

Supplementary Information

The driving factors of new particle formation and growth in the polluted boundary layer

Radical chemistry in CLOUD chamber

5 HO₂ is produced by the OH reactions with O₃ and VOCs in the experiments. The latter pathway dominates the HO₂ production rates, but also the RO₂ production rates (which means that in the absence of NO the RO₂-HO₂ ratios are fairly constant). The major sinks of HO₂ are self-reaction and reaction with NO. HO₂ concentrations are a few 10⁹ cm⁻³ based on calculations. The ratio of N containing HOMs to total HOMs reaches 50 % of its maximum at 60-120 ppt NO. Given $k_{\text{RO}_2+\text{NO}} = 10^{-11}$ molecule⁻¹ cm³ s⁻¹, and $k_{\text{RO}_2+\text{HO}_2} = 2.5 \times 10^{-11}$ molecule⁻¹ cm³ s⁻¹, the HO₂ concentration is estimated to be around $5 \times 10^8 - 1 \times 10^9$ molecules
10 cm⁻³ for aromatic oxidation experiments.

In the absence of NO (i.e., extremely low NO_x), HO₂ is expected to determine the lifetime of RO₂ because the HO₂+RO₂ channel is faster than the RO₂+RO₂ channel for most RO₂ radicals. There can be an exception for the highly oxygenated RO₂ radicals, which can self-terminate forming dimers (Berndt et al., 2018). In the ambient atmosphere, under low-NO_x conditions, OH reacts with CO and small oxygenated hydrocarbons to HO₂ radicals directly without first producing high molecular-weight
15 RO₂ radicals, which increases the importance of the HO₂+RO₂ channel compared to CLOUD, decreasing dimer formation (Schervish and Donahue, 2020). Therefore, dimer formation rates from aromatics and hence new-particle formation rates under low-NO_x conditions in CLOUD should be considered as upper bounds.

At the range of precursor concentrations studied here, a few hundred ppt of NO is sufficient to dominate the sink of both HO₂ and RO₂, confirmed by checking the ratio of N-containing HOMs to total HOMs vs NO concentration. The addition of NO
20 decreases both RO₂ and HO₂ but HO₂ would be recycled partially via RO₂+NO -> alkoxy radicals, which signifies that RO₂ self-termination is not at all favored compared to RO₂+NO and RO₂+HO₂. Therefore, under both low- and high-NO_x conditions, the dimer formation branching ratios would not be higher than simulated at CLOUD.

