SUPPORTING INFORMATION:

Sucralose-enhanced degradation of electronic cigarette liquids during vaping

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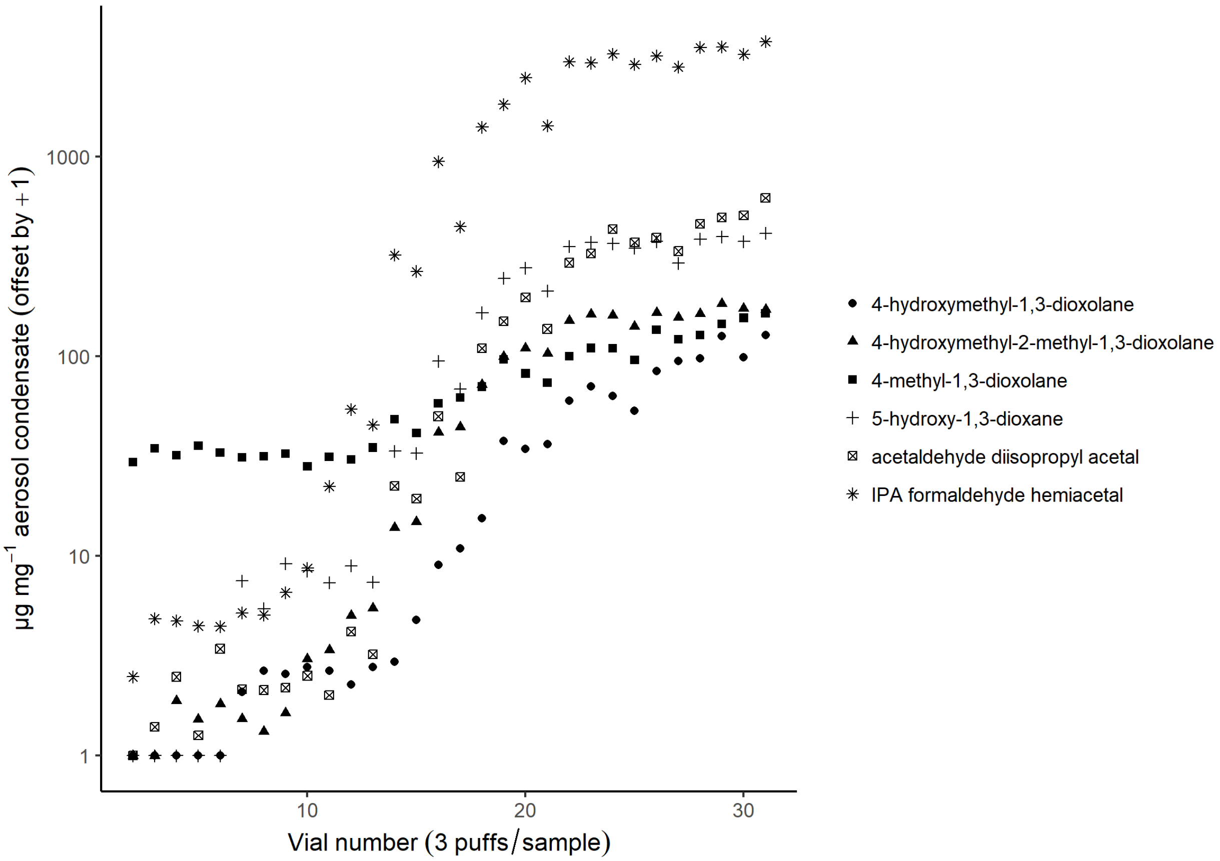

Figure S1: µg acetals and hemiacetal per mg aerosol condensate detected in each vial as detected by GC/MS or GC/FID generated using a 1.2 Ω coil at 20 watts containing 1:1 molar propylene glycol and glycerol.

Values of 1 represent compounds not detected as zero cannot be represented on a log scale. Cyclic acetals could go undetected with DNPH-derivatization detection methods. IPA hemiformal, higher than other formaldehyde equivalent analytes by a factor of ~10, represents free formaldehyde (less likely as gas phase was not collected) or propylene glycol (PG) and/or glycerol (GL) hemiacetals (more likely) captured in the aerosol and formed after addition of isopropanol to sample vials via exchange with the more abundant isopropanol. All acetals increase over the course of the puffing regime. Conditioning puffs were not employed in this sampling regime which highlights that toxicant levels may be underestimated if a limited number of puffs on a new atomizer are used.

