Supplementary information

S1: Estimation of the dissolved organic mass (DOM) concentrations in aqueous solutions after SOA extraction

The DOM concentrations in aqueous solutions were calculated as follows:

$$DOM(mg/L) = \frac{1}{V_{water}} \times \frac{V_{sample}}{t_{sample}} \times \sum_{t_i} \left(\frac{m}{V}\right)_{t_i} \times \Delta t_i \times 80\%$$

Where:

- V_{water} = volume of water used for SOA extraction (160 mL of water)
- V_{sample} = volume of {air + particles} sampled from the chamber (0.720 m^3 of air)
- t_{sample} = Sampling duration (2 hours)
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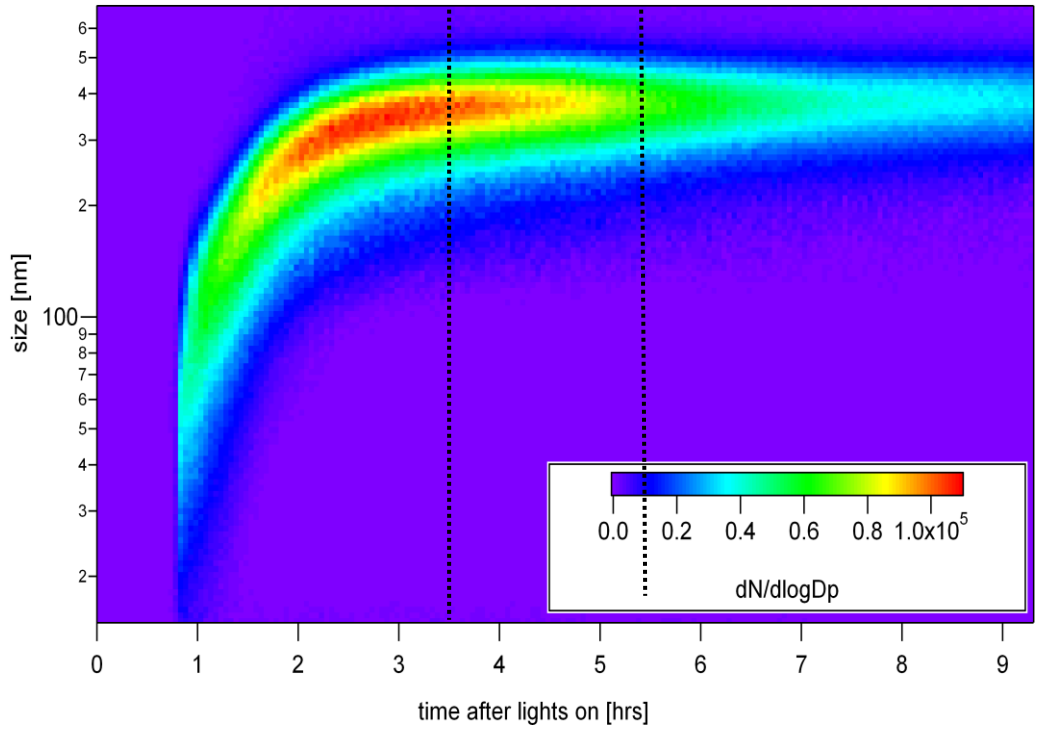
- $\frac{V_{sample}}{t_{sample}} \times \sum_{t_i} \left(\frac{m}{V}\right)_{t_i} \times \Delta t_i$ = total mass of particles sampled on the filter (µg). The HR-AMS provided a mass of organic particles per m^3 every 2 minutes $\left(\frac{m}{V}\right)_{t_i}$. Integrating this data during the filter collection time, multiplied by $\frac{V_{sample}}{t_{sample}}$, yields the total mass of particles sampled on the filter.
- The collection efficiency of SOA in water extracts was approximately 80%, as determined during previous experiments for SOA derived from α-pinene and isoprene.

