



” Ozone near surface measurements (science & techniques)”

Paolo Cristofanelli – paolo.cristofanelli@cnr.it

+39 051 6399597

<https://www.thoughtco.com/chemical-composition-of-air-604288>



IR0000032 – ITINERIS, Italian Integrated Environmental Research Infrastructures System

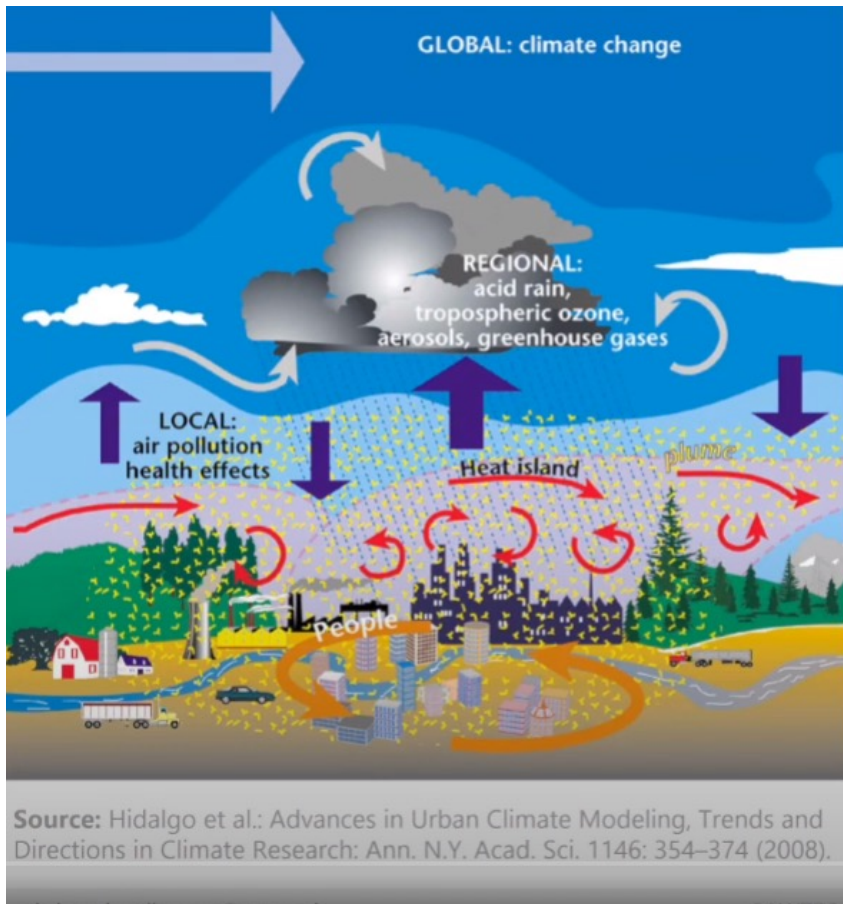
(D.D. n. 130/2022 - CUP B53C22002150006) Funded by EU - Next Generation EU PNRR-
Mission 4 “Education and Research” - Component 2: “From research to business” - Investment
3.1: “Fund for the realisation of an integrated system of research and innovation infrastructures”



A TALE OF TWO OZONES

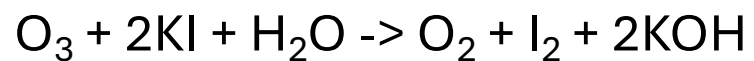
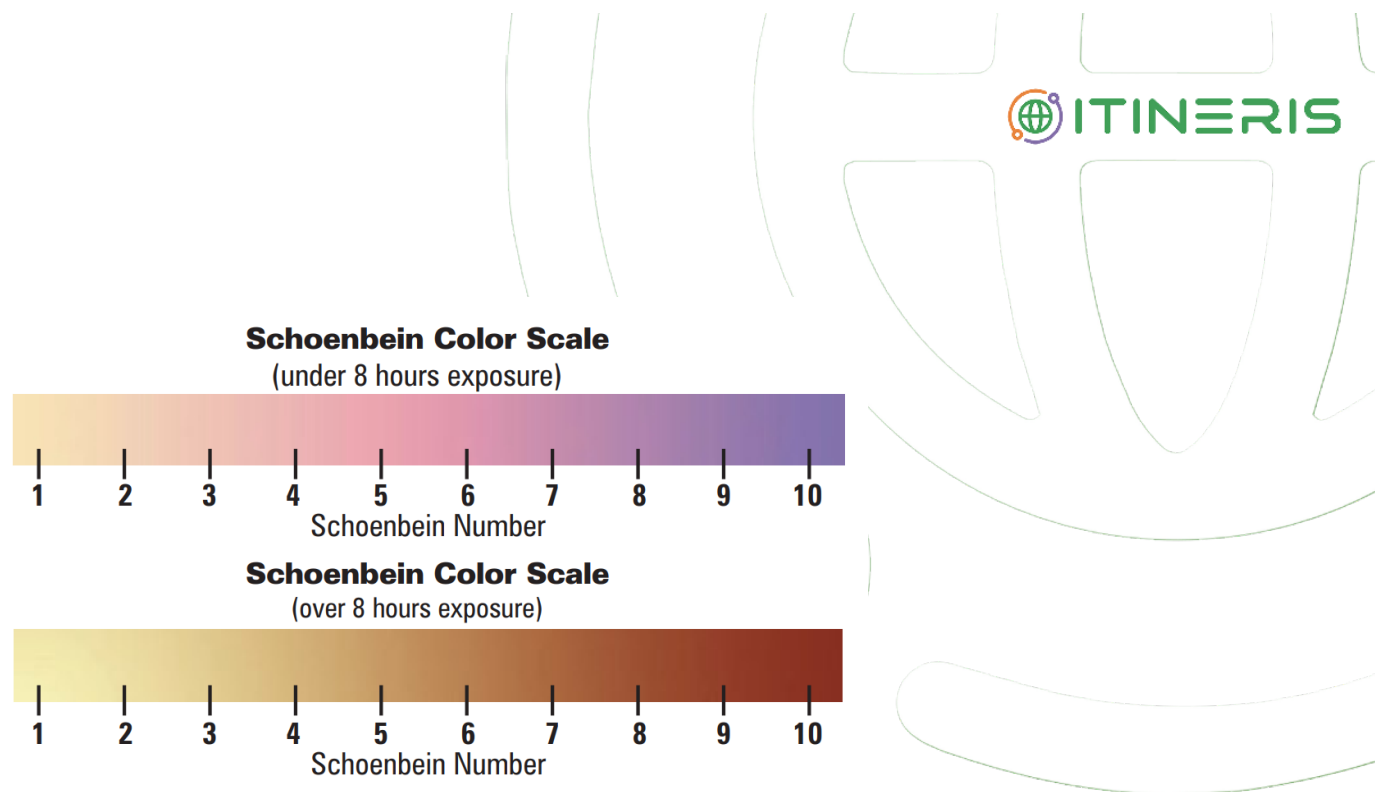
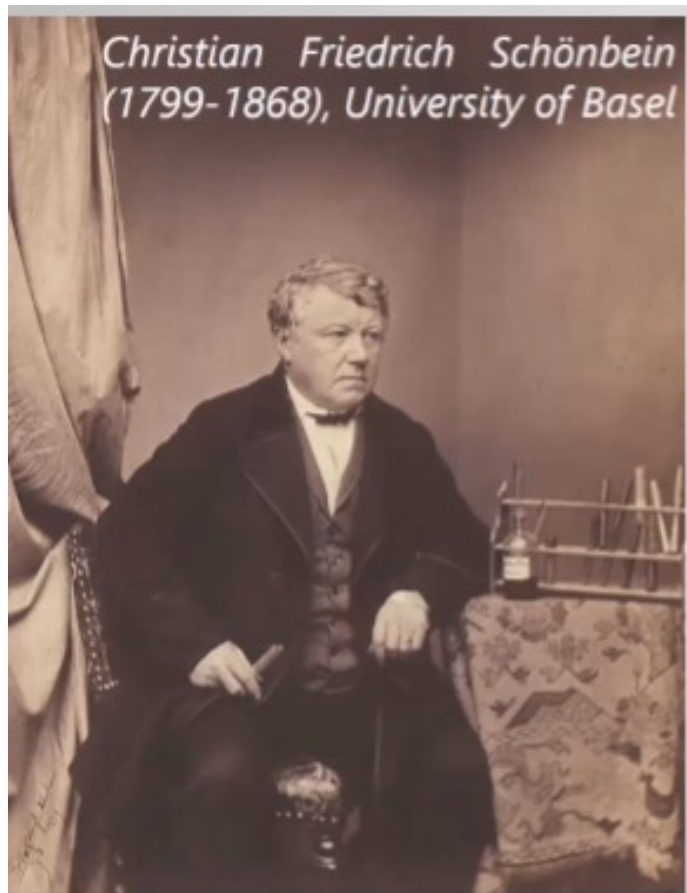


Rationale for near-surface ozone measurements



- In the lower troposphere, ozone is an air pollutant, threatening human health and ecosystems
- Elevated ground-level ozone can lead to leaf injury, crop loss and impact on food security
- In the free (upper) troposphere ozone is a (short-lived) greenhouse gas

Near-surface ozone

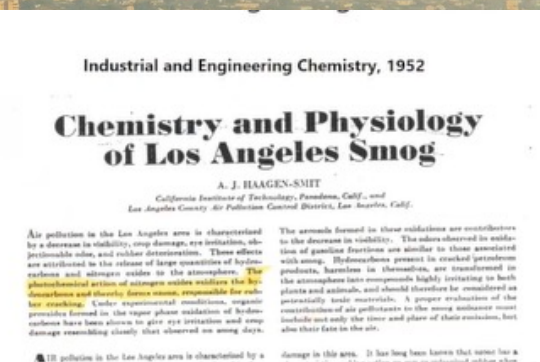


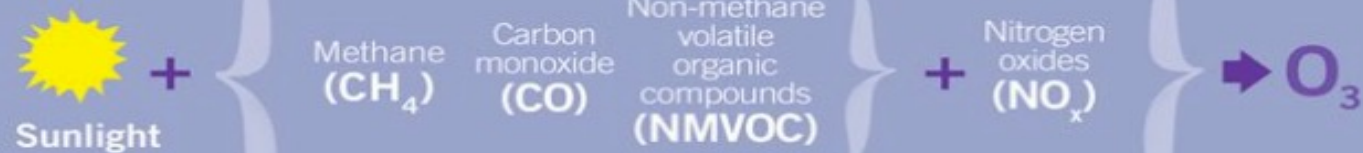
Near-surface ozone

Los Angeles 1940 – 1950 first investigation of photochemical smog



Arie Haagen-Smit
(1900-1977)