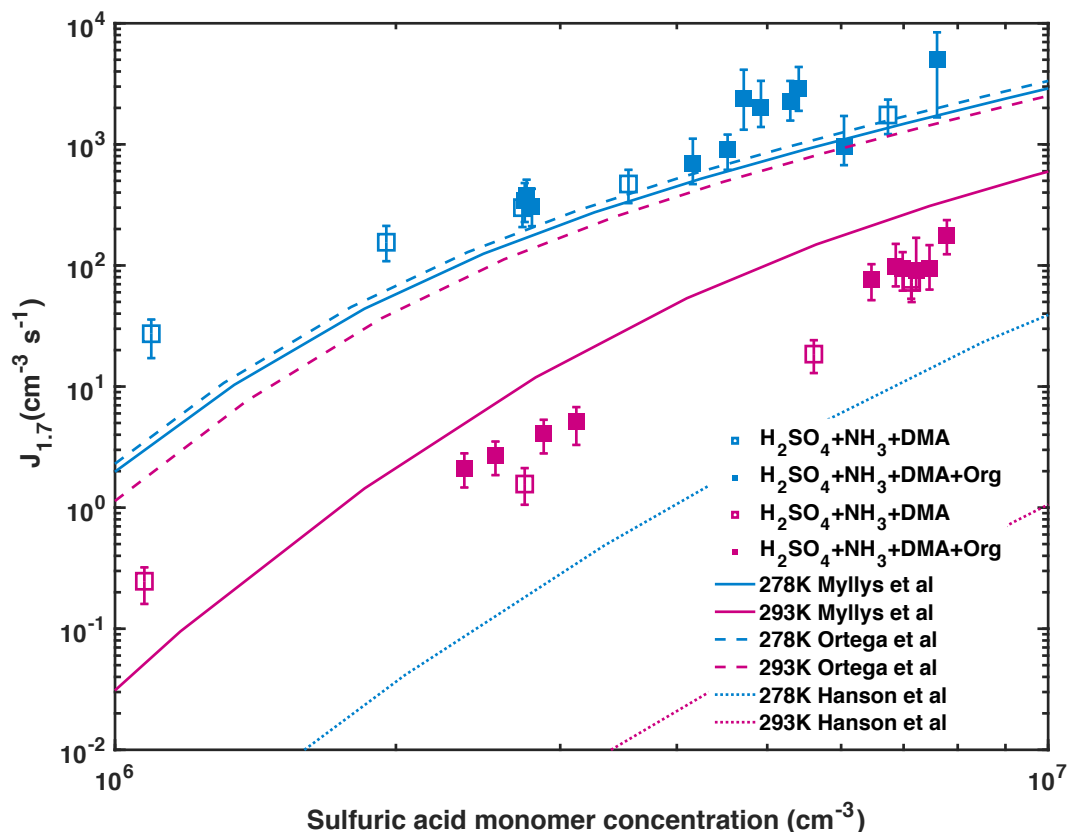
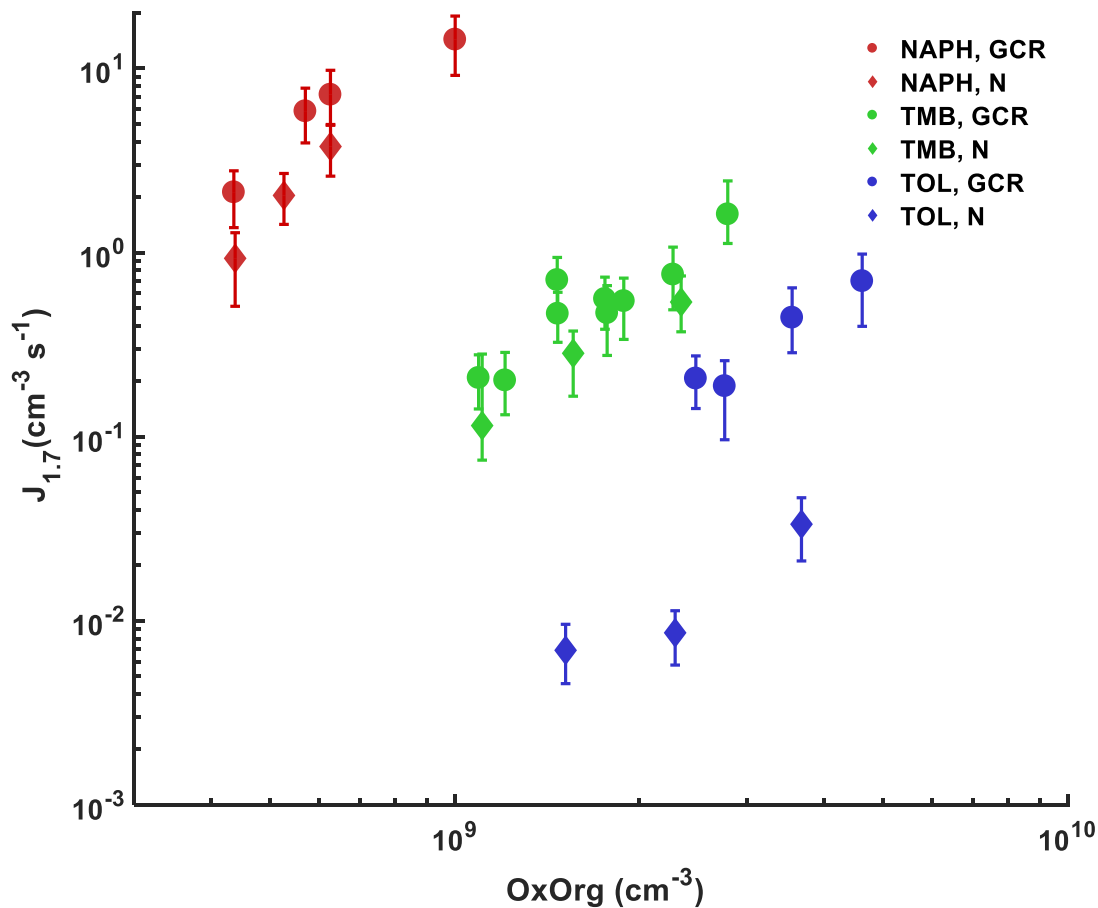


