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

Supplemental Information:

A streamlined workflow to study direct photodegradation kinetic and transformation products for persistence assessment of a fragrance ingredient in natural waters

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Preparation of stock solutions and test solutions

Aqueous stock solutions of **FI** were freshly prepared by pipetting an equivalent to 5-6 mg of **FI** into a 500 mL volumetric flask using a subtraction weighing method with an analytical balance. Water (18 MΩ) was added to the mark and the solution was sonicated to obtain a homogeneous aqueous stock solution of **FI**. The concentrations of the stock solution, in the range of 10 to 12 mg/L (ppm), were confirmed by GC-MS analysis after extraction with EtOAc using the method described in Section 2.5.2.

Test solutions (20 mL) of **FI** were prepared by pipetting required volumes of its stock solution and 18 MΩ water. The required volume (0.2 mL) of the SRNOM stock solution was also added to the test solutions by pipette to create reconstituted natural water (RNW) for total photodegradation experiments. The concentration of SRNOM in the test solutions was 5.32 mg C/L since in a survey of lakes, rivers, and ponds, humic substances in natural waters were found to be present at concentrations ranging from 0.3 to 30 mg C/L (Shinozuka, 1996). The concentration of **FI** was about 2 mg/L in the test solutions for kinetics experiments, and about 10 mg/L for the investigation of degradation products.

The stock solution of SRNOM was prepared by dissolving 52.0 mg in 50 mL 18 MΩ water at pH 10, with sonication, because the water solubility of SRNOM is higher under alkaline conditions. The pH of the resulting solution was pH 3.2, which was adjusted to pH 8.5 using 1 M aqueous NaOH solution. The stock solution was kept in a refrigerator in amber vials.

The stock solution of pyridine in ACN was prepared by weighing 2.0058 g of pyridine into a 25 mL volumetric flask, adding ACN to the mark and mixing. The resulting pyridine solution (1014.3 mM in ACN) was transferred into a vial and kept in a freezer until use.

The stock solution of PNA in ACN was prepared by weighing 383.45 mg of PNA into a 25 mL volumetric flask, adding ACN to the mark, and shaking to dissolve and mix. The resulting solution (100.1 mM or 15.338 mg/mL PNA in ACN) was transferred into an amber vial and kept in a freezer until use. This stock solution was freshly diluted 100 times in 18 MΩ water to obtain a 1000 μM aqueous solution of PNA to prepare test solutions of actinometer and calibration solutions for LC-UV determination of PNA.

Test solutions (20 mL) of actinometer (PNA/pyridine) were prepared by pipetting required volumes of the stock solutions of PNA (1000 μM in water) and pyridine (1014.3 mM in ACN), and 18 MΩ water into quartz test tubes.

The solution of **FI** for UV-Vis absorbance spectrum measurement was prepared by weighing **FI** (209.22 mg) into a 10 mL volumetric flask, adding HPLC grade ACN to the mark, and thoroughly mixing the contents to obtain 100.4 mM stock solution of **FI** in ACN. This stock solution was diluted 10 times in HPLC grade ACN to obtain a 1.004, 2.008 and 4.016 mM solution of **FI** for UV-vis absorbance spectrum measurement. Additionally, a 2mM solution was prepared in the same way from a separate weighing of **FI**.

The mobile phase solvent A used in UHPLC-HRMS analysis was prepared by weighing 77.08 mg of ammonium acetate into a 1 L HPLC solvent bottle, adding 1 L of 18 MΩ water using a graduated cylinder, and pipetting in 1 mL Optima LC/MS® acetic acid. The contents were thoroughly mixed and the pH of the solution was measured to be pH 3.5.

Quantitative and qualitative GC-MS analysis of ethyl acetate extracts

GC-MS analyses of the EtOAc extracts were performed on an Agilent 6890 gas chromatograph coupled to an Agilent model 5973N mass spectrometer. The system was installed with a Stabilwax®-MS column (30 m × 0.32 mm ID × 0.25 μm film thickness, Restek) at the front injector, and a Rxi-1 MS column (60 m × 0.32 mm ID × 0.25 μm film thickness, Restek) at the back injector. Helium was used as the carrier gas at a constant flow rate of 2.4 mL/min. The injection port was operated in splitless mode and the injection volume was 1 μL. The temperature of the GC injector was 250 °C. The oven temperature program: 70 °C to 180 °C at 8 °C/min, to 240 °C at 20 °C/min, and held at 240 °C for 0.25 min, giving a total run time of 17 min, when using the front polar column; or 110 °C to 240 °C at 8 °C/min, and held at 240 °C for 3.75 min, giving a total run time of 20 min, when using the back apolar column The mass spectrometer was operated in electron impact (EI) mode with an ionization voltage of 70 eV. The temperatures of the quadrupole and ion source were 150 °C and 230 °C, respectively. The MSD transfer line temperature was 280 °C.

For quantitative analysis of **FI**, the back nonpolar column was used and the mass spectrometer was operated in SIM mode monitoring m/z 150 and 208. Quantification was based on external calibration with **FI** standard solutions in EtOAc. Calibration solutions were run after every 12 sample injections.

For qualitative and semi-quantitative analysis of the degradation products, the mass spectrometer was operated in full scan mode with a scan range from m/z 29 to 450. In the preliminary study of the degradation products, the back nonpolar column was used, while the front polar column was used in the improved repeated study of the degradation products.

UHPLC-UV determination of PNA

This was performed using a Dionex™ UltiMate™ 3000 UHPLC system, consisting of an HPG-3400RS pump, a DAD-3000RS detector, a WPS-3000TRS autosampler, a TCC-3000RS column oven and an SRD-3600 degasser. Chromatography was performed on a 10 cm × 2.1 mm, 1.7 μm particle, Waters Acquity BEH C18 column held at 30°C. The mobile phase was 50% MeOH and 50% H_2O with a flow rate of 0.3 mL/min. The DAD wavelength was set at 300 nm with a band width of 4 nm. The sample injection volume was 10 μL. Quantification was based on external calibration with PNA standard solutions in MeOH / H_2O (1/1, v/v).

UHPLC-HRMS analysis of test solutions

LC was performed using a Dionex™ UltiMate™ 3000 UHPLC system, consisting of an HPG-3400RS pump, a WPS-3000TRS autosampler, a TCC-3000RS column oven and an SRD-3600 degasser. Mass spectrometry was performed on a Thermo Scientific™Q Exactive™ quadrupole-Orbitrap™ mass spectrometer.

Chromatography was performed on a 10 cm × 2.1 mm, 1.7 μm particle, Waters Acquity BEH C18 column kept at 30°C. Solvent A was 1 mM NH_4Ac in H_2O / 0.1% HAc (pH 3.6) and solvent B was MeOH. The flow rate was 0.3 ml/min.

The gradient for the characterization of **FI** degradation products was: 35% B increased to 100% B in 10 min; rinsed with 100% B for 2 min, equilibrated with 35% B for 3 min. Sample injection volumes were 25 µL.

The MS analyses were carried out on a Thermo Scientific Q ExactiveTM mass spectrometer using the electrospray technique in the positive ion mode. Positive H-ESI: 3500 V; capillary 320°C; heater 350°C; sheath gas 40; aux gas 8, sweep gas 0. S-lens RF level was 40. Full-scan MS range was m/z 65 to 500. High-resolution accurate mass (HRAM) full-scan MS and top 5 MS/MS spectra were collected in a data-dependent fashion at a resolving power of 70,000 and 17,500 at FWHM m/z 200, respectively. The Stepped NCE (Normalized Collision Energy) setting was 20, 40, 60.

Data analysis was performed using Compound Discoverer 2.0 (Thermo Scientific). A workflow combining both targeted and untargeted analyses was used (Fig. S3).