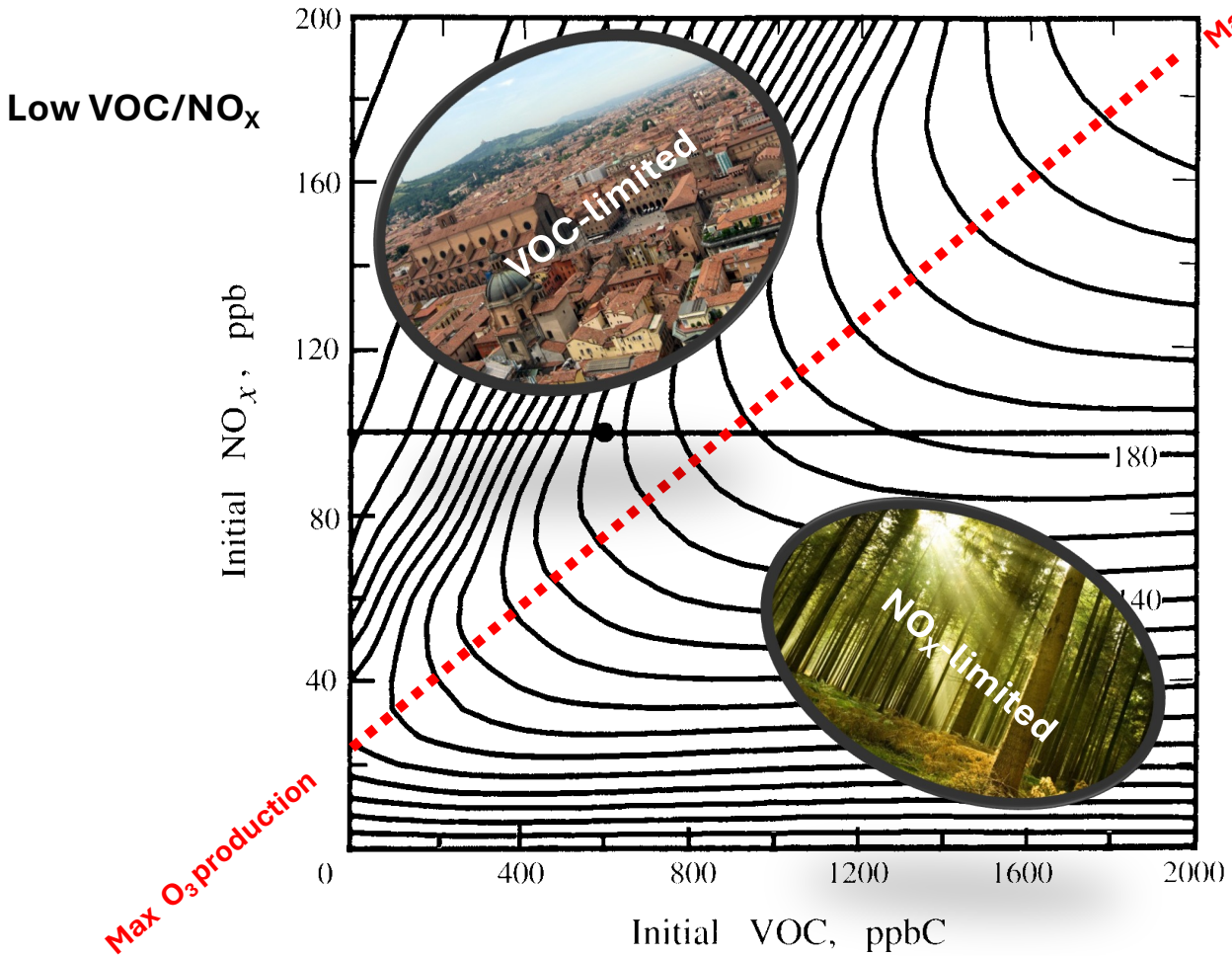


Precursor gas SOURCES



@CAC

Near-surface ozone



Near-surface ozone

SOURCES

Ozone (O₃)



Ozone is a gas formed when nitrogen oxides react with air pollutants known as 'volatile organic compounds' in the presence of heat and sunlight

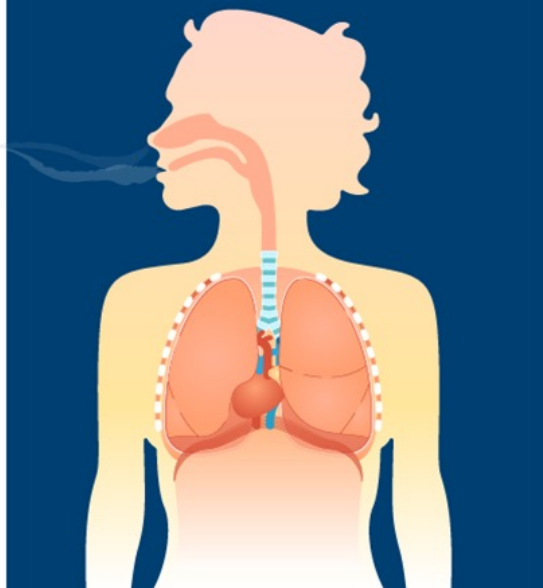
Sources include:

- motor vehicle exhaust
- industry
- bushfires



PATHWAY

Exposure to O₃ comes from the air we breathe.



HEALTH EFFECTS

Impacts:



respiratory system



cardiovascular system

Groups most at risk:



elderly



those with lung disease



children

Near-surface ozone



Ozone damage on plants at NCAR's Mesa Lab Cafeteria Patio garden progressed rapidly over several weeks. In the top photo, taken on August 3, 2015, there was little ozone damage on the potato (far left) and bean (center) plants, but in the bottom photo, taken on September 1, 2015, there is extensive damage.
Danica Lombardozi/NCAR



Brown patches on these potato leaves are evidence of moderate ozone damage.
Danica Lombardozi/NCAR

Content on this page edited from a blog post by Danica Lombardozi, a scientist at the National Center for Atmospheric Research (NCAR). Danica works in the Terrestrial Sciences group of the Climate and Global Dynamics Laboratory, and one of her research interests is the impact of ozone on plants.

© 2020 UCAR

What does ozone exposure do to sensitive plants?

When sufficient ozone enters the leaves of a sensitive plant, it can:

- Reduce photosynthesis, which is the process that plants use to convert sunlight to energy to live and grow.
- Slow the plant's growth.
- Increase sensitive plants' risk of:
 - disease
 - damage from insects
 - effects of other pollutants
 - harm from severe weather.



Also, some plants can show visible marks on their leaves when ozone is present under certain conditions.



The extensive yellow-ringed brown patches on the top and right side of this snap bean leaf are evidence of severe ozone damage, observed on September 1, 2015.
Danica Lombardozi/NCAR

<https://doi.org/10.5194/egusphere-2024-3742>
Preprint. Discussion started: 16 December 2024
© Author(s) 2024. CC BY 4.0 License.

Ozone causes substantial reductions in the carbon sequestration of managed European forests
Per Erik Karlsson¹, Patrick Büker², Sam Bland³, David Simpson⁴, Katrina Sharps⁵, Felicity Hayes⁵, Lisa

Near-surface ozone

B. Ozone target values

Objective	Averaging period	Target value	
Protection of human health	Maximum daily 8-hour mean ⁽³⁾	120 µg/m ³	not to be exceeded on more than 18 days per calendar year averaged over 3 years ⁽⁴⁾ ⁽⁵⁾
Protection of vegetation	May to July	AOT40 (calculated from 1-hour values)	18 000 µg/m ³ × h averaged over 5 years ⁽⁴⁾ From May to July



European Union

C. Long-term objectives for ozone (O₃) to be attained by 1 January 2050

Objective	Averaging period	Long-term objective	
Protection of human health	Maximum daily 8-hour mean within a calendar year	100 µg/m ³ not to be exceeded on more than 3 days per calendar year (99th percentile)	
Protection of vegetation	May to July	AOT40 (calculated from 1 h values)	6 000 µg/m ³ × h

A. Alert thresholds

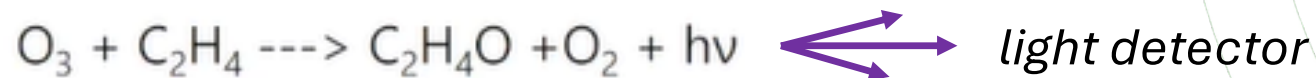
Pollutant	Averaging period	Alert threshold
Ozone	1 hour	240 µg/m ³

B. Information thresholds

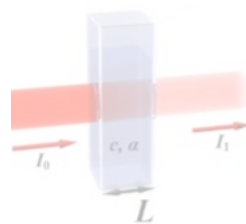
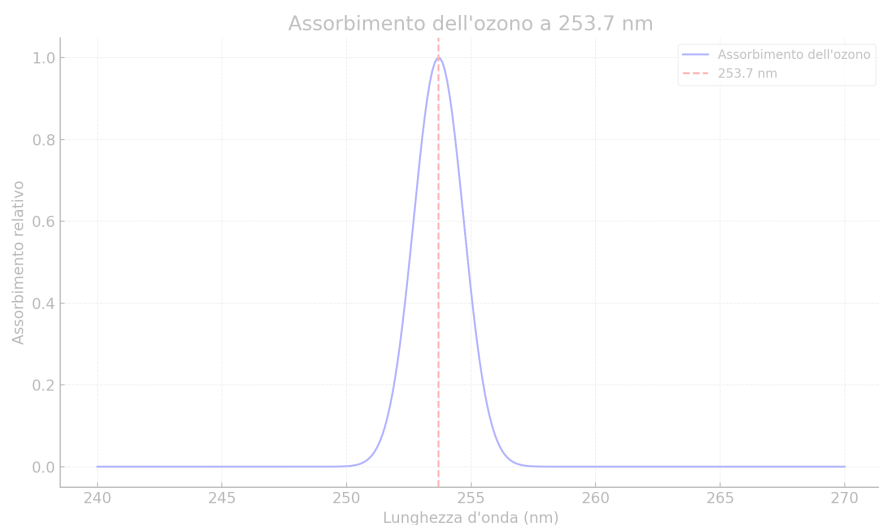
Pollutant	Averaging period	Information threshold
Ozone	1 hour	180 µg/m ³

In-situ ozone measurement techniques

- ❑ Chemiluminescence: reaction of ozone with ethene to form ethylen oxide



- ❑ UV-absorption (state-of-art technique).



$$C = \frac{-1}{2\sigma L_{\text{opt}}} \frac{T}{T_{\text{std}}} \frac{P_{\text{std}}}{P} \ln(D)$$

L_{opt} is the optical path length of one of the cells
 T_{mes} is the temperature measured in the cells
 T_{std} is the standard temperature (273.15 K)
 P_{mes} is the pressure measured in the cells
 P_{std} is the standard pressure (101.325 kPa)
 D is the product of transmittances of the two cells:

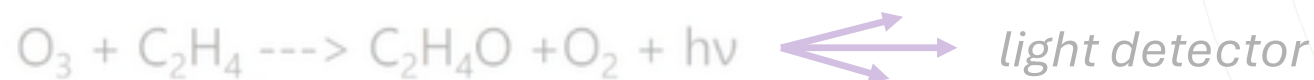
$$D = T_1 \cdot T_2$$

with the transmittance (T) of one cell defined as

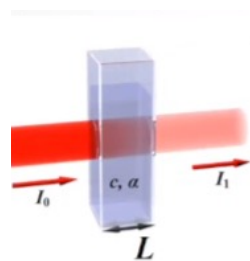
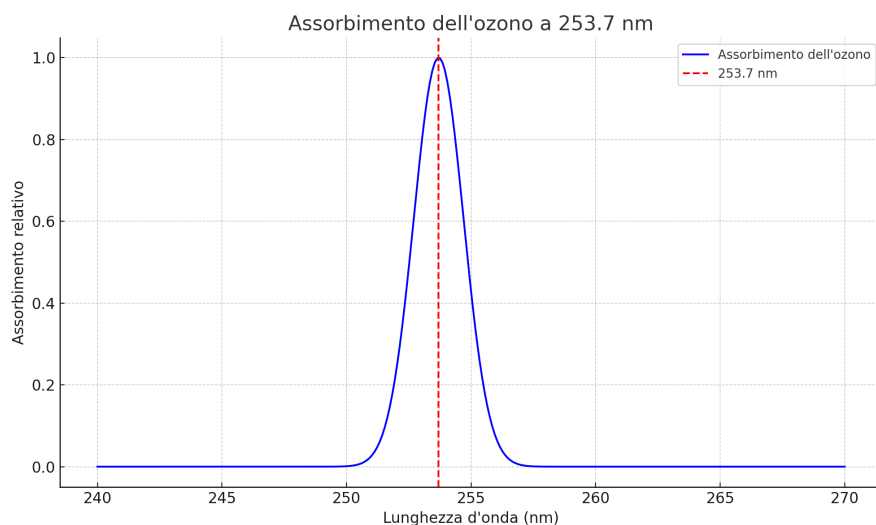
$$T = \frac{I_{\text{ozone}}}{I_{\text{air}}}$$

In-situ ozone measurement techniques

- Chemiluminescence: reaction of ozone with ethene to form ethylen oxide



- UV-absorption (state-of-art technique).



$$C = \frac{-1}{2\sigma L_{\text{opt}}} \frac{T}{T_{\text{std}}} \frac{P_{\text{std}}}{P} \ln(D)$$

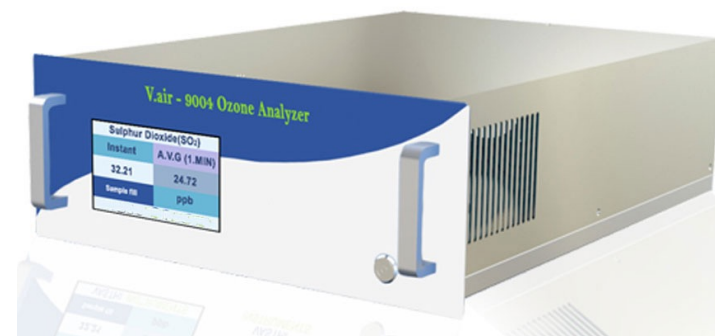
L_{opt} is the optical path length of one of the cells
 T_{mes} is the temperature measured in the cells
 T_{std} is the standard temperature (273.15 K)
 P_{mes} is the pressure measured in the cells
 P_{std} is the standard pressure (101.325 kPa)
 D is the product of transmittances of the two cells:

$$D = T_1 \cdot T_2$$

with the transmittance (T) of one cell defined as

$$T = \frac{I_{\text{ozone}}}{I_{\text{air}}}$$

In-situ ozone measurement techniques



In-situ ozone measurement techniques

- Despite other atmospheric species, no large changes in the measurement techniques in the past decades



? – 1995: 49/49PS Series

- Resolution 1 ppb
- Only analog output
- No remote control
- Significantly poorer performance compared to newer models



1996 – 2007: 49C/49C-PS Series

- Resolution 0.1 ppb
- RS-232 and analog output
- Remote control
- Better performance compared to 49-series



2008 – 2022(?): 49i/49i-PS Series

- Resolution 0.1 ppb
- Ethernet, RS-232 and analog output
- Remote access and control
- No further improvement regarding performance to 49C-series



2019 – ? : 49iQ/49iQ-PS Series

- Resolution 0.1 ppb
- Ethernet, RS-232 and analog output
- Remote access and control
- Cheaper components, no further improvement regarding performance to 49i-series

Zellweger C., "measurement of tropospheric ozone", GAWTEC Webinar Series. https://www.youtube.com/watch?v=_DksbpztnQU