(a) - Isoprene (exp 1)



(b) - Isoprene (exp 2)

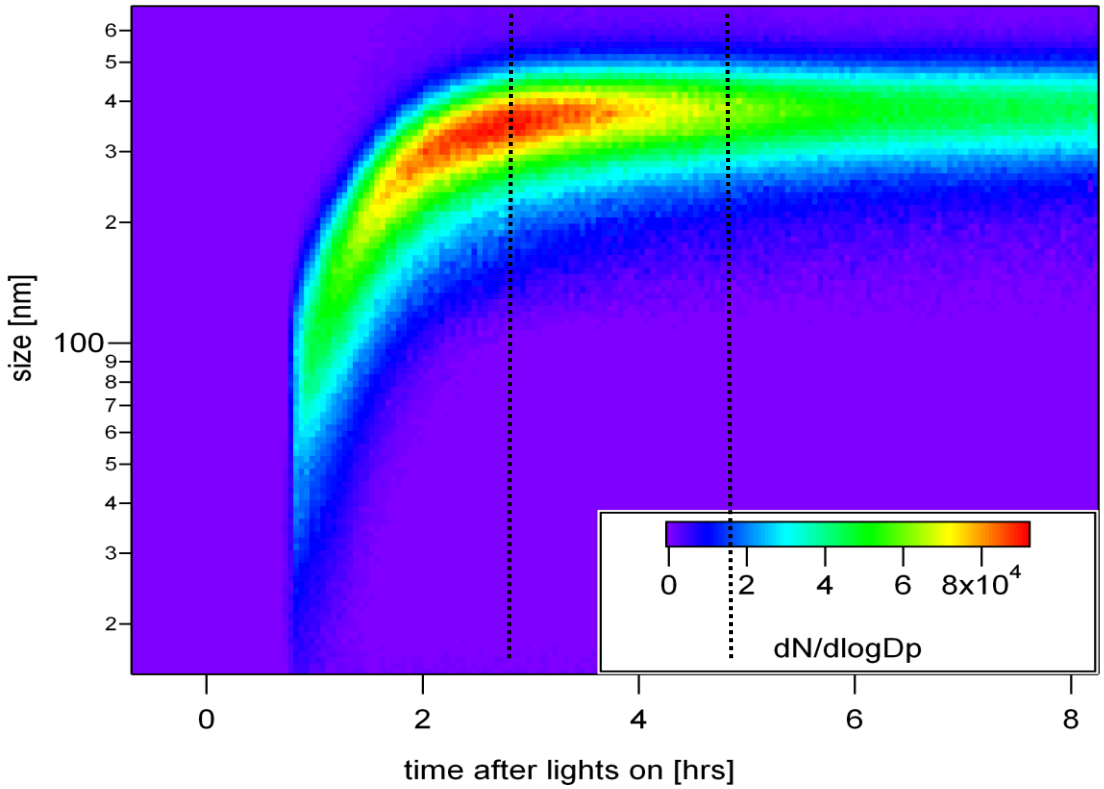
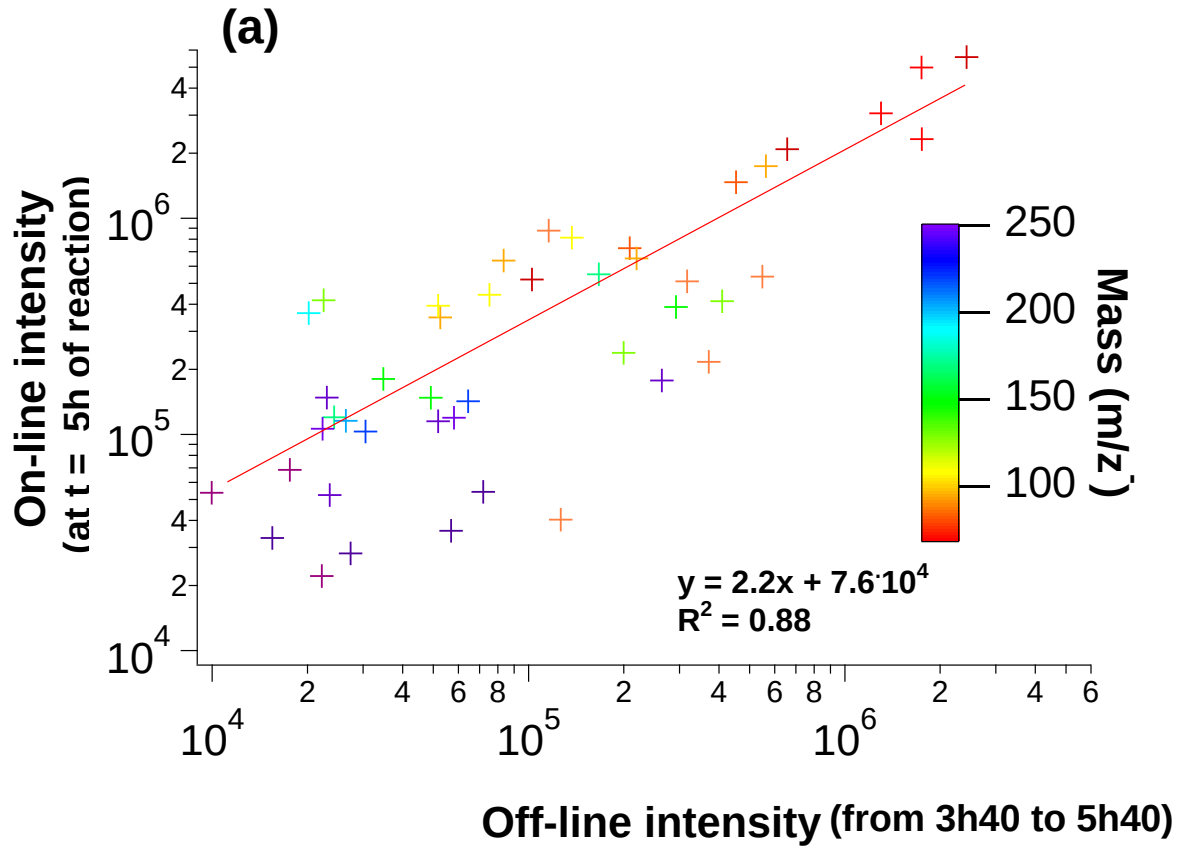


