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Concentrations of OH and HO₂ radicals during NAMBLEX: measurements and steady state analysis

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Abstract. OH and HO₂ concentrations were measured simultaneously at the Mace Head Atmospheric Research Station in the summer of 2002 during the NAMBLEX (North Atlantic Marine Boundary Layer Experiment) field campaign. OH was measured by laser-induced fluorescence employing the FAGE (Fluorescence Assay by Gas Expansion) technique, with a mean daytime detection limit of 2.7×10^5 molecule cm⁻³ (5 min acquisition period; signal-to-noise ratio = 1). HO₂ was detected as OH following its chemical conversion through addition of NO, with a mean detection limit of 4.4×10^6 molecule cm⁻³. The diurnal variation of OH was measured on 24 days, and that of HO₂ on 17 days. The local solar noon OH concentrations ranged between $(3-8) \times 10^6$ molecule cm⁻³, with a 24 h mean concentration of 9.1×10^5 molecule cm⁻³. The local solar noon HO₂ concentrations were $(0.9-2.1) \times 10^8$ molecule cm⁻³ (3.5–8.2 pptv), with a 24 h mean concentration of 4.2×10^7 molecule cm⁻³ (1.6 pptv). HO₂ radicals in the range $(2-3) \times 10^7$ molecule cm⁻³ were observed at night. During NAMBLEX, a comprehensive suite of supporting measurements enabled a detailed study of the behaviour of HO_x radicals under primarily clean marine conditions. Steady state expressions are used to calculate OH and HO₂ concentrations and to evaluate the effect of different free-radical sources and sinks. The diurnally averaged calculated to measured OH ratio was 1.04 ± 0.36 , but the ratio displays a distinct diurnal variation, being less than 1 during the early morning and late afternoon/evening, and greater than 1 in the middle of the day. For HO₂ there was an overprediction, with the agreement between calculated and measured concentrations improved by including reaction with measured IO and BrO radicals and uptake to aerosols. Increasing the concentration of IO radicals included in the calculations to above that measured by a DOAS instrument with an absorption path located mainly over the ocean, reflecting the domination of the inter-tidal region as an iodine source at Mace Head, led to further improvement. The results are compared with previous measurements at Mace Head, and elsewhere in the remote marine boundary layer.

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