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Prediction of Air Pollution in Latin America and the Caribbean

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Measurements and data analysis of ozone and volatile organic compounds

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Primary source of Hydroxyl radical

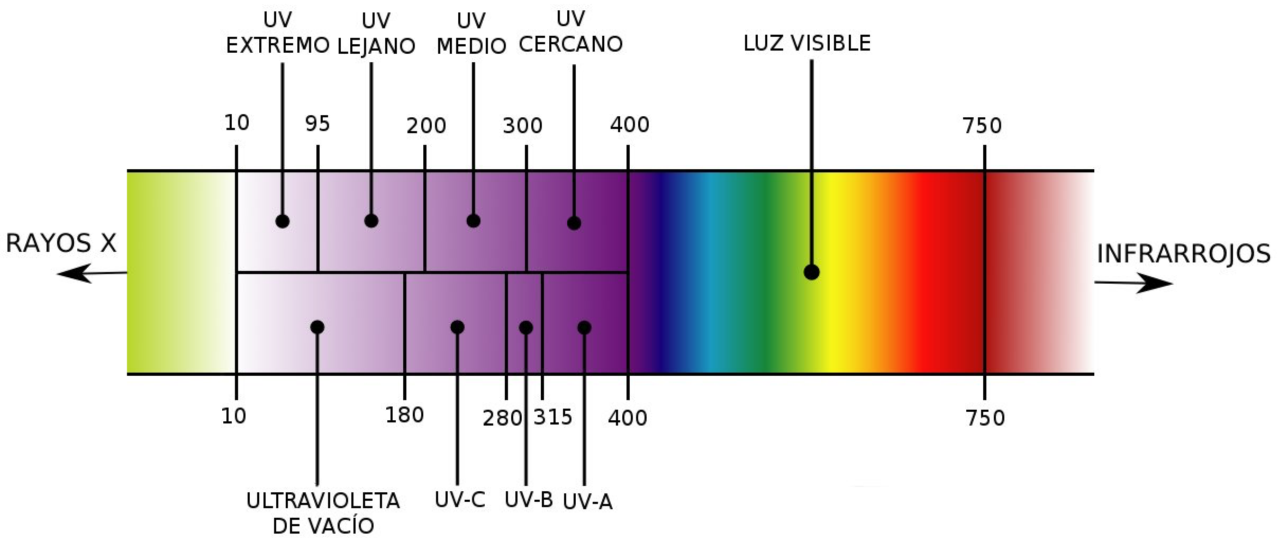
$$O_3 + h\nu \; (\lambda \leq 336) \rightarrow O_2 + O\,(^1D)$$

$$O\,(^1D) + H_2O \rightarrow 2\,^{\bullet}OH \; ; \; k\,(298\ K) = 2.2 \cdot 10^{-10} cm^{-3}\ molec^{-1}\ s^{-1}$$

$$O\,(^1D) + N_2O \rightarrow 2\,^{\bullet}NO \; ; \; k\,(298\ K) = 6.7 \cdot 10^{-11} cm^{-3}\ molec^{-1}\ s^{-1}$$

$$O\,(^1D) + M \rightarrow O\,(^3P) + M \; ; \; k\,(298\ K) \cong 3 \cdot 10^{-11} cm^{-3}\ molec^{-1}\ s^{-1}$$

- OH is unreactive toward O_2
- O_2 & O_3 have large bond energies



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VOC oxidation

$$CH_3CH_3 + {}^{\bullet}OH \rightarrow CH_3\dot{C}H_2 + H_2O$$

$$CH_3\dot{C}H_2 + O_2 \rightarrow CH_3\dot{C}H_2OO^{\bullet}$$

$$CH_3\dot{C}H_2OO^{\bullet} + NO \rightarrow CH_3CH_2O^{\bullet} + NO_2$$

$$CH_3CH_2O^{\bullet} + O_2 \rightarrow HO_2^{\bullet} + CH_3CHO$$

$$HO_2^{\bullet} + NO \rightarrow NO_2 + {}^{\bullet}OH$$

Ozone formation

$$RH + {}^{\bullet}OH \xrightarrow{O_2} RO_2^{\bullet} + H_2O$$

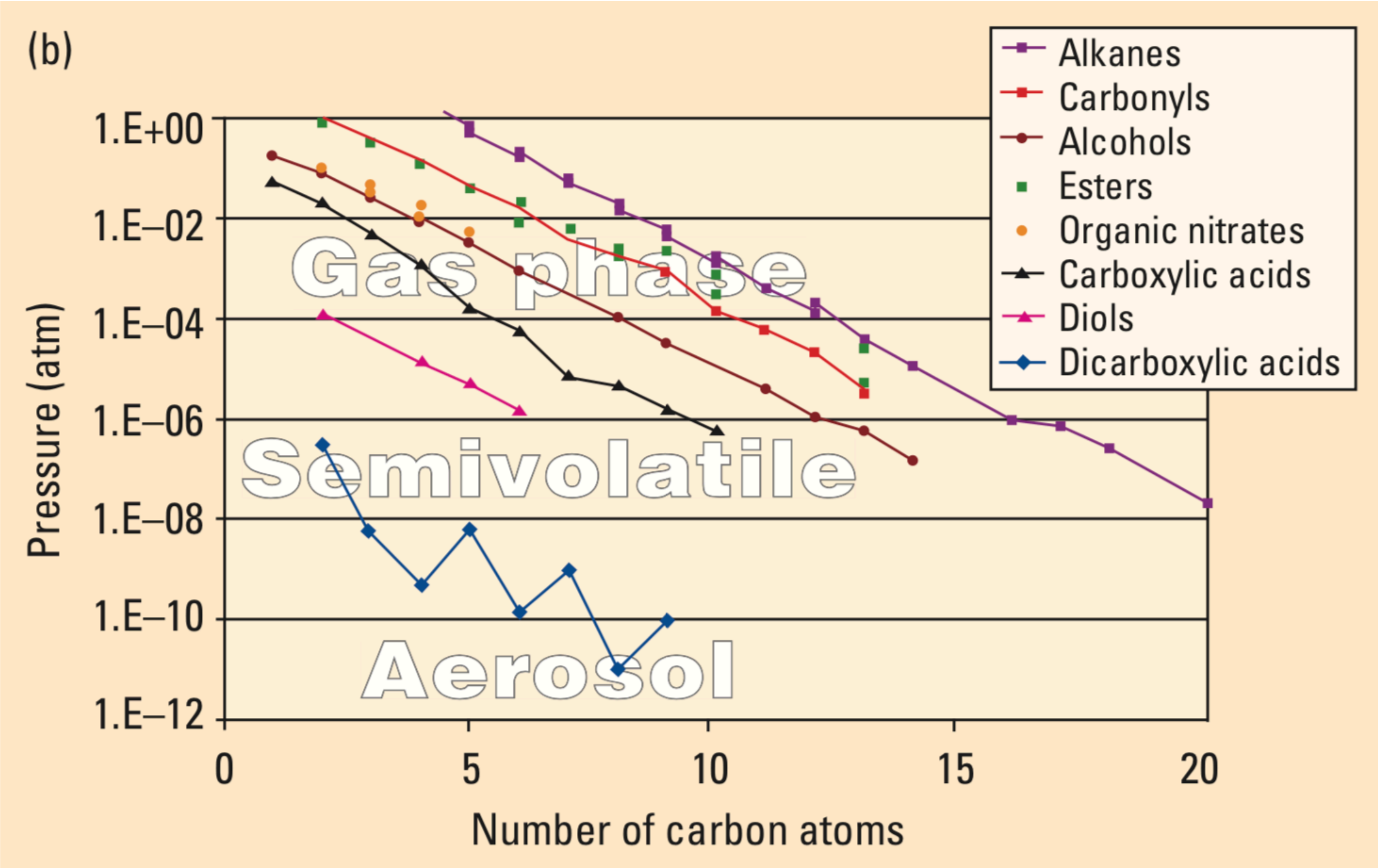
$$RO_2^{\bullet} + 2NO \xrightarrow{O_2} RCHO + 2NO_2 + {}^{\bullet}OH$$

$$2NO_2 + 2h\nu\ (\lambda \leq 424\ \text{nm}) \rightarrow 2O\,(^3P) + 2NO$$

$$2O\,(^3P) + O_2 \rightarrow 2O_3$$

- VOCs oxidation lead to ozone and aerosol production.

Gas particle partition as a function of nº of C & funcional group polarity



Goldstein AH, Galbally IE (2007) Known and Unexplored Organic Constituents in the Earth's Atmosphere Environmental science & technology 41:1514-1521 doi: 10.1021/es072476p

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Ozone and precursors

$$NO_2 + {}^{\bullet}OH \rightarrow HONO_2 \; ; \; k_{NO2+OH} = 1.7 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$$

$$VOC + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \; ; \; k_{VOC+OH} = 3.1 \times 10^3 \text{ ppmC}^{-1} \text{ min}^{-1}$$

$$[VOC]\, k_{VOC+OH} = [NO_2]\, k_{NO2+OH}$$

✓ $VOC:NO_2 = 5.5:1$

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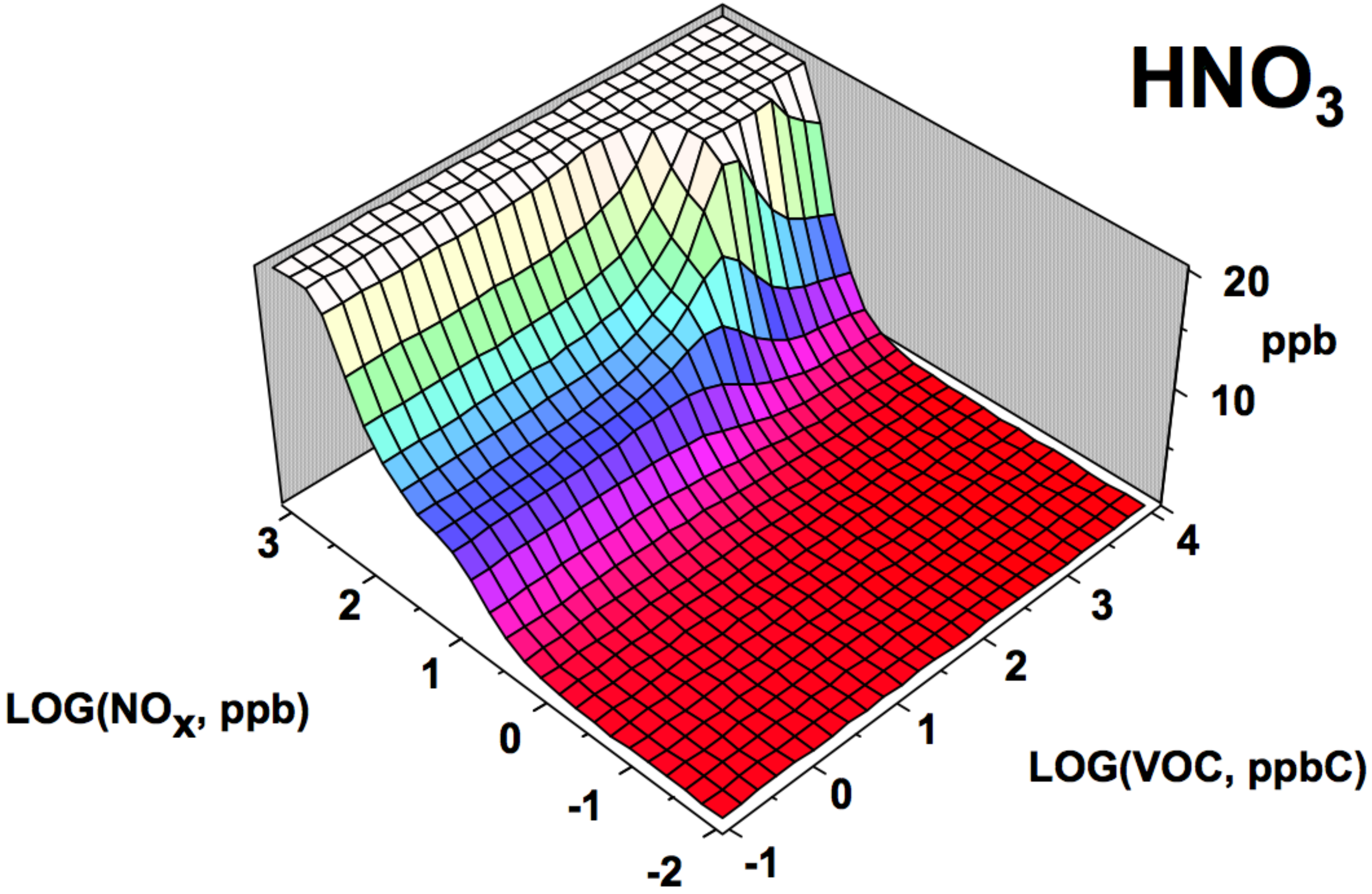
At low VOC/NO_x ratios



$$^{\bullet}OH + NO_2 + M \rightarrow HNO_3 + M$$

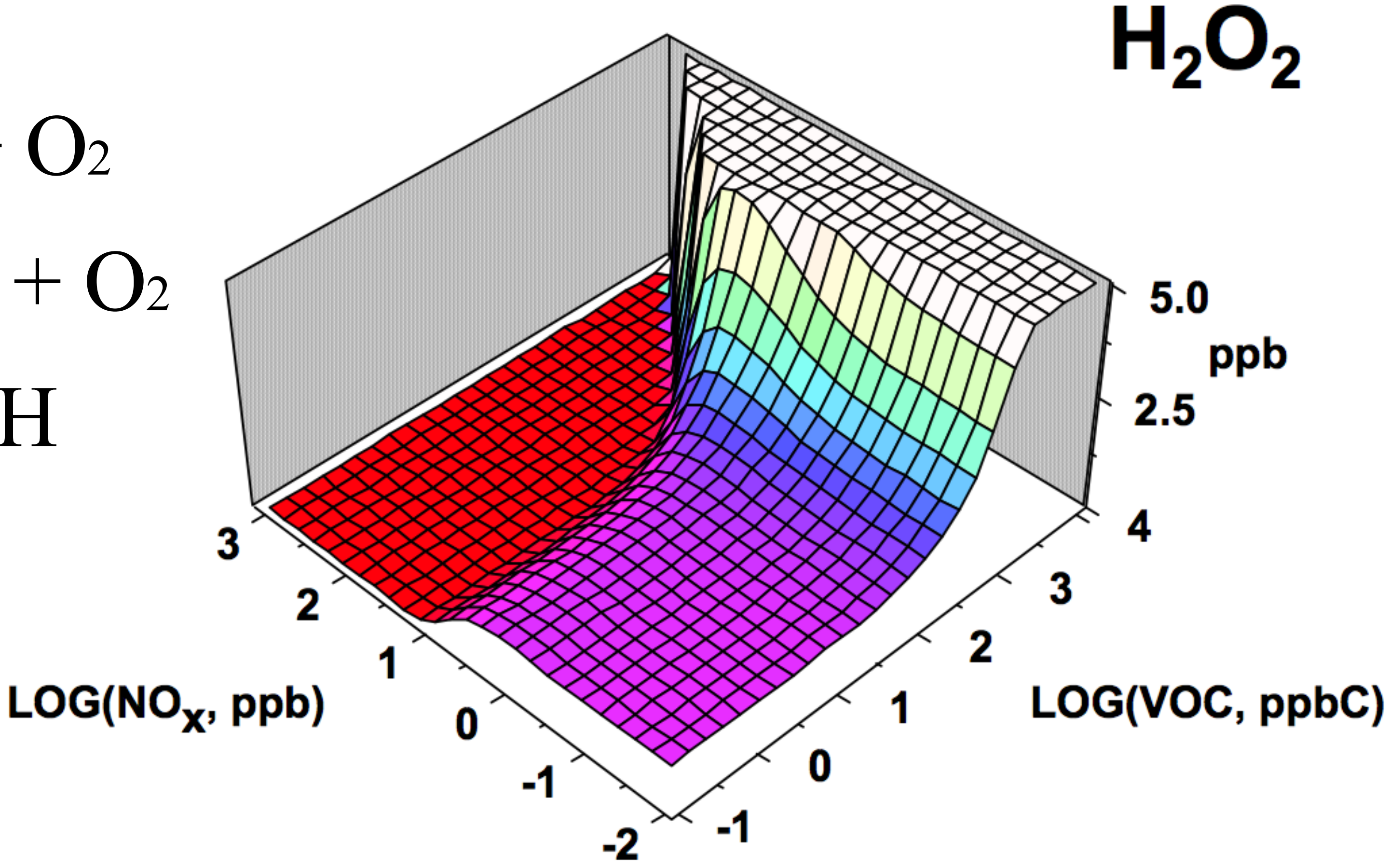
Fujita, E. Seminar "Photochemical smog in Chile and California: Experience, measures and recommendations", Organized by CENMA in collaboration with Desert Research Institute (DRI), Santiago, Chile. June 10, 2010.