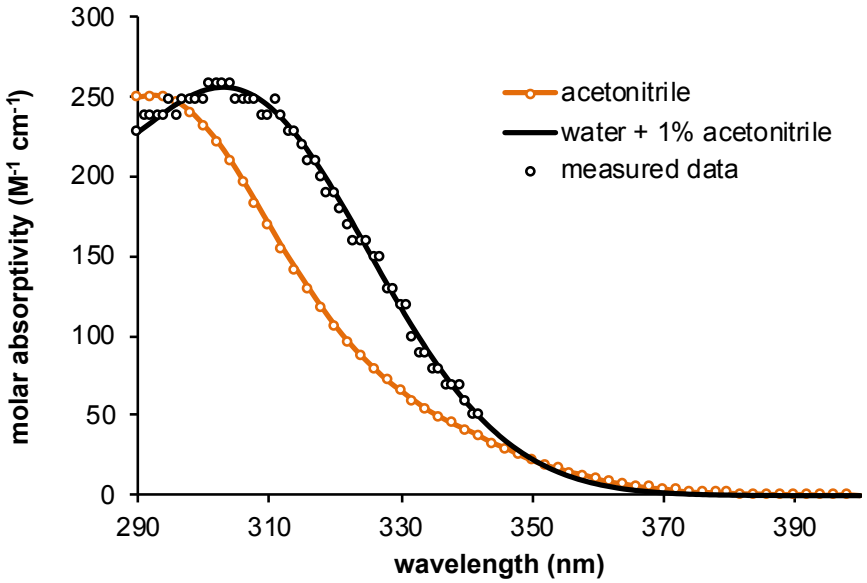


Fig. S1. Molar absorption spectrum of **FI** ($\varepsilon_{\lambda,c}$) in acetonitrile (orange line) and in water containing 1% acetonitrile (black line). The molar absorption spectrum was fit by a gaussian curve to obtain the values below the detection limit of the spectrophotometer.

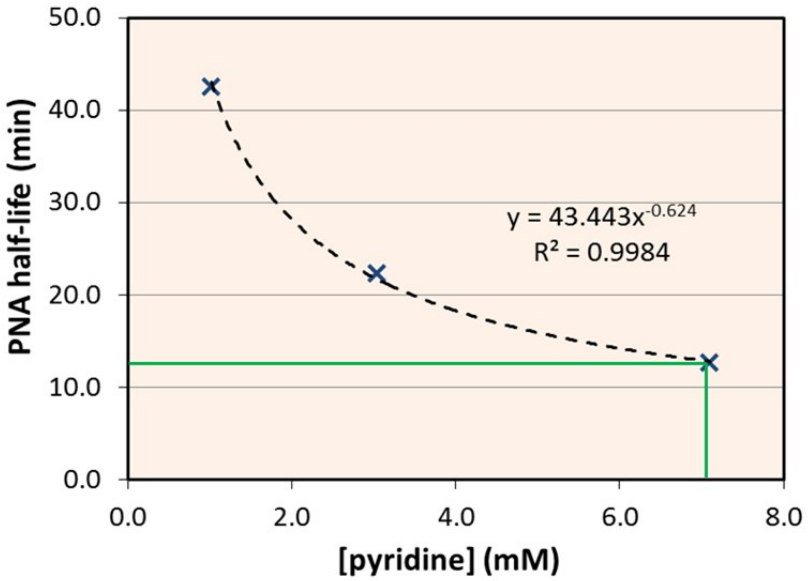


Fig. S2. Relationship between direct photodegradation half-life of PNA and pyridine concentration.

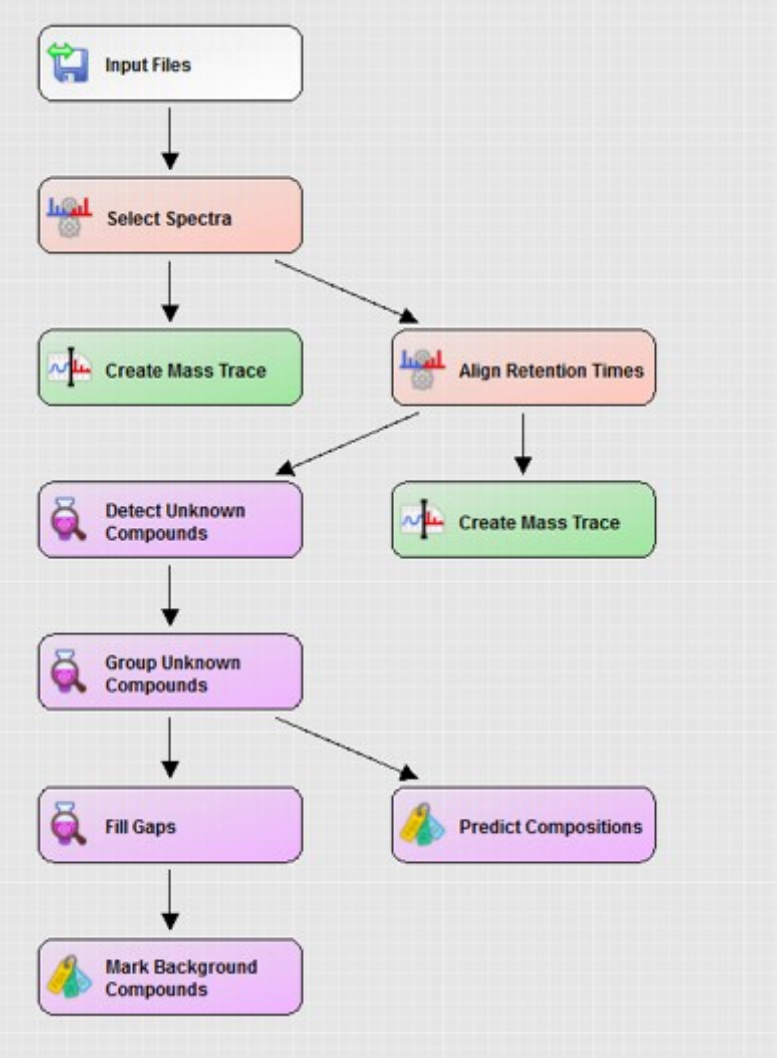


Fig. S3. The untargeted analysis workflow used to process LC-HRMS data in Compound Discoverer 2.0 and determine the molecular formulas of the photodegradation products.

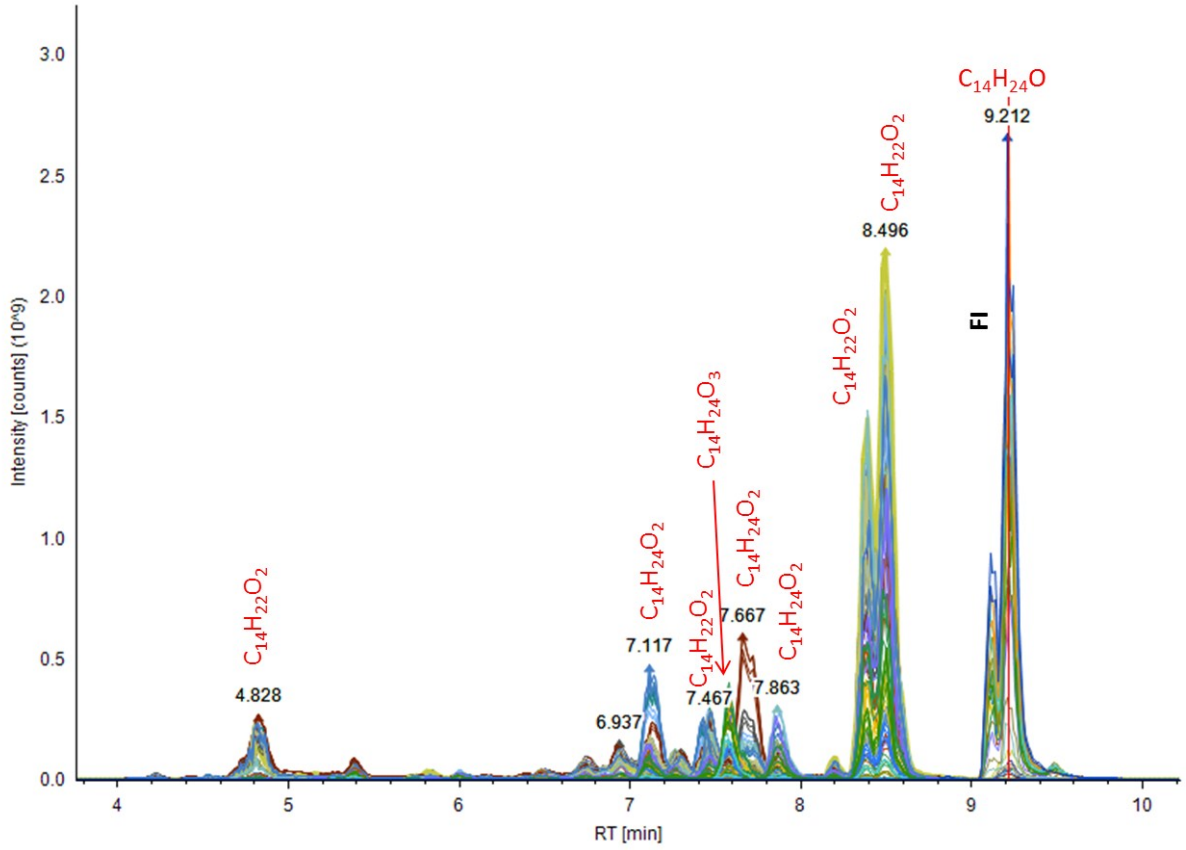


Fig. S4. The overlay of the base peak chromatograms of the ten major photodegradation products of **FI** in pure water or in RNW at all sampling time points.