Isopropanol hemiformal determination

The hemiacetal of isopropanol and formaldehyde is not stable therefore an authentic chemical standard is not available for purchase. A mixture containing isopropanol hemiformal was prepared by bubbling nitrogen gas into a vial containing a formaldehyde-enriched liquid solution via capillary tube. Another capillary tube was positioned in the headspace above the liquid level of formaldehyde solution and routed under the liquid level of another vial containing isopropanol. A capillary tube open to atmosphere was positioned in the isopropanol containing vial to allow release of excess gas. Gas from the headspace of the formaldehyde solution vial was allowed to bubble through isopropanol for approximately 30 minutes. The isopropanol solution was analyzed by GC/MS in both electron ionization (EI) and chemical ionization (CI). Retention time and spectra of the generated isopropanol hemiformal matched that of the suspected peak found in samples. The peak was not replicated when the above experiment was carried out substituting acetone for isopropanol. The suspected isopropanol hemiformal was observed to be stable at room temperature for weeks (as indicated by multiple injections over this time) along with hemiacetals of isopropanol and formaldehyde oligomers which were also identified by ^{1}H NMR testing of an aliquot the isopropanol solution.

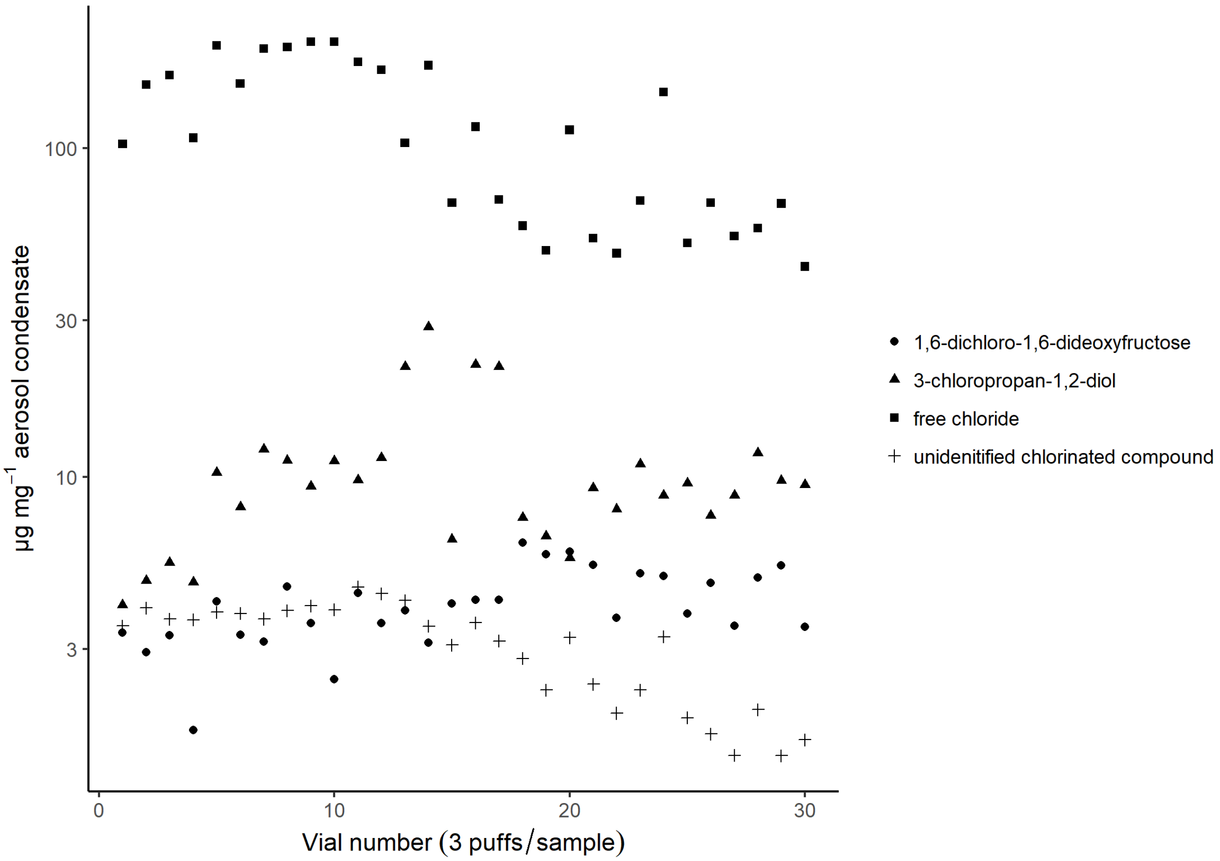

Figure S2: Chlorinated targets detected in each vaporized sample vial as detected by GC/MS, GC/FID, or IC generated using a 1.2 Ω coil at 20 watts containing 1:1 molar PG and GL.