Figure S1: Modelled particle formation rates at 1.7 nm diameter from sulfuric acid with NH₃ and DMA compared with our measurements at 293 and 278 K. Experiments were performed at 278 K (cyan) or 293 K (magenta) with 1 to 2 ppbv NH₃ and 4 pptv DMA. Filled and open symbols indicate presence or absence of organics, respectively. The error bars refer to the measurement uncertainties for the particle formation rates. Solid and dashed lines are calculated with the kinetic model by implementing sulfuric acid - DMA cluster evaporation rates based on thermodynamic data from Myllys et al. (2019) (solid line), Ortega et al. (2012) (dashed line) and from Hanson et al. (2017) (dotted line), respectively. Modelled results based on binding energies for H₂SO₄-DMA clusters from Myllys et al (2019). follow the same trends as our measurements while other published binding energies for H₂SO₄-DMA clusters fail to reproduce the temperature dependency of the measured $J_{1.7}$. The tightly bound clusters theoretically predicted by Ortega et al. (2012) result in minor evaporation, leading to formation rates close to kinetic limits even at high temperatures. Note that the quantum chemical method used tends to overestimate binding energy values (Leverentz et al., 2013), and a reduction of the values at 298 K for the H₂SO₄-DMA cluster (-15.4 to -11 kcal mol⁻¹) and for (H₂SO₄)₂-DMA (-19.48 to -18 kcal mol⁻¹), as suggested by Hanson et al. (2017), results in considerably lower $J_{1.7}$ values compared to our observations.

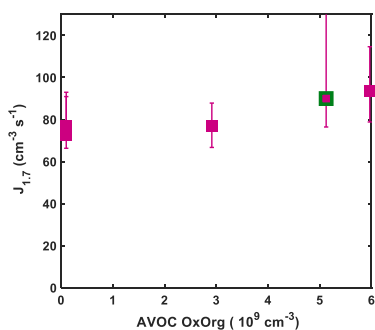


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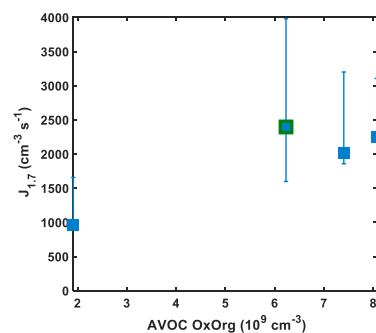
Figure S2: Dependence of particle formation rates from sulfuric acid and AVOC on OxOrg concentration at 293K. Experiments were conducted at 293 K with no addition of NO_x or NH_3 . H_2SO_4 concentration varied from 1×10^6 to $4 \times 10^7 \text{ cm}^{-3}$ in these experiments, but had no effect on the nucleation rate in the absence of ammonia (Lehtipalo et al., 2018). Concentration of precursors in the experiments: 2-8 ppbv naphthalene (NAPH), 4 ppbv 1,2,4-trimethylbenzene (TMB), 40 ppbv toluene (TOL). Experiments under both neutral (N) and GCR conditions are shown. The J values for NAPH are even higher than for pure biogenic nucleation from BVOC (Kirkby et al., 2016) for the same amount of VOC reacted. However, these values are not relevant for the ambient atmosphere, in contrast to the BVOC, as AVOC are typically emitted together with NO_x .