High VOC/NO_x ratios

$$^{\bullet}OH + HO_2^{\bullet} \rightarrow H_2O + O_2$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$$

$$RO_2^{\bullet} + HO_2^{\bullet} \rightarrow ROOH$$



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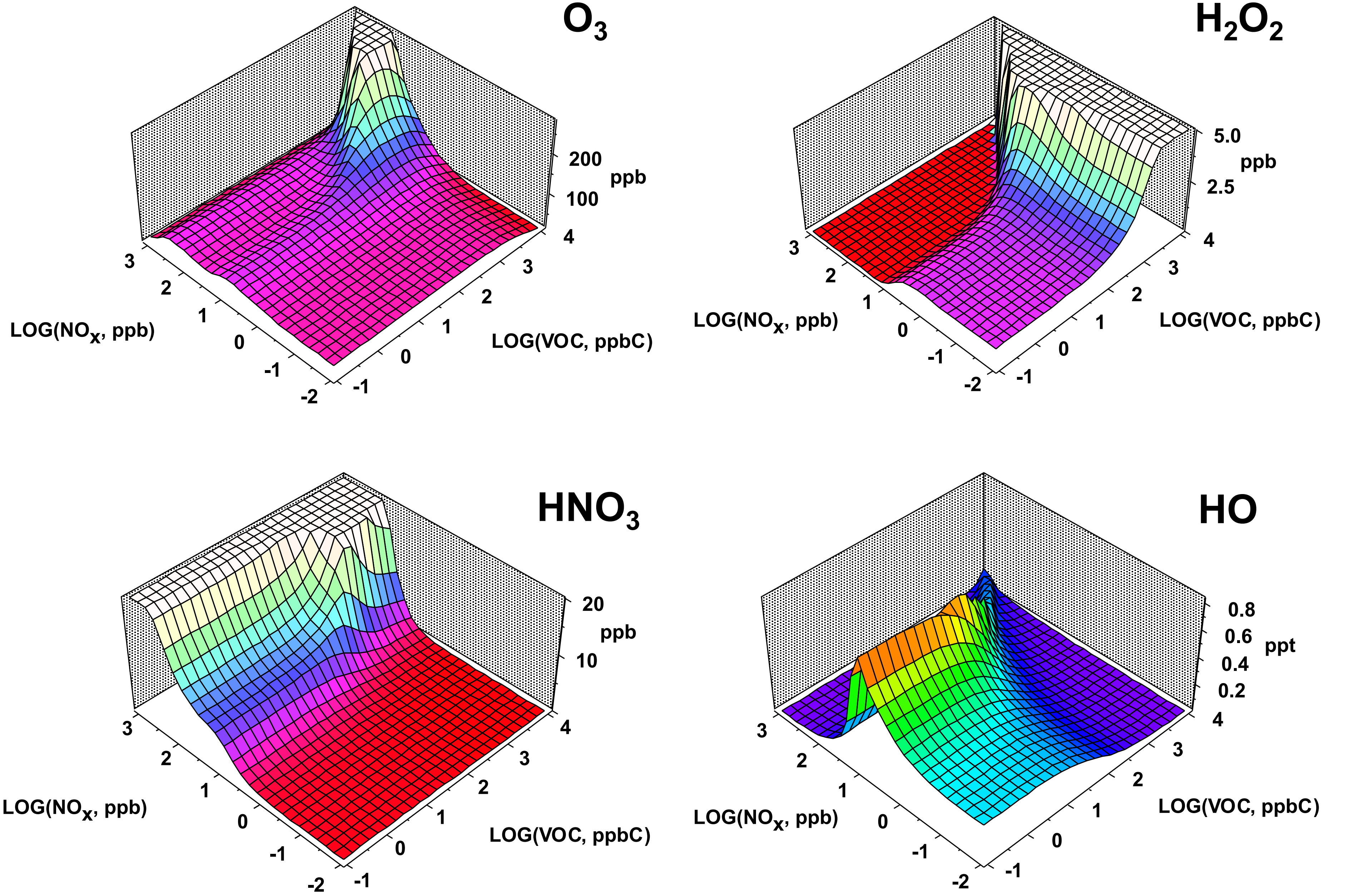
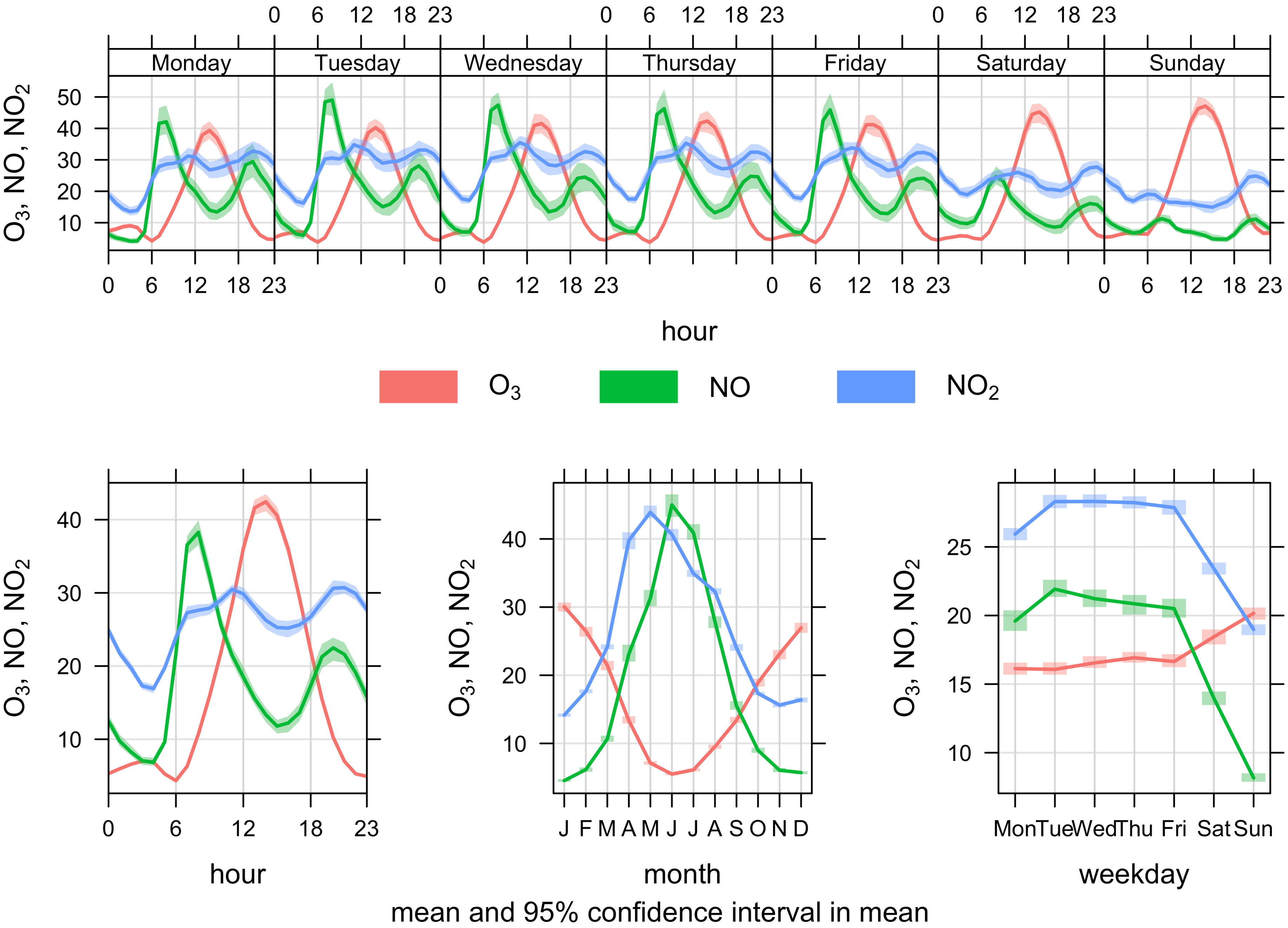


Fujita, E. Seminar “Photochemical smog in Chile and California: Experience, measures and recommendations”, Organized by CENMA in collaboration with Desert Research Institute (DRI), Santiago, Chile. June 10, 2010.



Seguel RJ, Gallardo L, Fleming ZL, Landeros S (2020) Two decades of ozone standard exceedances in Santiago de Chile Air Qual Atmos Health doi:10.1007/ s11869-020-00822-w

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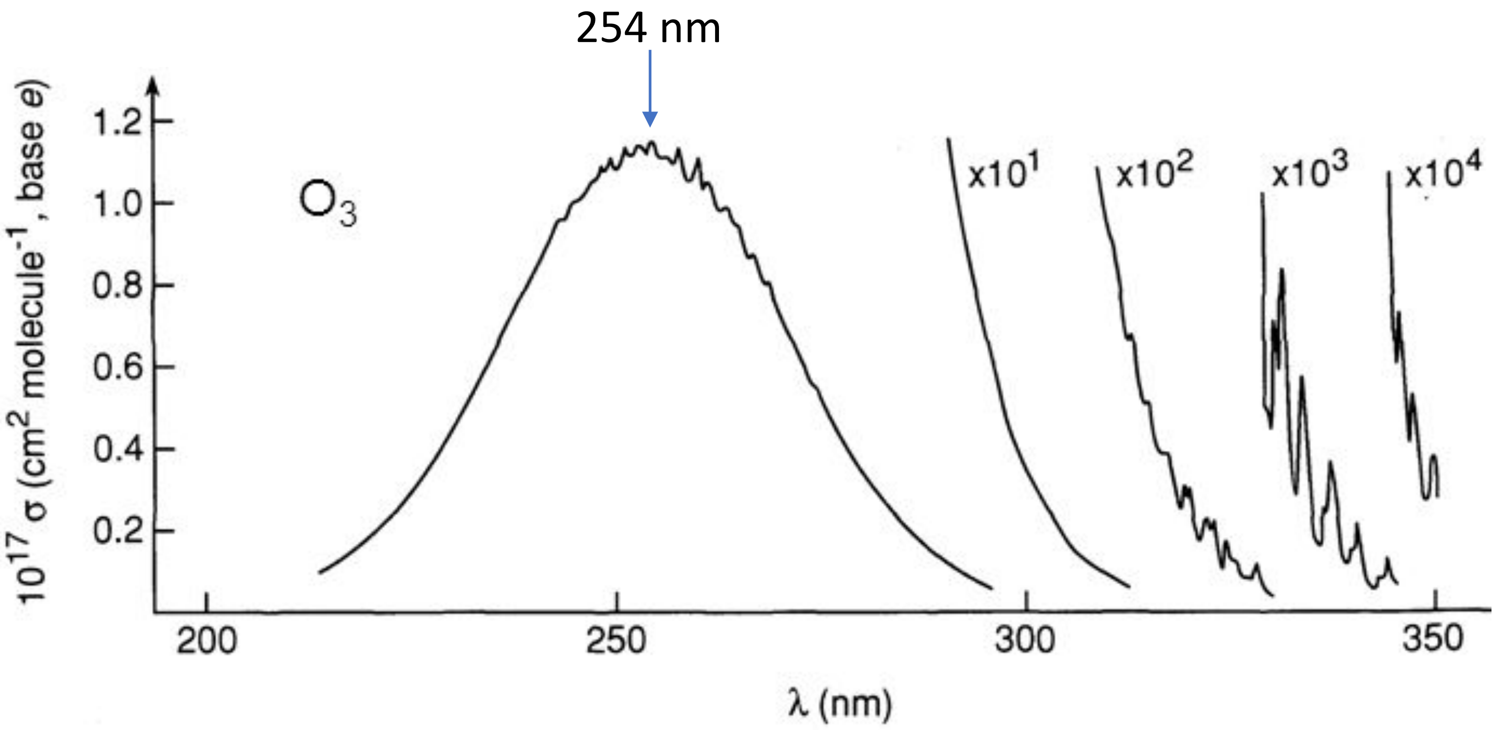
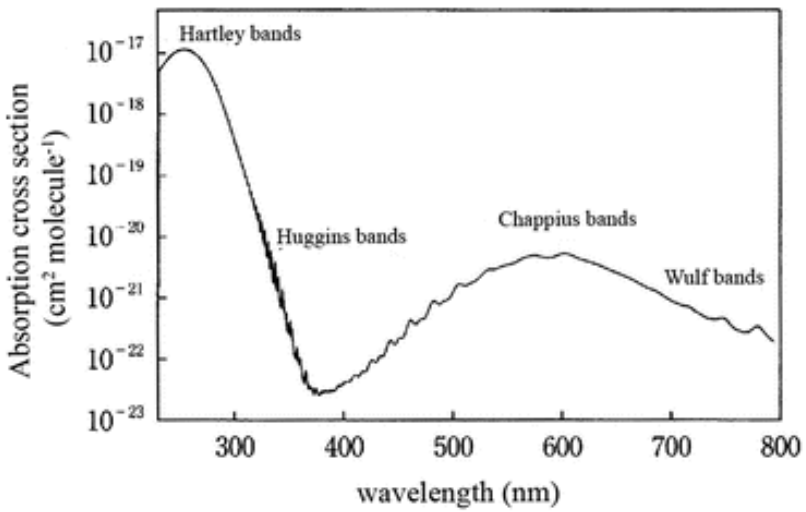
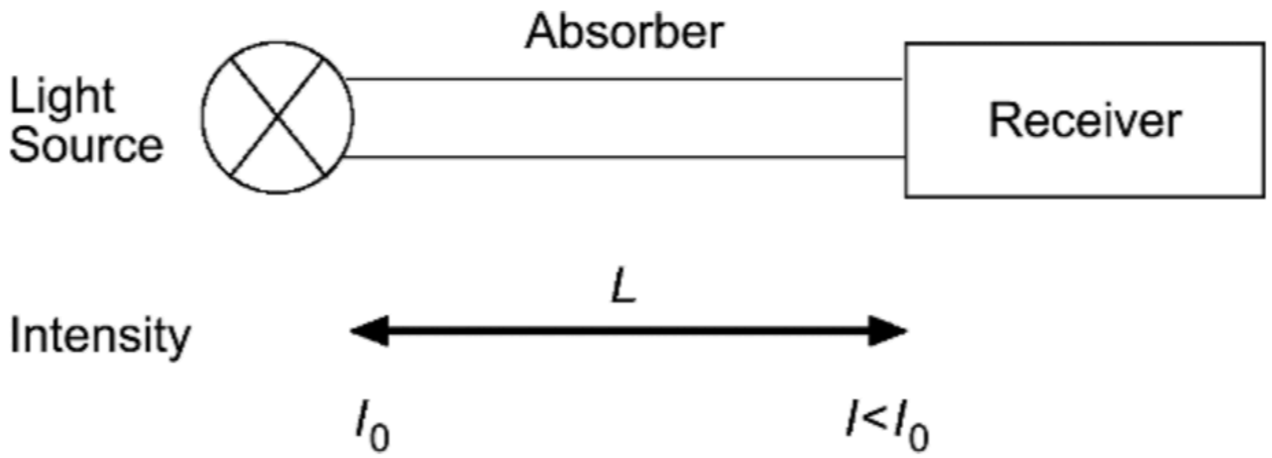
Absorption cross section of O_3





