Supplement of Atmos. Chem. Phys., 15, 1289–1298, 2015
http://www.atmos-chem-phys.net/15/1289/2015/
doi:10.5194/acp-15-1289-2015-supplement
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Atmospheric Chemistry and Physics Open Access

Supplement of

Evidence for an unidentified non-photochemical ground-level source of formaldehyde in the Po Valley with potential implications for ozone production

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Additional consideration of deposition

In the base case scenario, the model is constrained to all measurements with the exception of HCHO. Given the extensive constraints, deposition, emission, and advection are not treated explicitly. While such simplification is commonly performed in box models, the coupling between the surface layer and the overlying atmosphere can drive the behavior of many trace gases while chemistry plays a smaller role. The assumption is that with small enough time steps, constraining calculations to observed mixing ratios is functionally equivalent to having an inflow or outflow rate that accounts for net flux from the surface or emission sources. However, the impact on species that are not constrained could be a function of what the model sources and sinks of a given other species. For example, if an unconstrained HCHO precursor has a high deposition rate which is neglected, the model may overestimate loss to oxidation and create high concentrations of unconstrained oxidation products. This could lead to HCHO production, while deposition would not lead to HCHO formation. Furthermore, reaction with OH would be over-expressed, leading to erroneously high calculated OH reactivity.

To investigate the effect of neglecting model deposition, a model scenario which includes dry deposition of O_3, HNO_3, NO_x, H_2O_2, CH_3OOH, peroxyacetyl nitrate, CH_3CHO, HCHO, CH_3CO_3H, HCOOH, isoprene, methyl vinyl ketone, methacrolein, methylacetate, acetic acid, and methanol was constructed. Deposition velocities were calculated using the SCM without imposing any constraint on the soil moisture level. The deposition rates are generally based on species solubility and reactivity according to Wesely (1989), except for species which have been modified according to Ganzeveld and Lelieveld (1995) (O_3, HNO_3, NO_x), and peroxides (Ganzeveld et al., 2006). The base case model domain was extended down to the ground (rather than stopping at 100 m), and a first order deposition loss rate was applied to the surface layer. As observations were not available at these altitudes, the observed averages between 50-150 m are applied to the surface layer. All species except HCHO are constrained to measurements.

The results of this model run are shown in Fig. S1. Including deposition has negligible effects on calculated OH reactivity; however, calculated HCHO decreases significantly in the boundary layer, creating an inverted profile. To compensate for this potential depositional sink, an emission rate eight times greater than that used in the main text would be required. This suggests either net deposition and emission occur on separate surfaces, or the existence of a HCHO

compensation point at which the surface as a whole acts as a net source rather than a sink. Because calculated OH reactivity is largely unaffected by including deposition and because our base model scenario represents an upward bound on the calculated HCHO mixing ratio, the conclusions stated in the main text are unaffected by the deposition term. Our study represents a lower limit on the non-photochemical HCHO source, and therefore a lower limit on the sensitivity of ozone production to agricultural emissions of HCHO.

Model sensitivity to turbulent mixing

The eddy-diffusivities for tracer transport are taken from the SCM which simulates online the turbulent fluxes of momentum, heat and moisture transport according to the local-closure turbulent transport scheme of the climate model ECHAM4 including modifications for non-local contributions to the turbulent kinetic energy budget (Brinkop and Roeckner, 1995) and updated mixing length formulation (Lenderink and Holtslag, 2004). The simulated meteorology resembles the actual observed meteorological conditions quite well. The SCM simulations are constrained with the ECMWF (European Centre for Medium range Weather forecast) re-analysis data for the grid point resembling the location of the SPC site covering (e.g. Ganzeveld et al., 2006). The eddy diffusion constants are shown in context of the HCHO lifetime with respect to photolysis/reaction with OH in Fig. S2.

As seen in the case where direct HCHO emission is included in the model, the eddy diffusion constants may not accurately capture the speed of growth of the mixed layer. As a sensitivity analysis, the coefficients are increased uniformly by a factor of 10 in both the base case scenario and the scenario where emissions are included (Fig. S3). While faster mixing better captures the early growth of the mixed layer in the emissions included case, the effect on the base case is minimal. Therefore, we conclude that the uncertainties in eddy diffusion have minimal impact on the conclusion that HCHO is underestimated at the lowest altitudes while OH reactivity is well captured.

Finally, as a boundary condition, no mixing occurs between the uppermost model layer and the overlying atmosphere (i.e. all boundaries are reflective). Any mixing would only affect non-constrained species. It is probable that the concentrations of these species (e.g. RO_2, HCHO) is lower in the overlying layer and additional mixing would further dilute HCHO. Because our base

case model represents an upper estimate of model HCHO, i.e., a conservative estimate of missing HCHO, including mixing with the upper atmosphere would not affect our conclusions. Additionally, the reflective boundary conditions restict emitted species to the total model volume. This could artifically inflate the concentrations of emitted species if the actual atmopsheric mixing volume is greater than the model volume. According to the eddy diffusion coefficients, mixing significantly decreases at highest model altitude. Therefore, it is unlikely that the reflective boundary significantly inflate the increase in HCHO mixing ratios caused by emissions in the early morning.