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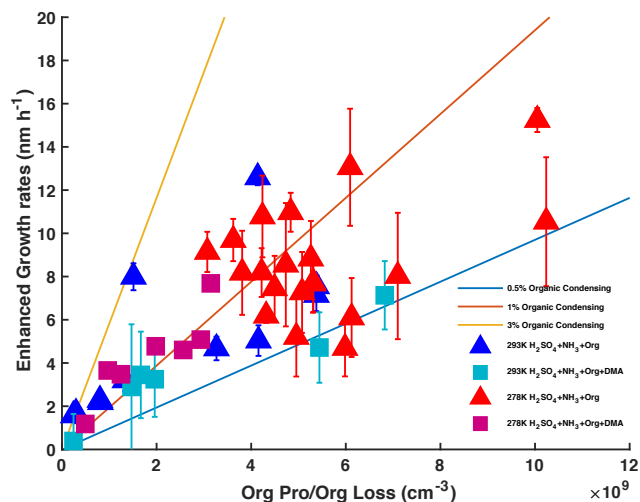
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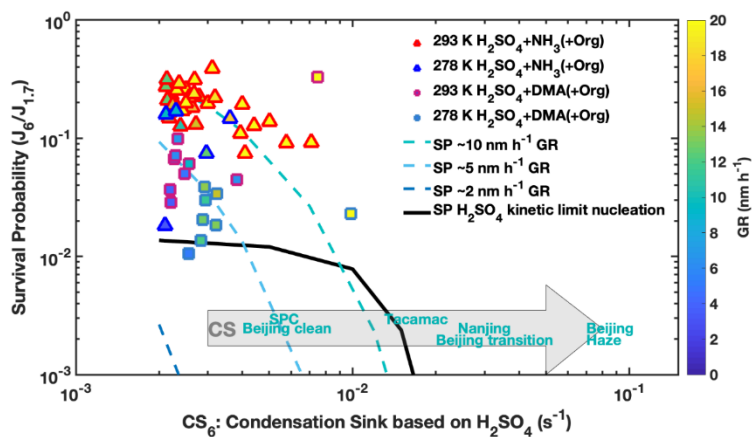
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- 50 **Figure S3. Dependence of particle formation rates from sulfuric acid, ammonia, DMA, and AVOC on OxOrg concentration at (A) 293 K and (B) 278 K.** (A) Experiments with $7.4 \pm 0.4 \times 10^6 \text{ cm}^{-3} \text{ H}_2\text{SO}_4$, 800 to 2000 pptv NH_3 , 4 pptv DMA and $0.71 \pm 0.18 \text{ ppbv NO}$ at 293 K, with NAPH:TMB:TOL of 1:5:15. Symbol highlighted with green outline also has 1 ppbv α -pinene added to the experiment. Error bars present variation of the measurements. (B) Experiments with $5.1 \pm 0.6 \times 10^6 \text{ cm}^{-3} \text{ H}_2\text{SO}_4$, 1000 to 1500 pptv NH_3 , 4 pptv DMA and $0.67 \pm 0.4 \text{ ppbv NO}$ at 293 K, with NAPH:TMB:TOL of 1:5:20. Symbol highlighted with green outline also has 1 ppbv α -pinene added to the experiment. Error bars present variation of the measurements.
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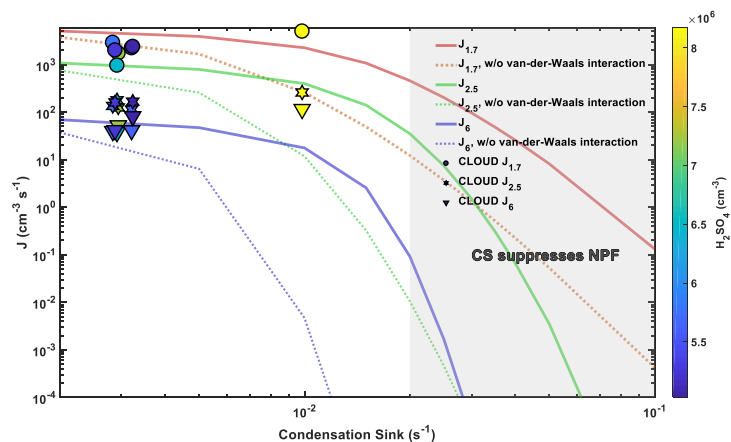


60 **Figure S4. Enhanced growth rates of sub-3 nm particles by OxOrg.** CLOUD data recorded at 278 K (blue and cyan) or 293 K (red and magenta) with 1×10^6 to 1×10^8 cm^{-3} H_2SO_4 and 1 to 2 ppbv NH_3 at GCR conditions. Experiments without DMA are shown by triangles, and with 4 pptv DMA by squares. Enhanced growth rates are calculated as measured growth rates minus the growth rates resulting from condensing sulfuric acid alone. Solid lines display the percentage contribution of 0.5, 1, and 3% of OxOrg to the growth rate. No NO_x dependence can be identified. The variability in condensable OxOrg yields is driven by NO_x concentrations, multi-generation chemistry and precursor composition, e.g., naphthalene oxidation leads to lower volatility products than the single-ring aromatics.