In-situ ozone measurement techniques

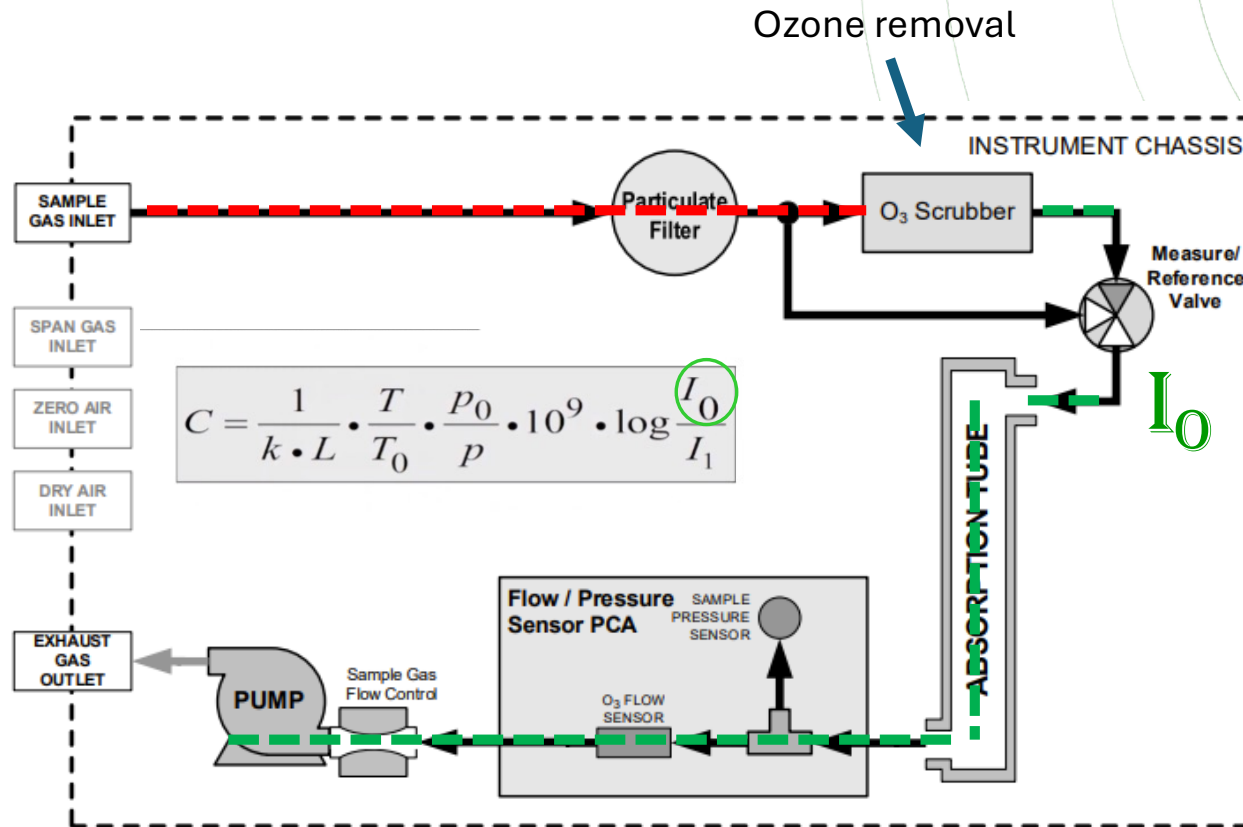


Figure 2-18. T400 Pneumatic Diagram – Basic Unit

In-situ ozone measurement techniques

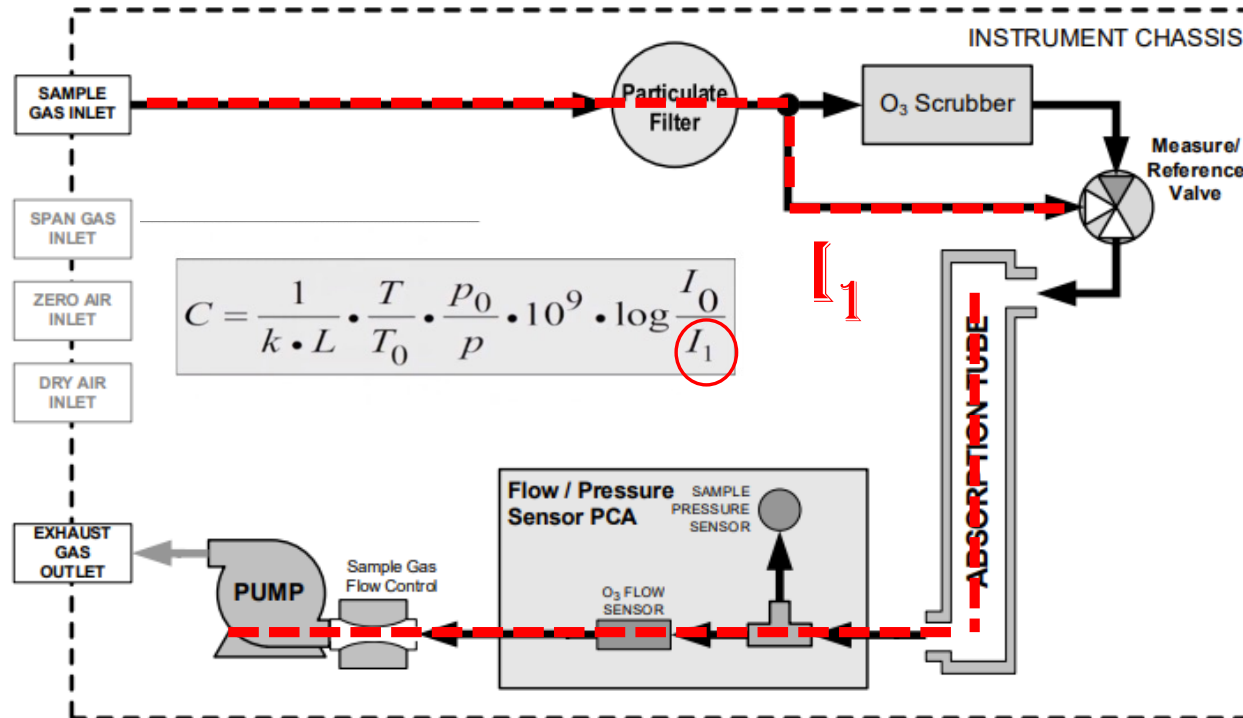
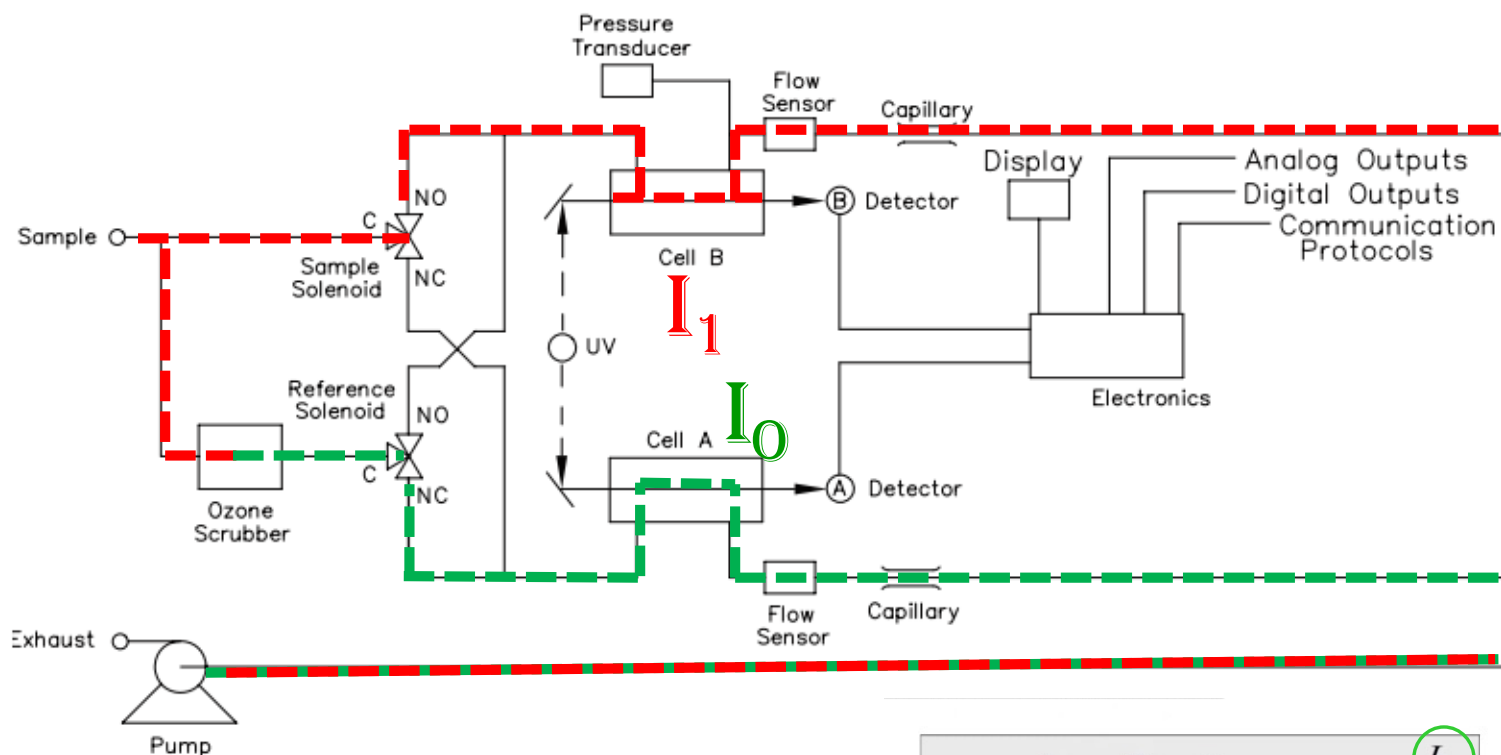


Figure 2-18. T400 Pneumatic Diagram – Basic Unit

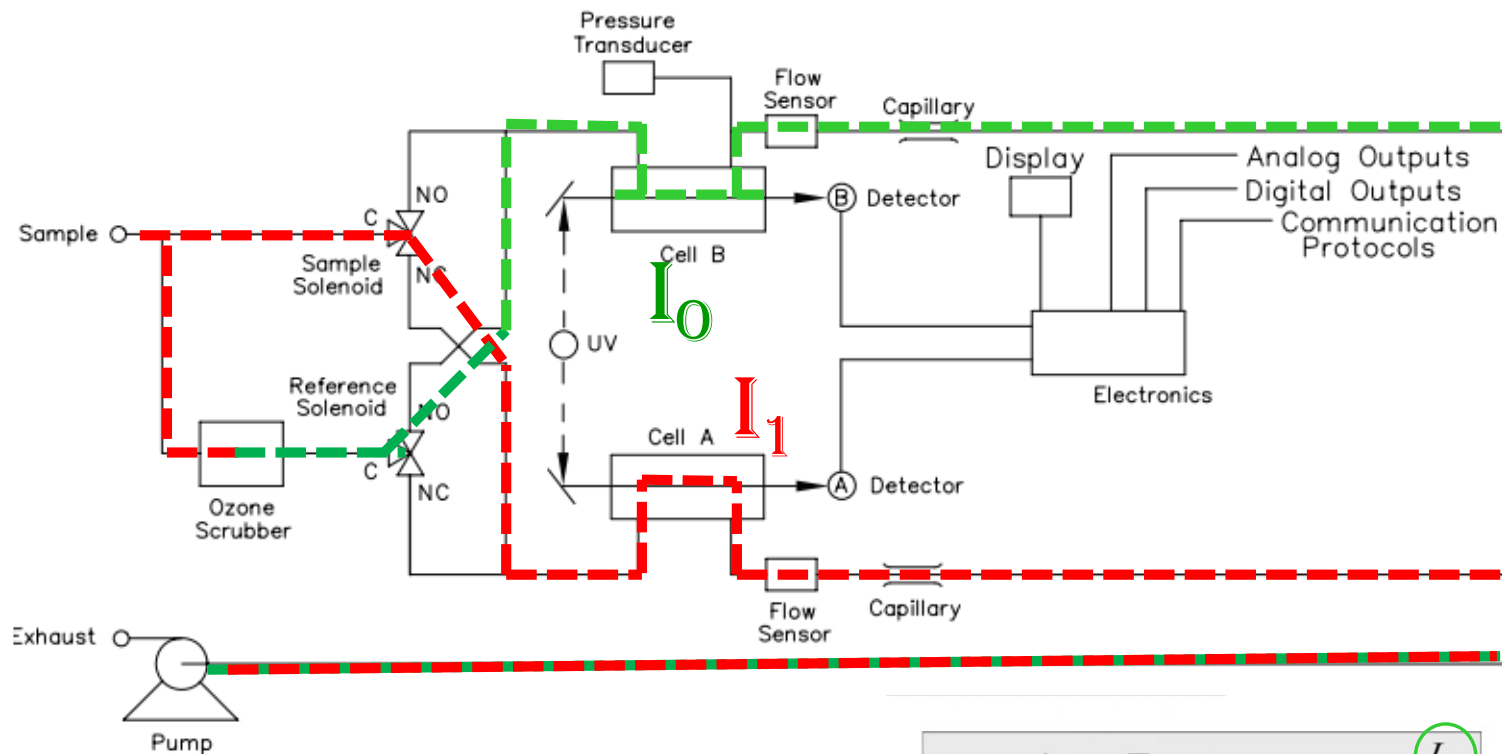
In-situ ozone measurement techniques



$$C = \frac{1}{k \cdot L} \cdot \frac{T}{T_0} \cdot \frac{p_0}{p} \cdot 10^9 \cdot \log \frac{I_0}{I_1}$$

Figure 1-1. Model 49i Flow Schematic

In-situ ozone measurement techniques



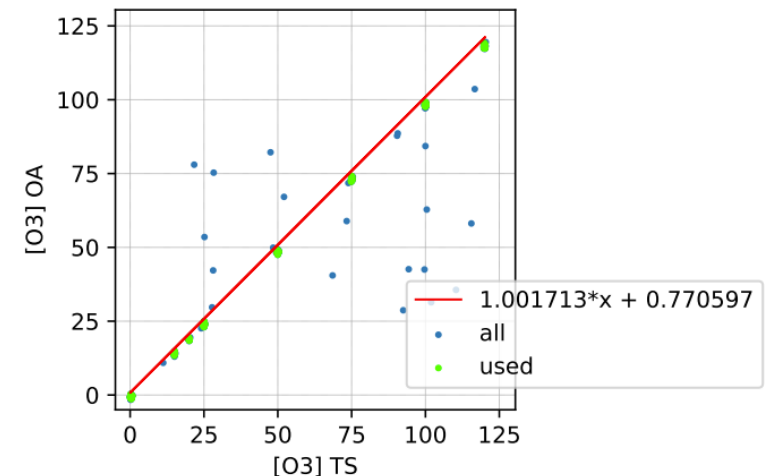
$$C = \frac{1}{k \cdot L} \cdot \frac{T}{T_0} \cdot \frac{P_0}{P} \cdot 10^9 \cdot \log \frac{I_0}{I_1}$$

Figure 1-1. Model 49i Flow Schematic

In-situ ozone measurement techniques

- ❑ Calibrations should be performed every ~12 months
- ❑ A Transfer Standard (TS) can be used to generate known ozone levels
- ❑ TS to be traceable to a SRP (Standard Reference Photometer): calibration certificate must be available
- ❑ Pressure sensors must be also calibrated. Check flows.

