

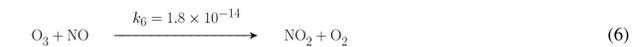
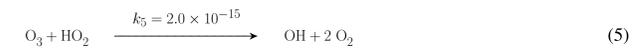
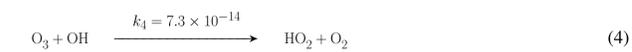
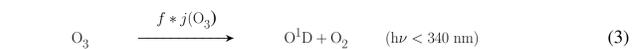
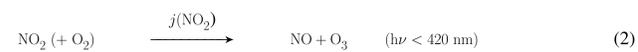
PEROXY RADICAL MEASUREMENTS FROM R/V BROWN DURING TEXAQS 2006

R. SOMMARIVA^{1,2,†}, S.S. BROWN¹, J.M. ROBERTS^{1,2}, A.E. PARKER³, P.S. MONKS³, D.M. BROOKES³, H.D. OSTHOFF^{1,2},
B.M. LERNER^{1,2}, E.J. WILLIAMS^{1,2}, F.C. FEHSENFELD^{1,2}, A.R. RAVISHANKARA^{1,4}, M. TRAINER¹

(1) EARTH SYSTEM RESEARCH LABORATORY, NOAA, BOULDER, CO, USA (2) CIRES, UNIVERSITY OF COLORADO, BOULDER, CO, USA
(3) DEPARTMENT OF CHEMISTRY, UNIVERSITY OF LEICESTER, LEICESTER, UK (4) DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY, UNIVERSITY OF COLORADO, BOULDER, CO, USA

Introduction

- Peroxy radicals are key intermediates of the oxidation of Volatile Organic Compounds (VOCs) in the troposphere. They are formed from the initial reaction of VOCs with OH, NO₃, Cl and O₃, followed by reaction with O₂.
- Peroxy radicals are central to the formation of ozone, because they oxidize NO to NO₂ (Eq. 1), whose photolysis is the only known source of ozone (Eq. 2). Ozone is destroyed instantaneously by photolysis (Eq. 3, where f the fraction of O¹D reacting with water, rather than recombining to form O₃) and by the reactions with OH, HO₂ and NO (Eq. 4–6).



- Measurements of total peroxy radicals, HO₂ + organic peroxy radicals (RO₂), were taken aboard the NOAA vessel *R/V Brown* during the TexAQS–GoMACCS 2006 campaign using a Chemical Amplification technique.
- Together with O₃, NO, NO₂, photolysis rates and the other chemical and physical parameters measured during the campaign, the measurements were used to estimate the Net Photochemical Ozone Production ($N(\text{O}_3)$) in Southern Texas and to study radical chemistry in the lower troposphere.

PERoxy Radical Chemical Amplifier (PERCA)

- The instrument deployed on the *R/V Brown* (Fig. 1, left) was a dual-channel PERCA (PERoxy Radical Chemical Amplifier) designed at the University of East Anglia (UK) and built at the University of Leicester (UK) [Green et al., 2006].
- The Chemical Amplification technique [Cantrell et al., 1984] is based on the radical-catalyzed conversion of NO and CO into NO₂ and CO₂. The yield of NO₂ and CO₂ is equal to $CL * ([\text{OH}] + [\text{HO}_2] + [\text{RO}_2])$, where CL is the chain length, *i.e.* the number of OH/HO₂ inter-conversion cycles that occur before removal of radicals from the inlet by heterogeneous loss on the walls and/or formation of HONO, HNO₃ and HO₂NO₂ (Fig. 1, right).

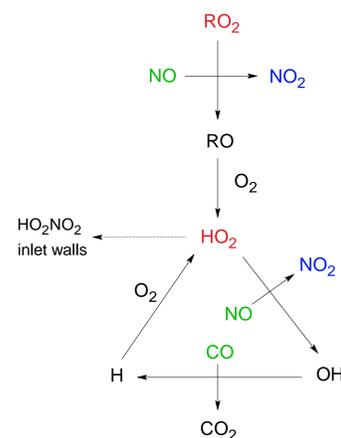
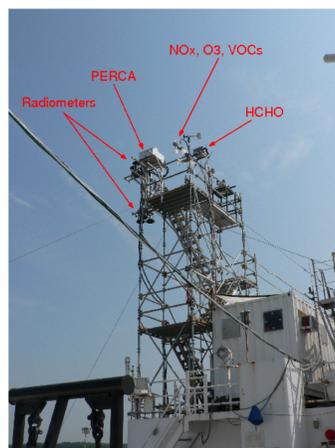


Figure 1: Measurements on the *R/V Brown* (left). Scheme of the Chemical Amplification technique (right).