65 **Figure S5. Survival probability (SP_6) of 6 nm particle vs condensation sink.** Survival probability of 6 nm particles (SP_6) is calculated as the ratio between the nucleation rates at 1.7 and 6 nm. CLOUD data were recorded at 60% RH and 278 K (blue and cyan contours) or 293 K (red and magenta contours) with 1 to 2 ppbv NH_3 . Experiments without DMA injection are shown by triangles and experiments with 4 pptv DMA by squares. The sub-3 nm growth rate is given by the colour of the symbols. The loss rates of newly formed particles are approximated by the condensation sink of sulfuric acid to particles larger than 6 nm (x-axis). Dashed lines are calculated survival probabilities of 6 nm particles with growth rates of 2, 5, and 10 nm h^{-1} . The solid line is the survival probability of 6 nm particles if 8×10^6 cm^{-3} sulfuric acid nucleates at the kinetic limit, which corresponds to a nucleation rate $J_{1.7}$ of 4000 $\text{cm}^{-3} \text{s}^{-1}$ (Fig. 1a) and a sub-3 nm growth rate of 11 nm h^{-1} (Fig. 4A) under CLOUD chamber wall loss conditions. The high production rate of nucleating clusters significantly reduces the survival

75 probability and simultaneously increases the growth rate, and the survival probability only becomes dependent on CS once the latter is greater than the loss due to cluster-cluster collisions.



80 **Figure S6. Dependence of particle formation rates at different diameters on condensation sink.** Solid lines are simulated formation rates at different particle sizes for 10^7 cm^{-3} sulfuric acid nucleating at the kinetic limit considering van-der-Waals interaction. Dashed lines present the formation rates if van-der-Waals interaction is ignored and only hard sphere collisions are considered. CLOUD measurements are shown for 278 K in the presence of DMA. Grey shading denotes the area where NPF is suppressed for our range of conditions.

Table S1. Experimental conditions of data in Figure 1.