- There is a new O_3 Cross-Section consensus value at 253.65 nm published in 2019 (Bureau International des poids et mesures)

Basic principle of surface ozone measurement



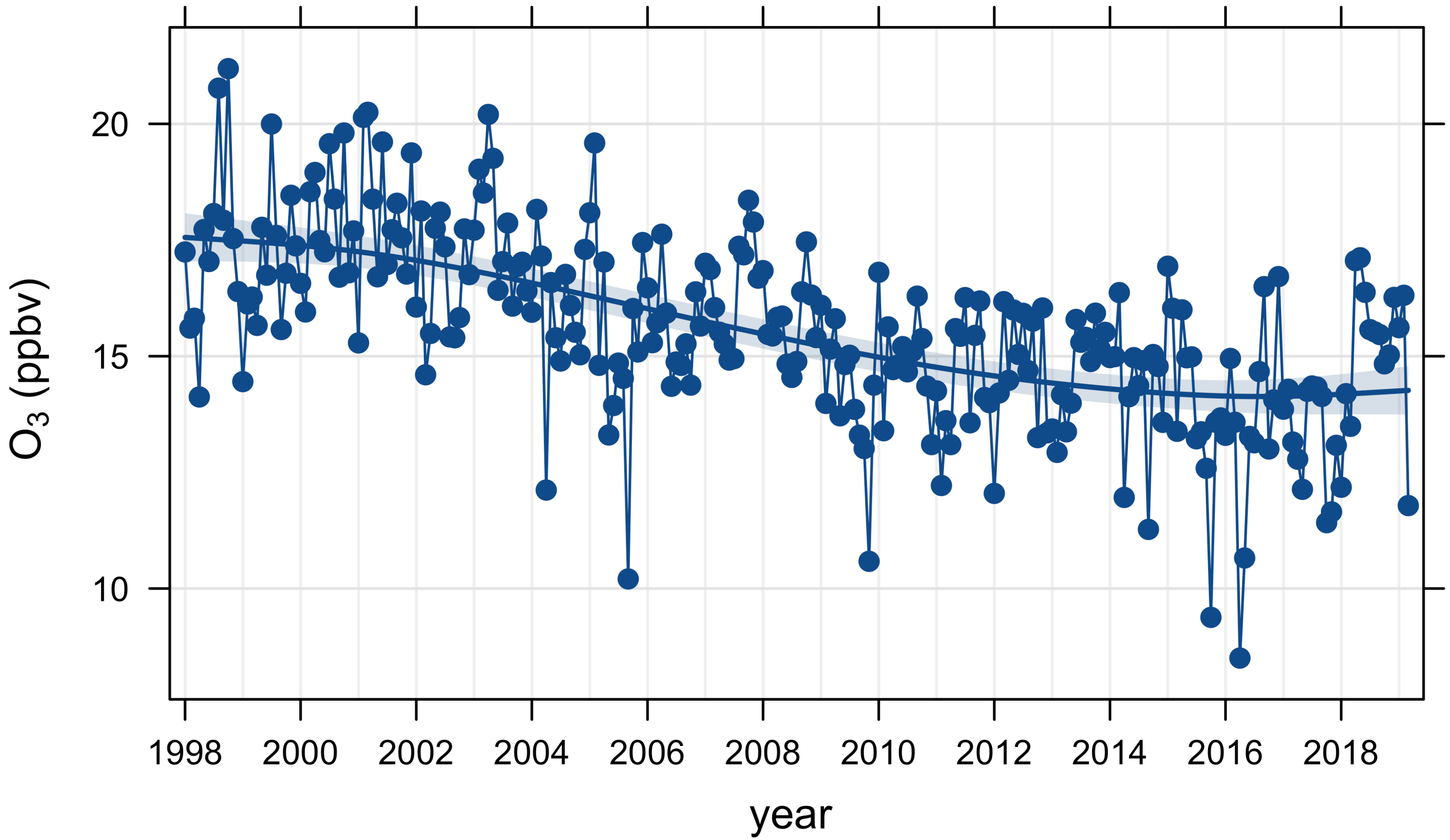
$$-\frac{dI}{dl}\alpha\ I$$

- Lambert–Beer's law

$$I(\lambda) = I_0(\lambda)\,\mathrm{e}^{[-L\,\sigma(\lambda)\,c]}$$

$$C_{O3} = \frac{1}{\sigma\ L}\ln\left(\frac{I_0}{I}\right)$$

Central Santiago



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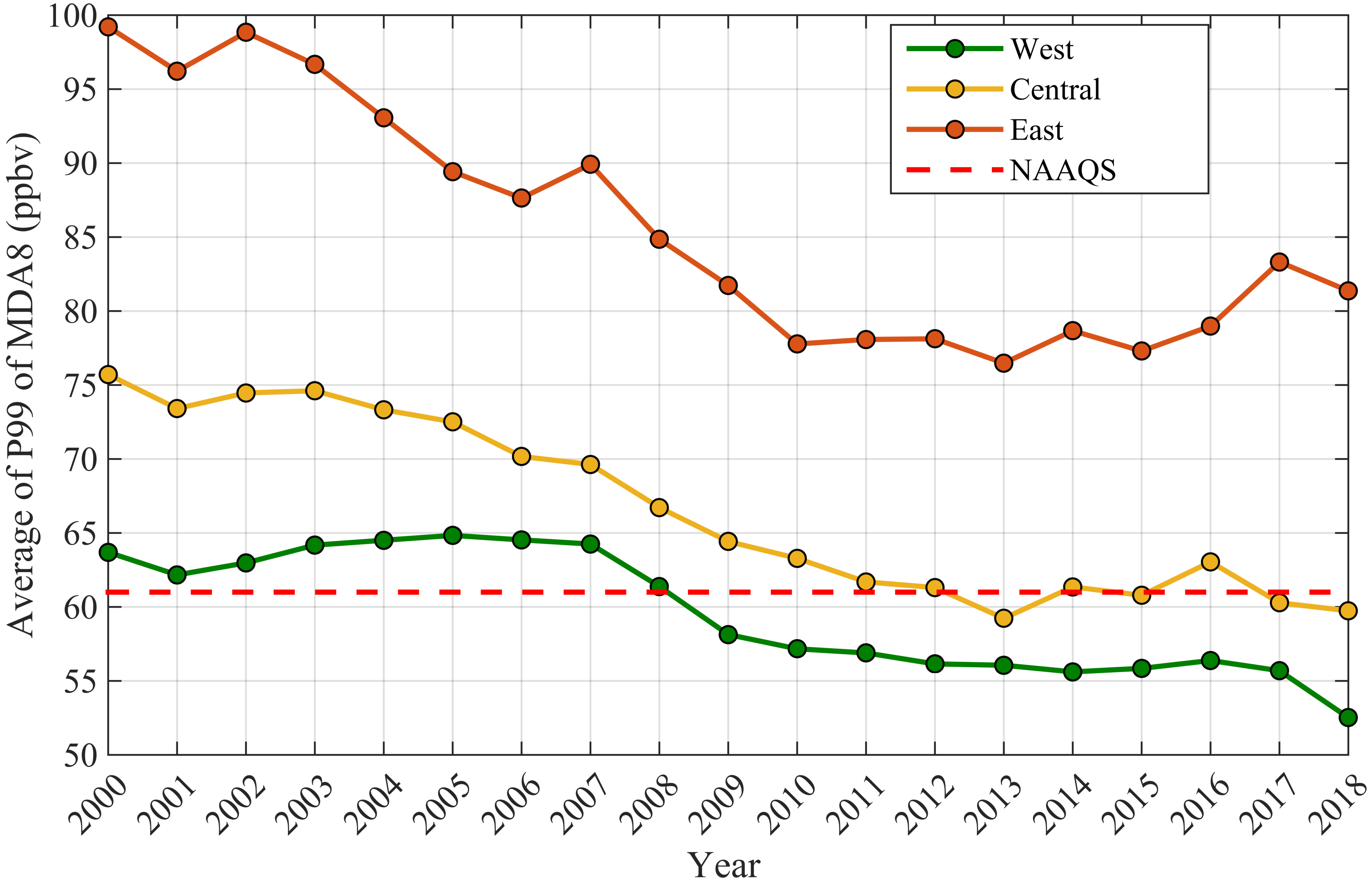

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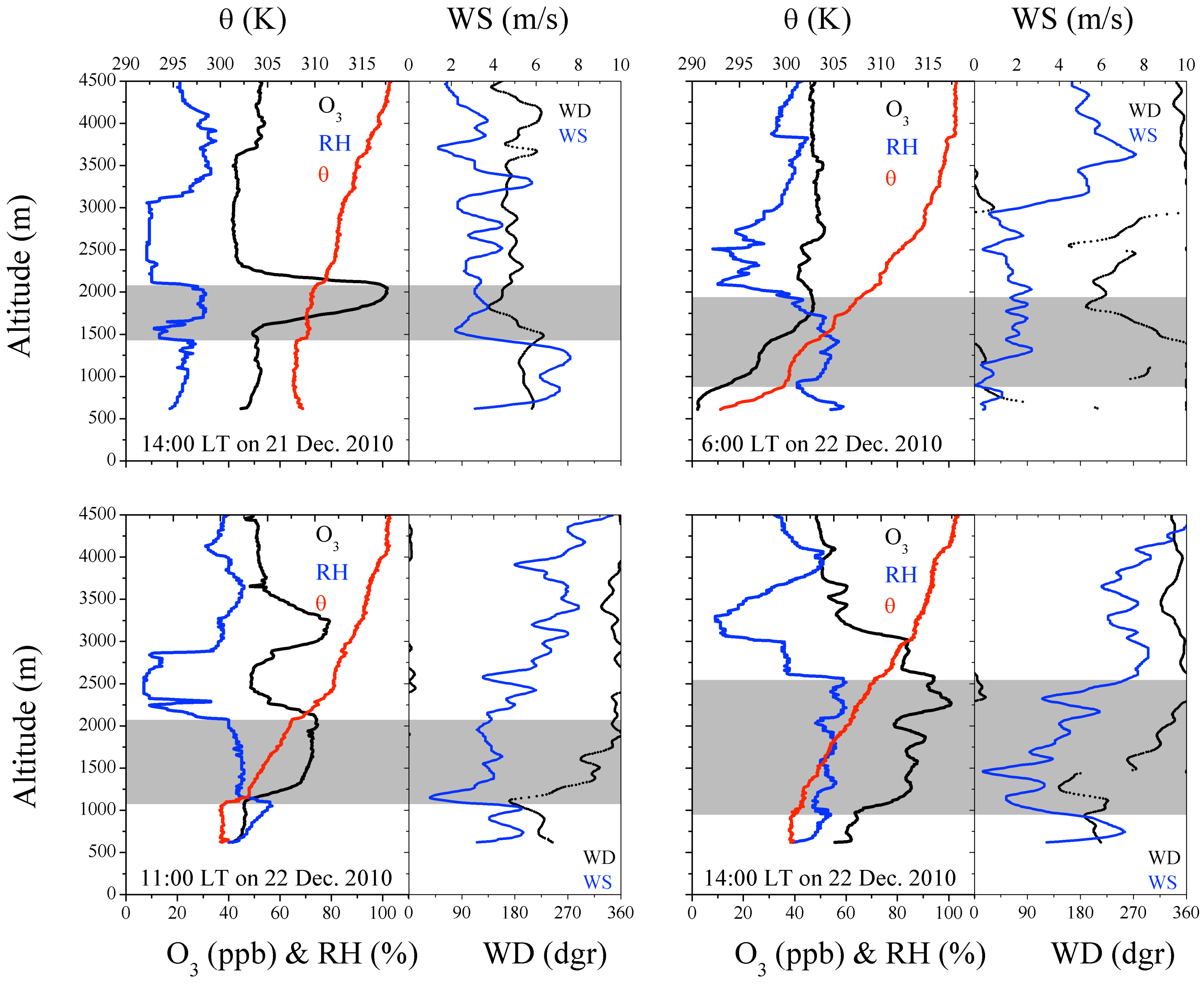


