Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supporting Information For:

Aqueous Autoxidation of Common Glycols in the Indoor Environment

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Section S1. Experiment Details

Section S1.1. Sample Preparation

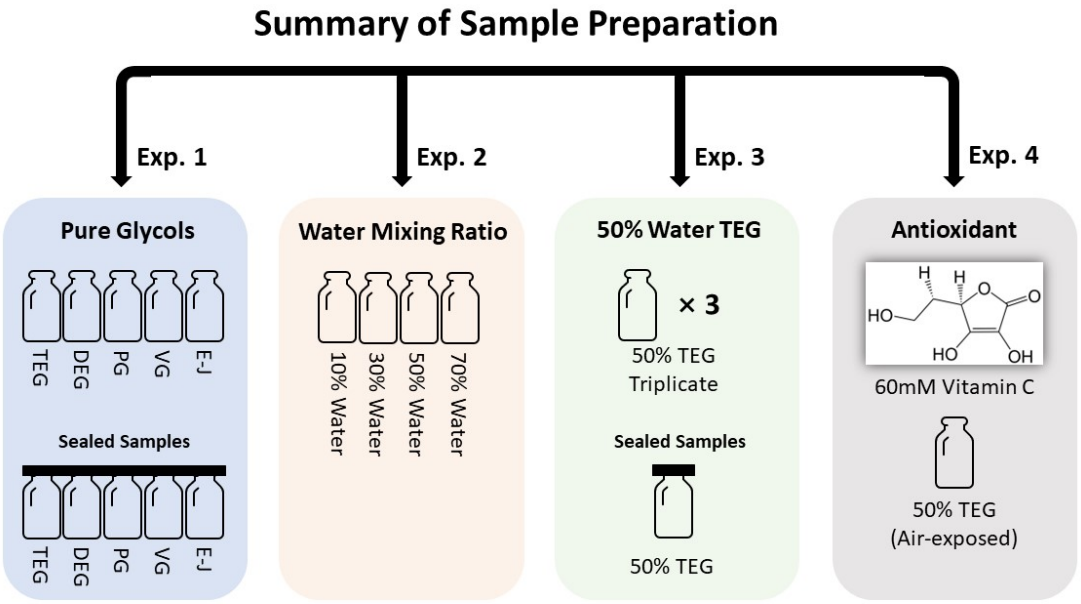

Figure S1. Summary of samples involved in this study; four sets of experiments were performed.

Experiment 1: Five different pure glycols were separated into two groups. The first group contains air-exposed samples, where 10 ml of the five glycols were added into 20 ml clear glass vials. These samples were exposed to room air all the time without vial caps while avoiding direct sunlight exposure. The second group was the same set of glycols, stored under the same condition as the first group, but with caps closed and sealed with parafilm.

Experiment 2: Three vials containing 10 ml of 50% (v/v) TEG were prepared by mixing 5 ml of water and 5 ml of TEG. The sealed 50% TEG was prepared in the same way. Triplicate 50% TEG samples were stored under room conditions without vial caps, and the sealed 50% TEG samples were capped with parafilm sealing. Masses of 50% TEG triplicate were monitored by an analytical balance, to track the water evaporation from the mixture.

Experiment 3: Four vials containing 10 ml of TEGs with varying water mixing ratios were prepared. Specifically, 1 ml, 3 ml, 5 ml, and 7 ml of water were added to different volumes of TEG to achieve a total volume of 10 ml. These four samples represent varying volumetric water mixing ratios of 10% to 70%. All samples were stored under room conditions without vial caps, their masses were monitored weekly to track water evaporation.

Experiment 4: 106 mg of L-ascorbic acid (Vitamin C) solid was added into 10 ml of 50% TEG mixture, resulting in a 60 mM final concentration of Vitamin C. This sample was stored under room conditions without the vial cap, and its mass was also recorded weekly.

