. Preheat a non-stick pan over medium heat. Add a small amount of butter to the pan;
- 5. Pour small portions of the pancakes mix onto the pan and cook until bubbles form on the surface (2-3 minutes);

 Flip each pancake with a wooden spatula and cook the other side for an additional 1-2 minutes or until golden brown.

1.1.2 Brussels sprouts

The following ingredients were used:

- 1 lb Brussels sprouts ("Natures great food")
- olive oil
- salt and pepper

The recipe used is the following:

- 1. Cut the Brussels sprouts in half;
- 2. In a non-stick pan, heat 2 tablespoons of olive oil over medium-high heat;
- 3. Add the Brussels sprout to the pan. ensuring they are in a single layer. Allow them to cook without stirring for a couple of minutes to develop a golden brown colour;
- 4. Stir the brissule sprouts occasionally to ensure cooking. Continue to cook until they are tneder on the inside and have a nice caramelized exterior (around 8-10 minutes);
- 5. Season with salt and pepper.

1.1.3 Vegetable stir-fry

The following ingredients were used for preparing this dish:

- Mann's vegetable medley (907g) that includes carrots, peas and broccoli;
- olive oil
- salt and pepper

The following recipe was used:

- 1. Heat 2 tablespoons of olive oil over medium-high heat;
- 2. Gradually introduce Mann's vegetable medley to the heated oil, adding the entire pack in stages;
- 3. Sprinkle salt into the mix and stir-fry the vegetables until they attain a slight tenderness and browning;
- 4. Add salt and pepper to taste.

1.2 Cooking setup



Figure S1: The cooking experiments were setup in the laboratory at UBC. Three instruments were sampling the cooking organic aerosols: the scanning mobility particle sizer (SMPS), the optical particle sizer (OPS) and the Coriolis impinger. All three instruments samples from the same location approximately 35 cm away from the cooking pan as indicated in the image. The picture is an example of the Brussels sprouts cooking experiment.

1.3 Illumination setup



(a) Windowsill sunlit experiments



(b) Rayonet photoreactor with UVA and fluorescent lights

Figure S2: Photochemical experimental setups for irradiation of the cooking organic aerosol extracts. Panel a) The indoor sunlit experiments were conducted on sunny days on the window sill of a south-facing window in the laboratory at UBC. Panel b) The experimental setup for the Rayonet irradiation used UVA and fluorescent bulbs. The test tubes were places inside a rotating carousel and every available space around the carousel was filled either with a sample solution or with a water blank to ensure that the light path length was constant throughout the project.

1.4 Sample absorbance



Figure S3: Absorbance of cooking aerosol extracts plotted as a function of wavelength zoomed in to 300-400nm and colour-coded by dish type: pancake BrCOA, Brussels sprout BrCOA and stir-fry BrCOA. The normalized irradiance of the three sources of indoor lighting (normalized for the 300-400nm range) is plotted on the right y-axis to visualize the overlap in absorbance between the BrCOA extracts and the irradiance. The sunlight spectrum was measured during the window sunlit experiment on May 15, 2022

2. Decay of the ${}^{1}O_{2}^{*}$ probe furfaryl alcohol (FFA) as a function of irradiation

2.1 Under UVA exposure



Figure S4: FFA decay under UVA irradiation for all the BrCOA extracts performed on different days. The first row is the raw data, and the second row is the data corrected to account for any deviation away from steady-state conditions. Steady state concentrations were then obtained from the slope of the decay and the rate constant of FFA + ${}^{1}O_{2}^{*}$.



2.2 Under fluorescent light exposure exposure

Figure S5: FFA decay under fluorescent light irradiation for all the cooking samples performed on different days. The first row is the raw data, and the second row is the data corrected to account for any deviation away from steady-state conditions. Steady state concentrations were then obtained from the slope of the decay and the rate constant of $FFA+{}^{1}O_{2}^{*}$

2.3 Under window sunlight exposure



Figure S6: FFA decay under Sunlight irradiation for all the cooking samples performed on different days. The first row is the raw data, and the second row is the data corrected to account for any deviation away from steady-state conditions. Steady state concentrations were then obtained from the slope of the decay and the rate constant of $FFA+{}^{1}O_{2}^{*}$.

2.4 FFA decay from Background Air



Figure S7: FFA decay under each irradiance source for background air samples. Dates of background experiments are 2021-10-20, 2021-10-15, and 2022-12-10 for UV, Fluorescence, and Sunlight respectively. There is no observed FFA decay for any irradiation type, therefore all FFA decay observed in cooking experiments is from cooking generated BrCOA.

2.5 FFA decay from the reference sensitizer (perinaphthenone)



Figure S8: FFA decay under all irradiation sources for the reference sensitizer of perinapthenone (PN). PN experiments were run alongside cooking samples in irradiation experiments, to ensure the same experimental conditions.

3. Chemical Actinometry



Figure S9: p-nitroanisole (PNA) decay resulting from the chemical actinometry experiments (p-nitroanisole + pyridine)¹ for a) Fluorescent irradiance source and b) UVA irradiance source. Different colours indicate triplicate measurements. Note the difference in y-axis scales.

