



Supplement of

Measurements of hydroperoxy radicals (HO_2) at atmospheric concentrations using bromide chemical ionisation mass spectrometry

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Supplementary Information 1 Experimental parameters

| day | H_2O | O_3 | VOC | VOC conc. | NO | NO_2 | CO |
|---------|--------|--------------------|--------------|--------------------|---------------------|--------------------|---------------------|
| 29 May | 1.8% | 140 ppbv | cis-IEPOX | 3.2 ppbv | $0.06\mathrm{ppbv}$ | 1.2 ppbv | 0.03 ppmv |
| 31 May | 1.6% | $50\mathrm{ppbv}$ | isoprene | $5\mathrm{ppbv}$ | $3.0\mathrm{ppbv}$ | $3.2\mathrm{ppbv}$ | $0.05\mathrm{ppmv}$ |
| 01 June | 1.6% | $140\mathrm{ppbv}$ | trans-IEPOX | $1.7\mathrm{ppbv}$ | $0.05\mathrm{ppbv}$ | $1.0\mathrm{ppbv}$ | $0.03\mathrm{ppmv}$ |
| 02 June | 1.7~% | $30\mathrm{ppbv}$ | cis-IEPOX | $4.3\mathrm{ppbv}$ | $3.0\mathrm{ppbv}$ | $1.8\mathrm{ppbv}$ | $0.06\mathrm{ppmv}$ |
| 14 June | 1.8% | $170\mathrm{ppbv}$ | 1,2-ISOPOOH | 2.4 ppbv | $0.06\mathrm{ppbv}$ | 1.3 ppbv | $0.02\mathrm{ppmv}$ |
| 15 June | 2.1% | $190\mathrm{ppbv}$ | 1,2-ISOPOOH | $0.7\mathrm{ppbv}$ | $0.04\mathrm{ppbv}$ | $1.0\mathrm{ppbv}$ | $0.03\mathrm{ppmv}$ |
| 19 June | 1.9% | $70\mathrm{ppbv}$ | none | | $0.14\mathrm{ppbv}$ | $2.1\mathrm{ppbv}$ | $0.9\mathrm{ppmv}$ |
| 20 June | 1.9% | $160\mathrm{ppbv}$ | 1,2-ISOPOOH | $1.9\mathrm{ppbv}$ | $0.04\mathrm{ppbv}$ | $1.2\mathrm{ppbv}$ | $0.04\mathrm{ppmv}$ |
| 21 June | 0.03% | $170\mathrm{ppbv}$ | 1,2-ISOPOOH, | 6.5 ppbv | $0.01\mathrm{ppbv}$ | $0.4\mathrm{ppbv}$ | $0.15\mathrm{ppmv}$ |
| | | | 4,3-ISOPOOH | $1\mathrm{ppbv}$ | | | |
| 22 June | 2.0% | $170\mathrm{ppbv}$ | 4,3-ISOPOOH | $9\mathrm{ppbv}$ | $0.04\mathrm{ppbv}$ | $1.0\mathrm{ppbv}$ | $0.1\mathrm{ppmv}$ |
| 24 June | 1.4% | $160\mathrm{ppbv}$ | none | | $0.06\mathrm{ppbv}$ | $0.8\mathrm{ppbv}$ | $3.0\mathrm{ppmv}$ |
| 26 June | 1.6% | $170\mathrm{ppbv}$ | none | | $0.05\rm ppbv$ | $0.9\mathrm{ppbv}$ | $0.02\mathrm{ppmv}$ |

Table S1. The maximum concentration of reactants present in the reaction chamber during the experiments used for the correlation plots show in the publication. The VOC concentrations for ISOPOOH and IEPOX are preliminary data and are having an higher uncertainty.

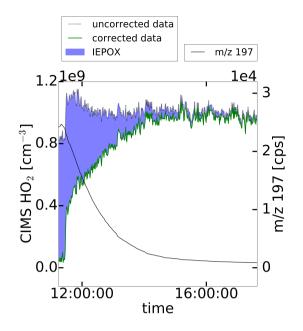


Figure S1. The HO_2 concentrations measured by the CIMS on 29 May, the blue shaded area indicates the correction for the IEPOX interference (see text for details). On the right axis the signal for mass 197 is shown, where IEPOX appears as cluster with bromide in the mass spectrum.

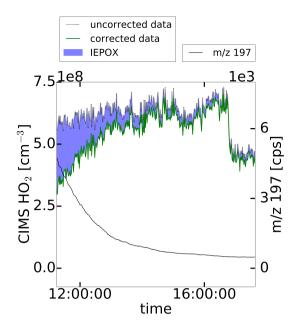


Figure S2. The HO_2 concentrations measured by the CIMS on 01 June, the blue shaded area indicates the correction for the IEPOX interference (see text for details). On the right axis the signal for mass 197 is shown, where IEPOX appears as cluster with bromide in the mass spectrum.

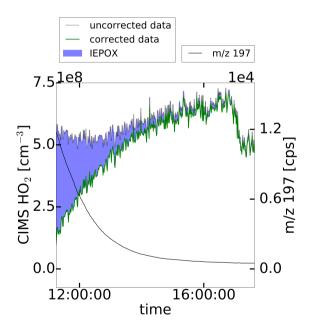


Figure S3. The HO_2 concentrations measured by the CIMS on 02 June, the blue shaded area indicates the correction for the IEPOX interference (see text for details). On the right axis the signal for mass 197 is shown, where IEPOX appears as cluster with bromide in the mass spectrum.

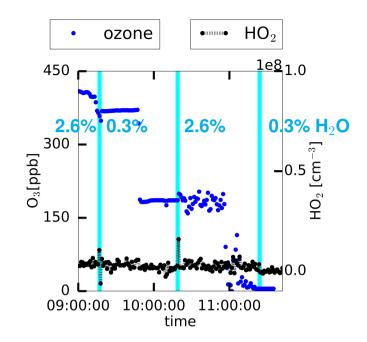


Figure S4. The plot shows the ozone concentration (left axis) applied to the inlet as blue dots and the normalized HO₂ signal (right axis) as black dots connected by a dashed line. The cyan lines indicate a change in the water mixing ratio applied. The water mixing ratio has been changed from 2.6% to 0.3% to 2.6% to 0.3%.

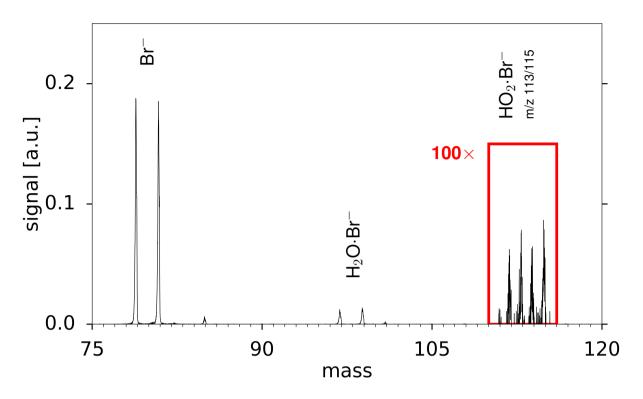


Figure S5. A mass spectrum showing a HO_2 measurement of 21 June, the intensity of masses shown in the red box is multiplied by a factor of 100.