

Investigation of the Tropospheric Oxidation Capacity and Ozone Photochemical Formation in the City of Santiago de Chile

-Field Measurements and Modelling Study-

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The physical and chemical properties of the atmosphere are influenced by the presence of trace gases like nitrogen oxides (NO_x) and volatile organic compounds (VOCs). The oxidising capacity of the atmosphere determines the rate of their removal, and hence controls the abundance of these trace gases. Understanding the processes and rates by which species are oxidized in the atmosphere is thus crucial to our knowledge of the atmospheric composition of harmful and climate forcing species. The relation between O_3 and its major anthropogenic precursors, VOCs and NO_x represents one of the major scientific challenges. Ozone is a major environmental concern because of its adverse impacts on human health and on crops and forest ecosystems. In addition, ozone is a major greenhouse gas, and changes in emissions of ozone precursors affect the global climate through a linked chemical system. Because ozone forms most rapidly in conditions with warm temperatures and sunshine, cities with warm climates are especially likely to experience high ozone events. In each of these locations it is necessary to understand how ozone depends on NO_x and VOC to develop an effective policy response.

This study provides a detailed analysis of the tropospheric photochemical oxidation processes and ozone photochemical formation under typical polluted urban conditions taking the city of Santiago de Chile as an example. Two field measurement campaigns were carried out in the city of Santiago de Chile during summer and winter, 2005 namely March 8 - 20 and May 25 - June 07, 2005, respectively. The measured species included HONO, HCHO, O_3 , NO_x , PAN, VOCs, CO, CO_2 , $j(\text{O}^1\text{D})$, $j(\text{NO}_2)$ and meteorological parameters. The OH radical budget was evaluated in both campaigns employing a photo stationary-state model (PSS) constrained with simultaneous measurements of HONO, HCHO, O_3 , PAN, NO, NO_2 , $j(\text{O}^1\text{D})$,

$j(\text{NO}_2)$, 13 alkenes and meteorological parameters. In addition, a zero dimensional photochemical box model based on the Master Chemical Mechanism (MCMv3.1) has been used for the analysis of the radical budgets and concentrations of OH, HO₂ and RO₂. Besides the above parameters, the MCM model has been constrained by the measured CO and other volatile organic compounds (VOCs) including alkanes and aromatics.

Average mixing ratios of HONO, CO, NO and NO₂ in winter were higher than their corresponding values during summer. However, average and maximum mixing ratios of the photo-oxidation products O₃, PAN and HCHO (partially photochemically formed) during summer were higher than their corresponding values during winter owing to the higher summertime photochemical activity. The higher mixing ratios of the emitted species (CO, NO, NO₂) observed during winter are due to the higher stability of the lower boundary layer during winter. During both, summer and winter campaign, daytime HONO concentrations were significantly higher than in other polluted urban areas with the average HONO mixing ratio in winter higher than in summer. The high mixing ratios of HONO and the daytime maximum of the HONO/NO_x ratio in Santiago point to a very strong daytime HONO source. This is also confirmed by the lower daytime HONO/NO_x ratio during winter (lower photochemical activity) in comparison to that during summer.

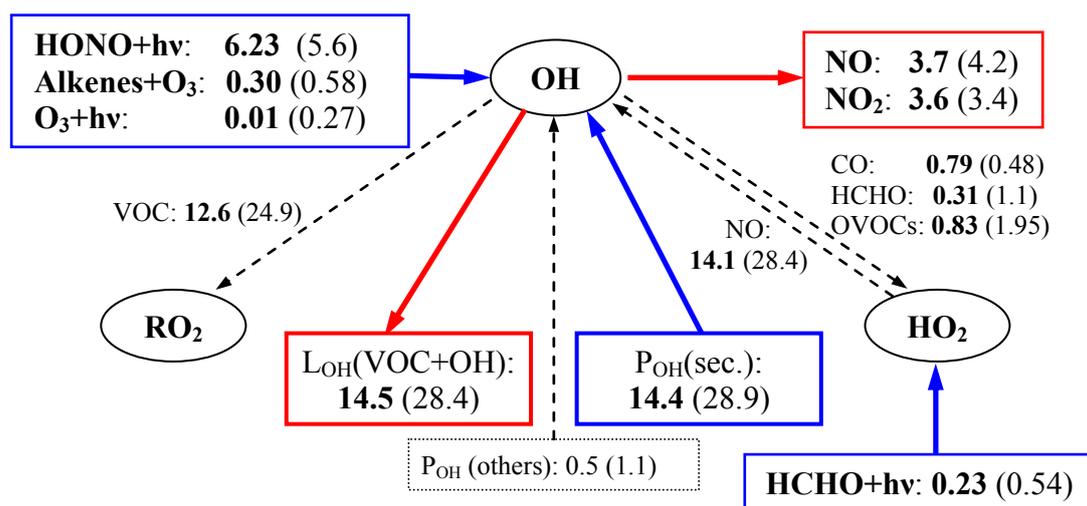


Fig.1: Average daytime fluxes of the radical sources and sinks for the city of Santiago de Chile calculated by the MCM model during winter (bold) and summer (in between brackets). See text for definitions. Units are in ppbv h⁻¹.