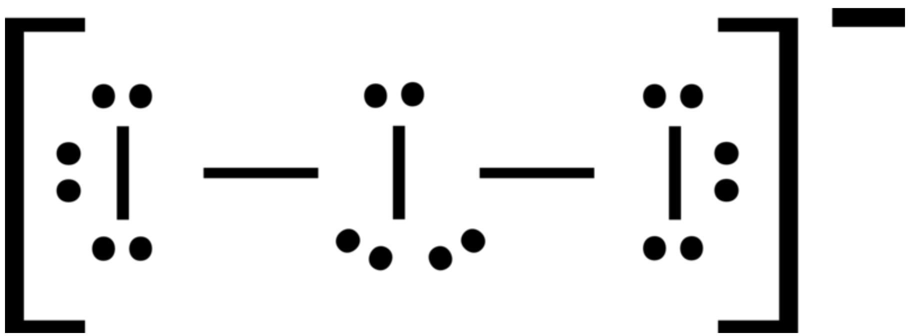
Seguel RJ, Mancilla CA, Rondanelli R, Leiva MA, Morales RGE (2013) Ozone distribution in the lower troposphere over complex terrain in Central Chile Journal of Geophysical Research: Atmospheres 118:2966-2980 doi: 10.1002/jgrd.50293

Ozonesondes: Electrochemical concentration cell (ECC)

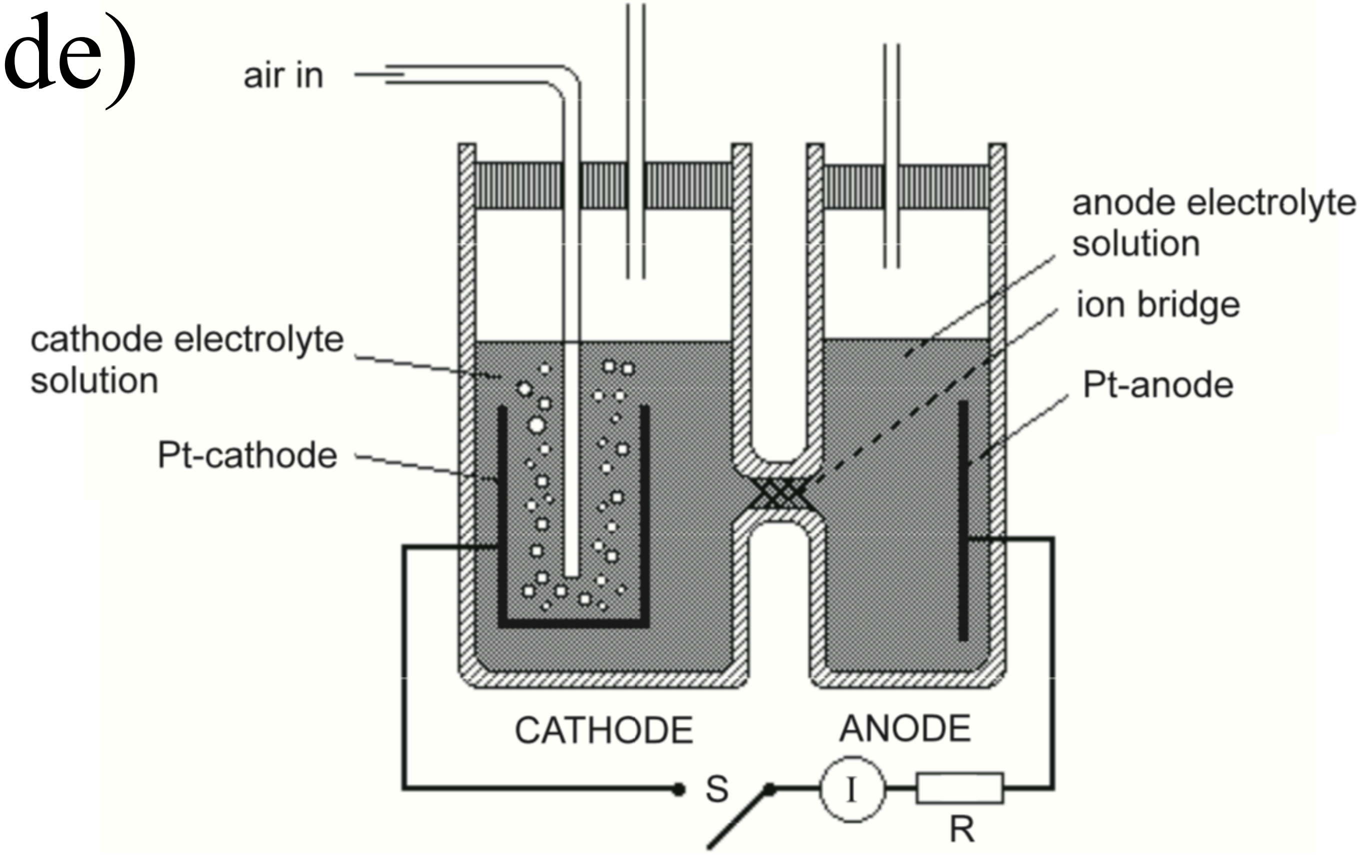
$$2\,KI + O_3 + H_2O \rightarrow 2\,KOH + I_2 + O_2 \text{ (Cathode)}$$

$$3\,I^- \rightarrow I_3^- + 2e^- \text{ (Cathode)}$$

$$I_2 + 2e^- \rightarrow 2I^- \text{ (Anode)}$$



Triiodide Lewis structure



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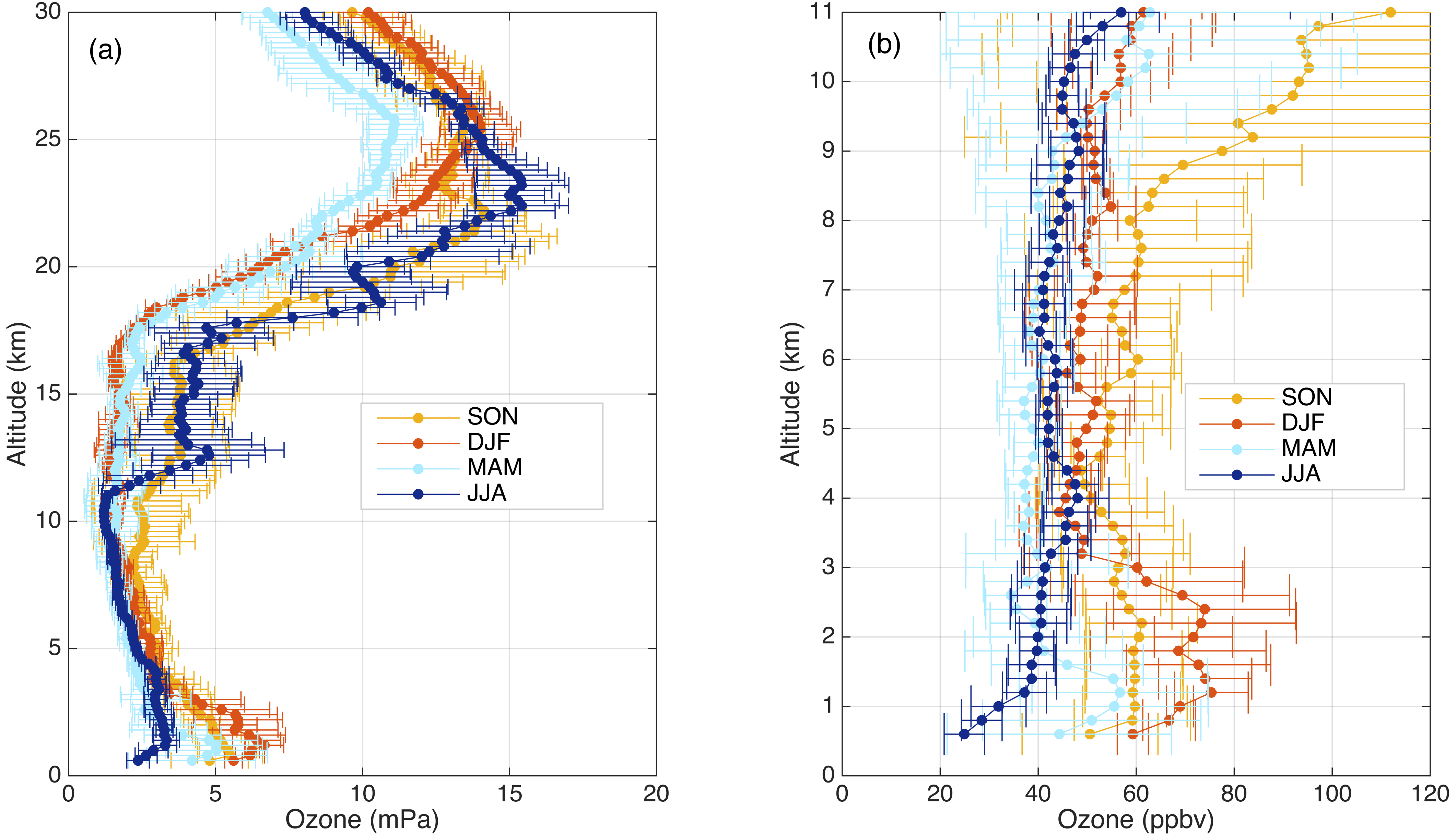
Estimation of the Ozone column by ECC

$$\text{Ozone Column} = \sum_i 3.9449 \cdot \left(p_{O_3 i} + p_{O_3 i+1} \right) \ln\left(\frac{p_i}{p_i + 1} \right)$$

- Where i represents the index for a measurement point.



(a)
Altitude (km)
Ozone (mPa)
SON
DJF
MAM
JJA
(b)
Altitude (km)
Ozone (ppbv)
SON
DJF
MAM
JJA

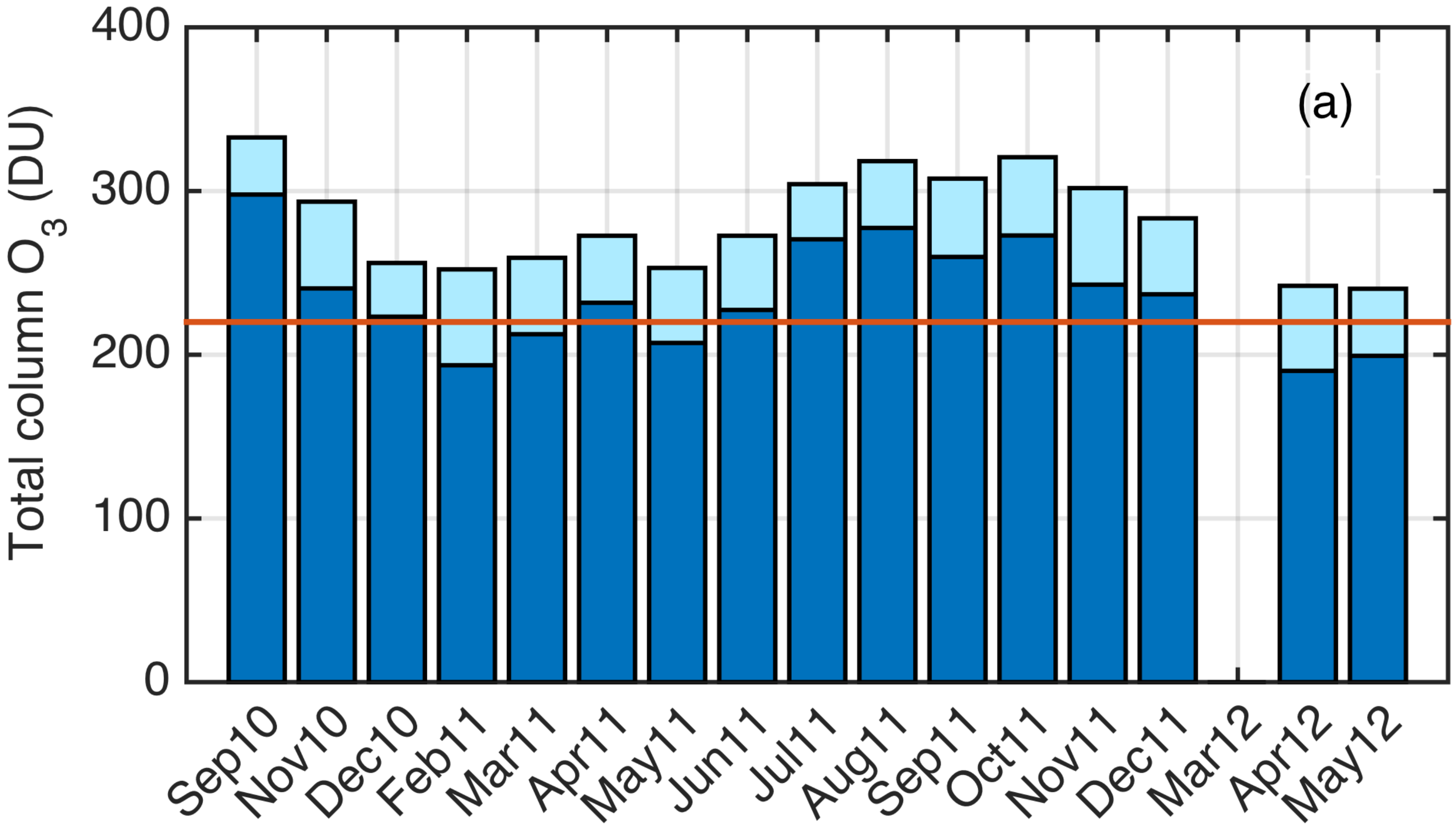
Estimation of the Total Column Ozone using a monthly average ozone climatology