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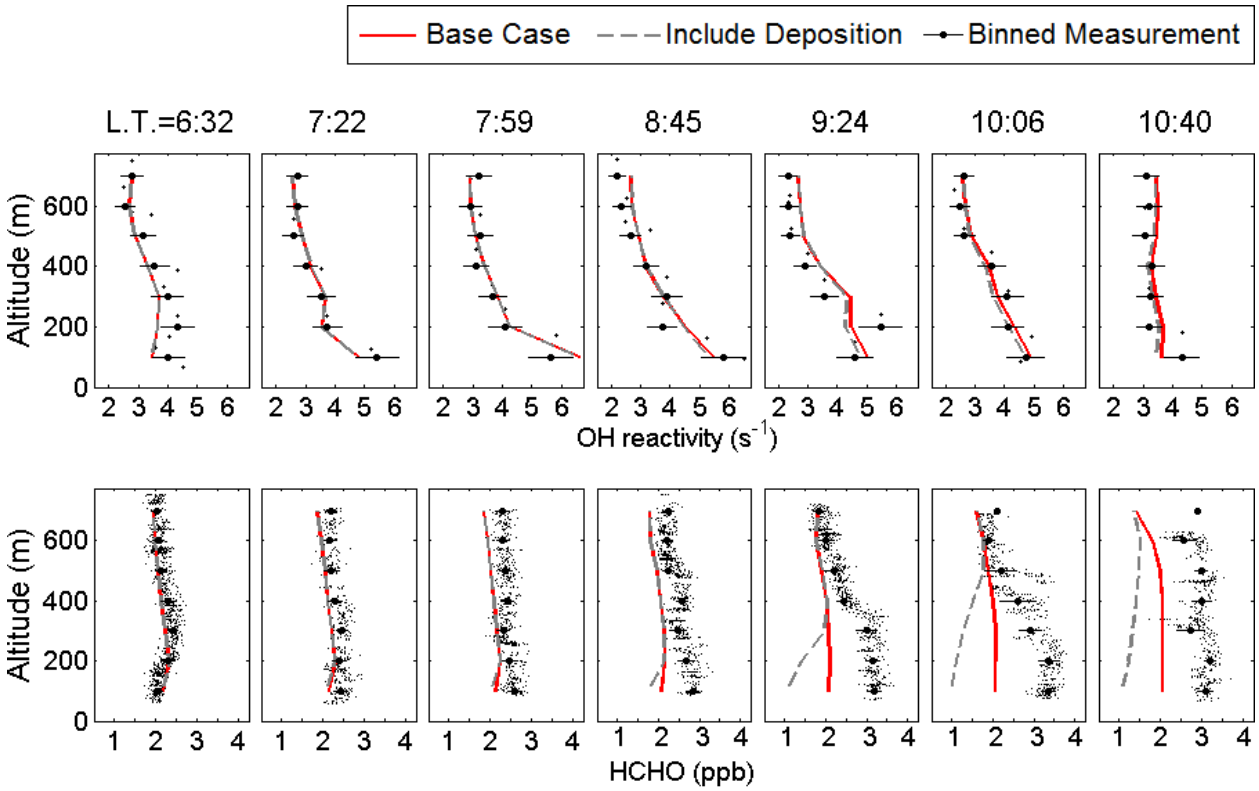

Figure S1. Measured and calculated OH reactivity and HCHO vertical profiles for every other Zeppelin ascent. Error bars on OH reactivity represent the measurement precision. Error bars on HCHO represent the standard deviation of the measurements in the given altitude bin.