Total production/destruction rates of the OH and HO₂ in winter are ~2 times lower than those during summer (see Fig.1), which is mainly due to the high NO_x levels and the lower photochemical activity during winter. The argument of the high NO_x conditions was further evidenced through an explicit analysis of the O₃-VOC-NO_x sensitivity analysis, performed during the summer. During both summer and winter, there was a balance obtained between the secondary production, P_{OH}(HO₂→OH) and destruction L_{OH}(OH + VOC) rates of OH which has been further investigated for other studies using a balance ratio, BR. Interestingly; a BR value of 1.0 was obtained from the slope of the correlation between the secondary production and destruction of OH for all field studies used for comparison (see Fig. 2). Therefore, initiation sources of HO₂ and RO₂ should not be considered as net OH sources under urban conditions.

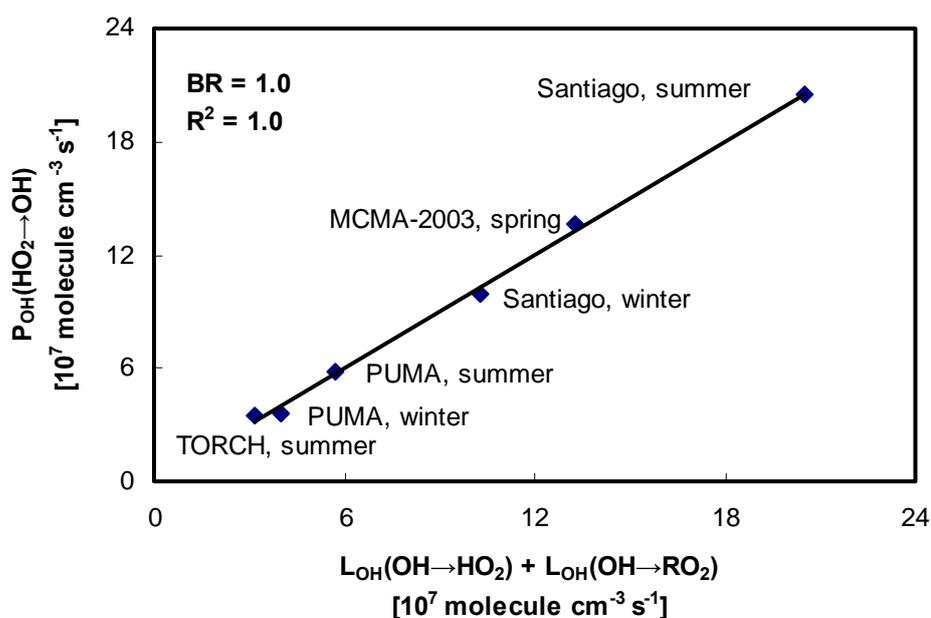


Fig. 2: Correlation between the average secondary radical production and destruction rates for different studies (for references see text).

The excellent agreement between the OH concentration profiles evaluated by the MCM and PSS models during both, summer and winter shows that the major OH radical sources and sinks are incorporated in the PSS model and that the secondary sinks, L_{OH}(OH + VOC) are balanced with the secondary sources P_{OH}(HO₂→OH). For daytime conditions during summer and winter, HONO photolysis has the highest contribution of (55 %, 84 %)

followed by alkenes ozonolysis (24 %, 9 %), HCHO photolysis (16 %, 6.5 %) and ozone photolysis (5 %, 0.5 %) to the OH initiation rate.