Comparison of NMR degradation data with the literature

Variability between individual experiments makes it difficult to readily compare degradation levels between this work and other studies reported in the literature. The coil resistance, wattage employed, device type, wicking material, puff duration, collection method, analysis method, etc. can all influence the resulting values.[1] Below are two studies that attempt to suggest how much degradation can be produced by e-cigarettes.

In this study, the amount of each degradation component was compared to the quantity of (PG) in each vaporized sample. The NMR data was used to calculate integration values for each component relative to the amount of PG in the sample, as found from its -CH_3 at 1.05 ppm (Figure S3). The LOD (as defined as the standard deviation of the noise X 3) and the LOQ (as defined as the standard deviation of the noise X 10) were 0.006% and 0.02% of the PG integration value, respectively.

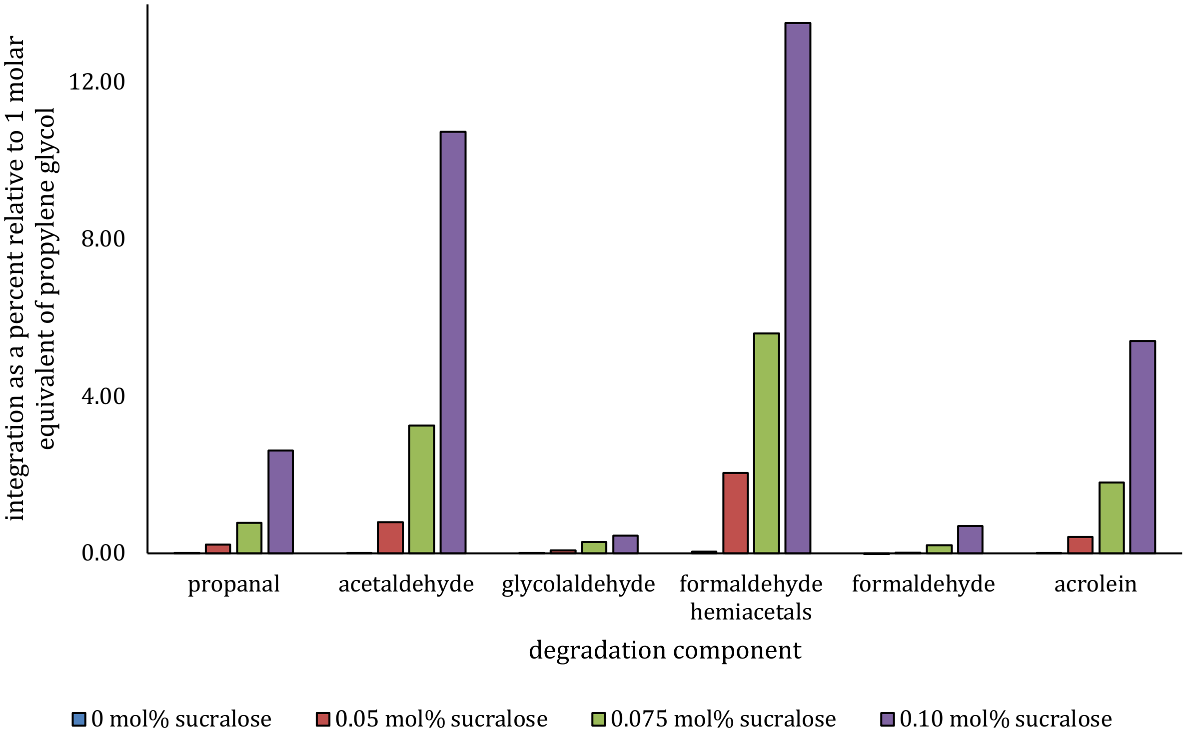

Figure S3: NMR integration values as a percent of the propylene glycol in each sample.

Salamanca et al. (2017)[1] reported the yields for formaldehyde and PG and/or GL + formaldehyde hemiacetals ("formaldehyde hemiacetals") at both 10 and 15 watts using a different resistance coil (2.2 Ω), e-cigarette device (KangerTech ProTank II atomizer), and collection method (DNPH collection method combined with qNMR analysis). Samples generated at 10 watts resulted in 1.20 µg of formaldehyde per mg e-liquid consumed and 16.75 µg of formaldehyde hemiacetals per mg e-liquid consumed.[1] At 15 watts, 4.43 µg formaldehyde and 65.70 µg formaldehyde hemiacetals were reported.[1]