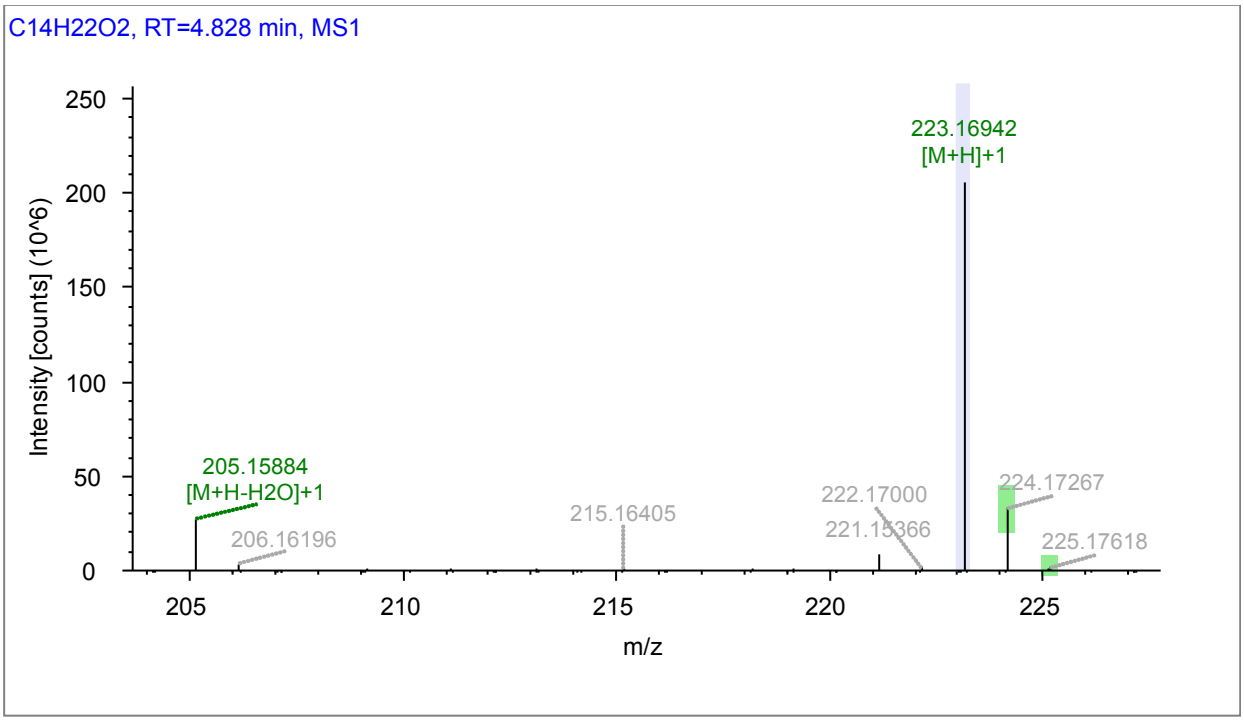


Fig. S5. HRMS spectrum of the photoproduct eluting at RT=4.83 min.

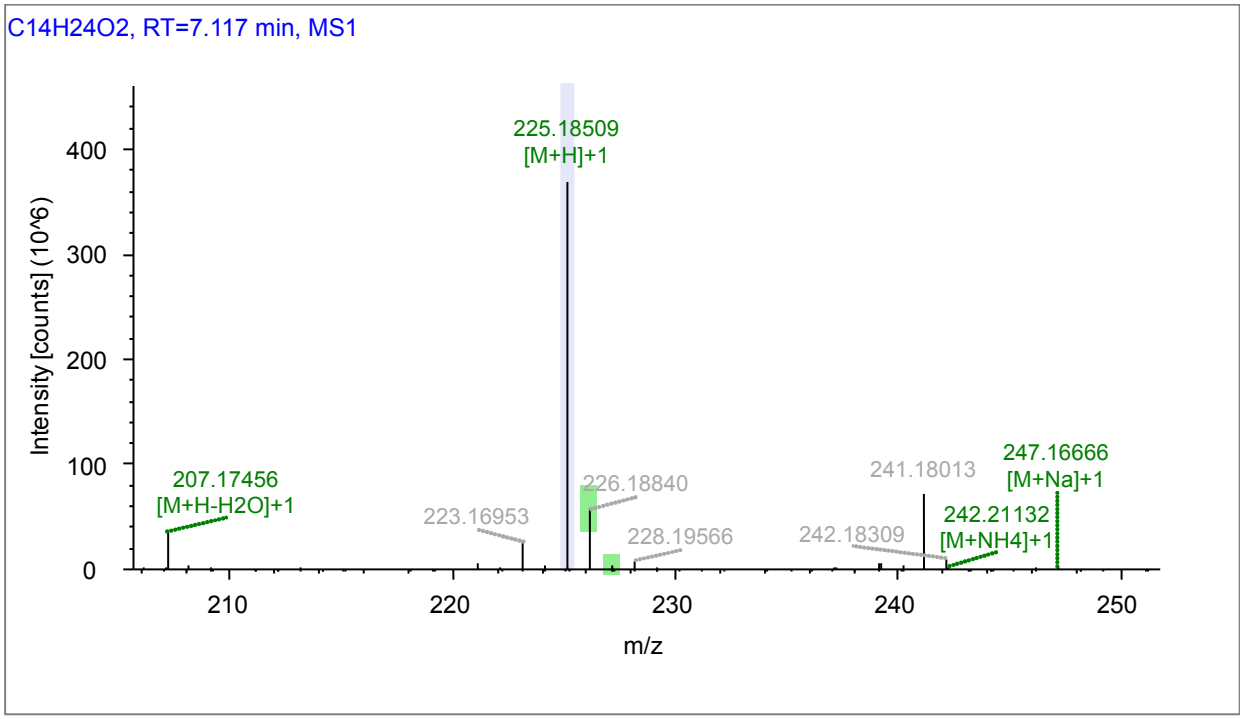


Fig. S6. HRMS spectrum of the photoproduct eluting at RT=7.12 min.