Table.1: Ozone forming potentials of the measured VOCs based on the $PIR_{adjusted}$ scale. The ten most important species are marked in bold.

compound name	PIR	$PIR_{adjusted}^{**}$	mixing ratio (ppbv)		
	$\Delta O_3/\Delta VOC$		Average	Median	Max
propene	0.25	0.39	3.80	1.56	38.8
1,3-butadiene	1.05	0.13	0.15	0.12	0.41
trans-2-butene	2.13	0.23	0.18	0.11	0.86
cis-2-butene	1.64	0.16	0.16	0.10	0.67
3-methyl-1-butene	0.72	0.10	0.19	0.14	1.22
1-pentene	0.70	0.13	0.30	0.18	1.77
isoprene	2.85	1.47	0.67	0.51	1.84
trans-2-pentene	2.13	0.30	0.24	0.14	1.41
cis-2-pentene	2.77	0.27	0.15	0.10	0.74
2-methyl-2-buten	2.97	0.58	0.33	0.20	2.10
1-hexene	0.94	0.13	0.20	0.14	0.80
2,3-dimethyl-2-butene	6.56	0.39	0.10	0.06	0.52
α-pinene	2.15	0.57	0.41	0.27	1.95
propane	0.01	0.07	41.8	11.5	475
i-butane	0.03	0.05	2.95	1.57	18.0
n-butane	0.04	0.10	3.89	2.32	18.3
i-pentane	0.08	0.32	5.75	4.08	27.6
3-methylpentane	0.10	0.09	1.40	0.92	6.09
2-methylhexane	0.10	0.02	0.35	0.22	1.71
n-heptane	0.06	0.03	0.55	0.42	2.50
n-octane	0.06	0.01	0.34	0.23	1.82
benzene	0.02	0.03	2.13	1.43	9.22
toluene	0.18	0.74	6.30	4.11	32.7
n-decane	0.07	0.03	0.60	0.42	2.94
ethylbenzene	0.25	0.29	1.38	1.14	6.06
o-xylene	0.60	0.91	1.81	1.50	7.72
n-propylbenzene	0.20	0.05	0.36	0.26	1.68
1,3,5-trimethylbenzene	2.35	0.90	0.58	0.38	2.79
4-ethyltoluene	0.47	0.10	0.30	0.21	1.40
1,2,3-trimethylbenzene	1.44	0.24	0.27	0.17	1.31
styrene	0.46	0.07	0.22	0.16	1.02

****** $PIR_{adjusted}$ scales were calculated by multiplying the median value of the mixing ratio of each VOC with the corresponding scale.

Summertime photochemical ozone formation in the urban area of Santiago, Chile has also been investigated using MCMv3.1. The results of the model simulations have been compared with a set of potential empirical indicator relationships. The ozone model sensitivity and the empirical indicator relationship analyses showed that photochemical ozone formation in Santiago is VOC limited. The ozone formation potentials of the different

measured VOCs have been determined using the PIR scale (see **Table.1**). The high ozone formation potential of isoprene and α -pinene suggests that other biogenic emissions can have a significant effect on summertime photochemical ozone formation in the urban centre of Santiago. Investigating the emissions of other unmeasured biogenic hydrocarbons may help elucidating the formation of the ozone afternoon shoulder.

HONO was found to account on average for ~37 % of the simulated ozone formation. This result stresses the absolute need to include measured HONO levels in ozone predicting models.

On a local scale, the reduction of VOCs was found to be the most effective way in reducing ozone formation in the city centre of Santiago de Chile. Thus, the design of air quality control measures should also consider reducing VOC emissions in addition to NO_x.

The results of this study has been published in the following peer reviewed articles:

- Elshorbany, Y. F., Kurtenbach, R., Wiesen, P., Lissi, E., Rubio, M., Villena, G., Gramsch, E., Rickard, A. R., Pilling, M. J. and Kleffmann, J.: Oxidation capacity of the city air of Santiago, Chile, *Atmospheric Chemistry and Physics*, 9, 2257-2273, 2009.
- Elshorbany, Y. F., Kleffmann, J., Kurtenbach, R., Rubio, R., Lissi, E., Villena, G., Gramsch, E., Rickard, A. R., Pilling, M. J. and Wiesen, P.: Summertime Photochemical Ozone Formation in Santiago de Chile, *Atmospheric Environment*, 43, 6398-6420, 2009.
- Elshorbany, Y. F., Kleffmann, J., Kurtenbach, R., Rubio, R., Lissi, E., Villena, G., Gramsch, E., Rickard, A. R., Pilling, M. J. and Wiesen, P.: Seasonal dependence of the oxidation capacity of the city of Santiago de Chile, *Atmospheric Environment*, 44, 5383-5394, 2010.
- Yasin Elshorbany: *Tropospheric Oxidation Capacity and Ozone Photochemical Formation*, Südwestdeutscher Verlag für Hochschulschriften AG Co. KG, ISBN 978-3-8381-1638-9, 2010.