To compare our values to those reported by Salamanca et al.,[1] the change in the mass of the vial (after collecting the sample into it) was used to calculate the mass of each component based on the molar ratios (as determined by NMR integration) and using the molecular weight of each component (Figure S4). Only PG, GL, propanal, acetaldehyde, glycolaldehyde, formaldehyde hemiacetals, formaldehyde, and acrolein were accounted for by NMR integration in this analysis. This means that values could be overestimated due to ignoring other components. Water, which generally comprises a significant portion of the vaped sample was not accounted for; this is a limitation. Other unknown degradation components were also excluded from this analysis. The change in the mass of the tank was used to calculate the volume of e-liquid consumed (in mL) in order to convert these degradation masses overall to µg degradation per mL of e-liquid consumed (also ignoring water in the starting e-liquid). Another limitation of this is that only a fraction of the total aerosol produced (as measured by the mL e-liquid consumed) was captured in the vial and tested by NMR. This may mean that the degradation values presented herein are an underestimation of the total quantity of degradation that was produced.

Furthermore, the PG and/or GL formaldehyde hemiacetals appear in the same region of the spectrum, and it is difficult to separate the PG and GL forms for analysis. Due to this, the masses of formaldehyde hemiacetals were approximated by using the molecular weight of the PG + formaldehyde hemiacetal. There was also a delay between the acquisition of the original spectrum (where the aldehyde degradation products were analyzed) and the addition of sodium bicarbonate so that the formaldehyde hemiacetals could be visualized. In solution, formaldehyde can continue to react with PG and GL and form more hemiacetals over time. Due to this, the quantitation of total formaldehyde products (in this case free formaldehyde and the formaldehyde hemiacetals) is likely overestimated due to the ongoing formation of the formaldehyde hemiacetals until there is no free formaldehyde remaining. The LOD and LOQ for these values in Figure S4 were 7 and 22 µg per mL of e-liquid vaped, respectively.

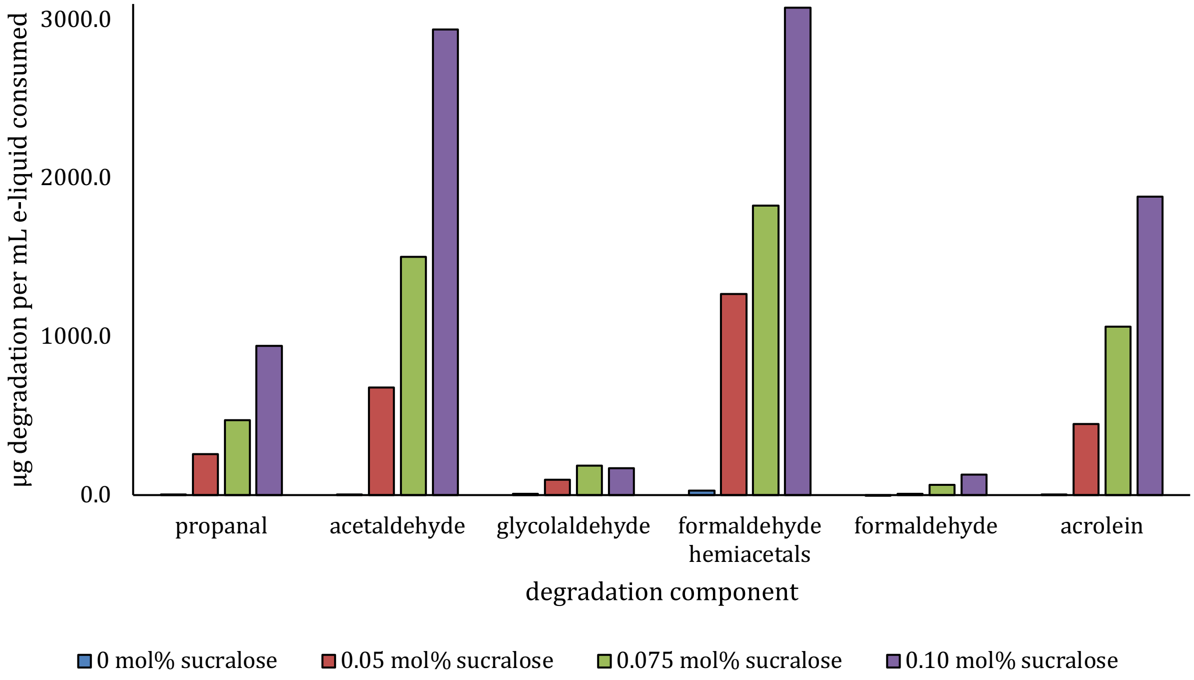

Figure S4: µg of each degradation component per mL of e-liquid consumed calculated from NMR integration values.