TSmean	TSstd	OAmean	OAstd	predicted	residual	deviation
0.139	0.132	-0.970	0.544	-0.157	0.296	-1.109
74.289	0.128	73.360	0.314	74.274	0.015	-0.929
49.458	0.086	48.460	0.276	49.340	0.118	-0.998
99.195	0.086	98.260	0.347	99.208	-0.013	-0.935
24.640	0.142	23.540	0.364	24.386	0.253	-1.100
118.983	0.112	117.900	0.219	118.875	0.109	-1.083
14.684	0.122	13.970	0.374	14.803	-0.120	-0.714
0.077	0.132	-0.640	0.310	0.173	-0.096	-0.717
24.564	0.094	23.800	0.283	24.647	-0.082	-0.764
99.112	0.116	98.220	0.214	99.168	-0.056	-0.892
49.463	0.102	48.670	0.215	49.550	-0.087	-0.793
74.349	0.148	73.440	0.398	74.354	-0.005	-0.909
19.670	0.133	18.910	0.298	19.750	-0.080	-0.760
119.026	0.098	118.180	0.442	119.155	-0.129	-0.846
0.130	0.132	-0.730	0.385	0.083	0.047	-0.860
49.497	0.158	48.580	0.447	49.460	0.037	-0.917
24.660	0.140	23.930	0.297	24.777	-0.117	-0.730
74.299	0.094	73.460	0.332	74.374	-0.075	-0.839
99.111	0.094	97.940	0.310	98.888	0.224	-1.171
119.008	0.088	118.110	0.359	119.085	-0.077	-0.898
-0.029	0.138	-0.680	0.376	0.133	-0.162	-0.651



In-situ ozone measurement techniques

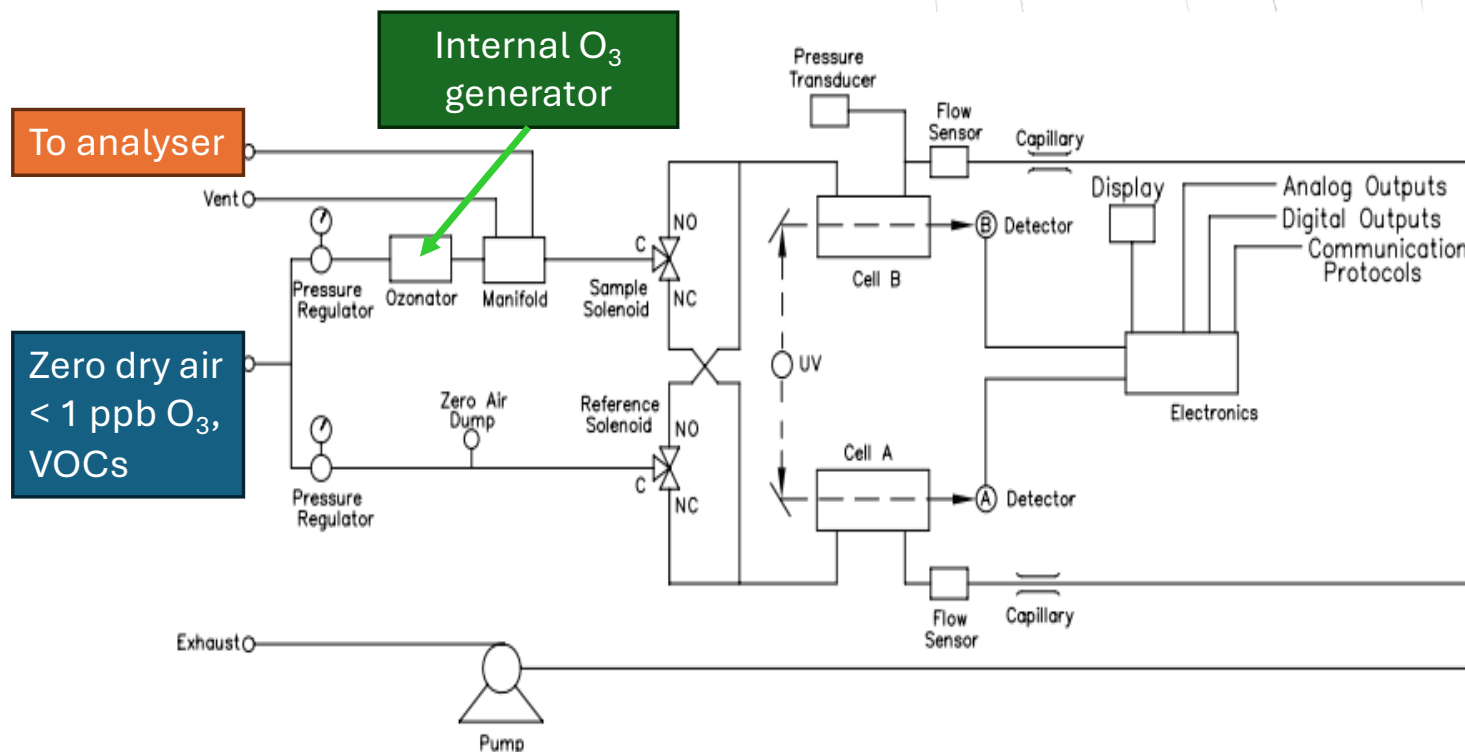


Figure 1-1. Model 49i Primary Standard Flow Schematic

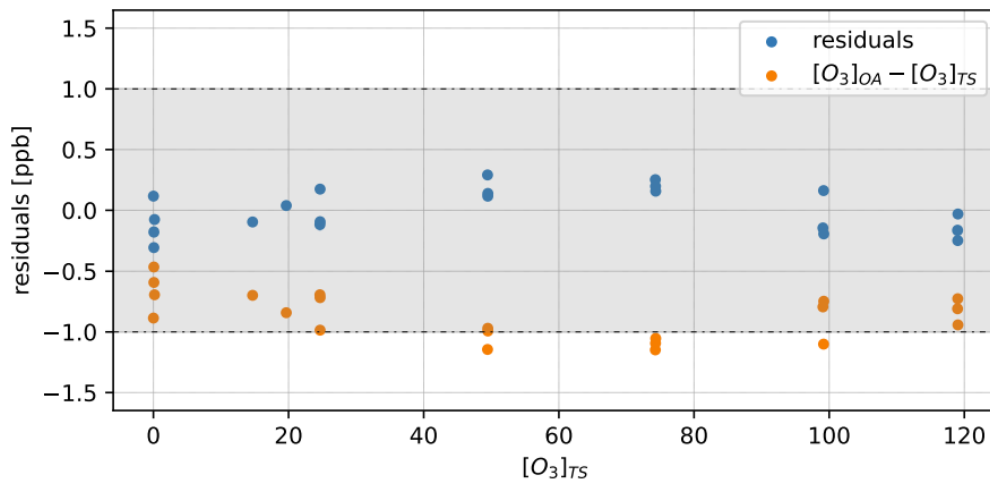
In-situ ozone measurement techniques

☐ Calibration equation

compensation equation to obtain unbiased concentration
 $[O_3]_{unbiased} = ([O_A] * 1.002) + 0.771$

☐ Uncertainty calculation (see DOI:10.1029/2003JD003710)

Ulinearity: Residual standard deviation	= 0.177
Urepeat = $\sqrt{U_{noise}^2 + U_{linearity}^2}$	= 0.407
Udrift = $\sqrt{0.58^2 + (0.0025 * C)^2}$	= 0.632
U = $\sqrt{U_{repeat}^2 + U_{drift}^2}$	= 0.751
C	= 100.0



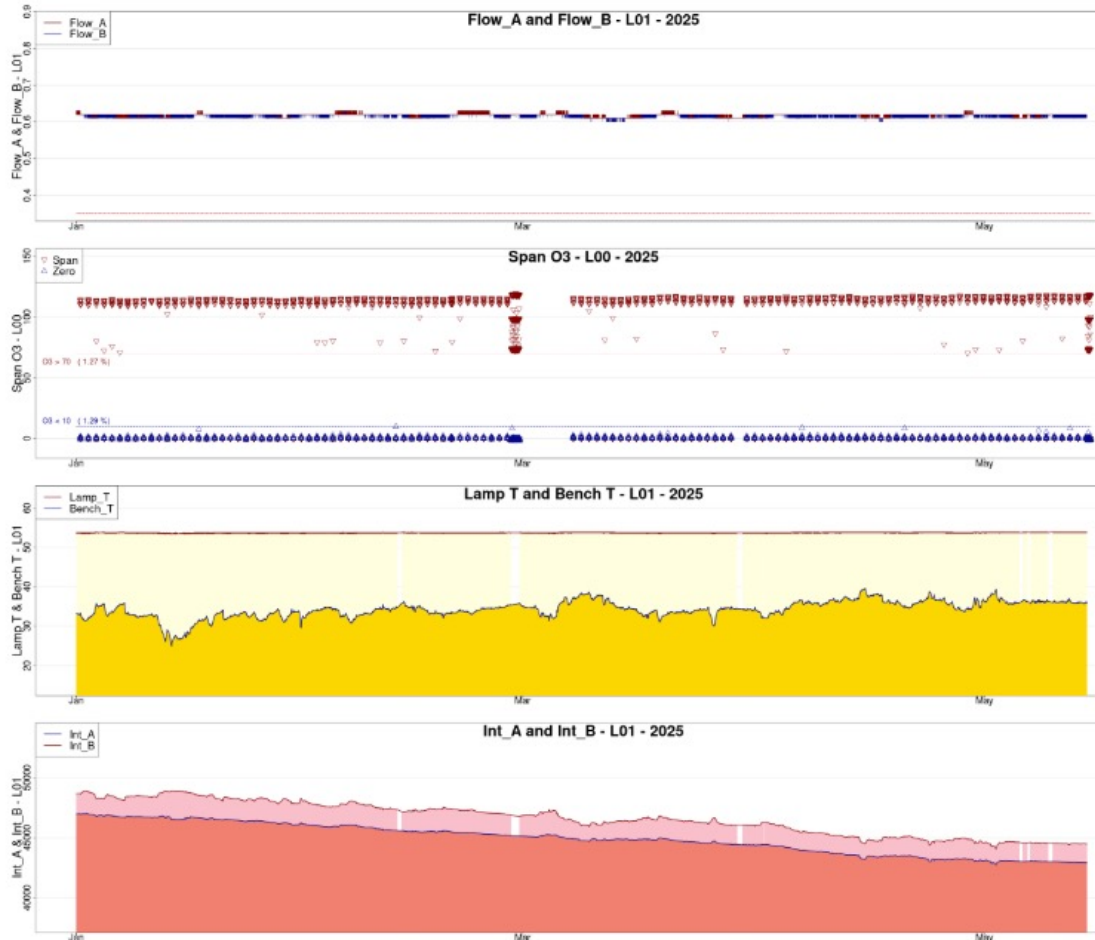
GUIDELINES FOR CONTINUOUS MEASUREMENTS OF OZONE IN THE TROPOSPHERE

Prepared by Ian E. Galbally and Martin G. Schultz

In collaboration with

B. Buchmann, S. Gilge, F. Guenther, H. Koide, S. Oltmans, L. Patrick, H.-E. Scheel, H. Smit, M. Steinbacher, W. Steinbrecht, O. Tarasova, J. Viallon, A. Volz-Thomas, M. Weber, R. Wielgosz and C. Zellweger