- Cumulative ozone above atmospheric Pressure levels for 10º from 70ºN to 70ºS

Press, mbar	January	February	March	April	May	June	July	August	September	October	November	December	S.D.
							30°–40°S						
1	1.2	1.3	1.3	1.3	1.4	1.4	1.4	1.4	1.4	1.3	1.2	1.2	0.06
2	4.1	4.3	4.5	4.8	5.3	5.4	5.2	5.1	4.9	4.5	4.1	4.0	0.24
3	8.4	8.7	9.1	9.6	10.3	10.5	10.2	10.1	9.8	9.2	8.5	8.3	0.44
4	13.8	14.3	15.0	15.8	16.7	16.8	16.4	16.4	16.2	15.4	14.3	13.8	0.69
5	19.5	20.0	20.7	21.5	22.2	22.3	21.9	22.0	22.0	21.3	20.1	19.5	0.86
6	25.9	26.3	27.0	27.6	28.1	28.0	27.6	27.9	28.2	27.7	26.5	25.9	1.03
7	32.8	33.1	33.8	34.1	34.2	34.0	33.7	34.2	34.9	34.7	33.6	32.8	1.20
8	40.3	40.5	41.0	40.9	40.6	40.2	40.0	40.8	41.9	42.1	41.1	40.4	1.37
9	46.3	46.4	46.7	46.4	45.8	45.3	45.1	46.1	47.4	47.8	47.0	46.4	1.51
10	52.4	52.5	52.6	51.9	51.0	50.4	50.3	51.4	52.9	53.6	53.0	52.5	1.66
11	58.6	58.6	58.5	57.5	56.2	55.5	55.4	56.7	58.5	59.4	59.0	58.7	1.80
12	64.9	64.8	64.5	63.1	61.4	60.5	60.6	62.0	64.1	65.2	65.1	65.0	1.95
13	71.3	71.1	70.5	68.7	66.6	65.6	65.8	67.4	69.7	71.1	71.3	71.4	2.09
14	77.8	77.5	76.6	74.3	71.8	70.7	71.0	72.7	75.2	77.0	77.5	77.9	2.22
15	84.4	83.9	82.7	79.9	77.1	75.8	76.2	78.1	80.9	82.9	83.8	84.5	2.36
16	91.0	90.5	89.0	85.7	82.3	80.9	81.4	83.5	86.6	88.9	90.2	91.2	2.50
17	95.5	94.8	93.3	89.9	86.6	85.2	85.7	87.8	91.0	93.4	94.6	95.6	2.59
18	99.8	99.2	97.6	94.1	90.7	89.4	90.0	92.2	95.4	97.8	99.0	100.0	2.67
19	104.1	103.4	101.8	98.3	94.9	93.6	94.3	96.5	99.8	102.2	103.3	104.3	2.75
20	108.3	107.6	105.9	102.3	99.0	97.7	98.4	100.8	104.1	106.5	107.6	108.6	2.83
21	112.5	111.8	110.1	106.4	103.0	101.8	102.6	105.0	108.4	110.8	111.8	112.8	2.91
22	116.7	115.9	114.2	110.4	107.0	105.9	106.8	109.2	112.7	115.0	116.0	117.0	2.99
23	120.8	120.1	118.2	114.4	111.1	110.0	111.0	113.4	117.0	119.3	120.1	121.2	3.07
24	124.9	124.1	122.2	118.4	115.0	114.1	115.1	117.6	121.2	123.5	124.2	125.3	3.14
25	128.9	128.1	126.2	122.3	119.0	118.0	119.1	121.7	125.3	127.6	128.3	129.3	3.21
26	132.9	132.1	130.1	126.2	122.9	122.0	123.2	125.8	129.5	131.7	132.3	133.3	3.28
27	136.9	136.0	134.0	130.0	126.8	126.0	127.2	129.9	133.6	135.8	136.3	137.3	3.36
28	140.8	140.0	137.9	133.9	130.6	129.9	131.2	134.0	137.7	139.8	140.3	141.3	3.42
29	144.7	143.8	141.7	137.7	134.4	133.8	135.2	138.0	141.7	143.9	144.2	145.2	3.49
30	148.6	147.7	145.6	141.4	138.3	137.7	139.2	142.0	145.8	147.9	148.1	149.2	3.56

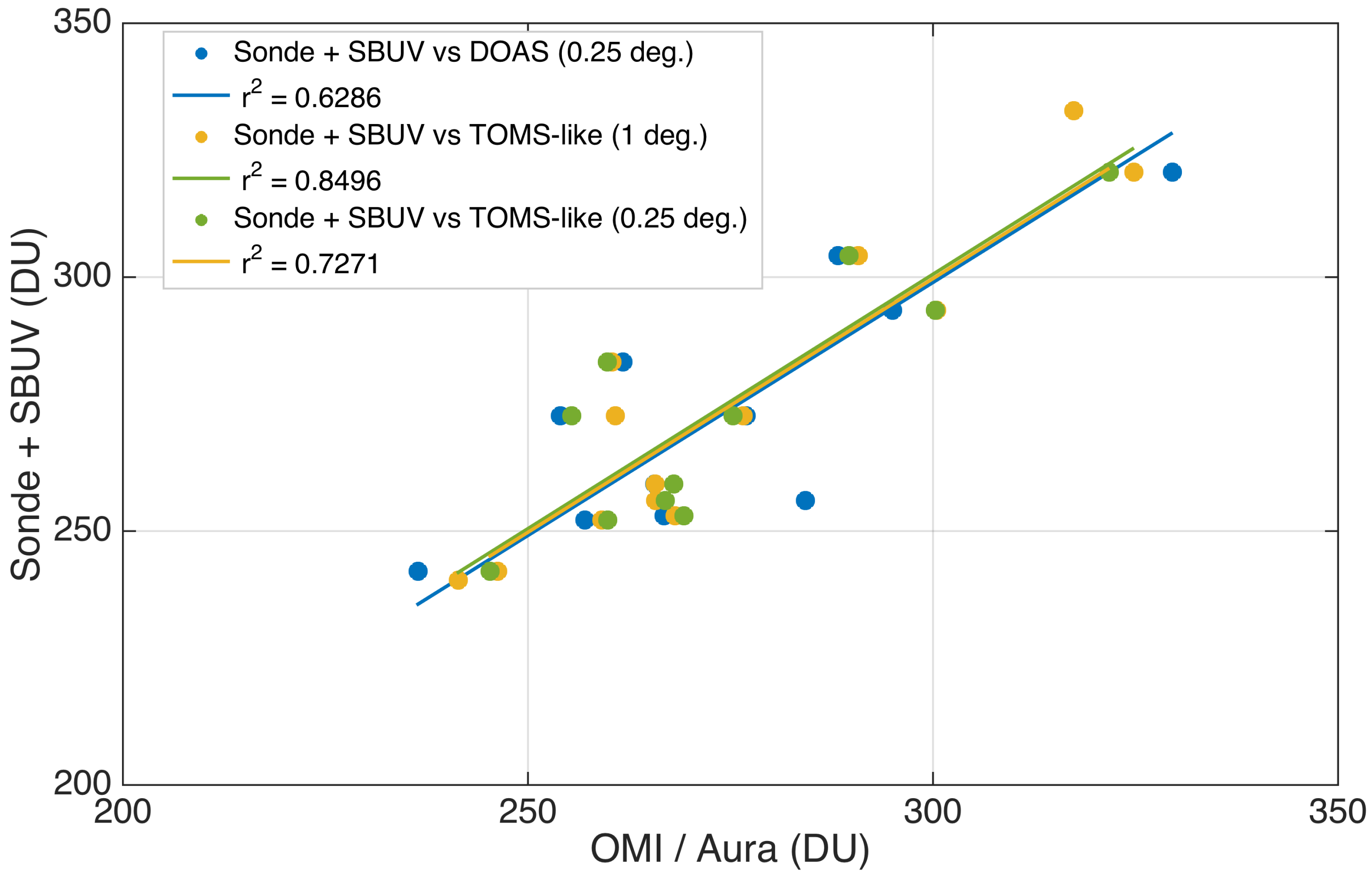
McPeters RD, Labow GJ, Johnson BJ (1997) A satellite-derived ozone climatology for balloonsonde estimation of total column ozone Journal of Geophysical Research: Atmospheres 102:8875-8885 doi:10.1029/96JD02977

Total column ozone measured by ozonesonde (blue) and extrapolation computed by adding SBUV climatological amounts (light blue)



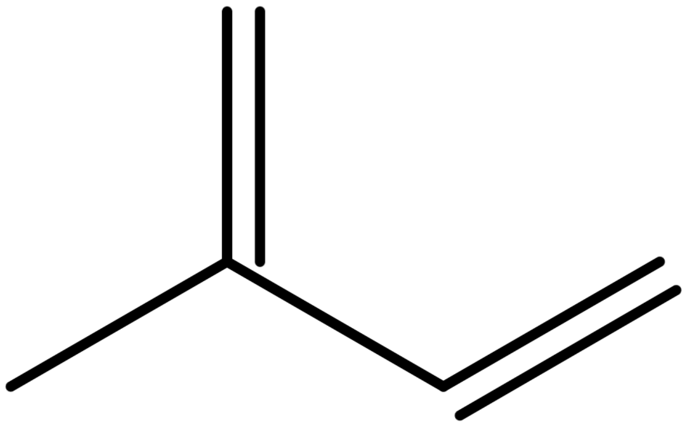
- The red line represents 220 DU, which is conventionally defined as an “ozone hole”

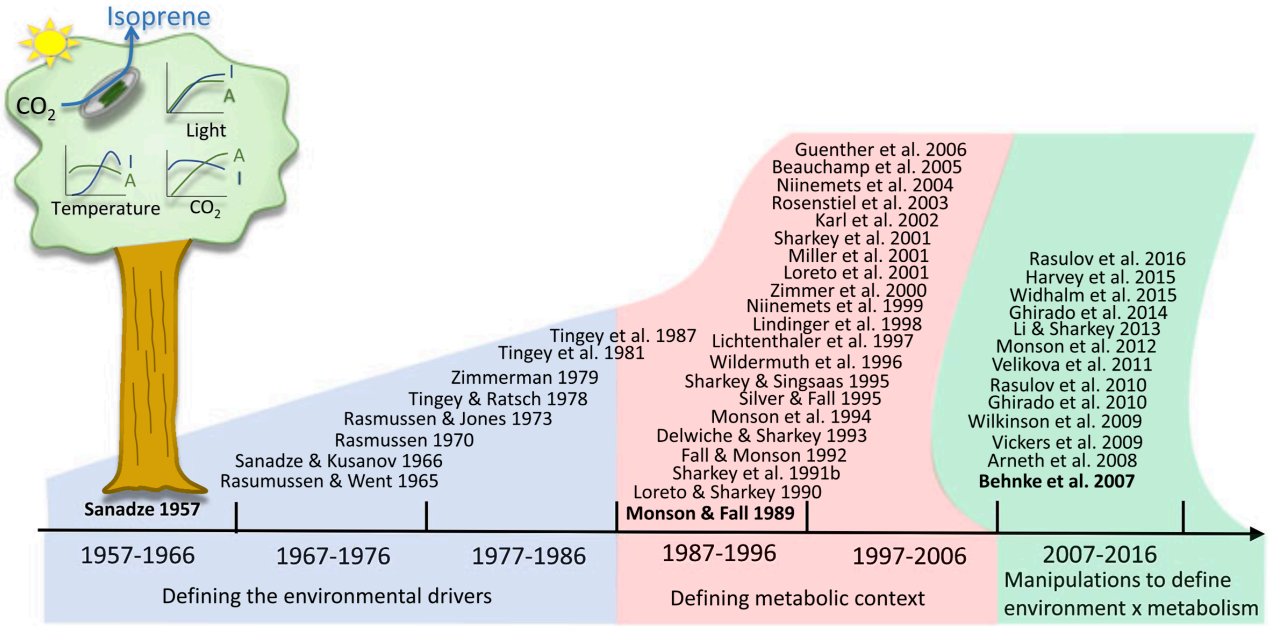
Total correlation between satellite products & and the total column O_3 computed by adding SBUV climatological amounts



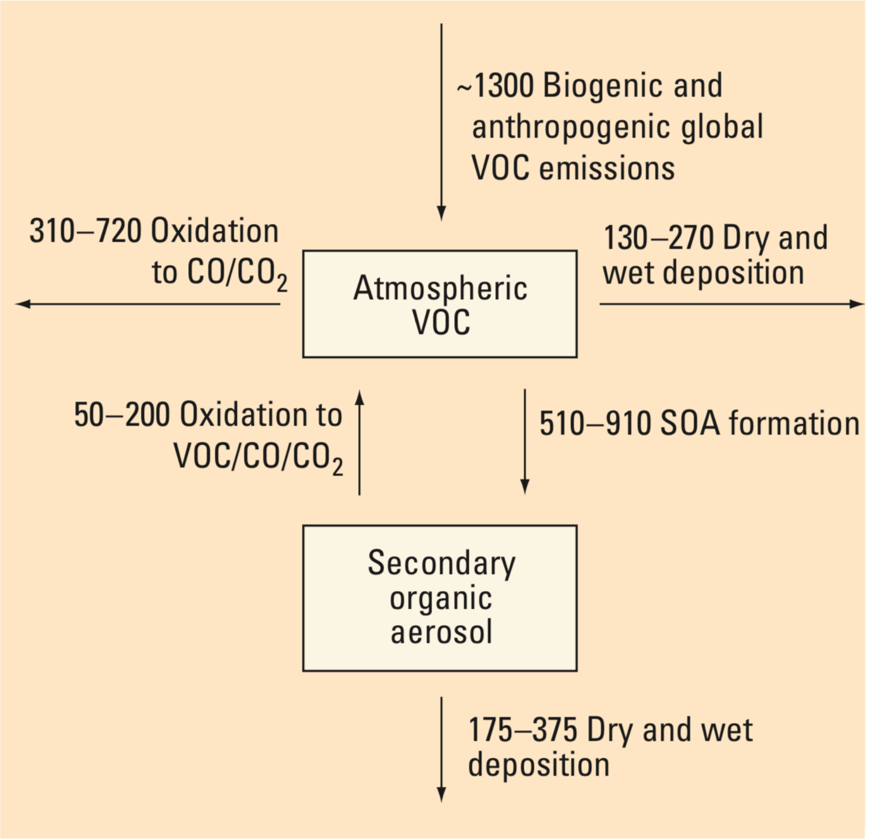
Biogenic emissions

- ~1000 TgC BVOCs per year (T: $1x10^{12}$)
- 440-660 TgC año^{-1} (isoprene)
- Biogenics: ~10 > Anthropogenics





Sharkey TD, Monson RK (2017) Isoprene research – 60 years later, the biology is still enigmatic Plant, Cell & Environment 40:1671-1678 doi:10.1111/pce.12930