Section S2. Instrumental Settings

Table S1. LC-MS instrument parameters

Injection volume	2 μL
Solvent A	0.1% (v/v) Formic Acid in MQ Water
Solvent B	0.1% Formic Acid in ACN
Flow Rate	400 μL/min
Gradient	See **Table S2**
Column	Luna Omega C18 column 150 mm x 2.1 mm x 3 μm
Acquisition Time	20 min
Scanning Mode	Negative
Spray Voltage	-3.5 kV
Sheath Gas Flow Rate	40 a.u.
Aux Gas Flow Rate	8 a.u.
Sweep Gas Flow Rate	0 a.u.
Capillary Temp	150 ℃
Capillary Voltage	-35 V
Tube Lens	-51.88 V
Electron Multiplier 1 Voltage	-783.44 V
Electron Multiplier 2 Voltage	-853.44 V
Collision Gas (MSMS)	Helium
Normalized Collison Energy	22~27 a.u.

Table S2. LC gradient for derived carbonyls			
Time /min	Flowrate μL/min	Solvent A	Solvent B
0.00	400	68.0	32.0
5.00	400	68.0	32.0
10.00	400	55.0	45.0
15.00	400	30.0	70.0
18.00	400	10.0	90.0
20.00	400	10.0	90.0

Section S3. Iodometry-UV-Vis Peroxide Quantitation [1]

Section S3.1 Solutions Involved

1 M CH_3COOH solution: prepared in MilliQ water and kept in the refrigerator for storage.

1.5 M KI solution: prepared in MilliQ water. KI solution is prepared fresh every time before the experiment.

H_2O_2 solution: Served as calibration standards, ranging from 0 to 50 μM. It is prepared from the concentrated 30% H_2O_2 stock solution and serial dilution. Prepared fresh before use.

Sample for analysis: One UV-Vis sample is consisting of 200 μL KI solution, 150 μL CH_3COOH solution, and corresponding volume glycol solution, and filled up with MQ water to a total volume of 5 ml. The volume of glycol was varying to reach the desired dilution (1:400 for TEG, 1:10 for PG, VG, and DEG). For instance, the TEG sample for UV-Vis contains KI solution, CH_3COOH solution, 11.6 μL of TEG, and 4.6 ml of water. UV-Vis samples were allowed to react under room conditions for one hour before the analysis. **Figure S2** justified the reaction completeness.