In-situ ozone measurement techniques



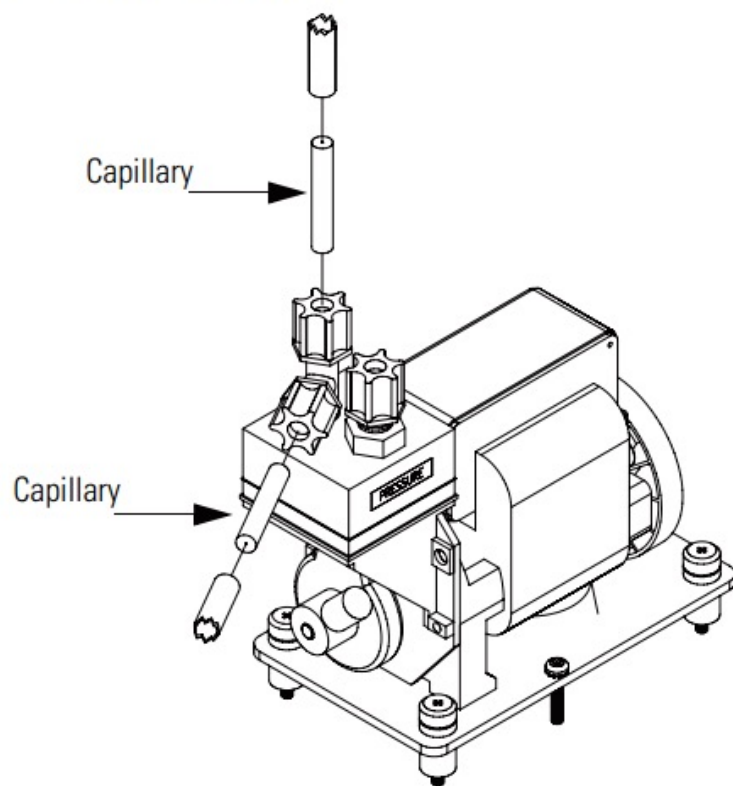
Low flow -> pump problems;
check capillaries

Span/Zero check -> leaks or
check scrubber efficiency

High T -> stability and integrity
issues

Lamp intensity -> check cells, to
regulate intensities

In-situ ozone measurement techniques

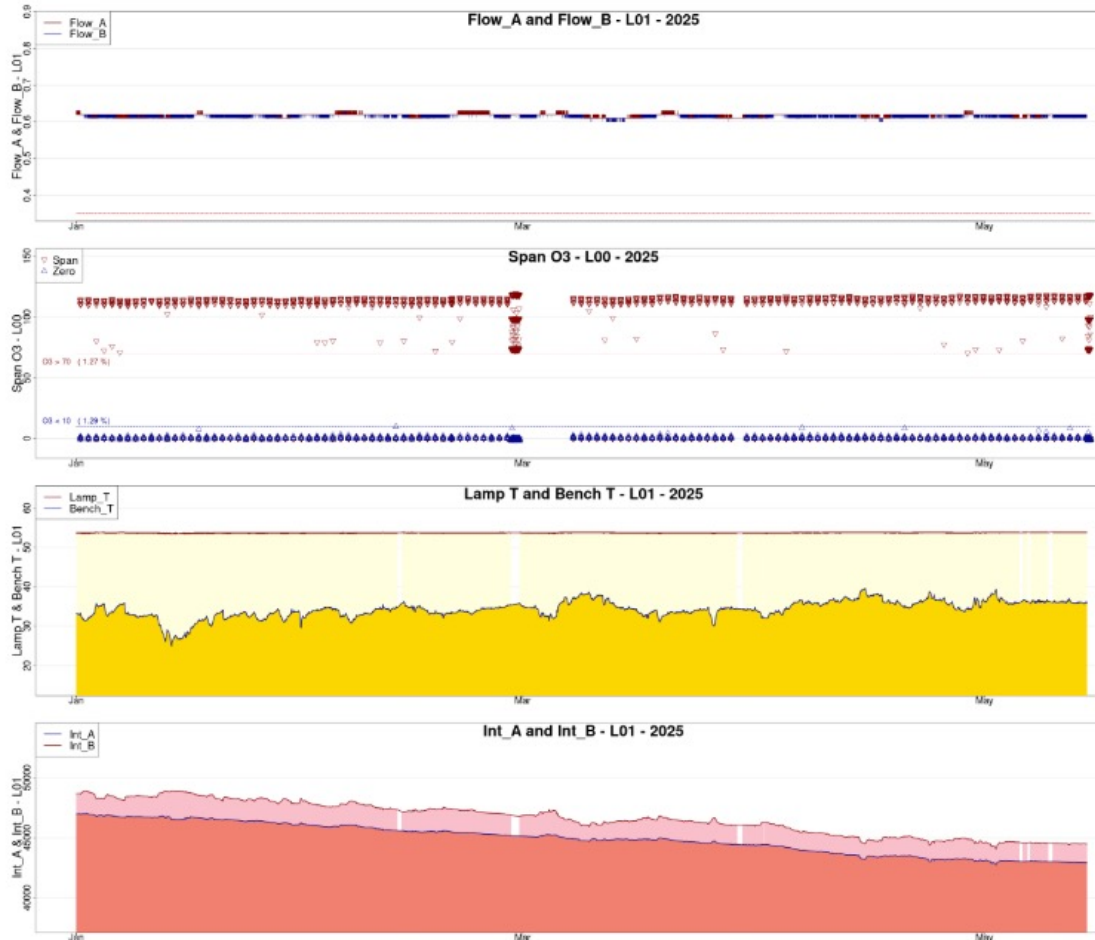


Capillaries limit and stabilize the gas flow (1-3 lt/min) into the measurement system. Maintain constant pressure conditions and residence time within the UV cell.

!!!Pump should be regularly maintained (diaphragm change every 1 yr)!!!

Figure 5-1. Capillary Location

In-situ ozone measurement techniques



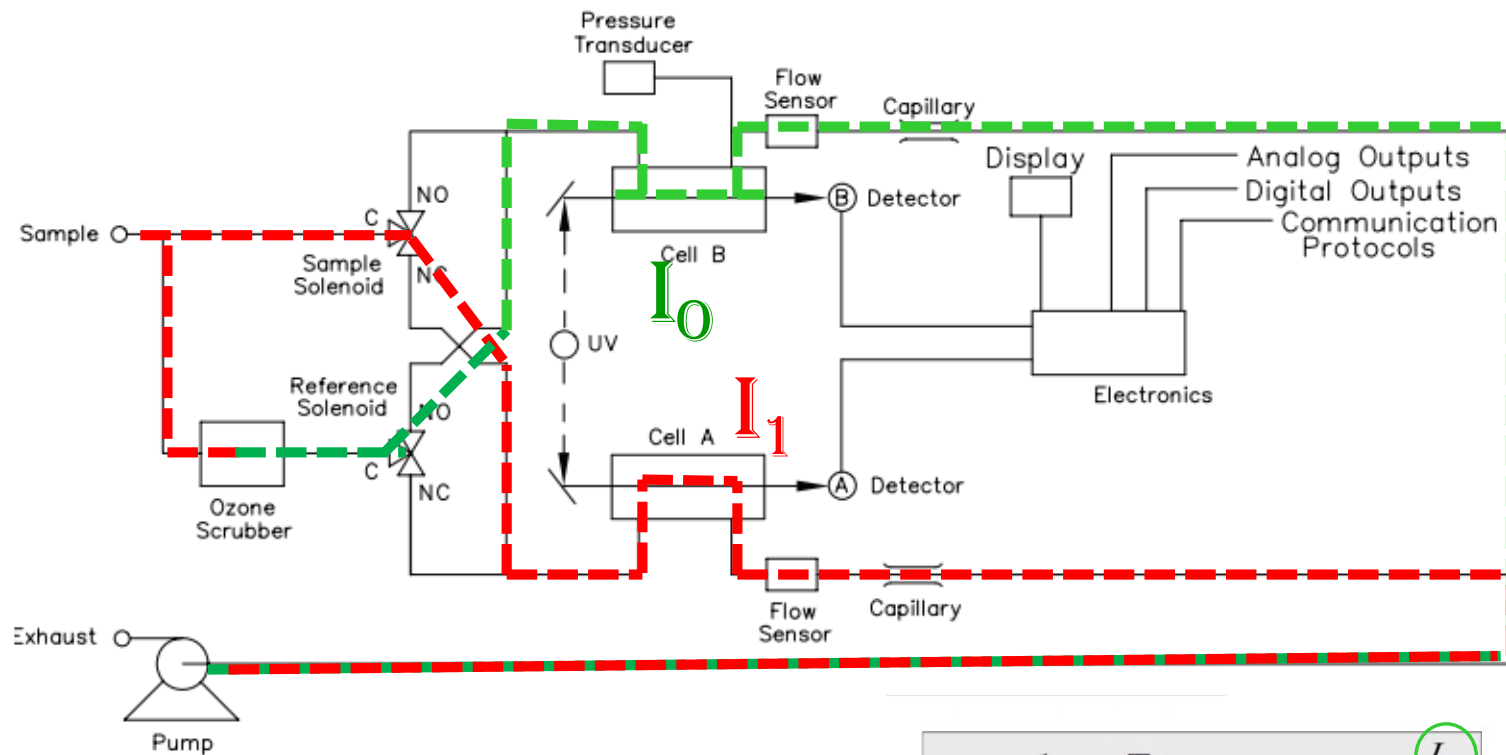
Low flow -> pump problems;
check capillaries

Span/Zero check -> leaks or
check scrubber efficiency

High T -> stability and integrity
issues

Lamp intensity -> check cells, to
regulate intensities

In-situ ozone measurement techniques



$$C = \frac{1}{k \cdot L} \cdot \frac{T}{T_0} \cdot \frac{P_0}{P} \cdot 10^9 \cdot \log \frac{I_0}{I_1}$$