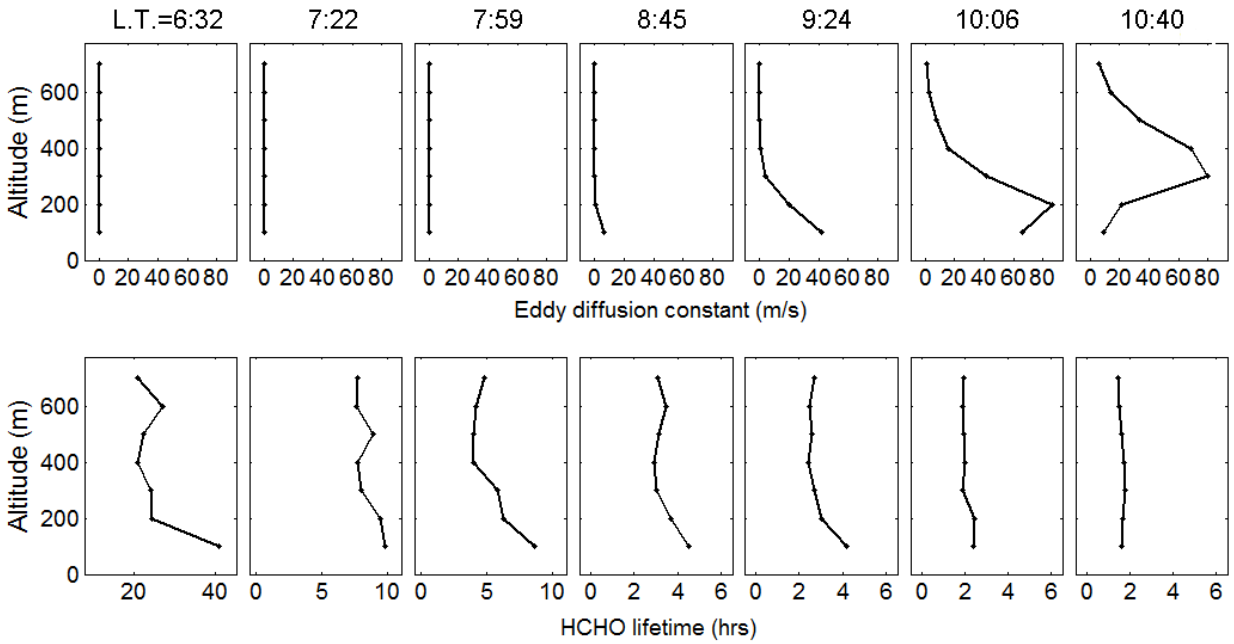

Figure S2. Calculated eddy diffusion constants and HCHO lifetime with respect to photolysis/reaction with OH.

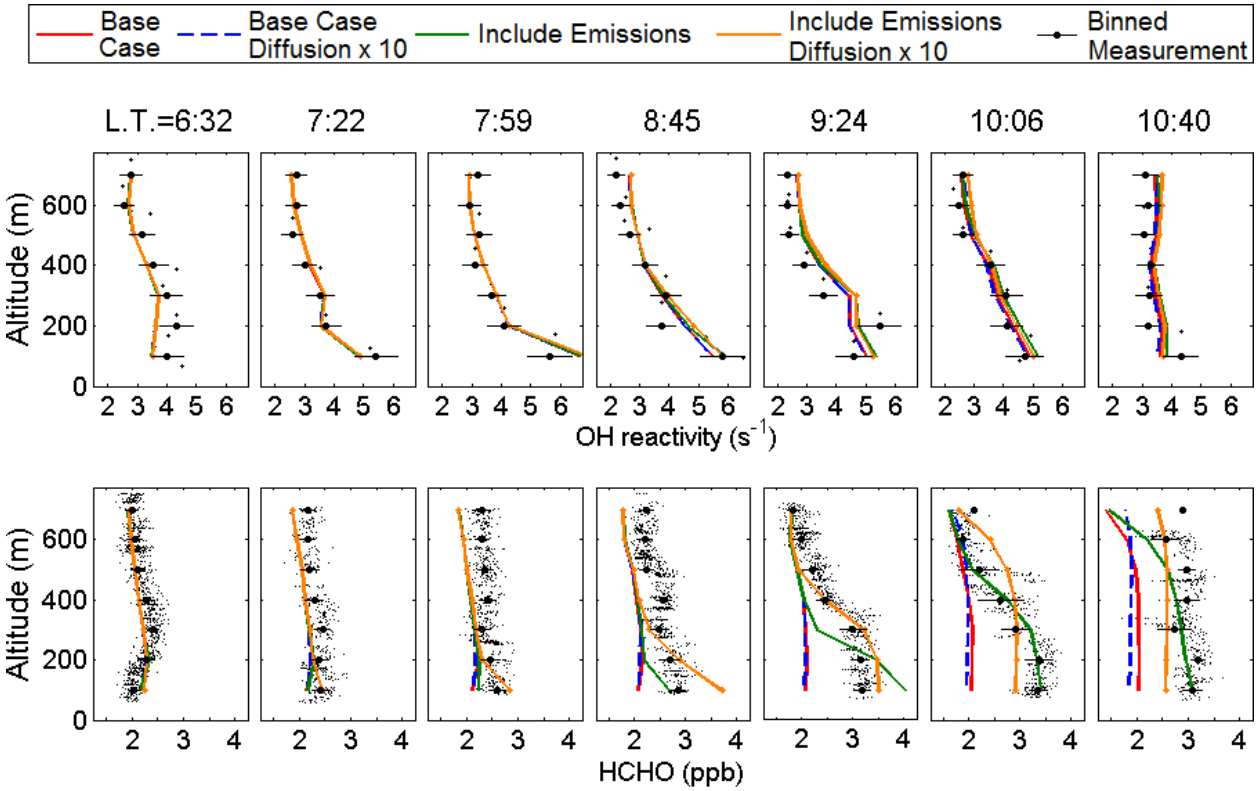

Figure S3. Sensitivity to eddy diffusion constants for calculated OH reactivity and HCHO vertical profiles in the base case scenario and including direct HCHO emissions. Increased eddy diffusivity in most cases does not change the average model-measurement discrepancy.