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Improved simulation of isoprene oxidation chemistry with the ECHAM5/MESSy chemistry-climate model: lessons from the GABRIEL airborne field campaign

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Abstract. The GABRIEL airborne field measurement campaign, conducted over the Guyanas in October 2005, produced measurements of hydroxyl radical (OH) concentration which are significantly higher than can be simulated using current generation models of atmospheric chemistry. Based on the hypothesis that this "missing OH" is due to an as-yet undiscovered mechanism for recycling OH during the oxidation chain of isoprene, we determine that an OH recycling of about 40–50% (compared with 5–10% in current generation isoprene oxidation mechanisms) is necessary in order for our modelled OH to approach the lower error bounds of the OH observed during GABRIEL. Such a large amount of OH in our model leads to unrealistically low mixing ratios of isoprene. In order for our modelled isoprene mixing ratios to match those observed during the campaign, we also require that the effective rate constant for the reaction of isoprene with OH be reduced by about 50% compared with the lower bound of the range recommended by IUPAC. We show that a reasonable explanation for this lower effective rate constant could be the segregation of isoprene and OH in the mixed layer. Our modelling results are consistent with a global, annual isoprene source of about 500 Tg(C) yr⁻¹, allowing experimentally derived and established isoprene flux rates to be reconciled with global models.

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