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Night-time radical chemistry during the NAMBLEX campaign

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Abstract. Night-time chemistry in the Marine Boundary Layer has been modelled using a number of observationally constrained zero-dimensional box-models. The models were based upon the Master Chemical Mechanism (MCM) and the measurements were taken during the North Atlantic Marine Boundary Layer Experiment (NAMBLEX) campaign at Mace Head, Ireland in July–September 2002.

The model could reproduce, within the combined uncertainties, the measured concentration of HO_2 (within 30–40%) during the night 31 August–1 September and of HO_2+RO_2 (within 15–30%) during several nights of the campaign. The model always overestimated the NO_3 measurements made by Differential Optical Absorption Spectroscopy (DOAS) by up to an order of magnitude or more, but agreed with the NO_3 Cavity Ring-Down Spectroscopy (CRDS) measurements to within 30–50%. The most likely explanation of the discrepancy between the two instruments and the model is the reaction of the nitrate radical with inhomogeneously distributed NO, which was measured at concentrations of up to 10 ppt, even though this is not enough to fully explain the difference between the DOAS measurements and the model.

A rate of production and destruction analysis showed that radicals were generated during the night mainly by the reaction of ozone with light alkenes. The cycling between HO_2/RO_2 and OH was maintained during the night by the low concentrations of NO and the overall radical concentration was limited by slow loss of peroxy radicals to form peroxides. A strong peak in [NO_2] during the night 31 August–1 September allowed an insight into the radical fluxes and the connections between the HO_x and the NO_3 cycles.

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