Online and Offline Mass Spectrometric Study of the Impact of Oxidation and Ageing on Glyoxal Chemistry and Uptake onto Ammonium Sulfate Aerosols

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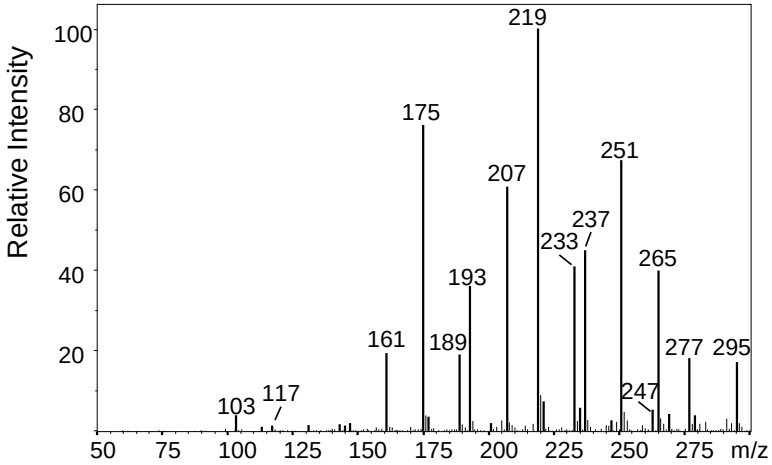
Supplementary Info

Chamber Cleaning

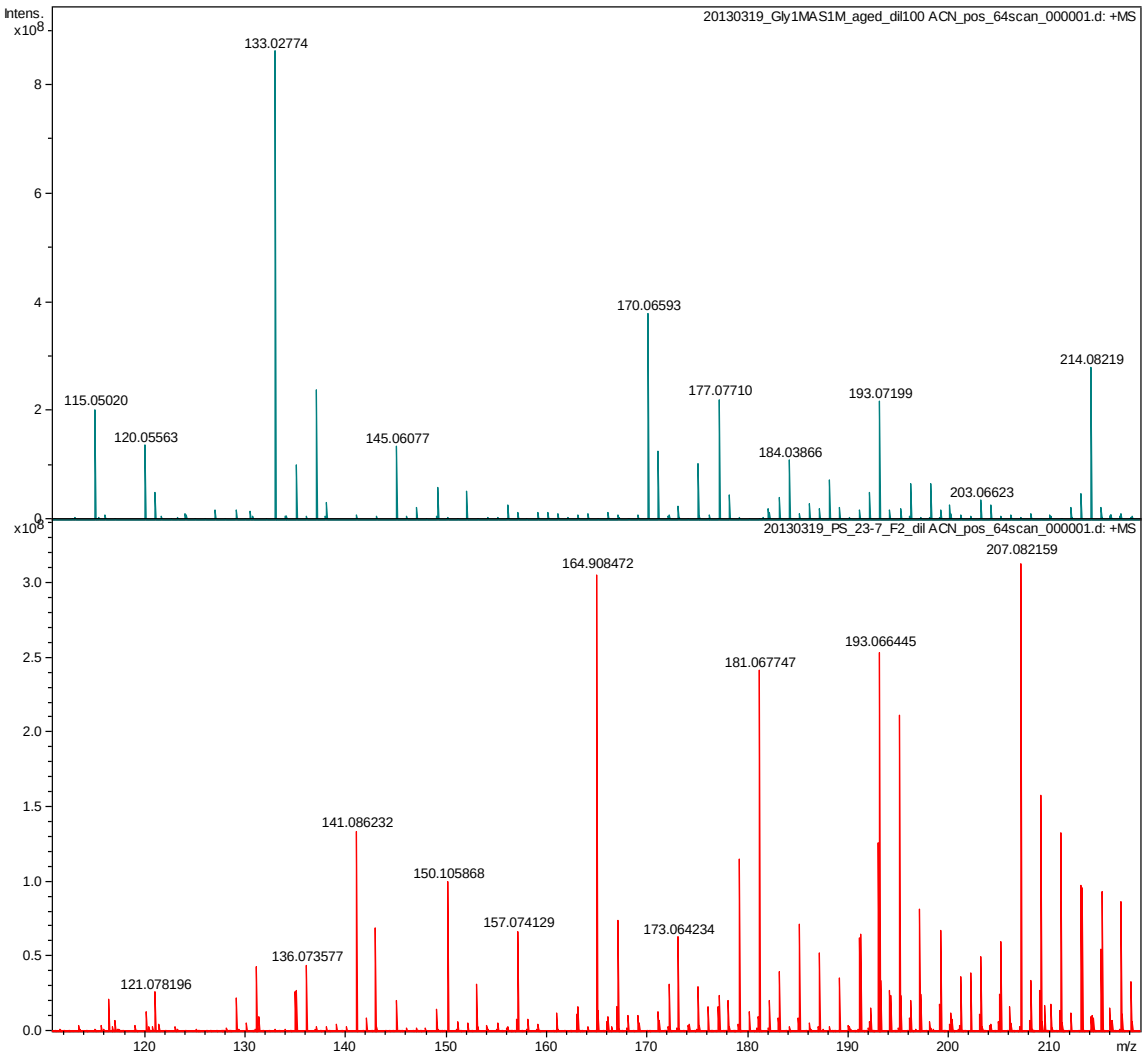
During a preliminary set of experiments at EUPHORE during June 2011, it was found that flushing the chamber with dry air did not produce a sufficiently clean background to carry out this type of experiment. When AS was added to the chamber it began to grow, even without the addition of glyoxal and a background glyoxal signal was detected by Broadband Cavity Enhanced Absoprtion Spectroscopy (BBCEAS). Thus, for the 2012 experiments, an extensive pre-cleaning regime was implemented. This involved cleaning the chamber wall by hand using water on a Friday and flushing over the weekend with high RH clean air