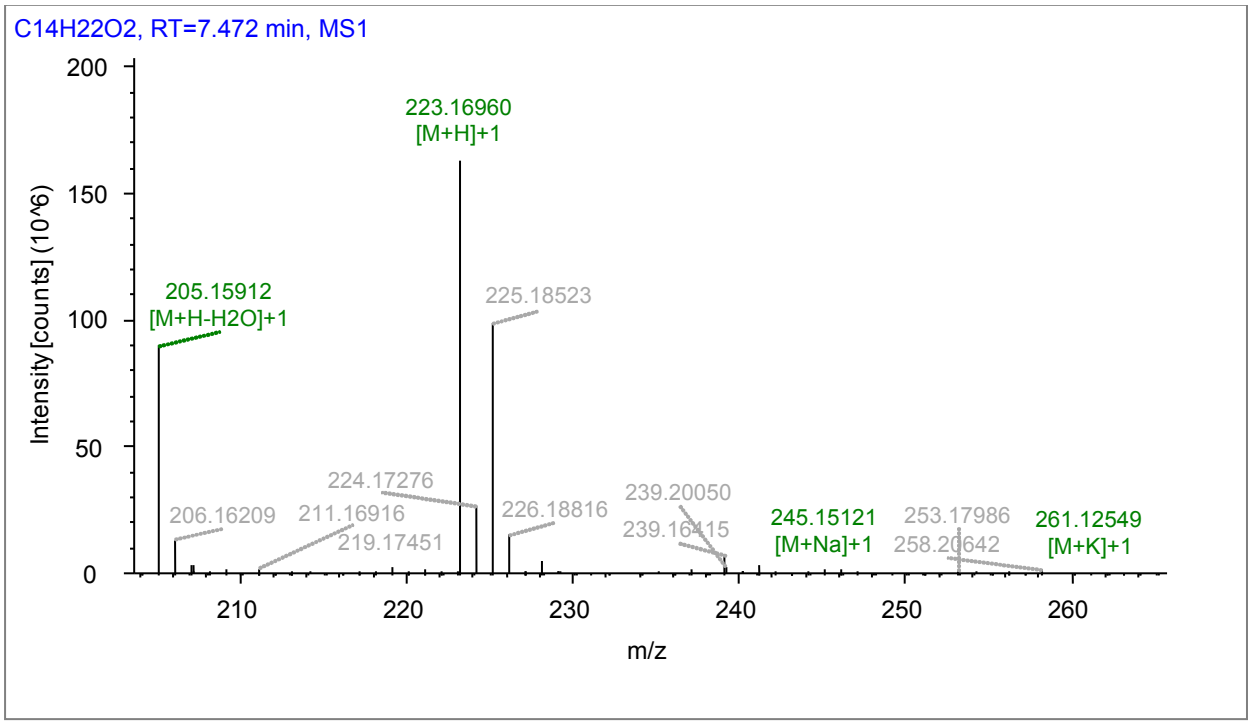


Fig. S7. HRMS spectrum of the photoproduct eluting at RT=7.47 min.

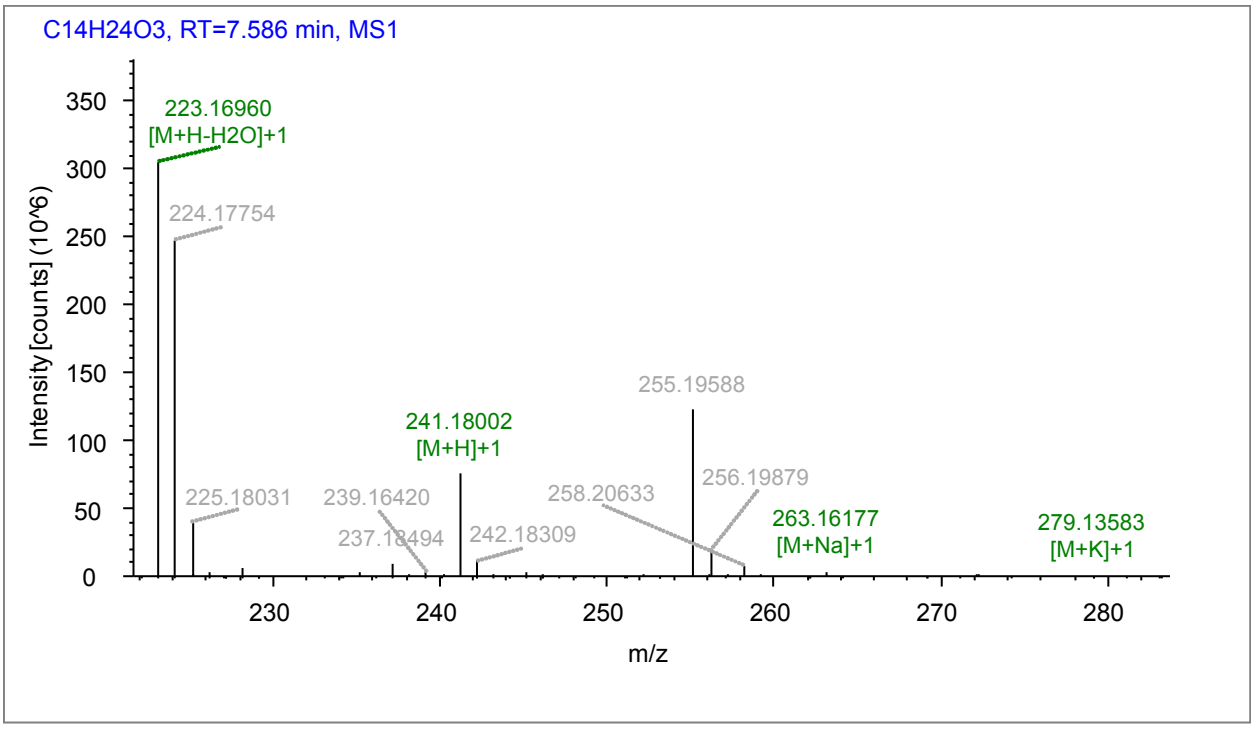


Fig. S8. First HRMS spectrum of the photoproduct eluting at RT=7.58 min.

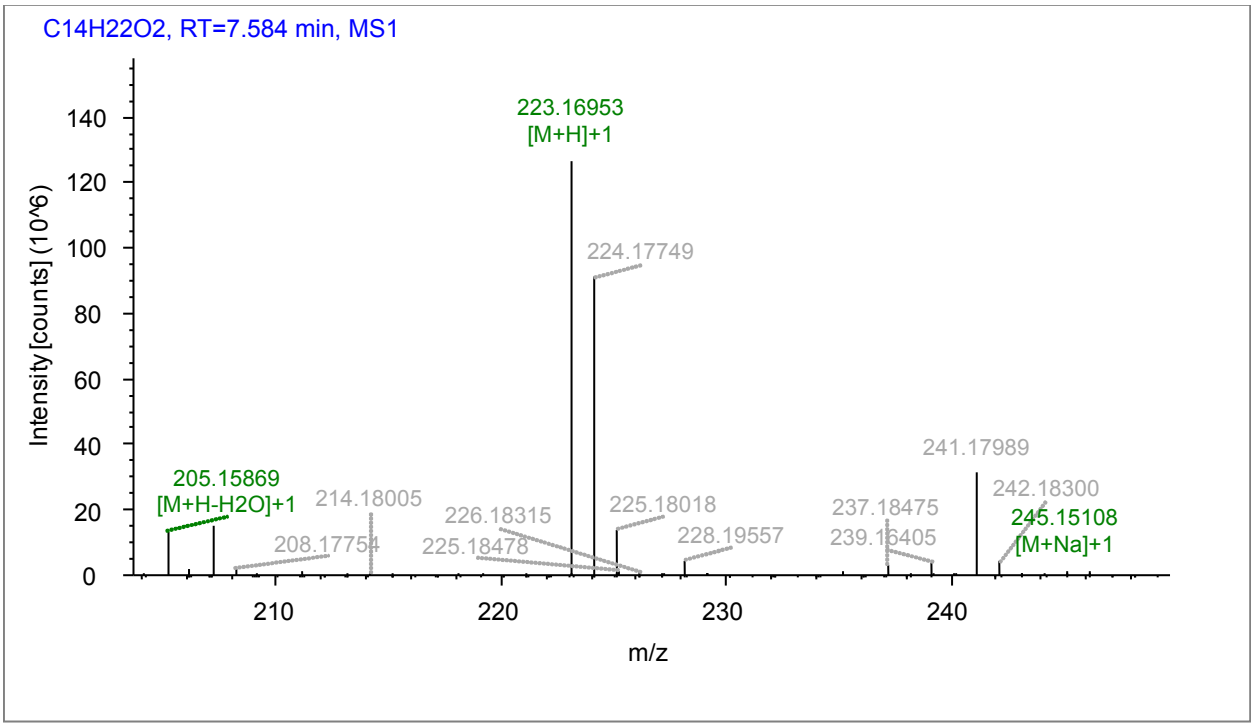


Fig. S9. Second HRMS spectrum of the photoproduct eluting at RT=7.58 min, which is possibly a fragmentation product of the photoproduct shown in Fig. S13.