Sample	Sample	Fluorescence	Sunlight
	Number	Conversion	Conversion
		Factor	Factor
Pancake	211008	0.06	0.32
Pancake	211013	0.08	0.39
Pancake	211020	0.07	0.36
Brussells Sprouts	211015	0.09	0.47
Brussells Sprouts	211115	0.09	0.46
Brussells Sprouts	211124	0.07	0.38
Stir-Fry	211027	0.06	0.33
Stir-Fry	211209	0.07	0.35
Stir-Fry	211210	0.07	0.35

Table S1: Fluorescent and sunlight conversion factors (normalized to UVA) calculated using Equations (9) & (10) in the main text.



4. Aerosol mass calculation based on SMPS and OPS data

Figure S10: Aerosol size distribution plots of Brussels sprout, pancake, and stir-fry experiments measured with the SMPS and OPS directly at the point source. Cooking plots are represented in the following order from top to bottom: Pancakes 10/08, Pancakes 10/13, Pancakes 10/20, Brussels Sprouts 10/04, Brussels Sprouts 11/15, Brussels Sprouts 11/24, Stir-Fry 10/27, Stir-Fry 12/09, Stir-Fry 12/10. The y-axis represents the size of the aerosols sampled (nm), the x-axis represents the duration of the experiment, and the z-axis represents the number concentration (dN/dlogDp). Background aerosols were always sampled for 1 h prior to cooking.

To calculate the ambient aerosol mass, we used the following steps and equations:

1. To convert from the number concentration to the mass concentration, we assumed a spherical particle with a density, ρ of 1.0 g/cm³.²

 $dN \times (4/3)\pi r^3 \times \rho = dM$

$$dN \times (4\pi/3)(D_p/2)^3 \times \rho = dM$$

$$dN \times (\pi/6) \times D_p^3 \times \rho = dM$$

Where dN is the number concentration (number of particles/ cm^3), D_p is the geometric midpoint of the particle, ρ is the density, and dM is mass concentration.

2. In order to calculate the mass-weighted total concentration, we must normalize the SMPS and OPS data. For the SMPS, the data is in the dM/dlogDp format. For the OPS, the data is in dM/dDp format. For the SMPS:

$$dM/dlogDp \times (log(UB) - log(LB)) = dM$$

For the OPS:

$$dM/dDp \times (UB - LB) = dM$$

Where dM/dlogDp = log normalized mass concentration ($\mu g/m^3$), dM/dDp = normalized mass concentration, ($\mu g/m^3$), UB = the upper size bin of the instrument (nm), LB is the lower size bin of the instrument (LB).

3. Next, we calculated the total mass concentration (M) by summing the mass concentrations (dM) of each instrument scan for the SMPS and OPS separately.

$$\sum_{s_1}^{s_n} dM = M$$

Where s_1 is the first bin of your scan, and s_n is the last bin of your scan. We do this calculation for each scan present in the data.

4. Then, we multiplied this total mass concentration value by the volume sampled by the instrument to obtain a total sampled mass (μ g) for each scan. This is done using the formula:

$$M_{instrument} \times V_{instrument} = C_{instrument}$$

where C_i is the total sampled mass measured by a specified instrument (µg) at one scan. $M_{instrument}$ is the total mass concentration (µg/m³) of a specified instrument at one scan. $V_{instrument}$ represents the volume of the air sampled during 1 scan which is determined by the scan length multiplied by the flow rate.

5. During these scans, we had a pre-cooking sampling period, and a during-cooking sampling period, while the Coriolis μ impinger sampled. Since the Coriolis was active for a total of 60 minutes per period, we took the sum of each scan of C_i . Before cooking period:

$$\sum_{Scan_1}^{Scan_n} C_{OPS} + \sum_{Scan_1}^{Scan_n} C_{SMPS} = C_{totalbackground}$$

During cooking period:

$$\sum_{Scan_1}^{Scan_n} C_{OPS} + \sum_{Scan_1}^{Scan_n} C_{SMPS} = C_{totalsample}$$

where similarly to the above equation, Scan 1 = the scan number the coriolis first starts sampling at, Scan n = the total number of samples (60 scans).

6. We also calculated the average total concentration of each period the Coriolis impinger sampled. Before cooking period:

$$\left(\sum_{Scan_{1}}^{n} M_{OPS}/n + \sum_{Scan_{1}}^{n} M_{SMPS} = M_{totalbackground}/n\right)/2$$

After cooking period:

$$\left(\sum_{Scan_{1}}^{n} M_{OPS}/n + \sum_{Scan_{1}}^{n} M_{SMPS} = M_{totalsample}/n\right)/2$$

References

- Laszakovits, J. R.; Berg, S. M.; Anderson, B. G.; O'Brien, J. E.; Wammer, K. H.; Sharpless, C. M. p-Nitroanisole/pyridine and p-nitroacetophenone/pyridine actinometers revisited: Quantum yield in comparison to ferrioxalate. *Environmental Science & Technology Letters* 2017, 4, 11–14.
- (2) Katz, E. F. et al. Quantification of cooking organic aerosol in the indoor environment using aerodyne aerosol mass spectrometers. *Aerosol Science* and Technology 2021, 55, 1099–1114, Publisher: Taylor & Francis _eprint: https://doi.org/10.1080/02786826.2021.1931013.