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OH and HO₂ chemistry in clean marine air during SOAPEX-2

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Abstract. Model-measurement comparisons of HO_x in extremely clean air ([NO] < 3 ppt) are reported. Measurements were made during the second Southern Ocean Photochemistry Experiment (SOAPEX-2), held in austral summer 1999 at the Cape Grim Baseline Air Pollution Station in north-western Tasmania, Australia.

The free-radical chemistry was studied using a zero-dimensional box-model based upon the Master Chemical Mechanism (MCM). Two versions of the model were used, with different levels of chemical complexity, to explore the role of hydrocarbons upon free-radical budgets under very clean conditions. The "detailed" model was constrained to measurements of CO, CH₄ and 17 NMHCs, while the "simple" model contained only the CO and CH₄ oxidation mechanisms, together with inorganic chemistry. The OH and HO₂ (HO_x) concentrations predicted by the two models agreed to within 5–10%.

The model results were compared with the HO_x concentrations measured by the FAGE (Fluorescence Assay by Gas Expansion) technique during four days of clean Southern Ocean marine boundary layer (MBL) air. The models overestimated OH concentrations by about 10% on two days and about 20% on the other two days. HO₂ concentrations were measured during two of these days and the models overestimated the measured concentrations by about 40%. Better agreement with measured HO₂ was observed by using data from several MBL aerosol measurements to estimate the aerosol surface area and by increasing the HO₂ uptake coefficient to unity. This reduced the modelled HO₂ overestimate by ~40%, with little effect on OH, because of the poor HO₂ to OH conversion at the low ambient NO_x concentrations.

Local sensitivity analysis and Morris One-At-A-Time analysis were performed on the "simple" model, and showed the importance of reliable measurements of j(O¹D) and [HCHO] and of the kinetic parameters that determine the efficiency of O(¹D) to OH and HCHO to HO₂ conversion. A 2σ standard deviation of 30–40% for OH and 25–30% for HO₂ was estimated

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for the model calculations using a Monte Carlo technique coupled with Latin Hypercube Sampling (LHS).

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