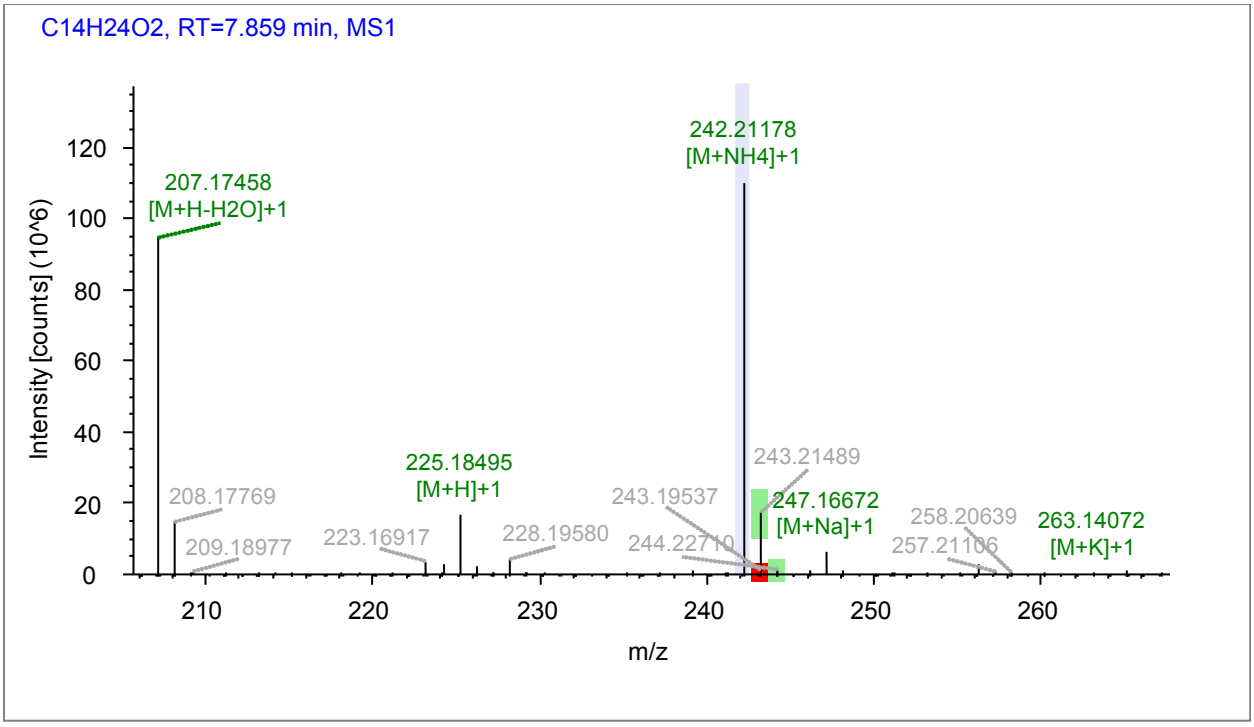


Fig. S10. HRMS spectrum of the photoproduct eluting at RT=7.86 min.

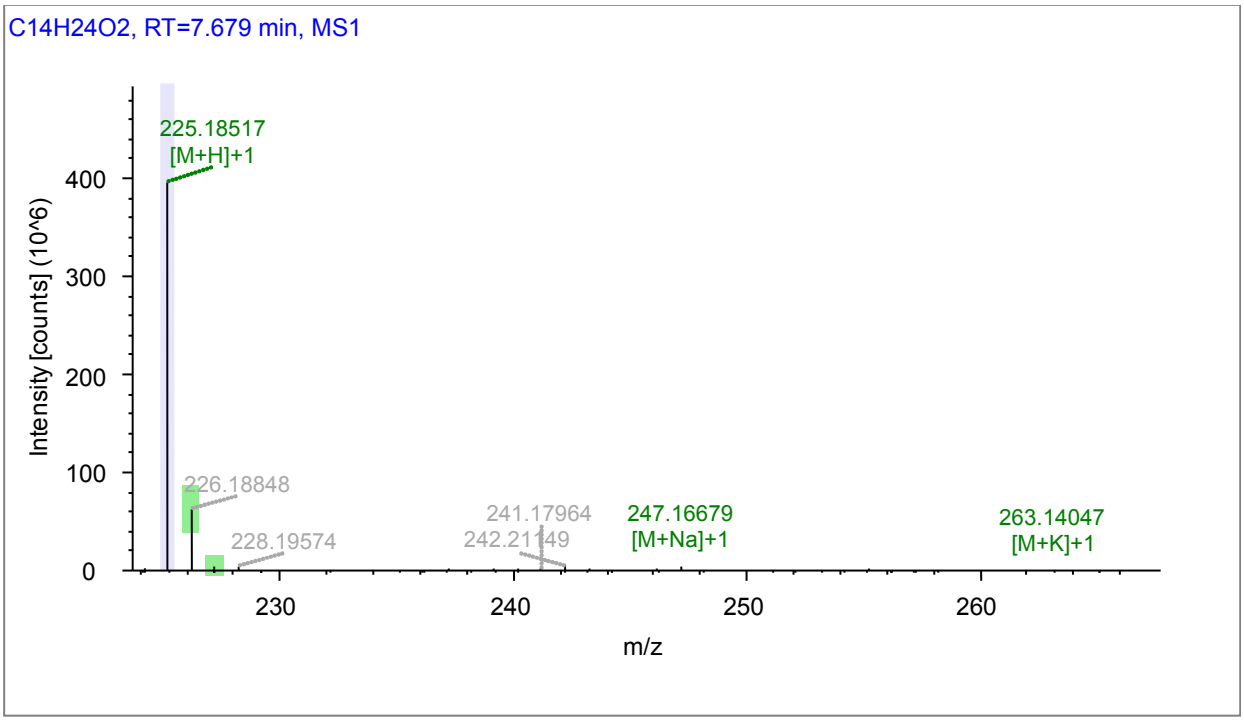


Fig. S11. HRMS spectrum of the photoproduct eluting at RT=7.69 min.

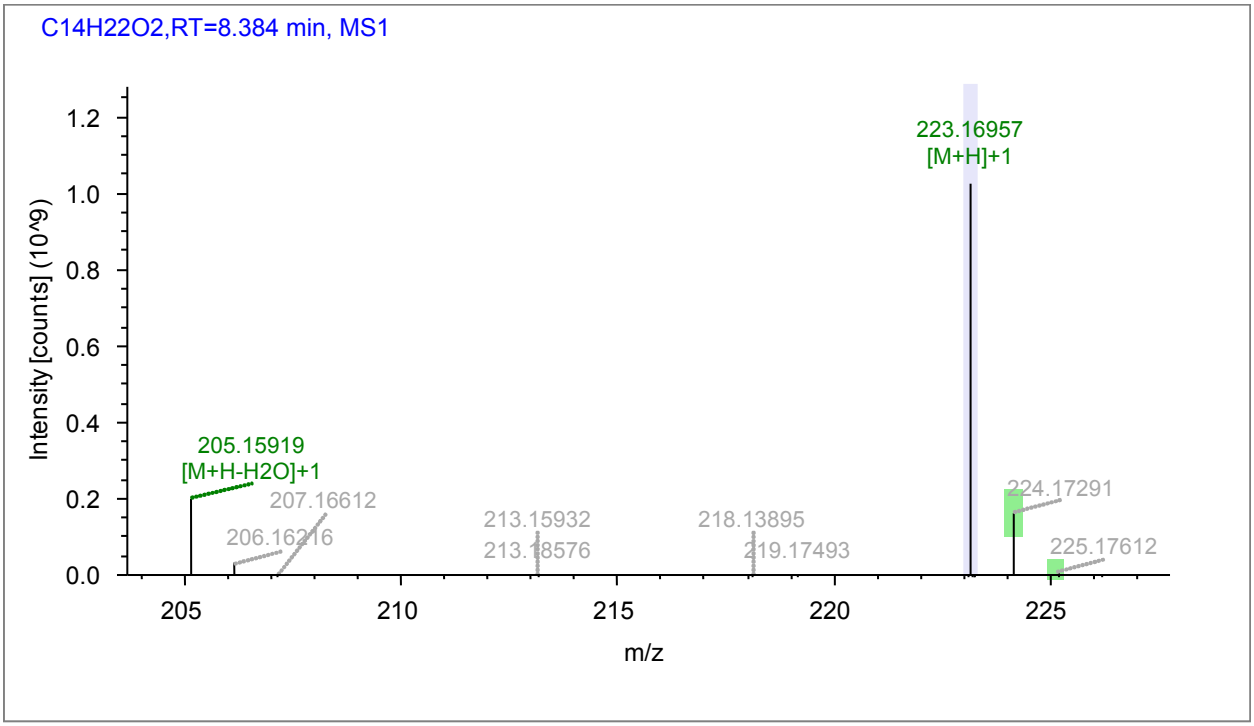


Fig. S12. HRMS spectrum of the photoproduct eluting at RT=8.39 min.