Geiss et al. (2016)[2] provided an overview of existing degradation concentrations, associated methods employed, e-cigarette device, and e-liquid. Of the studies included by Geiss et al., the highest concentrations of formaldehyde, acetaldehyde, and acrolein from all studies are as follows: 3400, 2600, and 2500 ng/puff.

To convert our values to the same units as those used by Geiss et al., the mass values for each degradation component (calculated based on the molar ratios and the trapped sample mass) that were used to calculate the µg of each degradation component per mL of e-liquid consumed in Figure S4 were converted to ng and divided by 3 since each sample was composed of 3 puffs. The LOD and LOQ for the values in Figure S5 were 147 and 488 ng/puff, respectively.

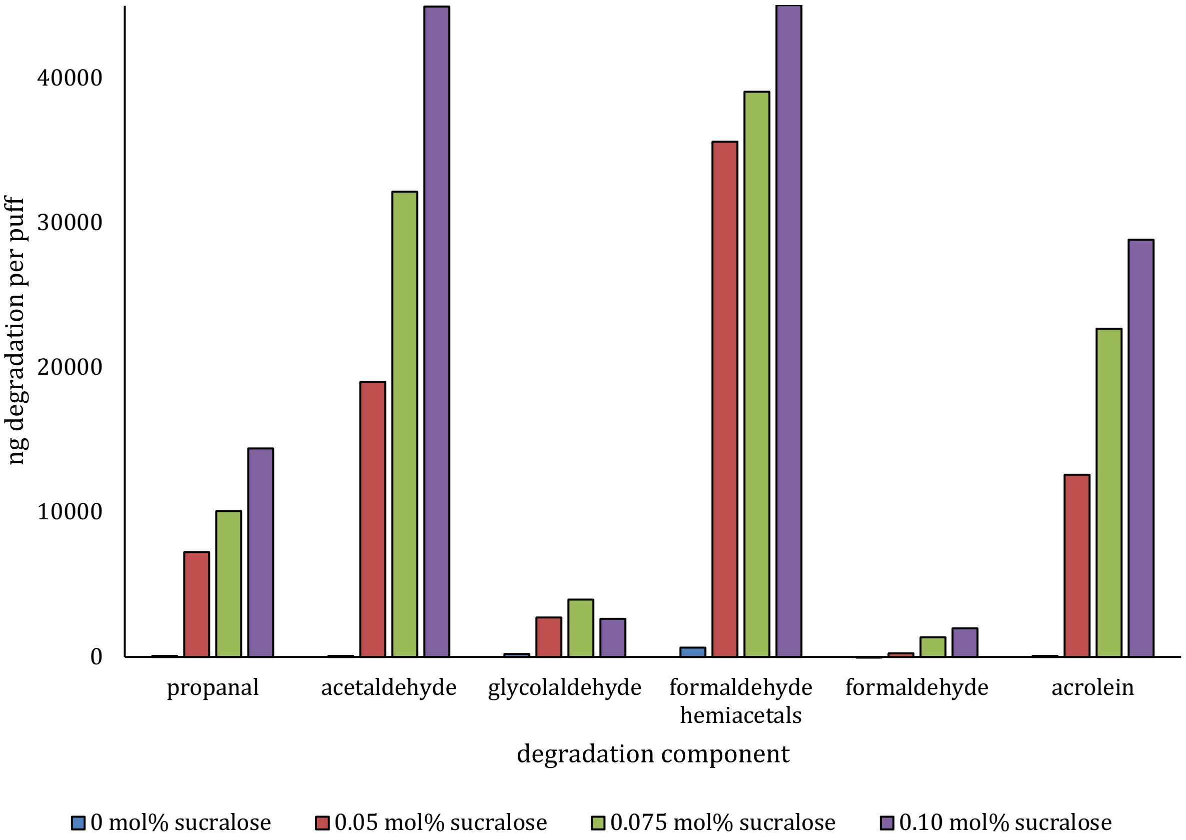

Figure S5: ng of each degradation component per puff.

References

1. Salamanca, J. C.; Munhenzva, I.; Escobedo, J. O.; Jensen, R. P.; Shaw, A.; Campbell, R.; Luo, W.; Peyton, D. H.; Strongin, R. M., Formaldehyde Hemiacetal Sampling, Recovery, and Quantification from Electronic Cigarette Aerosols. *Sci Rep* **2017,** *7* (1), 11044.

2. Geiss, O.; Bianchi, I.; Barrero-Moreno, J., Correlation of volatile carbonyl yields emitted by e-cigarettes with the temperature of the heating coil and the perceived sensorial quality of the generated vapours. *Int J Hyg Environ Health* **2016,** *219* (3), 268-77.