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Supplement of

A chamber study of the influence of boreal BVOC emissions and sulfuric acid on nanoparticle formation rates at ambient concentrations

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S1.1 Uncertainty analysis for expressions (6) and (7).

All measurements contain error. Generally, the errors can be random or systematic, and depending on the measurement method, errors can be proportional or independent of the measured value. Expression (6) for the nucleation rate depends on the gas-phase concentration measurements $[BVOC]_{SS}$, $[OH]_{SS}$, and $[H_2SO_4]_{SS}$, and the condensation sink CS, while expression (7) depends on the quantities Q_{BVOC} and $[H_2SO_4]_{SS}$. Q_{BVOC} in turn depended on the concentration measurement at the plant chamber and the flow measurement.

In our paper, we have shown that in the conditions of our experiments, these two expressions are equivalent, that is, they should produce the same result. However, when correlating the RHS of Eq. (6) with the observed J, we found very low correlation, while high correlation was observed performing the same comparison for Eq. (7).

The reason for this lies in the magnitude of the random error for the respective measurements. We can see that both expressions include the sulphuric acid concentration $[H_2SO_4]_{SS}$, and therefore the reason is unlikely to be found there. However, the only other factor in Eq. (7) is Q_{BVOC} , while for Eq. (6) we have a factor $[BVOC]_{SS} \times [OH]_{SS}/CS$. The key for correlation coefficients is the random error. For each measurement, we can estimate the random error from the standard deviation of measurements during times when concentrations are changing very little; in our case, the steady-state situations are a good fit for this.

When the UV-lights were on, BVOC concentrations in the reaction chamber dropped to values of 0.05-0.3 ppb with a mean of 0.14 ppb. The random uncertainty (estimated from the count statistics of the PTRMS instrument) was on average 0.2 ppb; therefore, the actual measured value was lower or similar to the random variation of the signal. The random uncertainty was the same for the measurements performed at the plant chamber, which acted as the source for BVOC; however, the observed values in the plant chamber during the UV-on times were 0.7-1.6 ppb, and thus the relative random error was at most ca. 25%.

The effect of this difference on the analysis can be demonstrated using an artificial dataset, in which we have introduced variable amounts of random error. In the figure below, we have produced simulated VOC and OH measurements, and also a dependent observation of J. The relation between J is simple; $J = A \cdot VOC \cdot OH$ (for simplicity). The result in correlation (without random error) can be seen in the leftmost panel. The centre panel shows the correlation when a random error of a similar magnitude than the VOC measurement is added to the VOC observation, and a smaller random error (25%) to the OH measurement. We see (middle panel) that the correlation gets very low (R^2 would be 0.09). With a lower error of ca 25% in the VOC measurement (rightmost panel), we still get a reasonably high correlation.

Effectively, using Eq. (6) would introduce a random factor of at least 100% into the computed value of the RHS (and likely more due to cumulative effects of OH and CS measurements, even though these are minor in comparison). In contrast, Eq (7) has a small relative error (even though the absolute magnitude of the random error stays the same), and it is multiplied only by the sulphuric acid concentration, which has a low random variation (ca 10% in our experiments). Thus, correlation analysis for Eq. (7) is successful, while for Eq. (6) it fails.

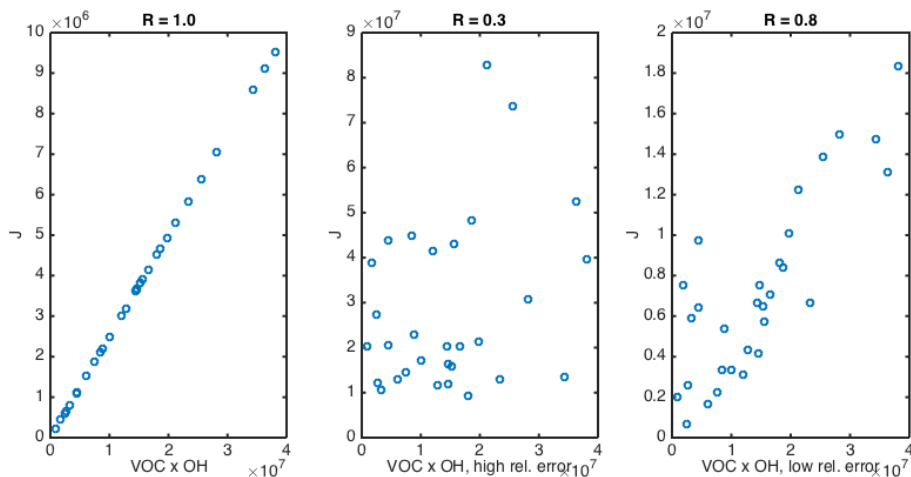


Figure 1: The effect of adding random error to measurements. See text for details.

S1.2 Data for individual experiments

Table 1: Characteristics of UV-on periods for which particle formation rates were determined. Given values are mean values over the selected time period.

Date of Sep 09	mean VOC (ppb)		OH	CS	O3
	Plant	Reaction	10^7 cm^{-3}	10^{-3} s^{-1}	ppb
17	3.09	0.14	6.5	5.3	32
18	1.31	0.12	7.6	3.4	31
19	1.17	0.08	8.0	2.25	30
20	1.08	0.02	7.5	1.9	29
21	0.90	0.08	5.7	0.4	33
22	0.91	0.15	10.0	0.9	35
23	0.88	0.26	1.1	0.003	0
24	0.87	0.12	7.4	0.3	37
26	0	0	11.0	-	29
27	-	0.28	6.3	0.06	34