Figure 1-1. Model 49i Flow Schematic

In-situ ozone measurement techniques

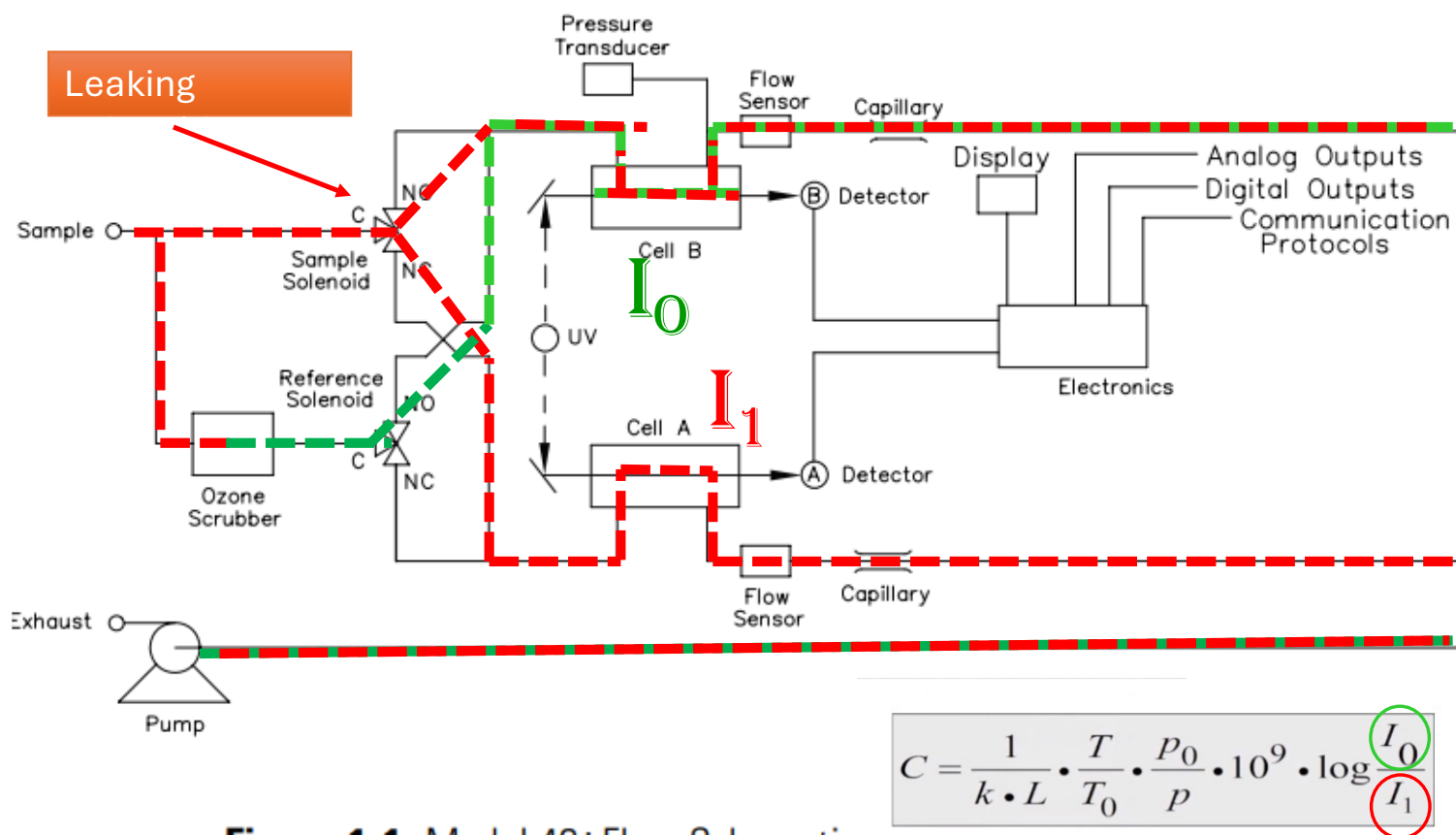




Figure 1-1. Model 49i Flow Schematic

In-situ ozone measurement techniques

- ❑ If a calibrator or an ozone generator is available, leaks through solenoids can be detected by using the «balance» cell A/B test
- ❑ At 500 ppb ozone, 10 consecutive readings of cell A and B should not deviate more than 3%
- ❑ If the case -> exchange cells to determine if the problem is related to one (dirty) cell.
- ❑ Then make a solenoid leak test (follow manual)



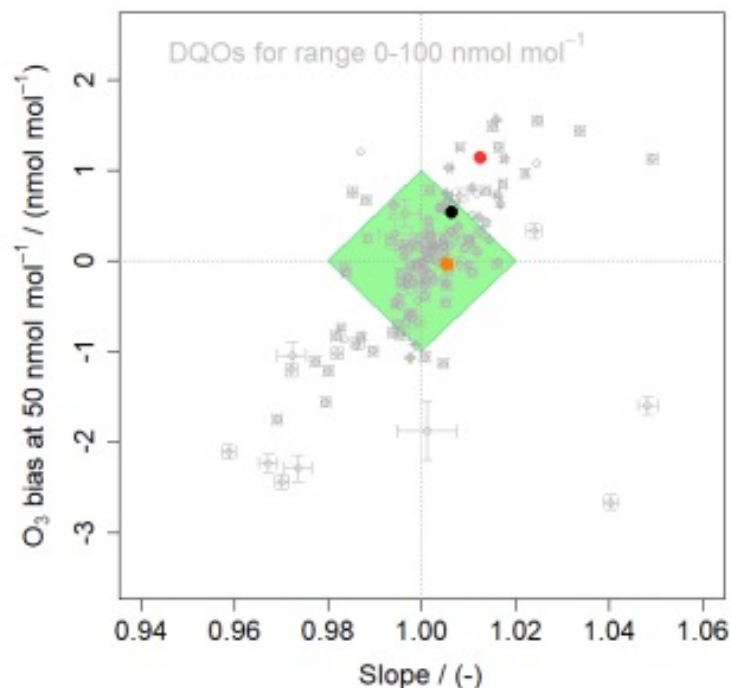
#	A	B
1	488	510
2	500	499
3	490	509
4	500	500
5	489	511
6	511	489
7	496	504
8	501	498
9	480	518
10	510	491
AVG	496.5	502.9
Difference	1.3%	



#	A	B
1	464	510
2	475	499
3	466	509
4	475	500
5	465	511
6	485	489
7	471	504
8	476	498
9	456	518
10	485	491
AVG	471.7	502.9
Difference	6.6%	

Data quality objectives (GAW Report No. 209)

- ❑ To **detect tropospheric ozone trend**, the combined measurement uncertainty must be approximately $\pm 1 \text{ nmol mol}^{-1}$ or less
- ❑ For **model assimilation and validation**, a combined uncertainty of less than $\pm 5 \text{ nmol mol}^{-1}$ is required



O₃ bias in the middle of the relevant amount fraction range compared to the slope of the WCC-Empa performance audits.

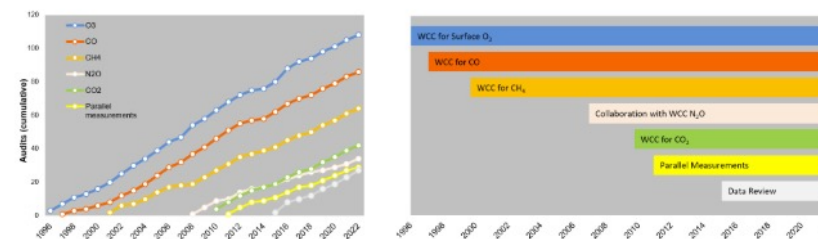
The coloured areas correspond to the WMO/GAW compatibility goals (green) and the extended compatibility goals (yellow).

Suggested citation: Zellweger, C., Steinbacher, M., and Emmenegger, L.: System and Performance Audit of Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide at the Global GAW Monte Cimone, Italy, September 2023. WCC-Empa Report 23/3, Dübendorf, Switzerland, 2024. This work is licensed under CC BY-NC 4.0.

WCC-Empa Report 23/3

World Calibration Centre (WCC-Empa) for Surface Ozone, Carbon Monoxide, Methane, Carbon Dioxide and Nitrous Oxide

WCC-Empa was established in 1996, assuming worldwide responsibility for surface ozone, carbon monoxide and methane comparisons at global GAW stations. WCC-Empa was also mandated to extend its activities to carbon dioxide in 2010 and nitrous oxide in 2025.

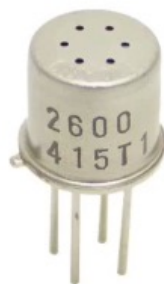


Cumulative number (left) and scope (right) of WCC-Empa audits since 1996

In-situ ozone measurement techniques

Instrument development: Low-end

Zellweger C., "measurement of tropospheric ozone", GAWTEC Webinar Series. https://www.youtube.com/watch?v=_DksbpztnQU



Metal oxide
~ CHF 5
~ 1960



Electrochemical / voltammetric
~ CHF 50
~ 1980

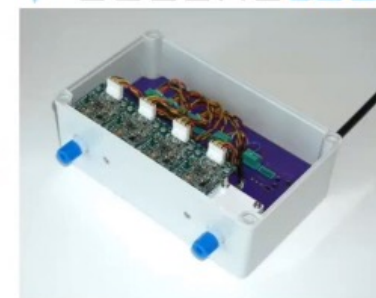


Photochemical
~ CHF 200
~ 1990



Model 106-L-OEM Ozone Monitor

Micro-optical
> CHF 100
~ 2000



Micro-electro-mechanical (MEMS) type device

Trend:

- Miniaturization
- Design improvements
- Integration into units
- Ancillary parameters (e.g. p, T)
- Multiple sensors
- Communication (LoRa / GSM)
- Cloud processing

■ Sensors: Challenging component diversity. Mainly 'old' technologies.

Tropospheric ozone (data repositories)



