



Supplement of

Measurements of carbonyl compounds around the Arabian Peninsula: overview and model comparison

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Figure S1. Wind map of each area and ship cruise. The number on the left top of each map represents the mean ± standard deviation of the wind speed in each area. The data used for map plotting was from public domain GIS data found on the Natural Earth web site (http://www.naturalearthdata.com) was read into Igor using the IgorGIS XOP beta.



Figure S2. Comparison of (a) benzene and (b) toluene measured by GC-FID and PTR-ToF-MS (data from PTR-Tof-MS was averaged to GC time resolution of 50 min).



Figure S3. Scatter plots between benzene and toluene mixing ratios for Arabian Gulf and Suez. Red dashed line represents the initial emission ratio (values with underlined numbers on the top right of each figure) determined for further OH exposure calculation.



Figure S4. Comparison of model results for carbonyls with and without input of the ethane and propane deep water source in the North Red Sea.



Figure S5. Scatter plots of carbonyls and ozone mixing ratios over the (a) Arabian Gulf (AG) and (b) Red Sea North (RSN).



Figure S6. Scatter plots between dimethyl sulfide (DMS) and acetaldehyde mixing ratios over the eight regions (10 minute average).



Figure S7. Estimated water concentration of acetaldehyde (nM) scaled according to solar radiation. The black dash line indicates the mean level 13.4 nM.



Figure S8. Scatter plots between measured and model simulated mixing ratios for acetaldehyde in different regions without ocean source (graph on the left side of each region labeled with No Ocean) and with ocean emission source (graph on the right side of each region labeled with Ocean E). The data points are further separated into day- and nighttime according to solar radiation.



Figure S9. Time series of ozone mixing ratios and measurement to model ratios of acetaldehyde, propene and ethene over the Arabian Gulf (shaded area represents daytime).

Table S1. Detection limit (LOD) and total uncertainty of standard gas calibrated trace gases during AQABA

| Compounds | Protonated | LOD (mean ± 36) | LOD Range | Total |
|------------------------|------------|-----------------|-----------|-----------------|
| | Masses | (ppt) | (ppt) | Uncertainty (%) |
| Methanol | 33.0335 | 105 ± 40 | 31-302 | 17 |
| Acetonitrile | 42.0339 | 13 ± 3 | 4-23 | 6 |
| Acetaldehyde | 45.0335 | 52 ± 26 | 10-194 | 8 |
| Acetone | 59.0492 | 22 ± 9 | 6-122 | 6 |
| DMS | 63.0263 | 13 ±5 | 2-30 | 12 |
| Isoprene | 69.0699 | 15 ± 10 | 2-98 | 6 |
| Methacrolein/ | 71.0492 | 7 ± 2 | 2-19 | 6 |
| Methyl Vinyl Ketone | | | / | |
| MEK | 73.0648 | 9 ± 6 | 3-80 | 6 |
| Benzene | 79.0543 | 6 ± 2 | 2-16 | 7 |
| Toluene | 93.0699 | 4 ± 1 | 1-8 | 8 |
| Xylene | 107.0856 | 4 ± 1 | 1-10 | 7 |
| 1,3,5-Trimethylbenzene | 121.1012 | 3 ± 1 | 1-13 | 7 |
| α-pinene | 137.1325 | 5 ± 3 | 2-38 | 7 |

Table S2. Protonated masses, chemical formula and limit of detection of carbonyl compounds.

| Protonated | Chemical | LOD Average | LOD Range |
|-----------------|------------------------|-------------|-----------|
| Masses | Formula | (ppt) | (ppt) |
| Aliphatic CCs | $C_nH_{2n}OH^+$ | | |
| 87.0805 | $C_5H_{10}OH^+$ | 10 | 4-28 |
| 101.0961 | $C_6H_{12}OH^+$ | 11 | 3-34 |
| 115.1118 | $C_7H_{14}OH^+$ | 7 | 1-22 |
| 129.1274 | $C_8H_{16}OH^+$ | 6 | 1-24 |
| 143.1431 | $C_9H_{18}OH^+$ | 5 | 1-28 |
| Unsaturated CCs | $C_nH_{2n-2}OH^+$ | | |
| 85.0648 | $C_5H_8OH^+$ | 12 | 3-34 |
| 99.0805 | $C_6H_{10}OH^+$ | 12 | 3-39 |
| 113.0961 | $C_7H_{12}OH^+$ | 6 | 1-19 |
| 127.1118 | $C_8H_{14}OH^+$ | 5 | 1-9 |
| 141.1274 | $C_9H_{16}OH^+$ | 4 | 1-12 |
| Aromatic CCs | CnH2n-8OH ⁺ | | |
| 107.0492 | $C_7H_6OH^+$ | 10 | 3-31 |
| 121.0648 | $C_8H_8OH^+$ | 7 | 2-21 |
| 135.0805 | $C_9H_{10}OH^+$ | 12 | 2-45 |