Figure S1: Evolution of the number size distribution (analyzed by SMPS) of the SOA formed in the smog chamber as a function of the reaction time during the gas-phase photooxidation of (a): isoprene experiment 1 and (b): experiment 2. The dashed lines indicate the filter sampling start and end times.



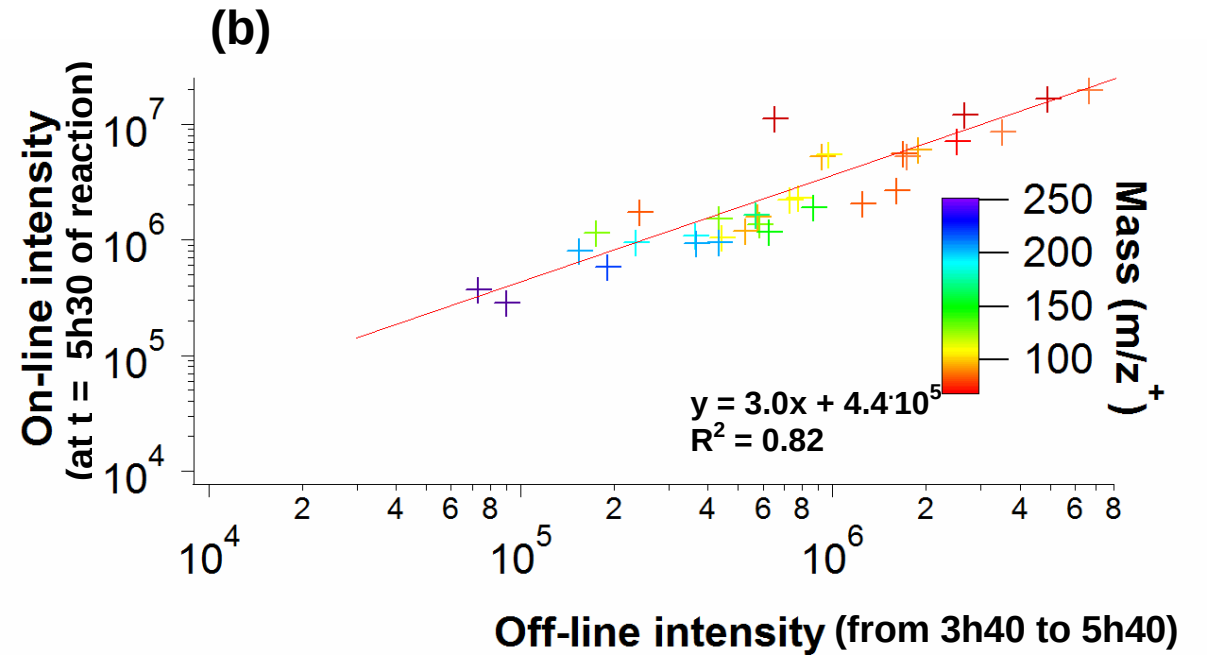


Figure S2: TD-API-AMS measurements (a) in the negative mode and (b) in the positive mode of the chemical composition of SOA formed during isoprene photooxidation (experiment 1). **C**orrelation between on-line (direct on-line measurement in the smog chamber) and off-line analysis (nebulization of "control" samples).