- NO₂ is measured with a luminol chemiluminescence detector (Scintrex LMA-3). The chain length was calibrated approximately every 3–4 days using CH₃O₂ radicals produced from CH₃I photolysis. The estimated systematic uncertainty in the measurements is about ± 30% [Clemittshaw et al., 1997].
- The chain length is sensitive to temperature and ambient humidity [Salisbury et al., 2002]. The data presented here have **NOT** been corrected for either. Experiments to determine the correction factors for the conditions encountered during TexAQS–GoMACCS 2006 are underway in the laboratory of the University of Leicester.

Total Peroxy Radicals Concentrations

- The diurnal cycles of HO₂+RO₂ measured at different locations during TexAQS–GoMACCS 2006 are shown in Fig. 2.
- On average, the measured concentration of HO₂+RO₂ was 20–40 ppt in the middle of the day and 10–20 ppt during the night. The comparatively little difference between day and night is likely due to day-time suppression of peroxy radicals by high [NO] during most of the cruise.
- The highest concentration during the cruise was 109 ppt, measured on September 7 at Jacinto Point at 9:15 GMT (04:15 LT). The daytime maximum was 86 ppt and was measured on September 7 in the Houston Ship Channel at 20:35 GMT (15:35 LT).

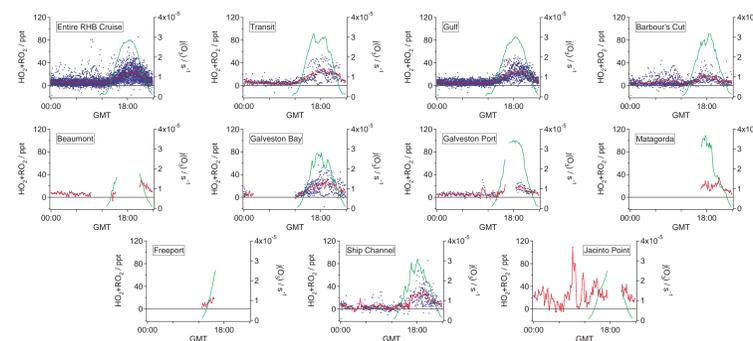


Figure 2: Average diurnal cycles of HO₂+RO₂ at different locations during the *R/V Brown* cruise.

Net Photochemical Ozone Production

- The Net Photochemical Ozone Production is the difference of the *in-situ* O₃ production and loss rates.
- Assuming that only peroxy radicals oxidize NO to NO₂ and that ozone is destroyed only by photolysis and reactions with OH and HO₂, the Net Photochemical Ozone Production ($N(\text{O}_3)$) is:

$$N(\text{O}_3) = (k_p * [\text{NO}] * [\text{HO}_2 + \text{RO}_2]) - (f * j(\text{O}_3) + k_4 * [\text{OH}] + k_5 * [\text{HO}_2]) * [\text{O}_3] \quad (7)$$

- OH was estimated using measured NO₂, $j(\text{O}_3)$ and $j(\text{NO}_2)$ and HO₂ was assumed to be a fraction of measured HO₂+RO₂. A generic rate coefficient (k_p) was used for the reaction of RO₂ with NO ($\sim 8.4 \times 10^{-12}$ molecule cm⁻³ s⁻¹).
- Sensitivity tests showed that $N(\text{O}_3)$ is relatively insensitive to the value of k_p (2–3%), to the concentration of OH (4–5%) and to the HO₂/HO₂+RO₂ ratio (7–10%).

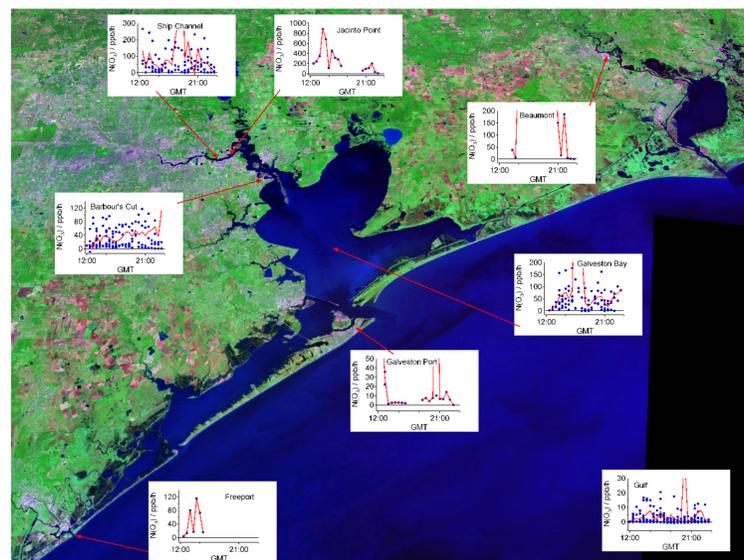


Figure 3: Average Net Photochemical Ozone Production at different locations during the *R/V Brown* cruise.