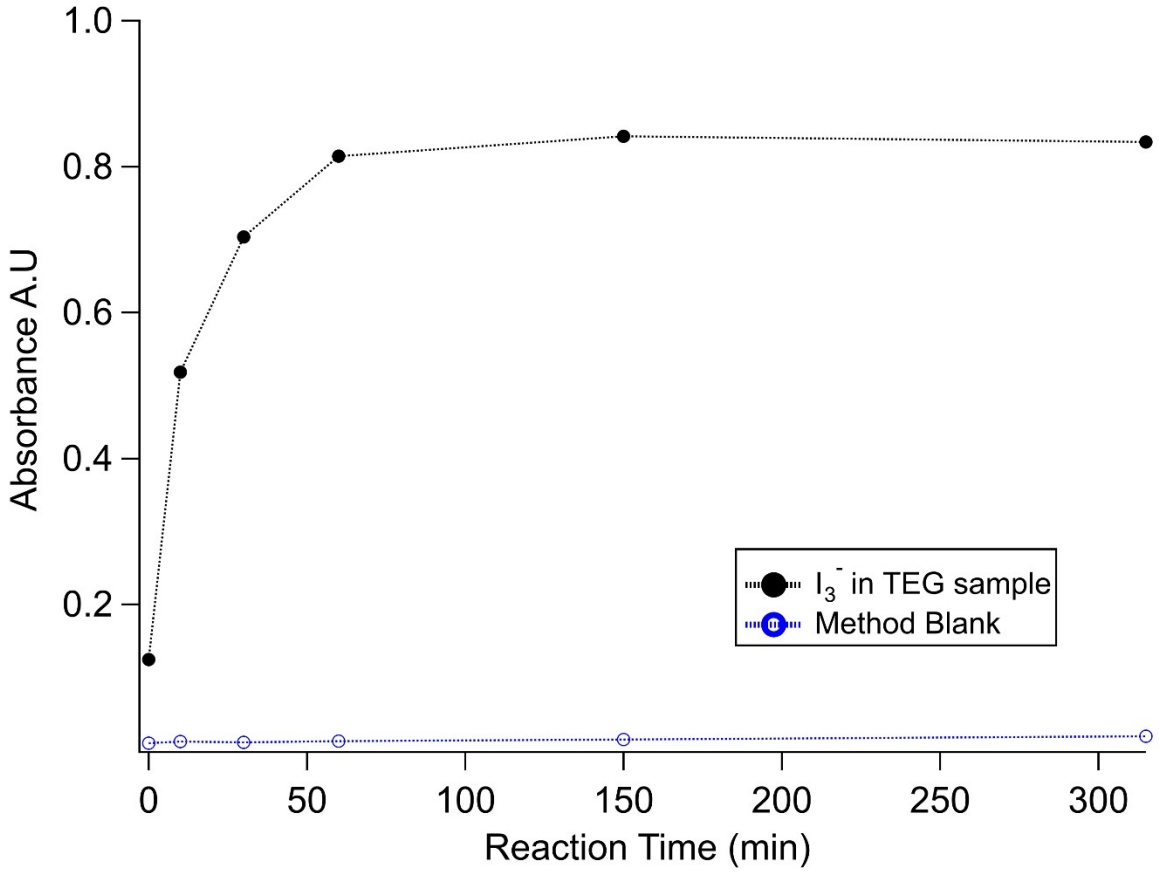

Figure S2. The absorbance of TEG sample in iodometry over time. We consider 60 min as the reaction completion time, due to the longer reaction time can be biased by the reaction between ambient oxygen and iodide ions.

Section S3.2 Instrumentation

The Agilent 8453 UV/VIS spectrophotometer was employed to obtain the absorbance value. The spectrum is collected from λ=200 to 1200 nm in a 1 cm path length semi-micro quartz cuvette from Fischer. A standard solution of 25 mM hydrogen peroxide was measured on every analytical day to prevent any instrumental variation.

Section S3.3 Calibration of Peroxide

Two calibration curves were constructed at the beginning and the end of the experiment, shown in **Figures S3 and S4** below, this is to evaluate the instrumental variation throughout the experiment.