Run	$J_{1,7}$	SA	NH ₃ (ppb)	DMA (ppt)	NPT (ppb)	TMB (ppb)	TOL (ppb)	NO (ppb)	Temperature
	(cm ⁻³ s ⁻¹)	(cm ⁻³)							
1833.04	17	5.89E+07	1.4	N/A	N/A	N/A	N/A	N/A	293 K
1833.06	29	7.76E+07	1.4	N/A	N/A	N/A	N/A	N/A	293 K
1833.1	4.5	2.59E+07	1.4	N/A	N/A	N/A	N/A	N/A	293 K
1833.12	18	6.04E+07	1.4	N/A	N/A	N/A	N/A	N/A	293 K
1833.17	26	7.04E+07	1.4	N/A	N/A	N/A	N/A	N/A	293 K
1833.23	0.2	7.48E+06	1.4	N/A	N/A	N/A	N/A	N/A	293 K
1843.02	2.4	1.02E+07	0.8	N/A	3.3	6.9	39	0.21	293 K
1843.04	7.9	1.24E+07	0.8	N/A	3.3	6.2	39	0.16	293 K
1843.06	9.3	1.19E+07	0.8	N/A	3.3	6.2	39	0.15	293 K
1843.09	12	1.18E+07	0.8	N/A	3.3	6.2	39	0.15	293 K
1844.01	8.4	2.16E+07	1	N/A	3.9	7.6	40	0.29	293 K
1844.02	24	2.44E+07	0.8	N/A	3.7	6.7	39	0.2	293 K
1844.04	26	2.88E+07	0.9	N/A	3.6	6.6	39	0.21	293 K
1844.05	19	2.16E+07	0.8	N/A	3.3	6.1	39	0.16	293 K
1845.02	2.1	1.87E+07	1	N/A	3.8	7.7	40	1.4	293 K
1845.03	11	3.02E+07	0.8	N/A	3.4	6.8	39	1.2	293 K
1845.04	18	3.16E+07	0.8	N/A	3.3	6	39	0.98	293 K
1845.06	24	3.31E+07	0.8	N/A	3.3	5.7	39	0.91	293 K
1845.07	18	3.16E+07	0.8	N/A	3.1	5.3	38	0.79	293 K
1846.05	8	2.44E+07	0.9	N/A	3.6	6.8	39	0.64	293 K
1846.09	17	3.16E+07	0.8	N/A	3.4	5.5	38	0.49	293 K
1846.15	35	2.88E+07	0.8	N/A	3.2	4.9	38	0.41	293 K
1847.01	2.3	1.73E+07	1	N/A	3.8	7.8	40	1.2	293 K
1847.02	9.7	2.59E+07	0.9	N/A	3.7	6.9	39	1.2	293 K
1847.03	10	2.73E+07	0.8	N/A	3.5	6.4	39	1.1	293 K
1847.05	14	2.59E+07	0.8	N/A	3.4	6.1	39	1.1	293 K
1847.07	26	3.02E+07	0.8	N/A	3.5	6	39	1	293 K
1847.12	4.6	2.16E+07	1	N/A	3.9	7.7	12	0.63	293 K
1847.13	18	3.02E+07	0.9	N/A	3.5	6.2	11	0.59	293 K
1847.14	29	2.88E+07	0.8	N/A	3.5	5.5	10	0.52	293 K

1847.15	39	2.73E+07	0.8	N/A	3.7	5.4	9.6	0.47	293 K
1848.01	6.1	2.30E+07	1.1	N/A	1.6	7.7	39	0.61	293 K
1848.02	18	3.31E+07	0.9	N/A	1.6	6.4	39	0.54	293 K
1848.04	34	3.45E+07	0.9	N/A	1.7	5.9	38	0.46	293 K
1848.06	81	3.74E+07	0.9	N/A	1.8	5.8	38	0.44	293 K
1849.01	12	2.88E+07	1.3	N/A	4.4	1.6	40	0.6	293 K
1849.02	30	3.31E+07	1.3	N/A	3.6	1.2	39	0.55	293 K
1849.03	34	2.88E+07	1.2	N/A	3.2	1.1	38	0.48	293 K
1849.05	130	3.02E+07	1.2	N/A	3.3	1.1	38	0.46	293 K
1969.18	1.1	7.80E+06	0.6	N/A	0.54	2.7	12	0.06	293 K
1969.2	2.3	9.20E+06	0.6	N/A	0.48	2.6	12	0.06	293 K
1970.02	2.7	9.60E+06	0.8	N/A	0.51	2.4	12	0.03	293 K
1970.03	1.8	8.90E+06	0.9	N/A	0.49	2.3	12	0.04	293 K
1970.06	3.8	1.10E+07	1	N/A	0.47	2.2	12	0.04	293 K
1970.09	3.7	1.20E+07	0.6	N/A	0.44	1.9	11	0.05	293 K
1970.12	2.2	1.10E+07	0.8	N/A	0.44	2.2	11	0.07	293 K
1971.02	1	9.40E+06	0.6	N/A	0.49	4.2	12	0.44	293 K
1971.05	1	1.10E+07	0.5	N/A	0.44	2.3	11	0.46	293 K
1971.08	1.7	1.30E+07	0.6	N/A	0.41	2.2	11	0.68	293 K
1971.11	1.6	1.20E+07	0.6	N/A	0.42	2.3	11	0.65	293 K
1971.22	16	5.00E+07	0.7	N/A	0.42	1.5	11	0.56	293 K
1971.25	10	3.00E+07	0.5	N/A	1.5	9.1	45	0.26	293 K
1974.07	19	5.60E+06	0.9	3.1	N/A	N/A	N/A	0.17	293 K
1974.12	1.6	2.70E+06	1	2.6	N/A	N/A	N/A	0.06	293 K
1974.14	72	7.10E+06	0.8	2.8	N/A	N/A	N/A	0.37	293 K
1974.16	77	7.10E+06	0.7	3.1	N/A	N/A	N/A	0.62	293 K
1974.19	0.3	1.10E+06	0.8	3	N/A	N/A	N/A	0.05	293 K
1975.02	5.2	3.10E+06	1.1	4.2	0.1	0.68	2.3	0.12	293 K
1975.03	94	7.50E+06	1.1	3.8	0.1	0.53	2.1	0.58	293 K
1975.05	4.1	2.90E+06	0.7	3.8	0.28	0.75	2.1	0.16	293 K
1975.06	98	6.90E+06	0.8	3.8	0.23	0.52	2	0.82	293 K
1975.08	2.1	2.40E+06	0.8	3.7	0.33	1.5	3.9	0.2	293 K
1975.09	77	6.50E+06	0.7	3.5	0.23	1.1	3.4	0.89	293 K