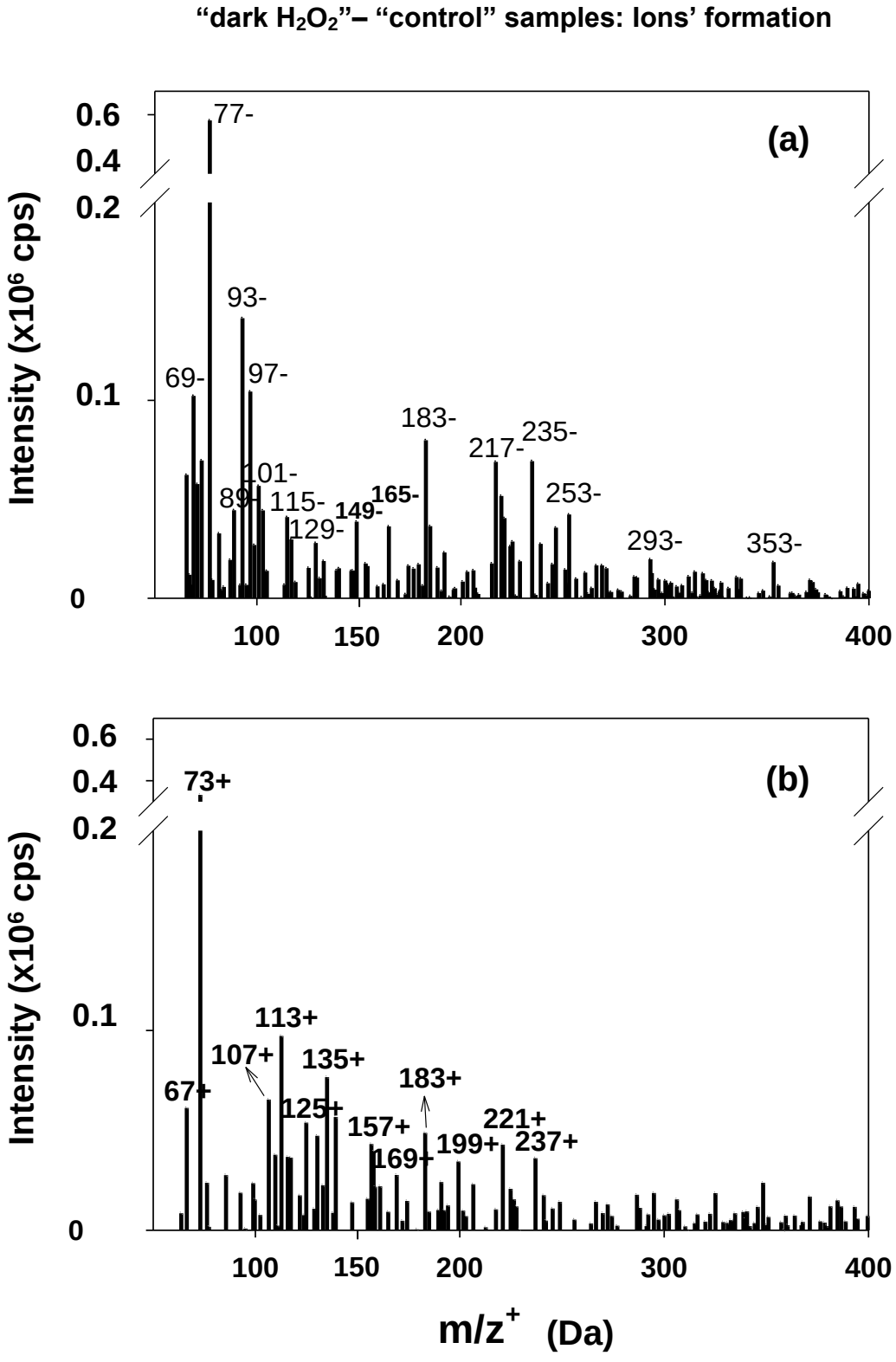


Figure S3 : Isoprene experiment (1). APCI-MS measurements of aqueous solutions by direct infusion of liquid solutions, in the negative mode (a) and in the positive mode (b). Mass spectra differences between "dark H_2O_2" samples and "control" samples show the ions formed during dark oxidation by H_2O_2 in the aqueous phase.

