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Statistical inference of OH concentrations and air mass dilution rates from successive observations of non-methane hydrocarbons in single air masses

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Bayesian inference has been used to determine rigorous estimates of hydroxyl radical concentrations ([OH]) and air mass dilution rates (K) averaged following air masses between linked observations of non-methane hydrocarbons (NMHCs) spanning the North Atlantic during the ITCT-Lagrangian-2K4 (Intercontinental Transport and Chemical Transformation) experiment (Summer 2004). The Bayesian technique obtains a refined (posterior) distribution of a parameter given data related to the parameter through a model, starting from prior beliefs about the parameter distribution. In this study, the model simply describes the loss of hydrocarbons through reaction with OH and mixing with a background concentration at rate K. The Lagrangian experiment, for the first time, provides direct observations of the hydrocarbon fingerprint at two time-points, rather than relying upon assumptions about composition or sources upwind of a single observation. The parameter estimates are sharpened by using many hydrocarbons with different reactivities and accounting for their variability and measurement uncertainty. A novel technique is used to construct the prior background distribution of many species, described by the variation of a single parameter (alpha), by making use of the high correlation of species in the atmosphere. The background is related to the first principal component obtained from hundreds of whole air sam-

ples collected throughout the Azores region during the ICARTT period. The Bayesian method then obtains posterior estimates of [OH], K and alpha following each air mass. Median [OH] values are typically between 0.5x10ˆ6 and 2.0x10ˆ6 molecule/cm3, but are elevated to between 2.5x10ˆ6 and 3.5x10ˆ6 molecule/cm3, in pollution advected at low levels ahead of a cold front. A comparison of [OH] estimates from absolute NMHC concentrations and NMHC ratios assuming zero background (the ‘‘photochemical clock” method) shows similar distributions, but reveals a systematic high bias in the estimates from ratios, compared with those from absolute concentrations. Estimates of K are on the order 0.1 dayˆ-1 but show more sensitivity to the prior distribution assumed. These results have important implications for previous [OH] and K estimates derived from less well-constrained NMHC concentration changes, and ad hoc choices of constant background concentrations.