(45 %) prior to the start of the experiment on a Monday morning. The background in the chamber was considerably lower than in 2011 (at or below LOD of BBCEAS for GLY, and aerosol <1 μg m^{-3}) and no growth was seen during the chamber background experiment after correcting for wall loss and dilution.

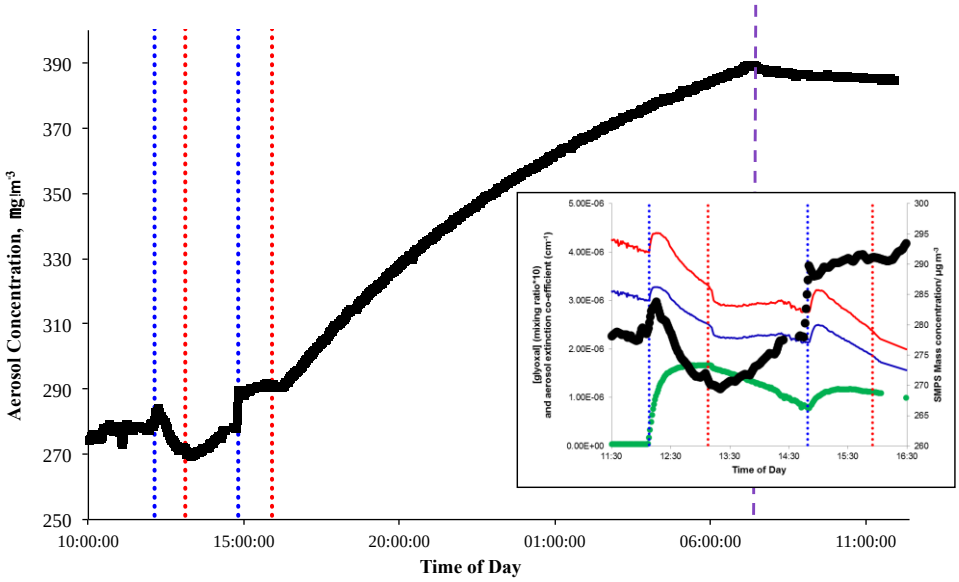
Supplementary figures



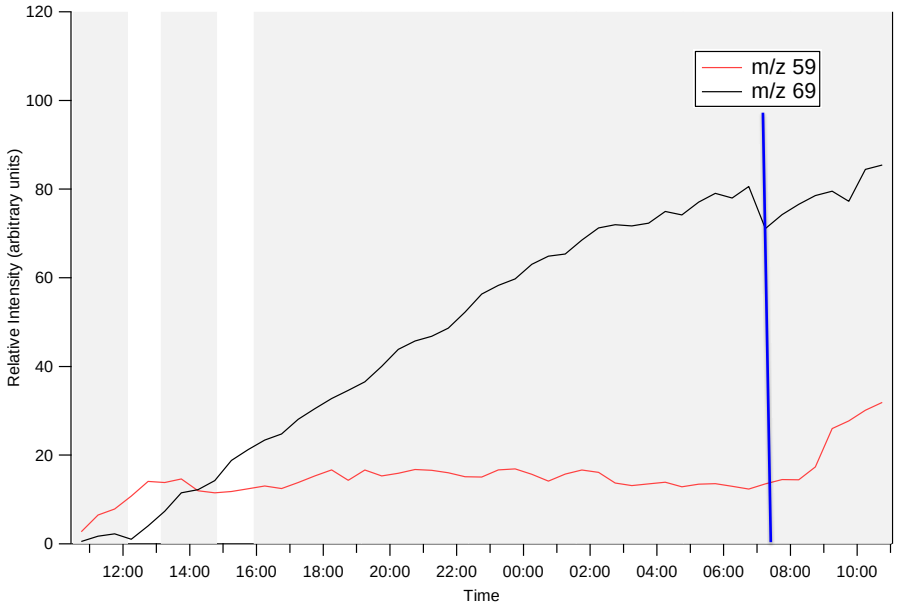
Supp Fig 1: ESI-MS positive ionization mass spectrum of GLY (1M) aqueous laboratory solution, aged 1 week.



