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What effect does VOC sampling time have on derived OH reactivity?

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State of the art techniques allow for rapid measurements of total OH reactivity. Unknown sinks of OH and oxidation processes in the atmosphere have been attributed to what has been termed ‘missing’ OH reactivity. Often overlooked are the differences in timescales over which the diverse measurement techniques operate. Volatile organic compounds (VOC) acting as sinks of OH are often measured by gas chromatography (GC) methods which provide low frequency measurements on a timescale of hours, while sampling times are generally only a few minutes.

We are presenting a study about the effect of the sampling time and thus the contribution of unmeasured VOC variability on OH reactivity. Measurements of VOC mixing ratios by proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS) conducted during two field campaigns (ClearfLo and PARADE) in an urban and a semi-rural environment were used to calculate OH reactivity. VOC were selected to represent variability for different compound classes. Data were averaged over different time intervals to simulate lower time resolutions and were then compared to the mean hourly OH reactivity. The results show deviations in the range of 1 to 25%. The observed impact of VOC variability is found to be greater for the semi-rural site. Similar effects were observed for a randomized data set. But, when comparing the sampling time needed to obtain a representative value for the hourly mean, the randomized data converge much faster to the range of their hourly standard deviation than the ambient VOC measurements.

The selected compounds were scaled by the contribution of their compound class to the total OH reactivity from VOC based on concurrent gas chromatography measurements conducted during the ClearfLo campaign. Prior to being scaled, the variable signal of aromatic compounds results in larger deviations in OH reactivity for short sampling intervals compared to oxygenated VOC (OVOC). However, once scaled with their lower share during the ClearfLo campaign this effect was reduced. No seasonal effect on the OH reactivity distribution across different VOC was observed at the urban site.