- Note that some places (Beaumont, Galveston, Freeport, Jacinto Point) were visited only once, so the values shown in Fig. 3 cannot be considered representative.

Case Studies

- Fig. 4 shows three case studies of radical chemistry: a change of chemical regime (from polluted to unpolluted), an example of night-time chemistry and an high ozone event.
- On 10 August (Fig. 4, left) the ship was on the Sabine River, leaving the industrial area of Beaumont towards the Gulf. A storm occurred in the early afternoon stopping photochemical production of radicals. After the storm, radicals increased again due to ozone photolysis. The ship was by now in the Gulf, far from emission sources, and the concentration of radicals was about half than before the storm, with much lower levels of HCHO.

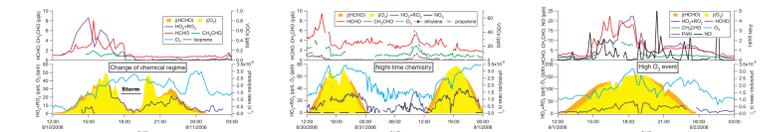


Figure 4: Photochemical activity on August 10 on the Sabine River (left), on August 30–31 in Barbour's Cut (middle) and on September 1 in Galveston Bay (right).

- HO₂+RO₂ concentrations were large (up to 20 ppt) on all nights (see also poster by Osthoff et al.). On the night of August 30–31 (Fig. 4, middle) a plume of hydrocarbons was sampled. Alkenes (*e.g.* ethylene and propylene) reactivity with ozone, and in part with NO₃, generated day-time levels of peroxy radicals (up to 40 ppt) and a large increase of oxidation products, like HCHO and CH₃CHO.
- The highest ozone concentration of the entire cruise (182 ppb) was measured on September 1 in Galveston Bay (Fig. 4, right). Total peroxy radicals peaked at 52 ppt during the event and were well correlated with HCHO, CH₃CHO and PAN. High concentrations of PAN (4.5 ppb) and HCHO (20 ppb) suggest that photochemical production of secondary pollutants occurred upwind, over the continent.

Summary and Future Work

- Measurements of total peroxy radicals (HO₂+RO₂) were made on board the *R/V Brown* during the TexAQS–GoMACCS 2006 campaign using a Chemical Amplification technique.
- The measurements were used to identify case studies of radical chemistry and to estimate the Net Photochemical Ozone Production at different locations. Values of $N(\text{O}_3)$ ranged from < 10 ppb/h in the Gulf up to 200 ppb/h in the Houston Ship Channel.
- The measurements of HO₂+RO₂ need to be corrected for temperature and humidity.
- Data analysis to come: the Photochemical Ozone Production can be estimated from the Photostationary State (PSS) and compared with the one calculated from the total peroxy radicals measurements; $N(\text{O}_3)$ can be correlated with VOCs reactivity and meteorological conditions.
- A box-model based on the MCM and constrained to the measurements will be built and used to model the concentrations of radicals (HO₂+RO₂ and NO₃) for comparison with the measurements, to estimate the concentration of OH, which was not measured during the campaign, and to study the details of the radical chemistry under the conditions encountered during the *R/V Brown* cruise.

Acknowledgements

S. Ciciora, J.A. de Gouw, W.P. Dubé, J.B. Gilman, P.D. Goldan, S.C. Herndon, G. Hübler, W.C. Kuster, H. Stark, T. Thompson, S. Tucker, C. Warneke, D. Welsh-Bon, M.S. Zahniser and the crew of the *R/V Ronald H. Brown*. The satellite picture is a Landsat-7 GeoCover Vis-IR image, courtesy of NASA.

References

- C. A. Cantrell, D. H. Stedman, and G. J. Wendel. Measurement of atmospheric peroxy radicals by chemical amplification. *Analytical Chemistry*, 56:1496–1502, 1984.
- K. C. Clemittshaw, L. J. Carpenter, S. A. Penkett, and M. E. Jenkin. A calibrated peroxy radical chemical amplifier for ground-based tropospheric measurements. *Journal of Geophysical Research*, 102(D21):25405–25416, 1997.
- T. J. Green, C. E. Reeves, Z. L. Fleming, N. Brough, A. R. Rickard, B. J. Bandy, P. S. Monks, and S. A. Penkett. An improved dual channel PERCA instrument for atmospheric measurements of peroxy radicals. *Journal of Environmental Monitoring*, 8:530–536, 2006.
- G. Salisbury, P. S. Monks, S. Bauguitte, B. J. Bandy, and S. A. Penkett. A seasonal comparison of the ozone photochemistry in clean and polluted air masses at Mace Head, Ireland. *Journal of Atmospheric Chemistry*, 41(2):163–187, 2002.