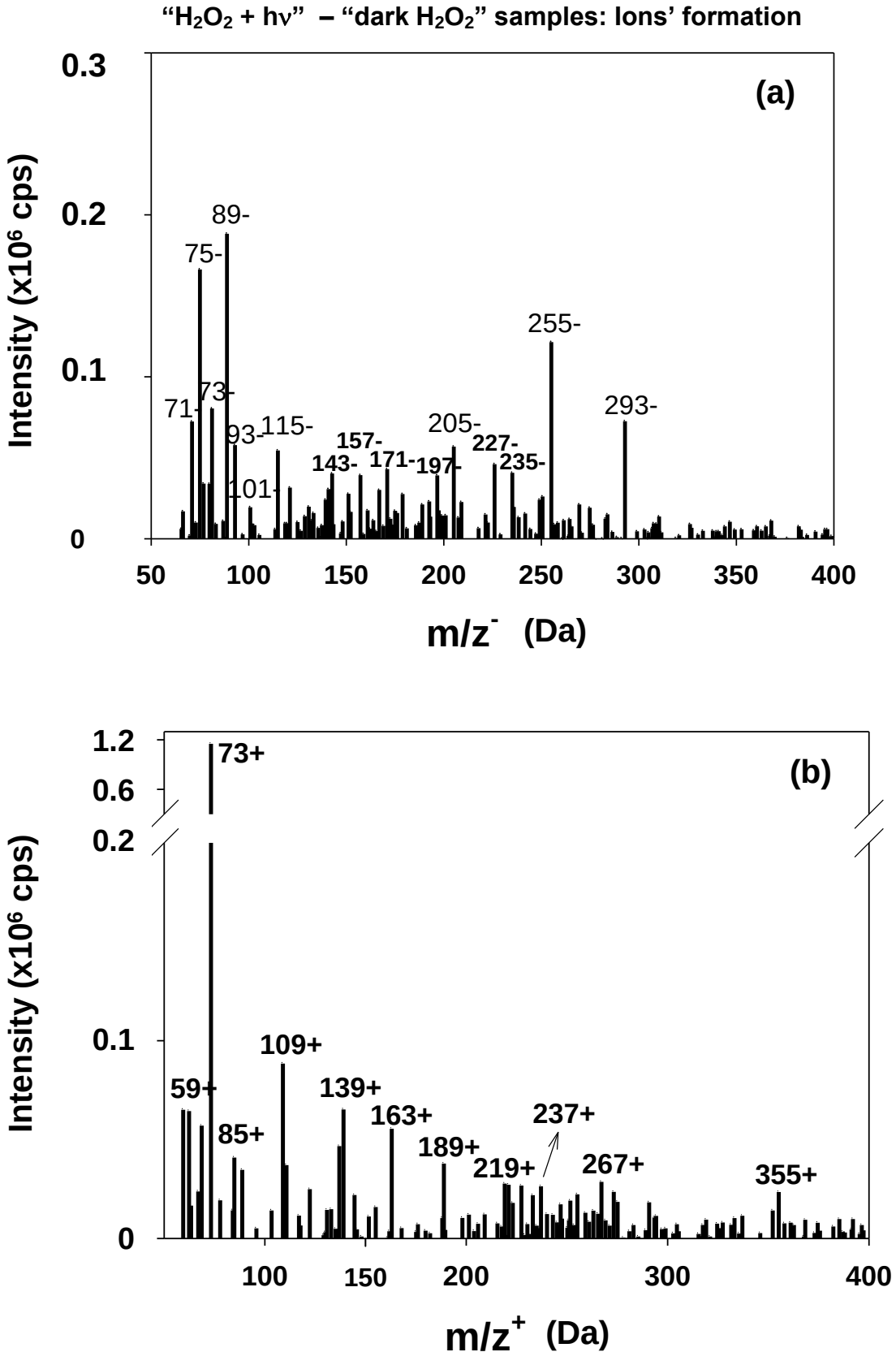


Figure S4 : Isoprene experiment (1). APCI-MS measurements of aqueous solutions by direct infusion of liquid solutions, in the negative mode (a) and in the positive mode (b). Mass spectra differences between "H_2O_2 + hν" samples and "dark H_2O_2" samples show the ions formed during the aqueous phase OH-oxidation of the solution.