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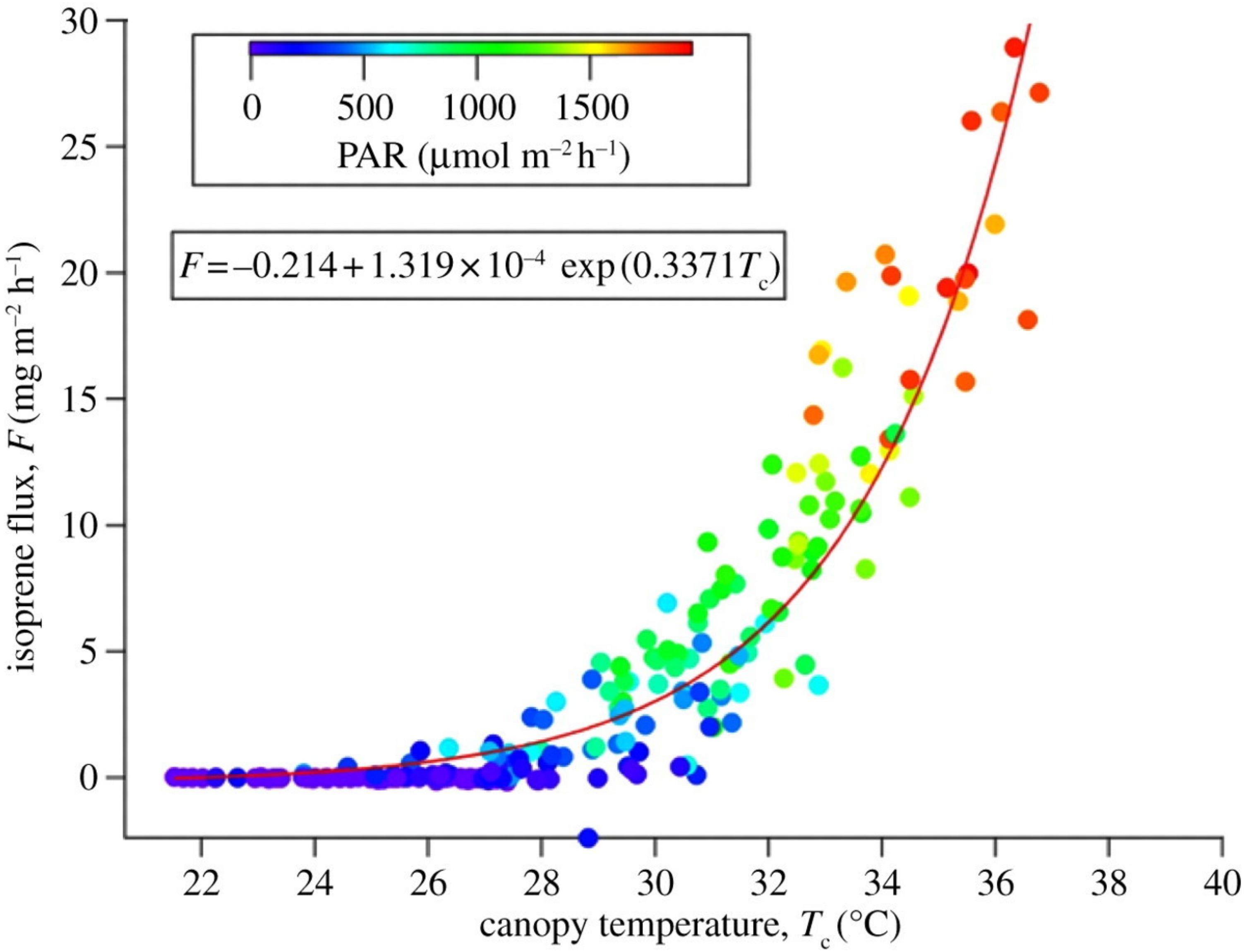
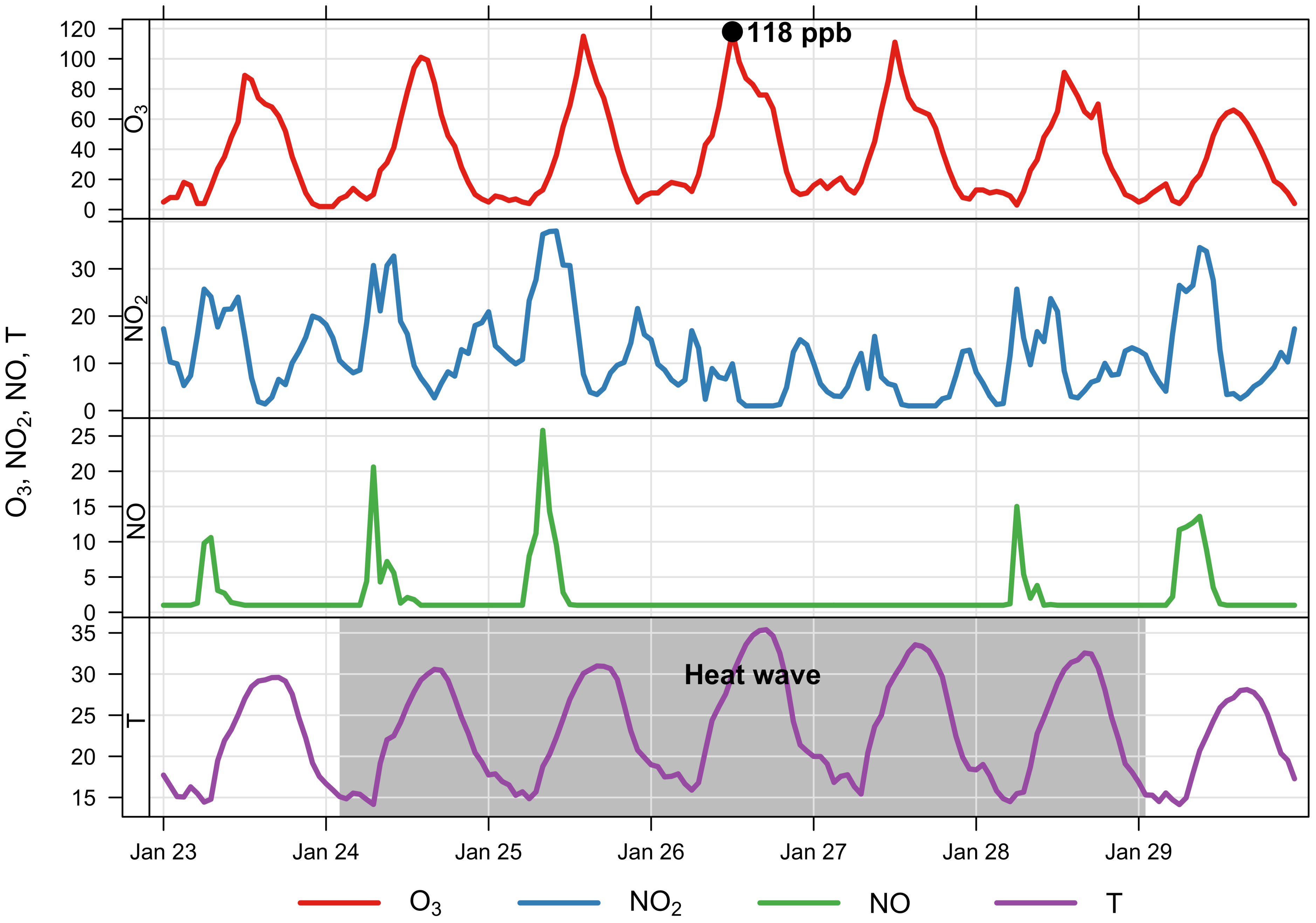


- Isoprene emission increases sharply with temperature up to ~38 °C and then falls off rapidly (Sanadze and Kalandaze 1966).



Seguel RJ, Gallardo L, Fleming ZL, Landeros S (2020) Two decades of ozone standard exceedances in Santiago de Chile Air Qual Atmos Health doi:10.1007/s11869-020-00822-w

USEPA Approach: Photochemical Assessment Monitoring Stations (PAMS) compound target list

- Priority compounds: 26 VOCs + 2 carbonyls
- Opcional compounds: 30 VOCs + 2 carbonyls + 2 organochlorides + 2 biogenics + ethanol

Priority compounds	Ozone precursor	Secondary organic aerosol precursors	Hazardous air pollutants
1-buteno	x		
1,2,3-trimetilbenceno	x	x	
1,2,4-trimeilbenceno	x	x	
2,2,4-trimetilpentano	x		x
Benceno	x	x	x
c-2-buteno	x		
Estireno	x	x	x
Etano	x		
Eteno (etileno)	x		
Etilbenceno	x	x	x
Formaldehído	x		x
Iso-butano	x		
Iso-pentano	x		
Isopreno	x		
m-etiltolueno	x	x	
m+p-xileno	x	x	x
n-butano	x		
n-hexano	x		x
n-pentano	x		
o-etiltolueno	x	x	
o-xileno	x	x	x
p-etiltolueno	x	x	
Propano	x		
Propeno (propileno)	x		
t-2-buteno	x		
Tolueno	x	x	x

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Optional compounds			
1-penteno	2,4-dimetilpentano	Ciclopentano	n-octano
1,3 butadieno	3-metilheptano	**Etanol**	n-propilbenceno
1,3,5-trimetilbenceno	3-metilhexano	Etino (acetileno)	n-undecano
2-metilheptano	3-metilpentano	Isopropilbenceno	p-dietilbenceno
2-metilhexano	**Acetona**	m-dietilbenceno	t-2-penteno
2-metilpentano	**Alfa pineno**	metilciclohexano	**Tetracloroetileno**
2,2-dimetilbutano	**Benzaldehído**	Metilciclopentano	**Tetracloruro de carbono**
2,3-dimetilbutano	**Beta pineno**	n-decano	
2,3-dimetilpentano	c-2-penteno	n-heptano	
2,3,4-trimetilpentano	Ciclohexano	n-nonano	

Canister for sampling VOCs

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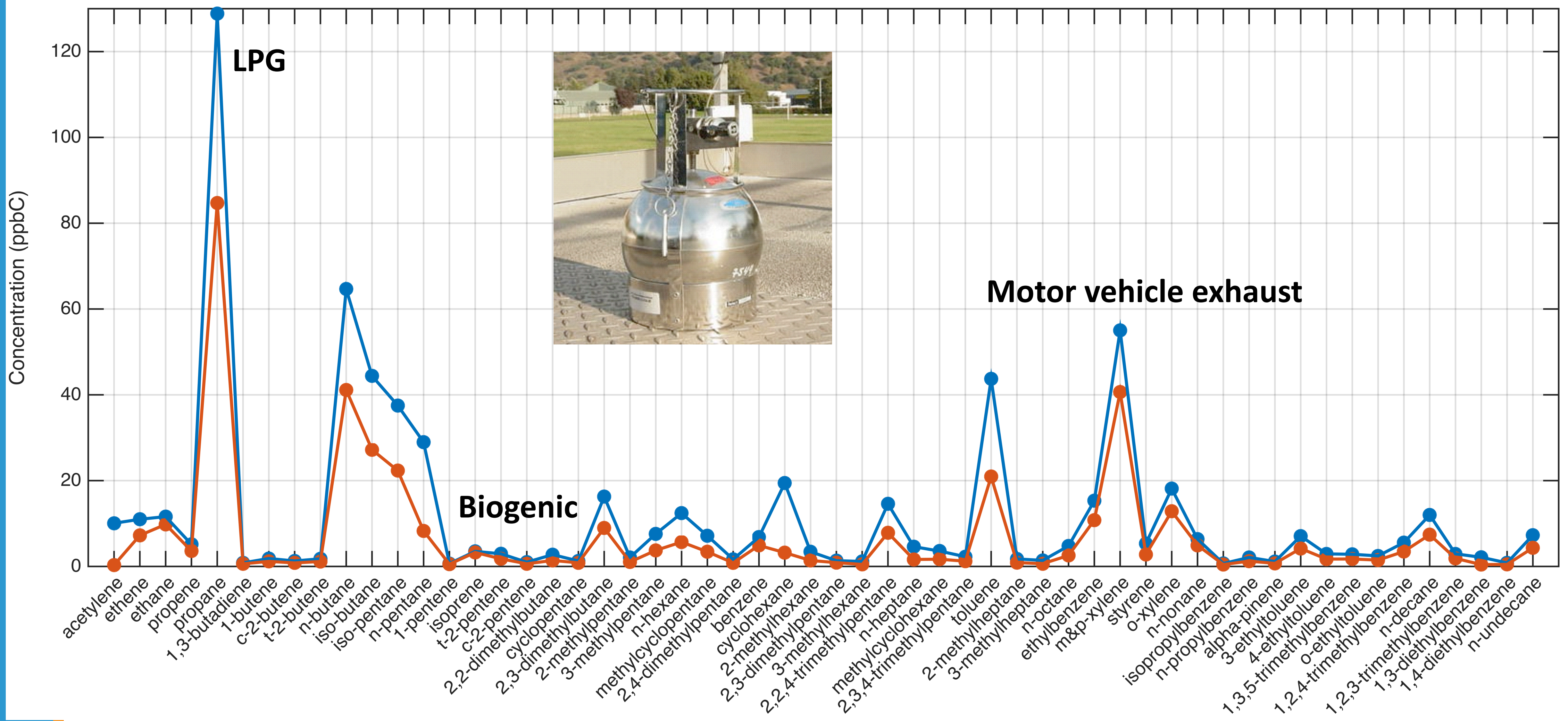
VOC Canister sampler

- Canister Based on 3 crates / weight: 409 kgs, 900 lbs/ chargeable
- Weight: 567 kgs, 1,250 lbs (Dims: 3 @ 64"x27"x40")