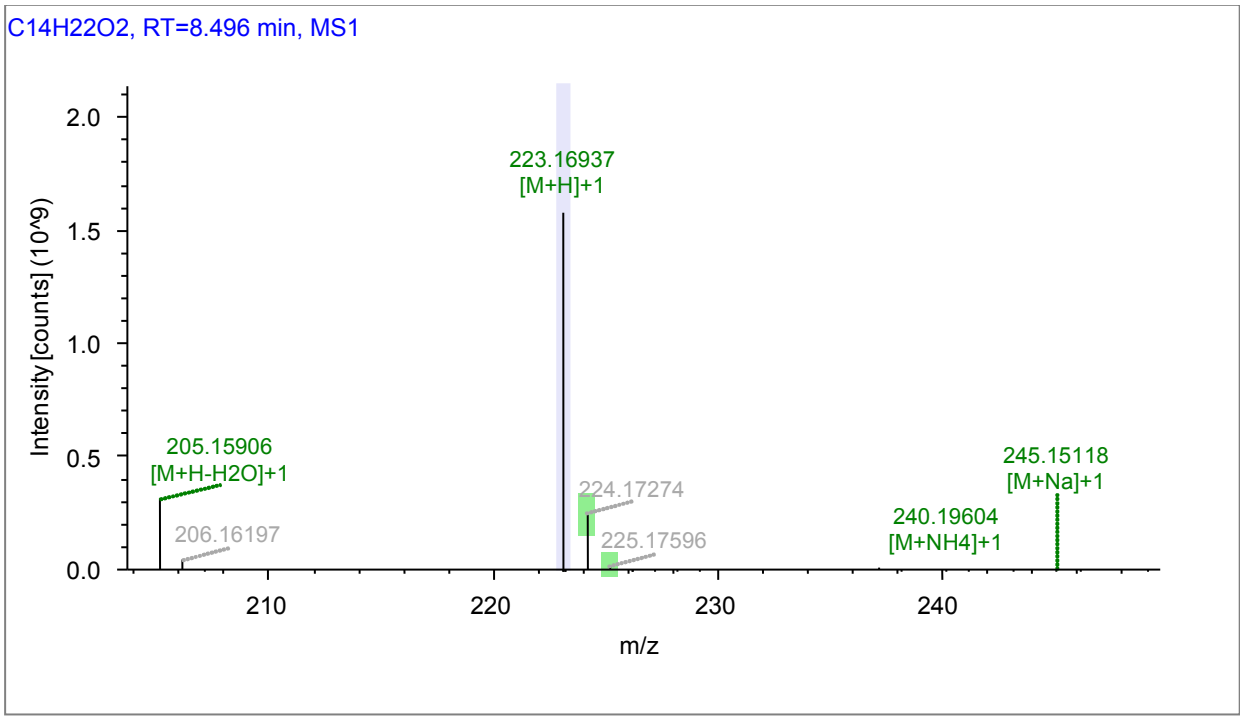


Fig. S13. First HRMS spectrum of the photoproduct eluting at RT=8.50 min.

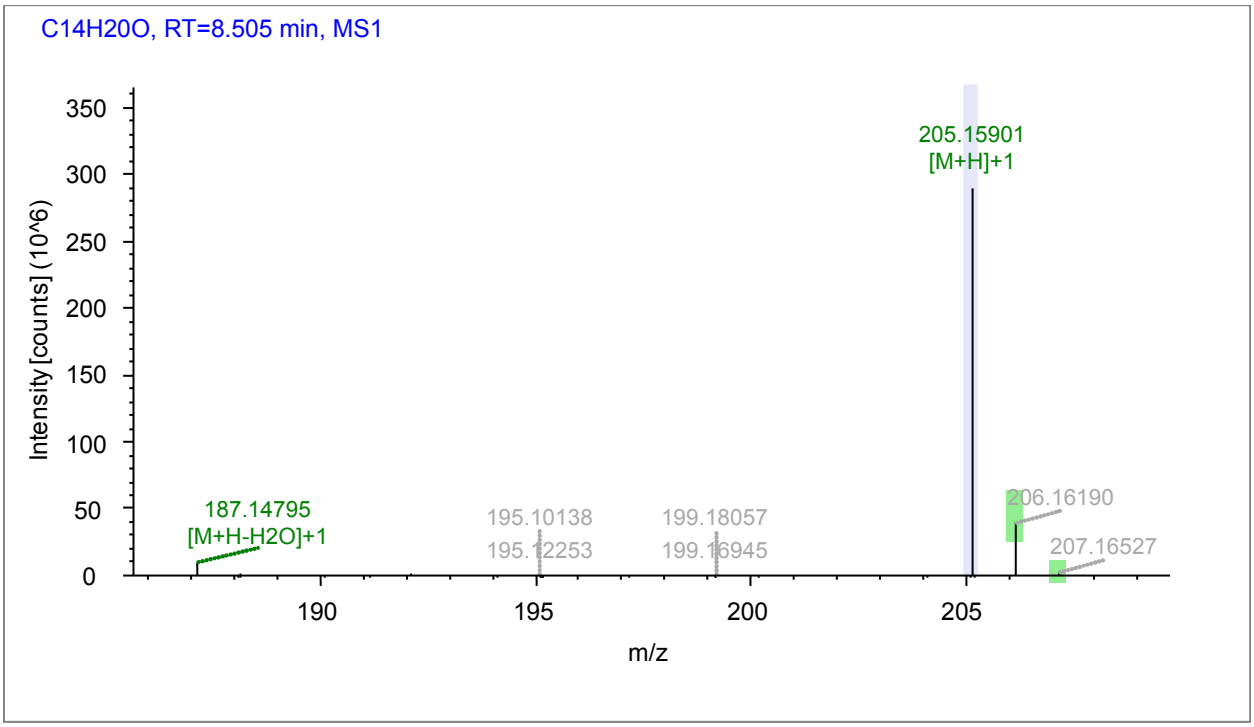
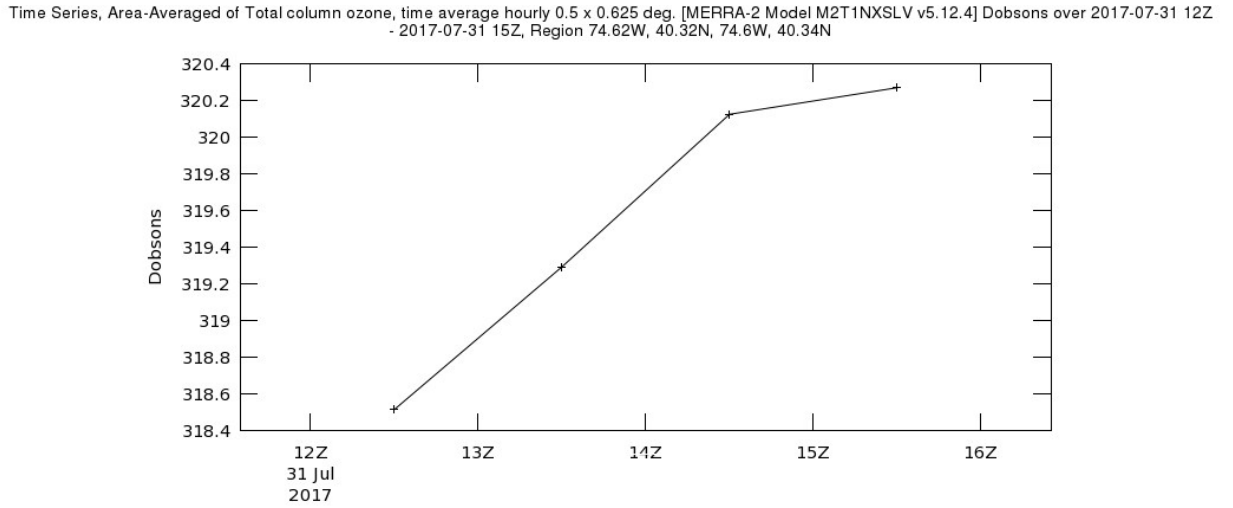


Fig. S14. Second HRMS spectrum of the photoproduct eluting at RT=8.50 min, which is possibly a fragmentation product of the photoproduct shown in Fig. S18.