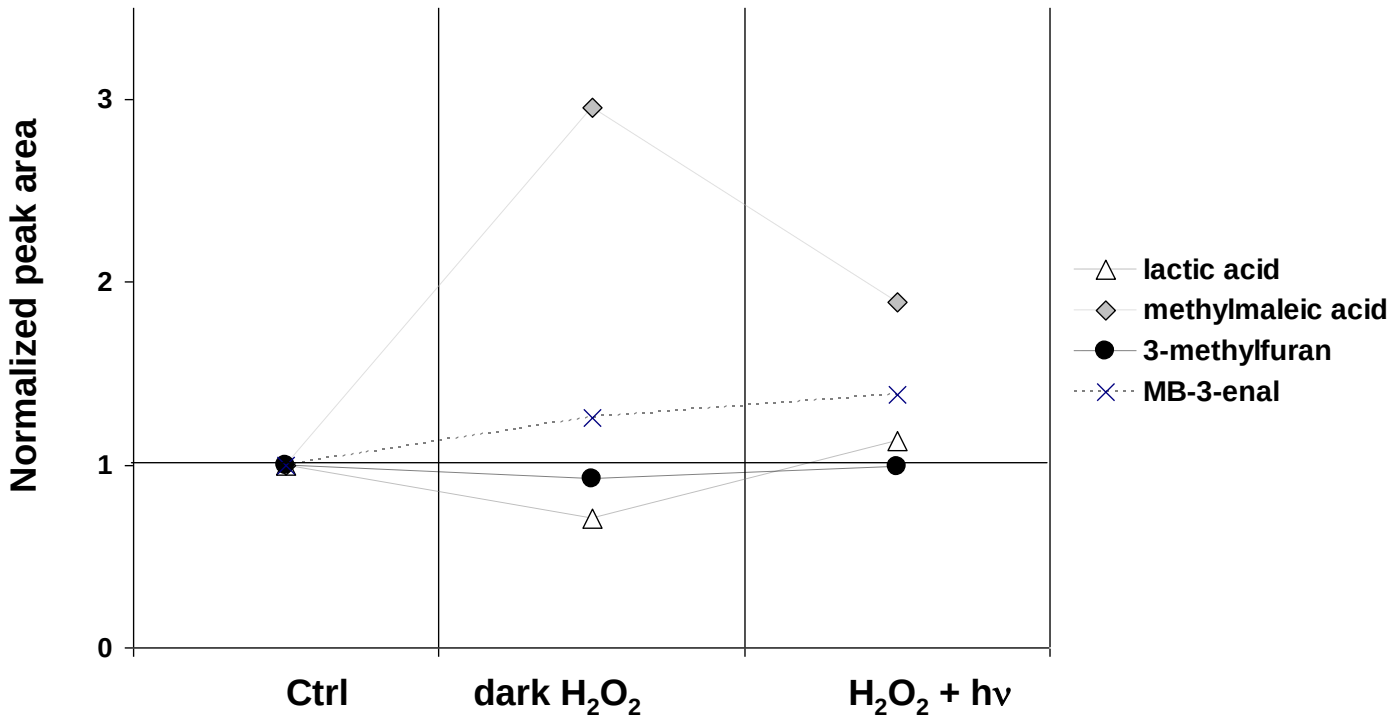


Figure S5: Evolution of four identified and quantified reaction products from "control", "dark H_2O_2" to "H_2O_2 + hν" samples in the mass range 60 – 120 Da (experiment 2). All peak areas were normalized to "control" samples. MB-3-enal = 3-methylbut-3-enal. Quantification was performed using the conditions indicated in Table 1.