| Formula | 'ormula Compound | | k (OH) cm ³ molecule ⁻¹ s ⁻¹ at 298K | |
|---------------------|----------------------------------|----------|---|--|
| Alkanes | | | | |
| CH4 | methane* | 74-82-8 | 6.40E-15 | |
| C2H6 | ethane [*] | 74-84-0 | 2.40E-13 | |
| C3H8 | propane [*] | 74-98-6 | 1.10E-12 | |
| C4H10 | i-butane | 75-28-5 | 2.12E-12 | |
| C4H10 | n-butane [*] | 106-97-8 | 2.35E-12 | |
| C5H12 | i-pentane | 78-78-4 | 3.60E-12 | |
| C5H12 | n-pentane | 109-66-0 | 3.80E-12 | |
| C6H14 | i-hexane | 107-83-5 | 5.20E-12 | |
| C6H14 | n-hexane | 110-54-3 | 5.20E-12 | |
| C7H16 | n-heptane | 142-82-5 | 6.76E-12 | |
| C8H18 | octane | 111-65-9 | 8.11E-12 | |
| Alkenes | | | | |
| C2H4 | ethene | | 8.52E-12 | |
| Aliphatic Carbonyls | | | | |
| CH2O | formaldehyde* | 50-00-0 | 8.50E-12 | |
| C2H4O | acetaldehyde [*] | 75-07-0 | 1.50E-11 | |
| C3H6O | acetone* | 67-64-1 | 1.80E-13 | |
| C4H8O | methyl ethyl ketone [*] | 78-93-3 | 1.10E-12 | |
| | 2-pentanone | 107-87-9 | 4.40E-12 | |
| C5H10O | 3-pentanone | 96-22-0 | 2.00E-12 | |
| | 3-methyl-2-butanone | 563-80-4 | 2.90E-12 | |
| | 3,3-dimethyl-2-butanone | 75-97-8 | 1.20E-12 | |
| | 2-hexanone | 591-78-6 | 9.10E-12 | |
| C6H12O | 3-hexanone | 589-38-8 | 6.90E-12 | |
| | 4-methyl-2-pentanone | 108-10-1 | 1.30E-11 | |
| | 3-methyl-2-pentanone | 565-61-7 | 6.90E-12 | |
| | 2,4-dimethyl-3-pentanone | 565-80-0 | 5.00E-12 | |
| C7H14O | 2-heptanone | 110-43-0 | 1.10E-11 | |
| | 5-methyl-2-hexanone | 110-12-3 | 1.00E-11 | |
| C8H16O | 2-octanone | 111-13-7 | 1.10E-11 | |

Table S3. OH rate constant of hydrocarbons and carbonyls mentioned in the study

Compounds marked with * represent k(OH) taken from Atkinson et.al. (2006). Otherwise k (OH) were taken from Atkinson and Arey (2003).

Calculation of acetaldehyde yield from pyruvic acid photolysis

In order to verify the contribution from the photolysis of pyruvic acid to acetaldehyde, we calculated the expected acetaldehyde produced through pyruvic acid photolysis over different regions assuming: (1) m/z 89.0234 is fully assigned to pyruvic acid; (2) the loss of pyruvic acid is only through photolysis; (3) 60% is the yield of acetaldehyde via pyruvic acid photolysis recommended by IUPAC (2019); (4) the loss of acetaldehyde is only through OH oxidation. The acetaldehyde produced via pyruvic acid photolysis can be calculated using following equation (consecutive reactions):

$$[Acetaldehyde] = [Pyruvic acid] \frac{J_{PA}}{k_{OH}[OH] - J_{PA}} [\exp(-J_{PA}\Delta t) - \exp(-k_{OH} \times [OH]\Delta t)]$$
Eq. S1

[*Pyruvic acid*] is the mean of pyruvic acid mixing ratio in each region. J_{PA} represents the mean photolysis rate constant of pyruvic acid during the daytime (dawn to dusk) in each region calculated from the wavelength resolved actinic flux data using quantum yield of 0.2 as suggested by IUPAC (2019). The k_{OH} is the rate constant of acetaldehyde reacting with OH radical (1.5×10^{-11} cm³ molecule⁻¹s⁻¹, Table S3). The [*OH*] concentrations in each area were the mean values during the daytime obtained from the EMAC model. The maximum acetaldehyde level as well as the corresponding time (Δt) can be derived from Eq. S1 as Δt is the only variable. The results are shown in Table S4.

| acetaidenyde yleid from pyruvic acid photolysis, maximum acetaidenyde and its fraction accounting the mean level over regions. | | | | | | |
|--|-----------------------------|-------------------------------------|---|----------------|-------------------------------|---------------|
| Regions | J_{PA} (s ⁻¹) | OH (molecules cm ⁻³) | m/z 89.0234 pyruvic acid (H ⁺) (ppt) | Δt (h) | Acetaldehyde maximum (ppt) | Fractions (%) |
| MS | $3.51 	imes 10^{-5}$ | $6.52 	imes 10^6$ | 39 ± 8 | 5.6 | 5.6 | 1.85 |
| SC | $3.44 	imes 10^{-5}$ | $7.42 	imes 10^6$ | 42 ± 9 | 5.2 | 5.3 | 0.85 |
| RSN | $3.52 	imes 10^{-5}$ | $7.14	imes10^{6}$ | 35 ± 14 | 5.2 | 4.7 | 0.92 |
| RSS | $3.00 	imes 10^{-5}$ | $8.74	imes10^6$ | 61 ± 15 | 4.9 | 6.2 | 1.98 |
| GA | $3.11 	imes 10^{-5}$ | $7.20 	imes 10^6$ | 57 ± 12 | 5.5 | 6.8 | 3.60 |
| AS | $2.74 	imes 10^{-5}$ | $4.35 	imes 10^6$ | 59 ± 12 | 7.8 | 9.4 | 5.88 |
| GO | $3.31 	imes 10^{-5}$ | $7.89 	imes 10^6$ | 65 ± 10 | 5.0 | 7.6 | 2.91 |
| AG | $3.29\times10^{\text{-5}}$ | $7.81 	imes 10^6$ | 110 ± 53 | 5.1 | 12.9 | 0.75 |

Table S4. Mean photolysis rate constant of pyruvic acid, OH concentrations, relative time (Δt) needed to reach the maximum acetaldehyde yield from pyruvic acid photolysis, maximum acetaldehyde and its fraction accounting the mean level over regions

References

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