1975.11	2.7	2.60E+06	0.6	3.7	0.56	3.1	7.8	0.17	293 K
1975.12	94	7.00E+06	0.5	3.6	0.41	2.3	6.7	0.69	293 K
1975.14	90	7.20E+06	0.4	3.4	0.06	2.2	6.7	0.81	293 K
1975.21	180	7.80E+06	0.6	3.8	0.43	2.7	9.5	0.8	293 K
1972.07	17	4.40E+06	1.1	N/A	0.55	2.6	15	0.24	278 K
1972.1	37	6.50E+06	0.9	N/A	0.45	2.2	15	0.34	278 K
1972.13	50	8.30E+06	0.6	N/A	0.35	1.8	15	0.58	278 K
1972.18	43	7.00E+06	0.7	N/A	0.44	2.2	15	0.44	278 K
1972.21	7.8	4.90E+06	0.6	N/A	0.11	0.64	3.9	0.08	278 K
1973.03	21	8.20E+06	0.6	N/A	0.06	0.25	3.5	0.68	278 K
1973.06	18	8.30E+06	0.8	N/A	0.01	0.13	1	0.78	278 K
1973.1	190	1.60E+07	0.6	N/A	0.26	1.8	13	1.3	278 K
1976.02	21	9.90E+05	0.8	4.2	N/A	N/A	N/A	1.6	278 K
1976.04	1.7	6.30E+05	0.6	5.4	N/A	N/A	N/A	0.14	278 K
1976.05	27	1.10E+06	0.6	5.3	N/A	N/A	N/A	0.13	278 K
1976.07	160	2.00E+06	0.6	4.6	N/A	N/A	N/A	0.34	278 K
1976.09	300	2.70E+06	0.5	4.6	N/A	N/A	N/A	0.88	278 K
1976.11	470	3.60E+06	0.4	3.9	N/A	N/A	N/A	1.9	278 K
1976.13	1700	6.70E+06	0.7	3.8	N/A	N/A	N/A	1.6	278 K
1977.01	690	4.20E+06	0.7	4.8	DL	0.63	2.7	0.3	278 K
1977.05	970	6.00E+06	0.8	3.8	DL	0.48	2.5	1.1	278 K
1977.07	310	2.80E+06	0.7	5	0.19	0.61	2.7	0.24	278 K
1977.09	2900	5.40E+06	0.6	5	0.12	0.48	2.6	0.93	278 K
1977.11	370	2.80E+06	0.5	5.5	0.23	1.2	4.5	0.25	278 K
1977.13	2200	5.30E+06	0.5	5.2	0.2	0.96	4.4	0.94	278 K
1977.15	340	2.70E+06	0.6	6.1	0.46	2.7	8.8	0.23	278 K
1977.17	2000	4.90E+06	0.6	6.1	0.42	2.2	8.6	0.68	278 K
1977.19	2400	4.70E+06	0.7	5.2	0.41	2.1	8.7	0.66	278 K
1977.2	5000	7.60E+06	0.7	4.7	0.29	1.3	8	0.46	278 K
1977.22	910	4.50E+06	0.7	4.5	0.3	1.6	8.1	0.64	278 K

N/A: not added.

85 DL: detection limit.

Reference:

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