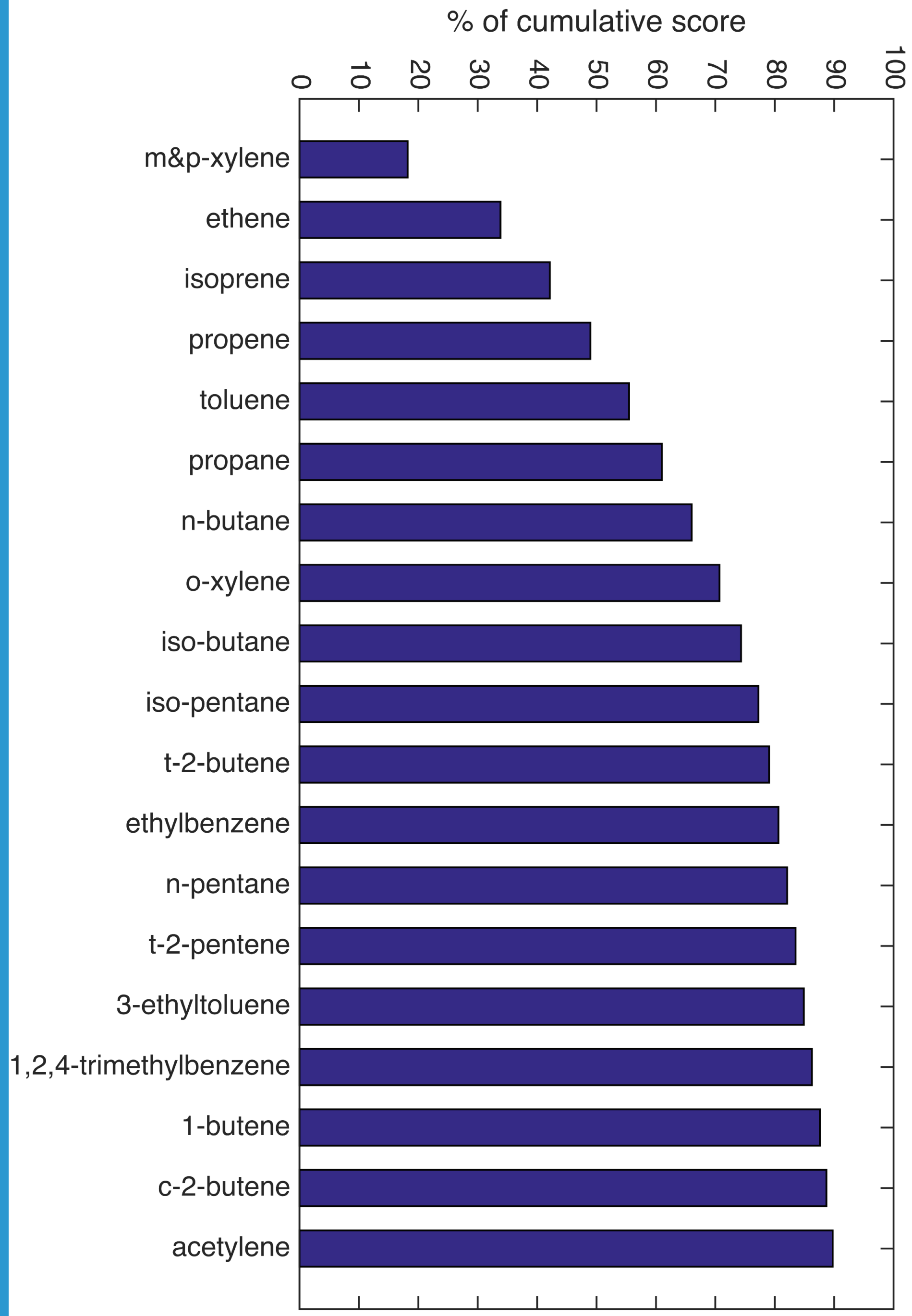
Automated VOC Analyzer ENTECH

- Canister GC/MS System

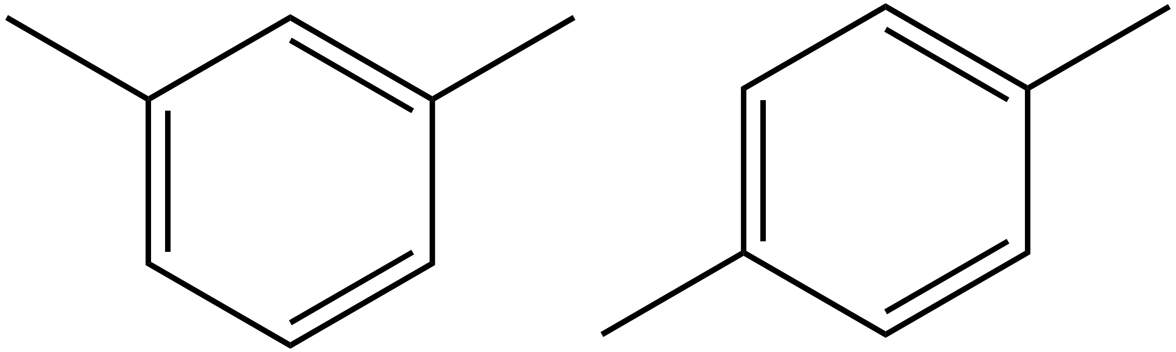
Parque O'Higgins: 16 & 17 Dec 2009 (6:00-10:00 AM)



Isoprene diurnal mixing ratio ranged 0.13–1.9 ppbv



Ozone formation potential



and 18 species...

$$VOC\ (+\ \dot{O}H,\ NO_3,\ O_3,\ h\nu) \xrightarrow{O_2} \alpha R\dot{O}_2$$

$$\alpha R\dot{O}_2 + \beta NO\ (+\ NO_2) \rightarrow \gamma NO_2 + \delta \dot{O}H + \varepsilon(\text{products})$$

Carter WPL (1994) Development of Ozone Reactivity Scales for Volatile Organic Compounds Air & Waste 44:881-899 doi:10.1080/1073161X.1994.10467290

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On-line monitoring of VOCs at ppt levels by means of Proton-transfer-reaction Mass Spectrometry (PTR-MS)

- Chemical ionization

$$H_3O^+ + R \rightarrow RH^+ + H_2O$$

Lindinger W, Hansel A, Jordan A (1998) On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research International Journal of Mass Spectrometry and Ion Processes 173:191-241 doi:https://doi.org/10.1016/S0168-1176(97)00281-4

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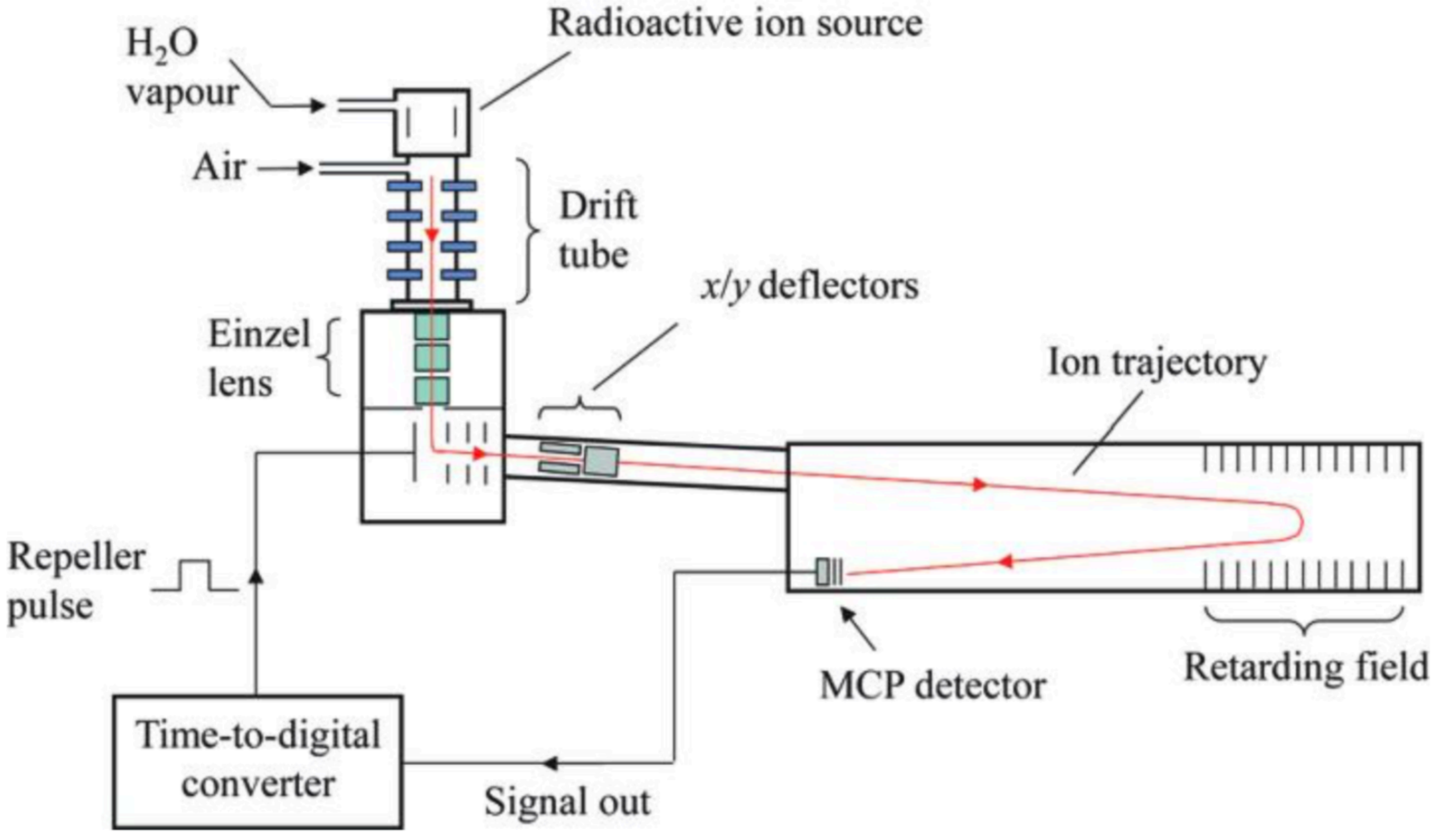
Proton affinities

Classification	Molecule	Basicity (kJ mol^{-1})	Proton affinity (kJ mol^{-1})
Inorganic gases	O_2	396	421
	N_2	465	494
	CO_2	516	541
	O_3	626	626
	H_2O	660	691
	NH_3	819	854
Alkanes	Methane	521	544
	Ethane	570	596
	Propane	608	626
	i-Butane	671	678
	Cyclopropane	722	750
Alkenes	Ethene	652	681
	Propene	723	752
Alkynes	Acetylene	617	641
	Propyne	723	748
Aromatic hydrocarbons	Benzene	725	750
	Toluene	756	784
	o-xylene	768	796
	p-xylene	767	794
	Naphthalene	779	803

Lindinger W, Hansel A, Jordan A (1998) On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research International Journal of Mass Spectrometry and Ion Processes 173:191-241 doi:https://doi.org/10.1016/S0168-1176(97)00281-4

Proton-Transfer Reaction Time-of-Flight Mass Spectrometry

- PTR-TOF-MS collects data across the entire mass range essentially instantaneously allowing to monitor complex trace VOC gas mixtures in the atmosphere



Blake RS, Whyte C, Hughes CO, Ellis AM, Monks PS (2004) Demonstration of Proton-Transfer Reaction Time-of-Flight Mass Spectrometry for Real-Time Analysis of Trace Volatile Organic Compounds Analytical Chemistry 76:3841-3845 doi:10.1021/ac0498260

Hydroxyl radical reactivity

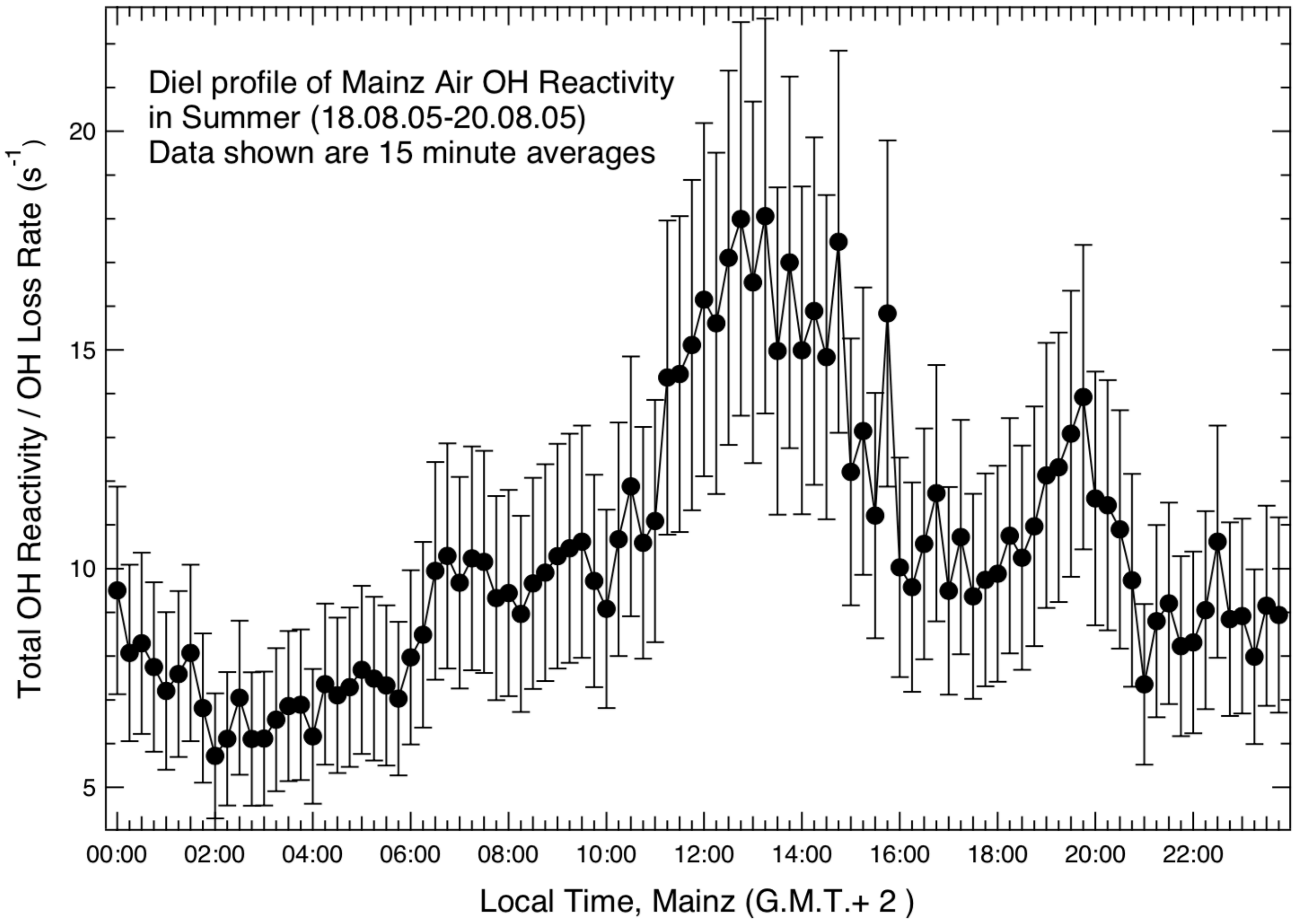
- Frequency of gas phase reactions with OH and is the inverse the lifetime of the OH.
- The Total OH Reactivity of an air mass can be defined in terms of the total loss rate of OH radicals due to the presence of OH reactants in the air mass

$$\text{Total OH reactivity } (s^{-1}) = \sum k_{(X_i + \text{OH})} [X_i]$$

- Missing reactivity

Sinha V et al. (2012) Constraints on instantaneous ozone production rates and regimes during DOMINO derived using in-situ OH reactivity measurements Atmos Chem Phys 12:7269-7283 doi:10.5194/acp-12-7269-2012

OH reactivity determined by CRM



Sinha V, Williams J, Crowley JN, Lelieveld J (2008) The Comparative Reactivity Method – a new tool to measure total OH Reactivity in ambient air Atmos Chem Phys 8:2213-2227 doi:10.5194/acp-8-2213-2008

Measured versus simulated OH reactivity

- Implications for the local photochemistry and the tropospheric ozone budget
- and other radiatively active gases, e.g., CH_4

$\downarrow$ OH reactivity ; $\uparrow$ [OH] ; $\downarrow$ lifetime of O_3 & CH_4

