Geophysical Research Abstracts, Vol. 5, 12036, 2003

MEASUREMENT OF PEROXY RADICALS IN THE EUROPEAN MARINE BOUNDARY LAYER WITH A NEW DUAL INLET PERCA INSTRUMENT

Z.L. Fleming (1), P.S. Monks (1), A.R. Rickard (1), N. Brough (2), T.J. Green (2), S.A. Penkett (2)

(1) Department of Chemistry, University of Leicester, UK, (2) School of the Environment, University of East Anglia, UK (zf5@le.ac.uk)

Measurements of peroxy radicals (HO_2 + $\sum RO_2$) carried out with the new dual inlet UEA/Leicester PEroxy Radical Chemical Amplification (PERCA) instrument during the North Atlantic Marine Boundary Layer Experiment (NAMBLEX 2002) are presented.

The PERCA instrument measures HO_2 and the sum of organic peroxy radicals ($\sum RO_2$) by detecting the NO_2 produced from a chain reaction involving CO and NO. The instrument works in two phases termed background and amplification; in background mode the NO added to the inlet reacts only with the ozone present naturally in the atmosphere to form NO_2. In amplification mode this background ozone and the concentration of peroxy radicals that react to form NO_2 are both measured. Using a dual inlet instrument, background and amplification modes are measured simultaneously and hence after subtraction, give the peroxy radical levels on up to a second timescale.

Over thirty days of continued measurements during the NAMBLEX 2002 campaign at the Mace Head Atmospheric Research Station in county Galway, on the west coast of Ireland, show a variety of peroxy radical diurnal cycles, depending on the pollution loads of the air masses (NO_x and VOC levels) and photochemical activity. On the majority of measurement days, clean westerly air masses with low pollutant levels were observed. This clean air resulted in high peroxy radical levels (up to 25 pptv) during the daytime as the OH formed from ozone photolysis reacts with methane and carbon dioxide.

The peroxy radical diurnal cycle generally showed a broader cycle than the ozone

photolysis rate coefficient, j(O^1D), especially in the evenings, where high levels persisted until just before sunset. Photolysis of other compounds such as formaldehyde (or other carbonyls) or nitrous acid appears to be the cause. Peroxy radical concentrations at night indicate that nighttime formation from ozone-alkene and/or NO_3-alkene reactions occurs in the European marine boundary layer.