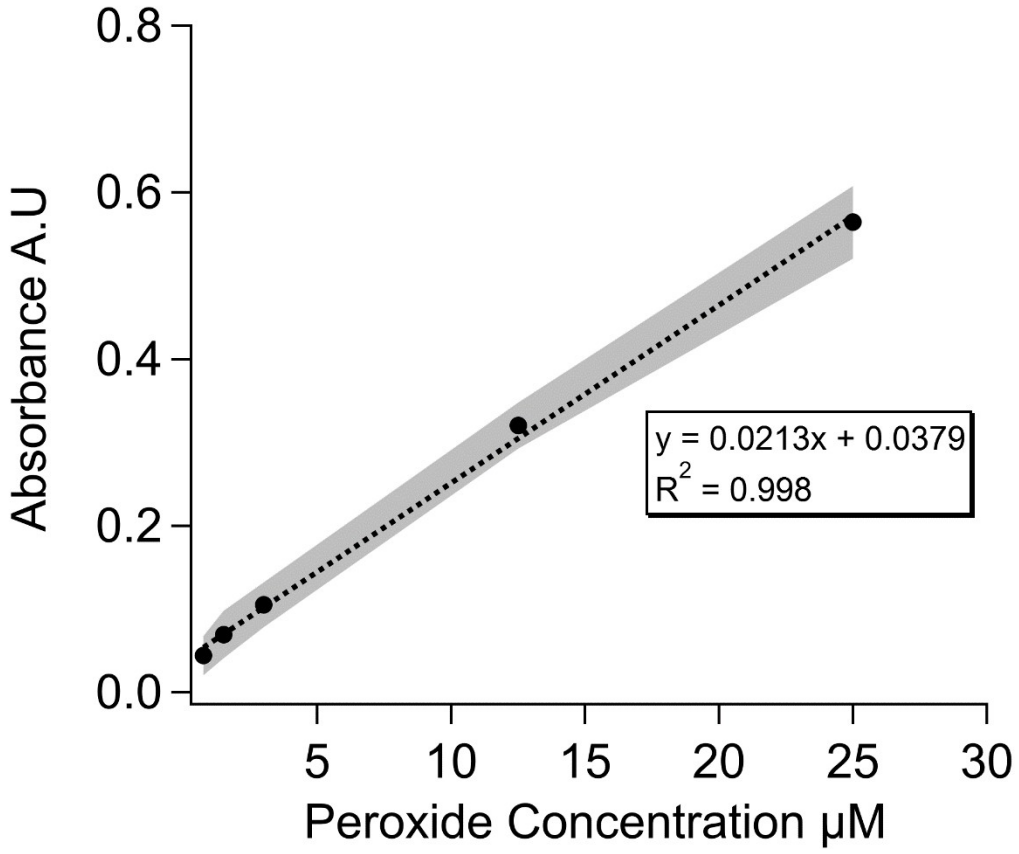

Figure S3. Iodometry-UV-Vis calibration curve at the beginning of the experiment, done in triplicates. Plotted is the average absorbance of three curves against concentration. The shaded area is the standard deviation of the triplicates.

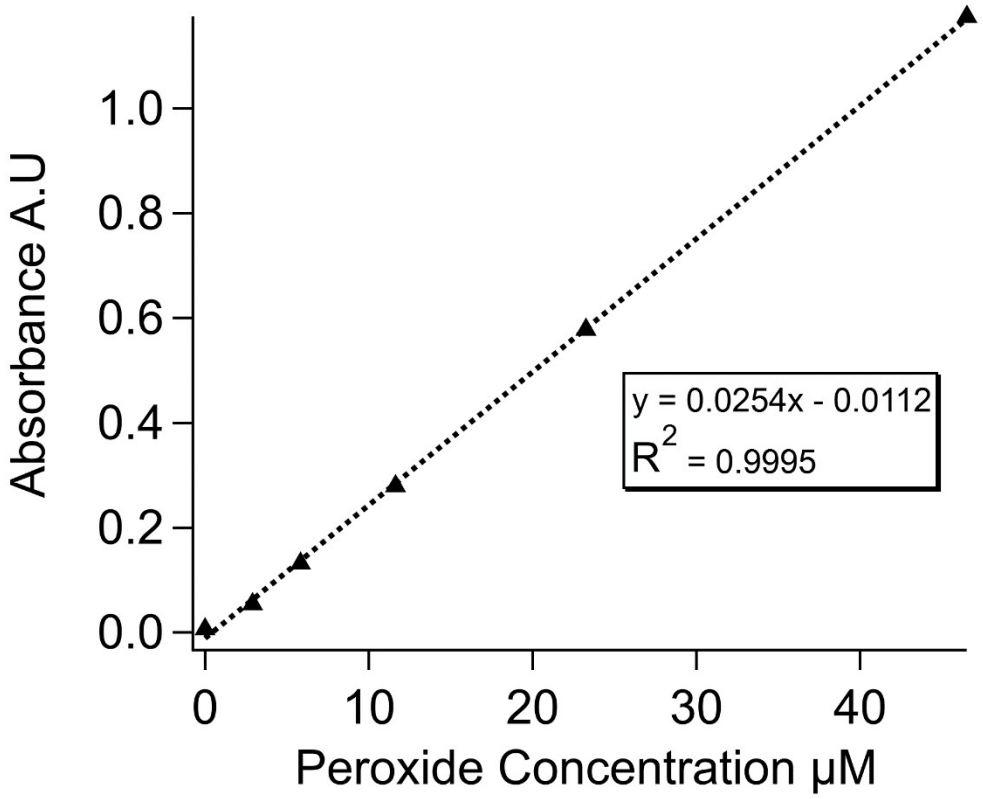

Figure S4. Iodometry-UV-Vis calibration curve at the end of the experiment. This calibration has only been done once.

Section S4. Quantification of Carbonyls

Table S3. Detailed Carbonyl Concentrations (µM)

	Week 1-2		Week 6-8	
	Formaldehyde	Glycolaldehyde	Formaldehyde	Glycolaldehyde
Air-PG	119	154	274	207
Sealed-PG	95	95	126	130
Air-DEG	144	140	153	140
Sealed-DEG	150	155	158	160
Air-VG	273	303	353	278
Sealed-VG	202	156	187	169
Air-EJ	618	592	952	590
Sealed-EJ	553	495	625	617
Air-TEG	1951	2859	3317	6377
Sealed-TEG	2024	3063	2391	4414

Section S5. Quality Control

We identified two major factors that can potentially induce bias in our results. The first one is the loss of water, causing increased concentrations of chemicals. We monitored the loss of water from all water gradients and fitted a first-order decay of the remaining solution, shown in **Figure S5**:

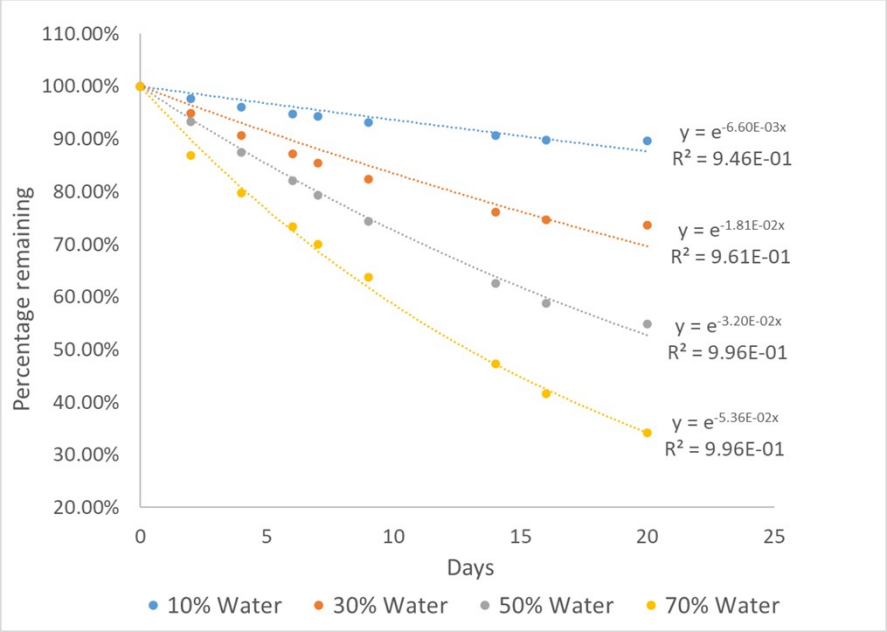

Figure S5. First-order fitment of remaining glycol solution time during constant water evaporation.

We also observed a varying recovery rate of formaldehyde in pure glycol and 50% glycol samples, despite standard addition being applied. Thus, we assumed a linear fitment of recovery rate from 0% to 50% of water, and extrapolated to 70%, shown in **Figure S6**:

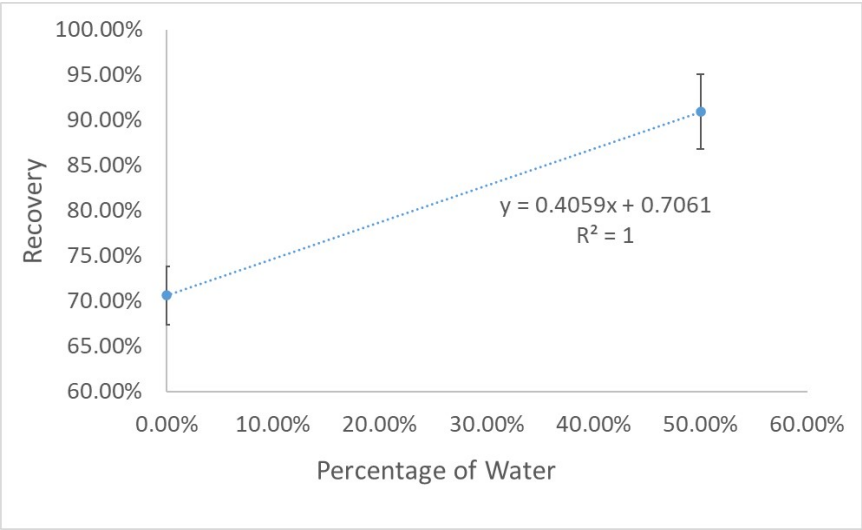

Figure S6. Assumed linear recovery rate in different mixing ratios of water. The error bar represents the standard deviation of recovery rates obtained from four replicates.

Reference

1. Mutzel (formerly Heinold), Anke & Rodigast, Maria & Iinuma, Yoshiteru & Böge, Olaf & Herrmann, Hartmut. (2013). An improved method for the quantification of SOA bound peroxides. Atmospheric Environment. 67. 365-369. 10.1016/j.atmosenv.2012.11.012.