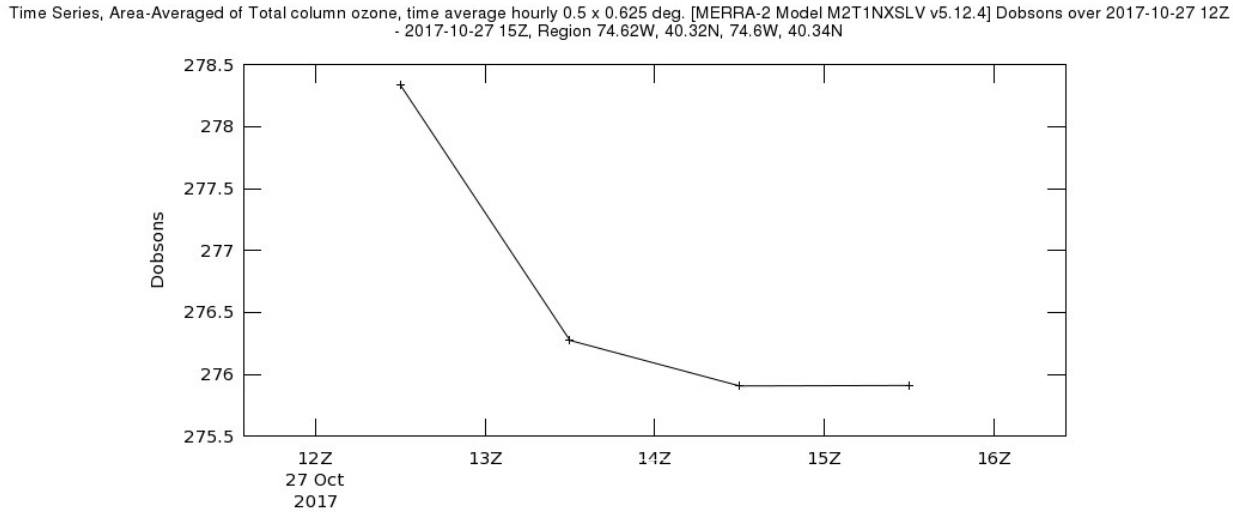


Figure S15. Hourly ozone concentrations (DU) available from remote sensing measurements (accessed at giovanni.gsfc.nasa.gov) from July 31, 2017 and October 27, 2017.

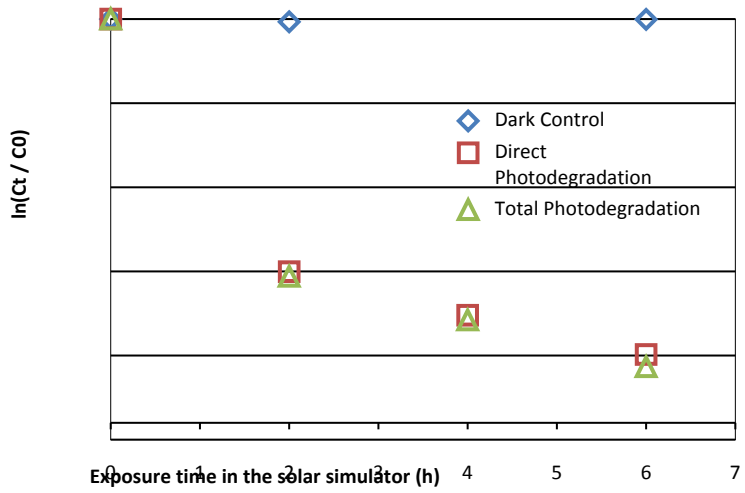


Fig. S16. Semi-logarithmic plot for the photodegradation screening of FI in solutions of pure water (red square) and in solutions containing 5.3 mg C/L of SRNOM (green triangle).

Table S1. Predicted near-surface half-lives (days) for direct photodegradation of **FI** at different northern latitudes in near-surface, clear water conditions.

northern latitude	21-Mar	21-Jun	22-Sep	22-Dec	Yearly Ave
0°	0.07	0.08	0.07	0.08	0.08
10°	0.07	0.07	0.07	0.09	0.08
20°	0.08	0.07	0.08	0.12	0.08
30°	0.09	0.07	0.09	0.19	0.09
40°	0.12	0.07	0.11	0.33	0.11
50°	0.16	0.07	0.15	0.79	0.14
60°	0.24	0.08	0.22	3.9	0.19
70°	0.45	0.09	0.40	--	0.25

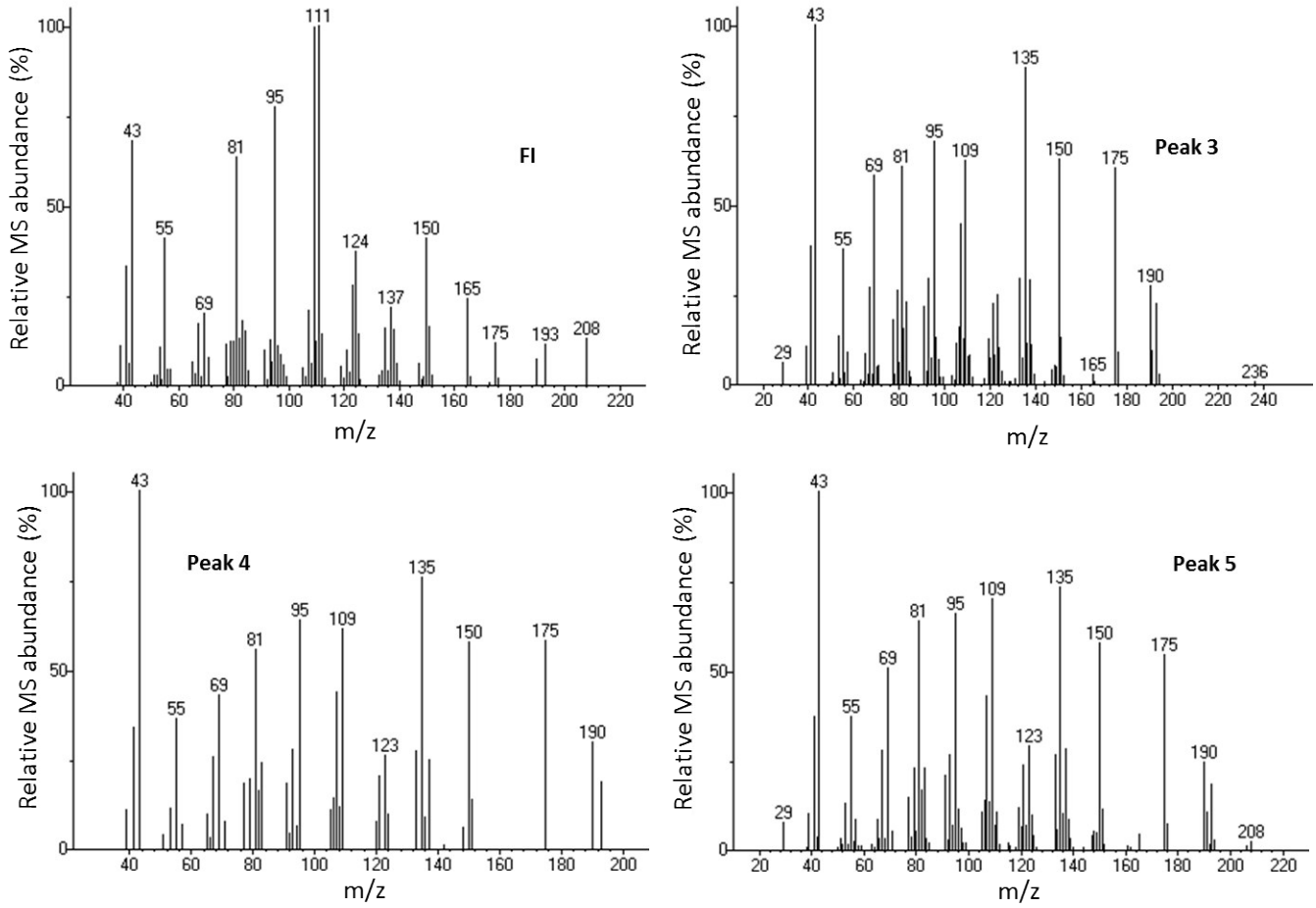


Fig. S17. EI mass spectra of **FI** and the three volatile photodegradation products labeled in Fig. S7.

