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Peroxy radical chemistry and the control of ozone photochemistry at Mace Head, Ireland during the summer of 2002

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Abstract. Peroxy radical (HO_2+ΣRO_2) measurements, using the PEroxy Radical Chemical Amplification (PERCA) technique at the North Atlantic Marine Boundary Layer EXperiment (NAMBLEX) at Mace Head in summer 2002, are presented and put into the context of marine, boundary-layer chemistry. A suite of other chemical parameters (NO, NO_2, NO_3, CO, CH_4, O_3, VOCs, peroxides), photolysis frequencies and meteorological measurements, are used to present a detailed analysis of the role of peroxy radicals in tropospheric oxidation cycles and ozone formation. Under the range of conditions encountered the peroxy radical daily maxima varied from 10 to 40 pptv. The diurnal cycles showed an asymmetric shape typically shifted to the afternoon. Using a box model based on the master chemical mechanism the average model measurement agreement was 2.5 across the campaign. The addition of halogen oxides to the model increases the level of model/measurement agreement, apparently by respeciation of HO_x. A good correlation exists between j(HCHO).[HCHO] and the peroxy radicals indicative of the importance of HCHO in the remote atmosphere as a HO_x source, particularly in the afternoon. The peroxy radicals showed a strong dependence on [NO_2] with a break point at 0.1 ppbv, where the radicals increased concomitantly with the reactive VOC loading, this is a lower value than seen at representative urban campaigns. The HO_2/(HO_2+ΣRO_2) ratios are dependent on [NO_x] ranging between 0.2 and 0.6, with the ratio increasing linearly with NO_x. Significant night-time levels of peroxy radicals were measured up to 25 pptv. The contribution of ozone-alkenes and NO_3-alkene chemistry to night-time peroxy radical production was shown to be on average 59 and 41%. The campaign mean net ozone production rate was 0.11±0.3 ppbv h^{-1}. The ozone production rate was strongly dependent on [NO] having linear sensitivity (dln($P(O_3)$)/dln(NO)=1.0). The results imply that the $N(O_3)$ (the in-situ net photochemical rate of ozone production/destruction) will be strongly sensitive in the marine boundary layer to small changes in [NO] which has ramifications for changing NO_x loadings in the European continental boundary layer.

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