Introduction to the Tropospheric Ozone Assessment Report – Phase II

On behalf of the TOAR-II SC

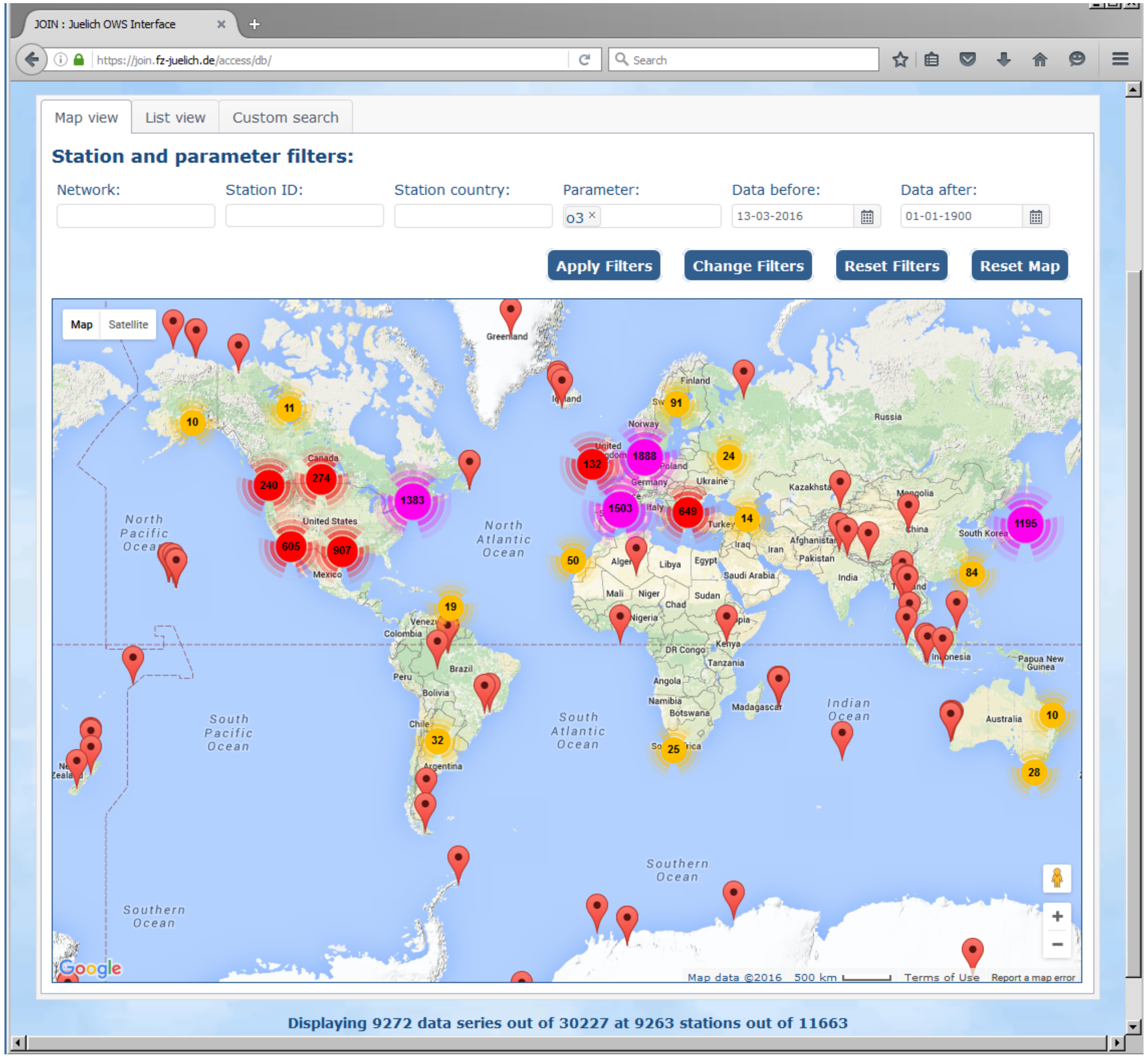
https://igacproject.org/activities/TOAR/TOAR-II https://join.fz-juelich.de/accounts/login/

TOAR Database

TOAR has built the world's largest database of ozone metrics.

Ozone observations from over 9000 monitoring sites in dozens of countries including 42 stations in South America:

Brazil, French Guiana, Chile, Argentina, Bolivia



R. J. Seguel on behalf of the TOAR-II SC
PAPILA summer school, April 2020

https://igacproject.org/activities/TOAR/TOAR-II

TOAR tropospheric ozone assessment report Phase II

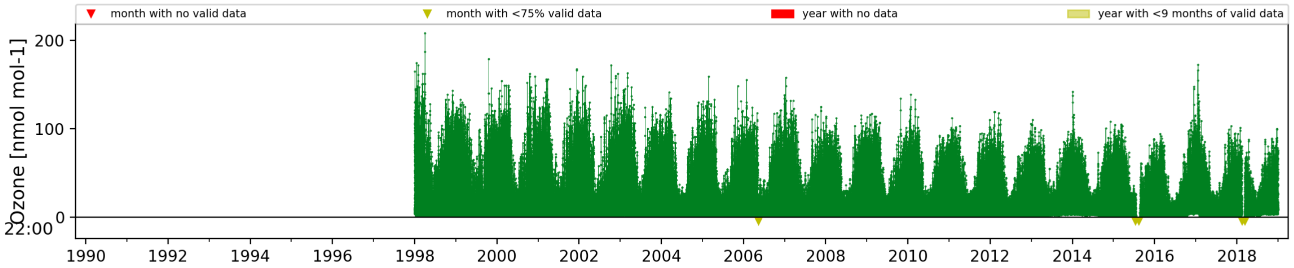
OTHER LASCONDES(CL002) O3
-33.38°N -70.52°E 795 m

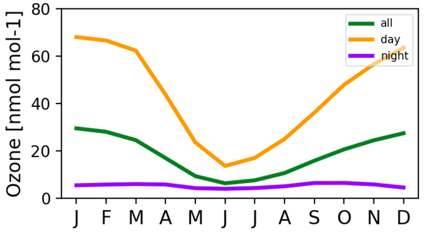
Dataset id: 31332

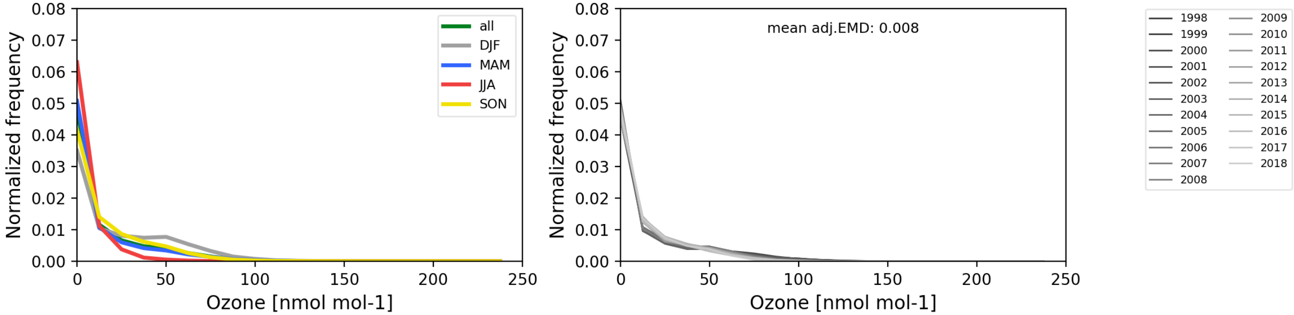
Contributor: Ministry of Environment
Country: Chile

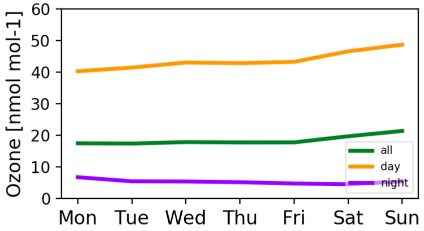
station type: other
station area type: urban
station category: local
data from 01 Jan 1998 01:00 to 31 Dec 2018 22:00

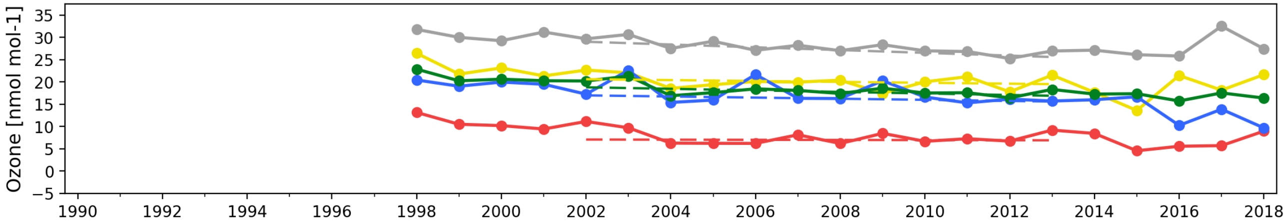
N years: 21
N years with > 75% data: 21
N hours: 180435

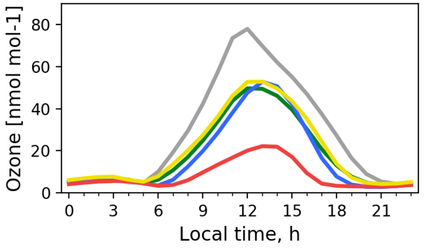




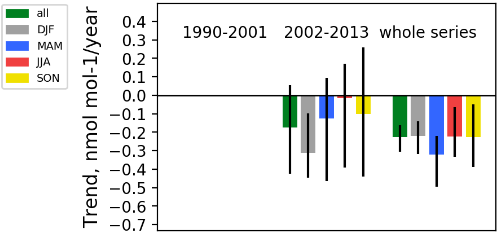








Trend statistics



Mann-Kendall p / Theil-Sen estimate (90% conf. int.)

	1990-2001	2002-2013	whole series
all		0.244 / -0.17 (-0.42..0.06)	0.000 / -0.23 (-0.31..-0.16)
DJF		0.002 / -0.31 (-0.44..-0.10)	0.001 / -0.22 (-0.32..-0.14)
MAM		0.193 / -0.13 (-0.46..0.09)	0.001 / -0.32 (-0.50..-0.22)
JJA		0.837 / -0.02 (-0.39..0.17)	0.006 / -0.22 (-0.33..-0.06)
SON		0.732 / -0.10 (-0.44..0.26)	0.027 / -0.23 (-0.39..-0.05)

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TOAR tropospheric ozone assessment report Phase II

TOAR-II in a nutshell

TOAR-II continues the successful work of TOAR-I and lasts until 2024

TOAR-II will provide updated and extended metrics on tropospheric ozone.

TOAR-II will provide an updated state of the science estimate of ozone's global distribution and trends relevant to climate, human health and vegetation

TOAR-II will further enhance the TOAR data portal and web services

TOAR-II will extend the statistical toolbox and trend analyses

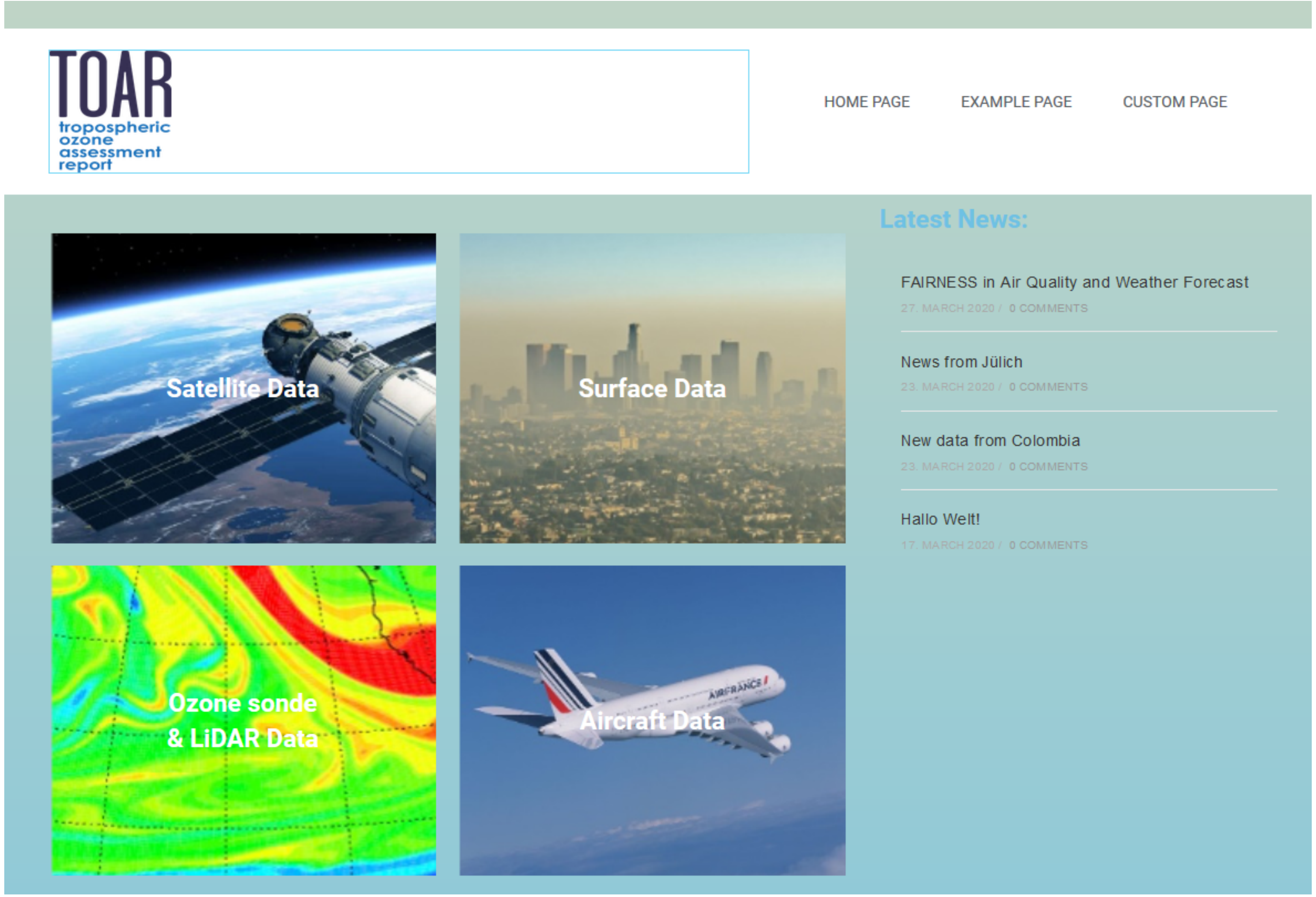
TOAR-II will maximize exploitation of the TOAR Surface Ozone Database

TOAR-II reaches out to the international scientific community

https://igacproject.org/activities/TOAR/TOAR-II

TOAR tropospheric ozone assessment report Phase II

Design of a new TOAR data portal



TOAR database: new content

Extend ozone time series to 2022 and extend coverage

Add ozone precursor and meteorological data

Provide new statistics (e.g. linear trends, flux calculations)

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PAPILA summer school, April 2020

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TOAR tropospheric ozone assessment report Phase II

TOAR-II Status and roadmap

2020
- Selection of new steering committee
- Planning of objectives and roadmap
- Formation of working groups
- Development of enhanced data infrastructure

2021
- First TOAR-II workshops
- Beginning of new data collection
- Bring data infrastructure online

2022
- WGs: Preparation of analyses and planning of manuscripts
- Develop new metrics and populate database

2023
- Finalize data
- Perform new and updated analyses
- Draft manuscripts

2024
- Publication of TOAR-II

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TOAR tropospheric ozone assessment report Phase II