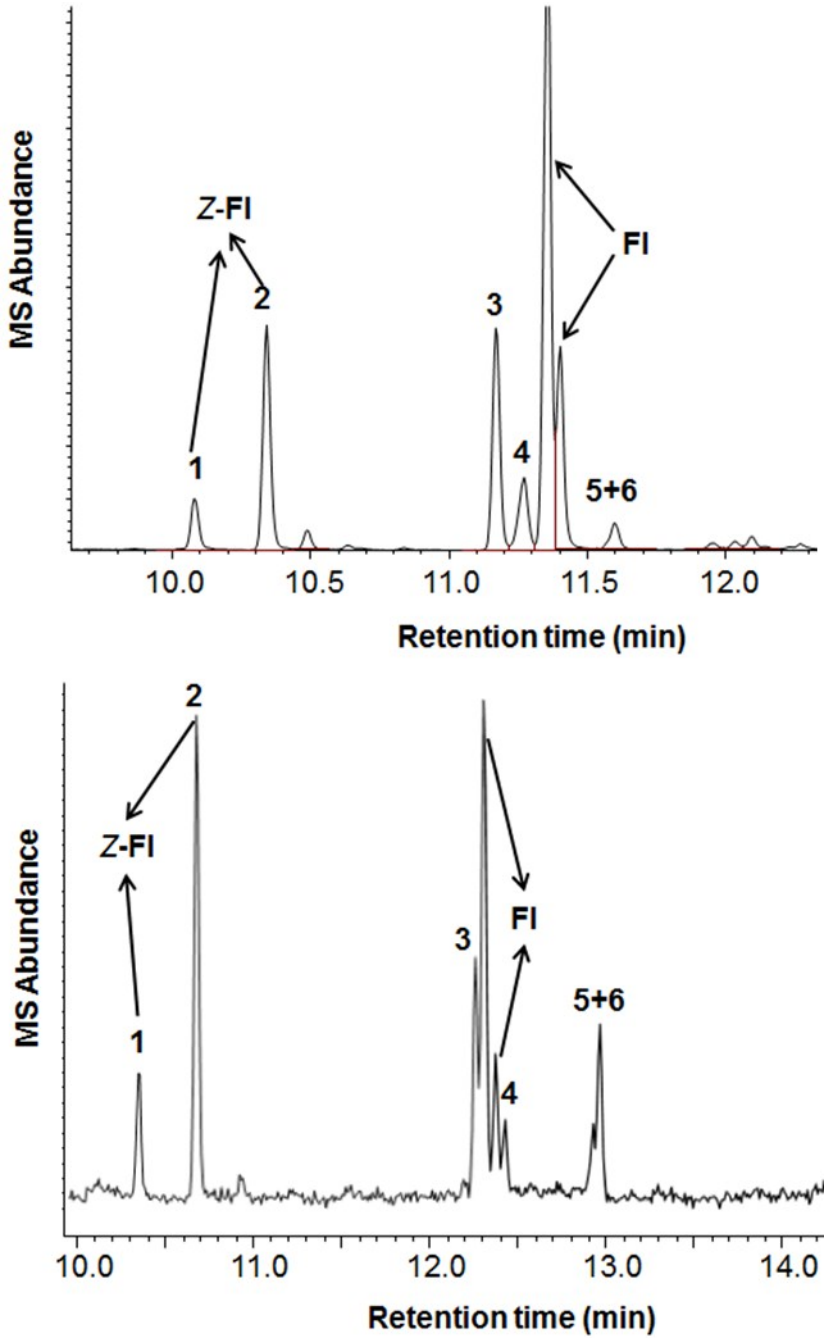


Fig. S18. Photodegradation products of **FI** detected by GC-MS on a non-polar column (top) and on a polar column (bottom). Two different reaction mixtures were injected on the two columns.

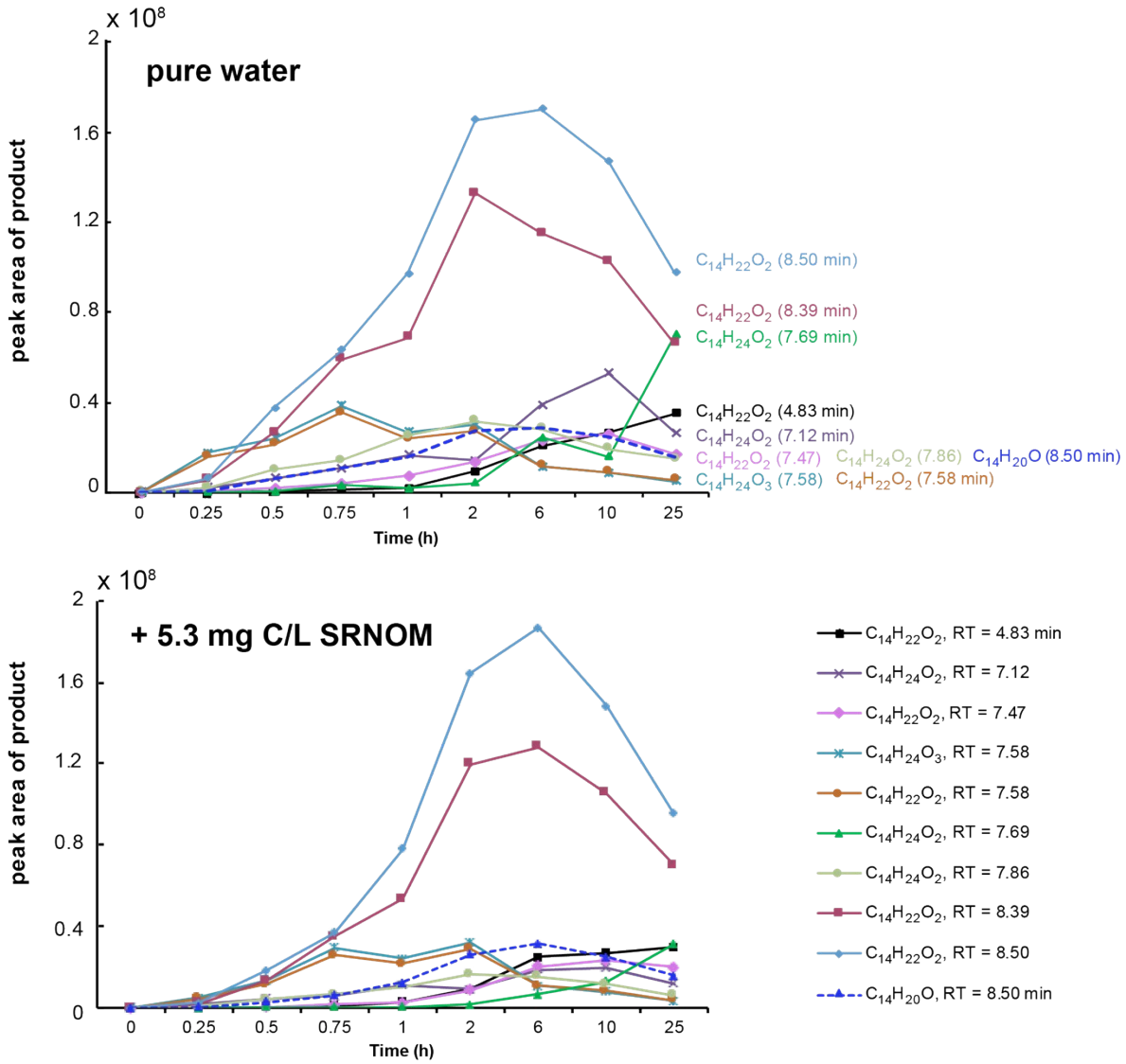


Fig. S19. Time profiles of the ten major photodegradation products of **FI** in pure water (top) or in water containing 5.3 mg C/L SRNOM (bottom) obtained by UHPLC-HRMS analysis.

Table S2. The times that the top ten products reached their maximum levels (T_{max}) in pure water and in RNW, along with their molecular formulae and retention times.

Product	Molecular formula	RT (min)	T_{max} (h) in pure water	T_{max} (h) in RNW
1	$C_{14}H_{22}O_2$	8.50	6	6
2	$C_{14}H_{22}O_2$	8.36	2	6
3	$C_{14}H_{24}O_2$	7.69	> 25	> 25
4	$C_{14}H_{24}O_2$	7.12	10	6
5	$C_{14}H_{24}O_3$	7.58	2	2
6	$C_{14}H_{22}O_2$	7.58	2	2
7	$C_{14}H_{22}O_2$	4.83	> 25	10-25
8	$C_{14}H_{20}O$	8.50	2	6
9	$C_{14}H_{24}O_2$	7.86	2	2
10	$C_{14}H_{22}O_2$	7.47	10	10