Supp Fig 2: FTICR-MS positive ionization mass spectra. Upper: 1 M GLY + 1M AS lab solution (aged 6 months). Lower: Filter F2 aqueous extract from 23/07/12 GLY+AS+HONO+light experiment.

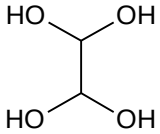
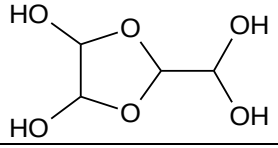
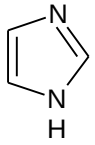
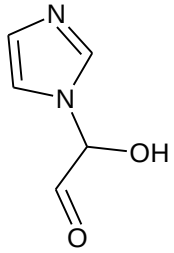


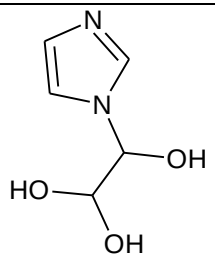
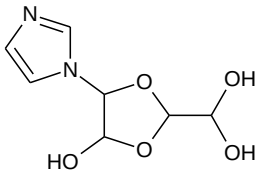
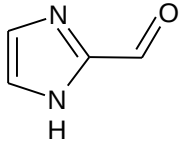
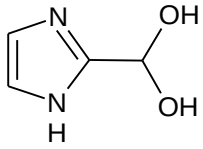
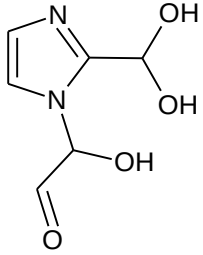
Supp Fig 3a: Main figure: SMPS aerosol mass concentration for 23/07/12 corrected for dilution and wall losses. Inset: Data obtained during the photochemical portion of the experiment. GLY mixing ratio (multiplied by 10; green), aerosol extinction coefficient (red: mean continuum 440 nm and blue: mean continuum 480 nm) and SMPS mass concentrations (black; corrected for dilution and wall loses. Vertical lines indicate the chamber condition; Blue = chamber opened, Red = chamber closed; Purple = chamber flushing begins

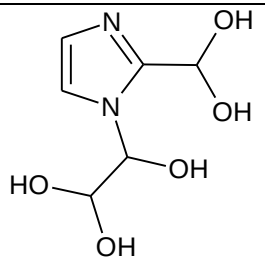
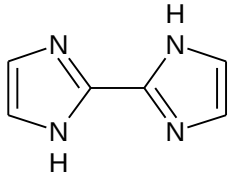
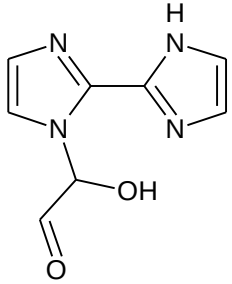
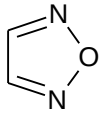


Supp Fig 4: Temporal evolution of ATOFMS *m/z* 59 and *m/z* 69 ions during the experiment on 23-24/07/2012. Shaded grey areas = chamber closed. White shaded areas = chamber open. Vertical blue line = flushing begins.

Supp Table 1: Compound structures and abbreviations of organic nitrogen species

Compound [abbreviation used in the text]	Structure	Formula	ESI-MS *m/z* of $[M+H]^+$	Note
Glyoxal only products				
Di-hydrated glyoxal [Gly+2H_2O]		$C_2H_6O_4$	117 (Na adduct)	a, b
Di-hydrated glyoxal dimer [2Gly+2H_2O]		$C_4H_8O_6$	175 (Na adduct)	a, b
ON products				
1H-Imidazole [IM]		$C_3H_4N_2$	69	a, b
Glyoxal substituted IM [GI]		$C_5H_6O_2N_2$	127	a

Hydrated GI [HGI]		$C_5H_8O_3N_2$	145	a
Hydrated glyoxal dimer substituted IM [HGGI]		$C_7H_{10}O_5N_2$	203	a
1H-Imidazole-2-Carbaldehyde [IC]		$C_4H_4ON_2$	97	a
Hydrated IC [HIC]		$C_4H_6O_2N_2$	115	a, b
Glyoxal substituted HIC [GHIC]		$C_6H_8O_4N_2$	173	a, b

Hydrated GHIC [HGHIC]		$C_6H_{10}O_5N_2$	191	a, b
2,2'-bisimidazole [BI]		$C_6H_6N_4$	135	a, b
Glyoxal substituted BI [GBI]		$C_8H_8O_2N_4$	193	a, b
1,2,5-oxadiazole		$C_2H_2ON_4$	71	b
a) Product found in lab solution b) Product found in chamber experiments				