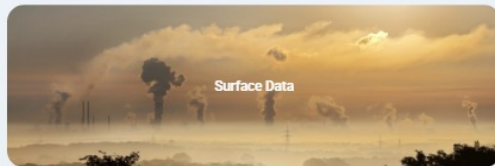
<https://toar-data.org/surface-data/>



<https://ebas-data.nilu.no/>

TOAR Data Portal

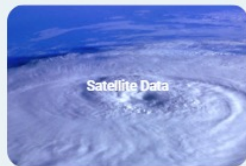
The Home of Tropospheric Ozone Data



Surface Data



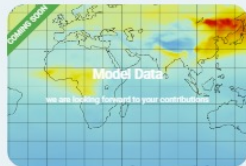
TOAR data infrastructure documentation



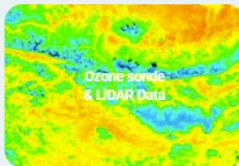
Satellite Data



Aircraft Data



Model Data



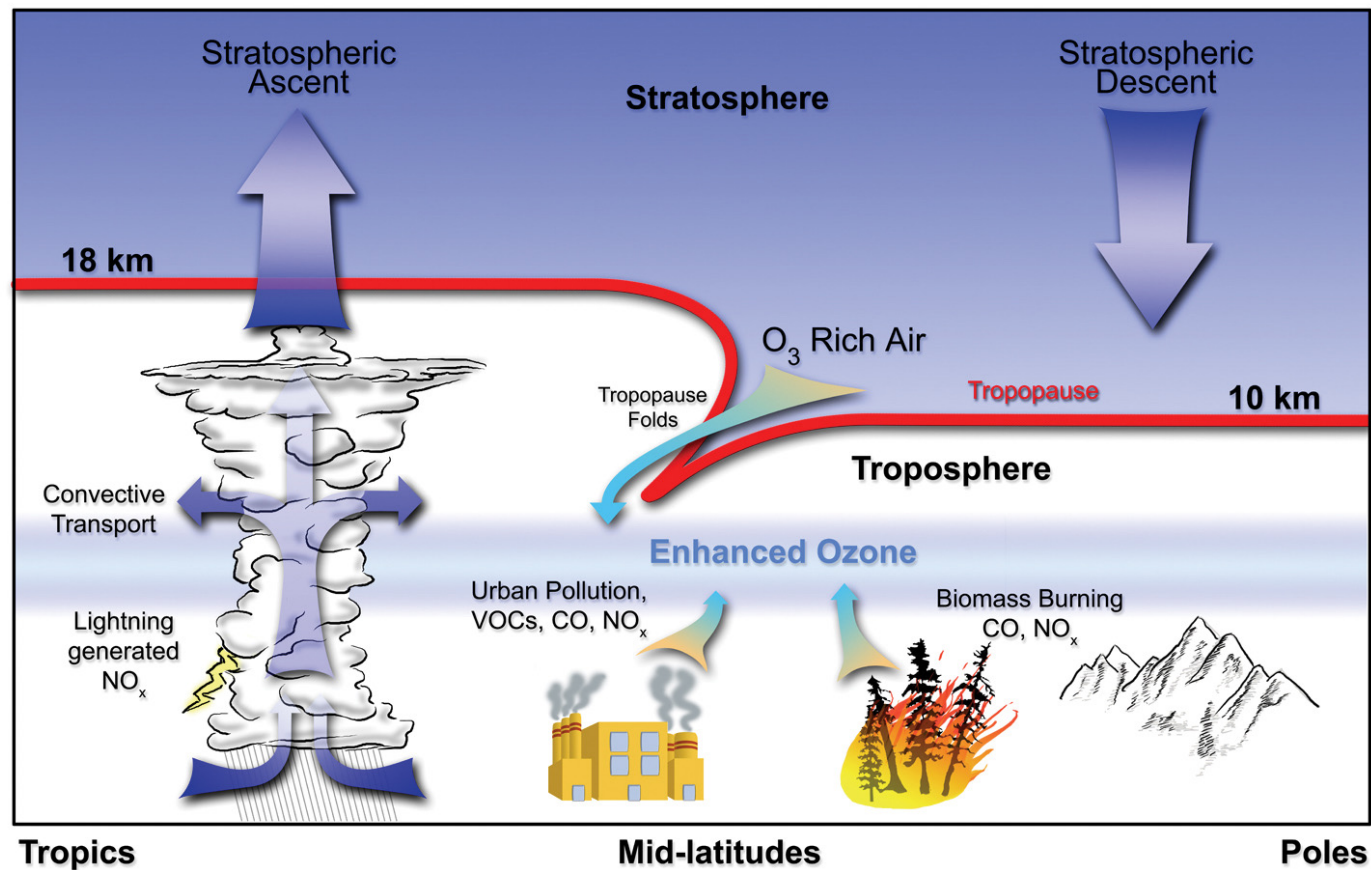
Ozone sonde & LIDAR Data

The screenshot shows the Ebas-Data portal interface with the following search filters:

- Framework [17]**: >>All, AMAP, AMAP_public, CAMP, CAMPAIGN, EMEP, EMEP_NRT, ELISΔΔR
- Country [57]**: >>All, Algeria, Argentina, Armenia, Australia, Austria, Barbados, Belgium
- Station [324]**: >>All, Achenkirch, Agia Marina Xyliatou / Cyprus Atmospheric Observatory, Alert, Algoma, Aliartos, Amberg, Ammannäs
- Instrument type [2]**: >>All, ECC_ozone_monitor, uv_abs
- Component [868]**: organic_mass, oxalate, oxalic_acid, oxychlorane, ozone, p-cymene, p-xylene
- Matrix [1]**: >>All, air

Additional interface elements include: Home, Acknowledgment, Data policy, username field, Login button, and a footer indicating "Available datasets: 929" with "Reset" and "List datasets" buttons.

Tropospheric ozone (investigation of processes)



Tropospheric ozone: deep stratospheric intrusions

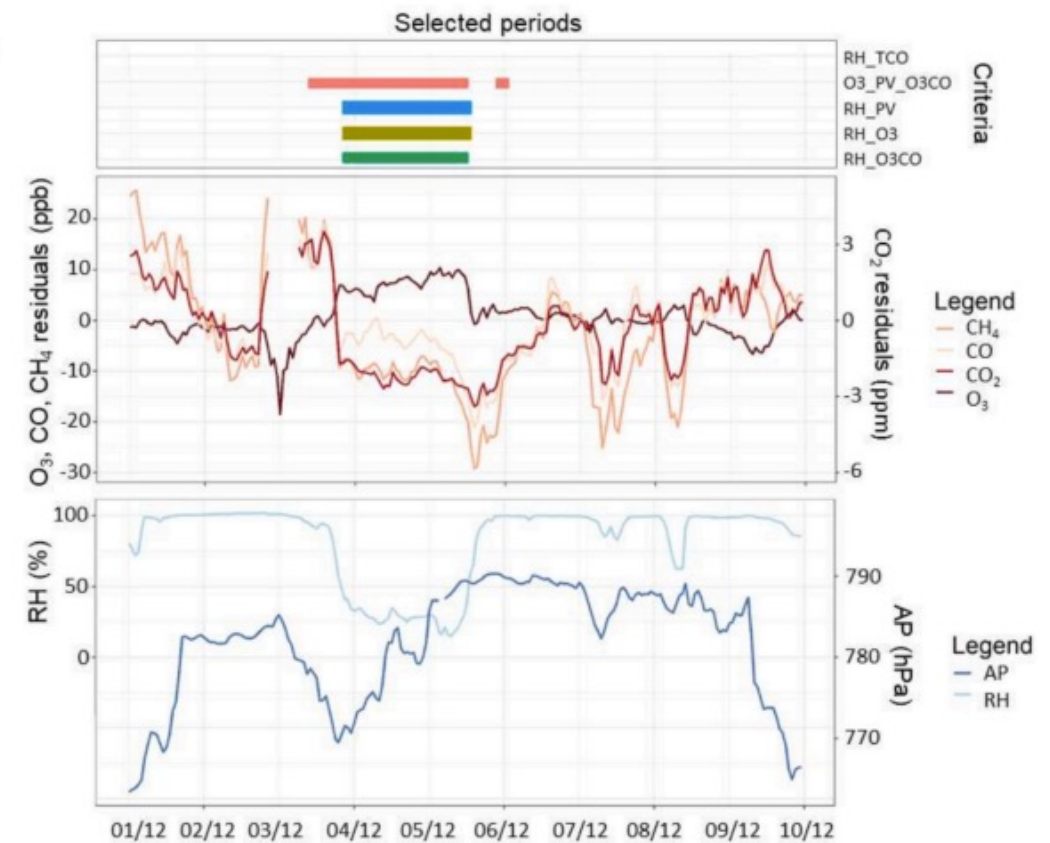
Influence of deep stratosphere-to-troposphere transport on atmospheric carbon dioxide and methane at the Mt. Cimone WMO/GAW global station (2165 m a.s.l., Italy): A multi-year (2015–2022) investigation

Pamela Trisolino^a, Davide Putero^{b,*}, Jgor Arduini^c, Stefano Amendola^d, Francescopiero Calzolari^a, Paolo Cristofanelli^a

<https://doi.org/10.1016/j.atmosres.2024.107627>

Criteria for selecting STT events

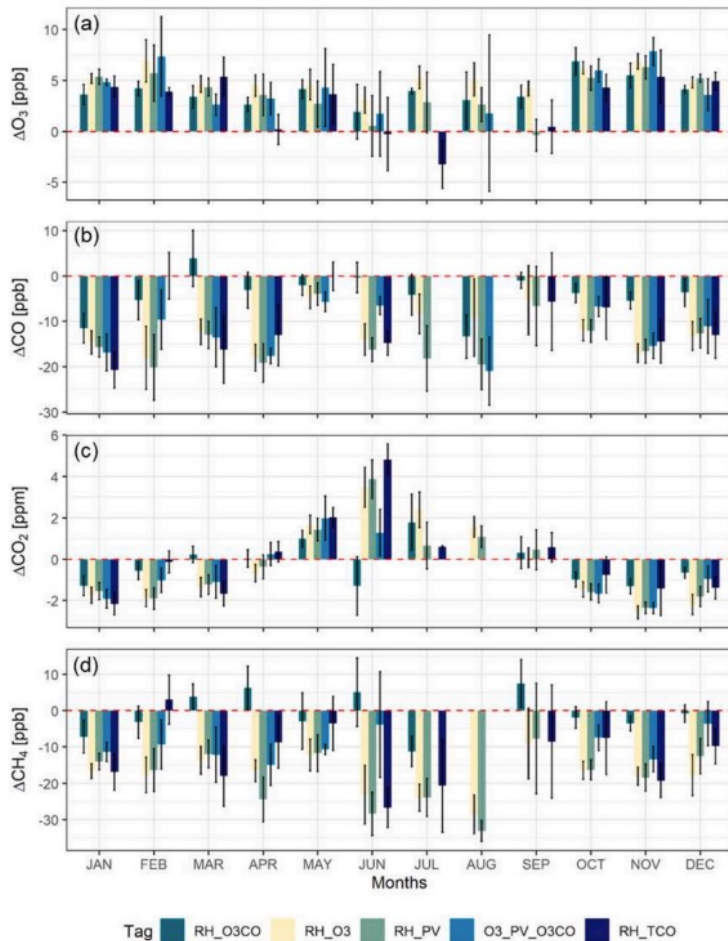
1. RH 6-h running mean lower than 40% and significant O₃ increase (denoted as "RH_O3")
2. RH 6-h running mean lower than 40% and negative O₃ vs CO correlation ("RH_O3CO")
3. significant O₃ increase with at least one back-trajectory/day with PV ≥ 2.0 pvu and negative O₃-CO correlation ("O3_PV_O3CO")
4. RH 6-h running mean lower than 40% and significant TCO increase ("RH_TCO")
5. RH 6-h running mean lower than 40% and at least one back-trajectory/day with PV ≥ 2.0 pvu ("RH_PV")



Tropospheric ozone: deep stratospheric intrusions

Influence of deep stratosphere-to-troposphere transport on atmospheric carbon dioxide and methane at the Mt. Cimone WMO/GAW global station (2165 m a.s.l., Italy): A multi-year (2015–2022) investigation

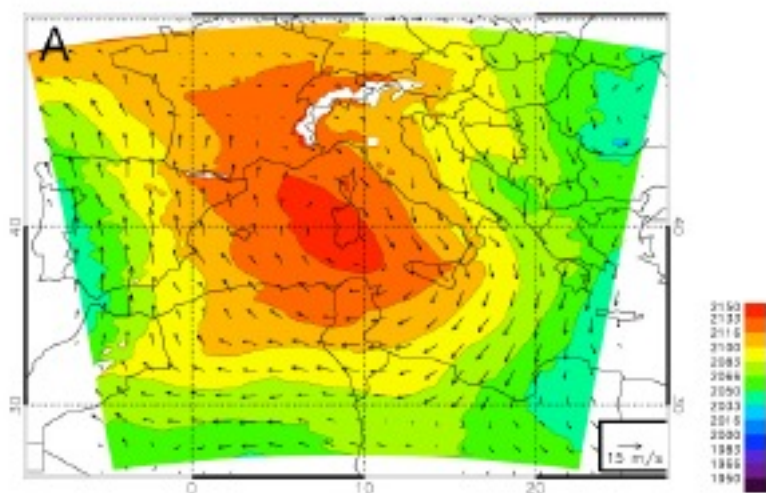
Pamela Trisolino^a, Davide Putero^{b,*}, Jgor Arduini^c, Stefano Amendola^d,
Francescopiero Calzolari^a, Paolo Cristofanelli^a
<https://doi.org/10.1016/j.atmosres.2024.107627>



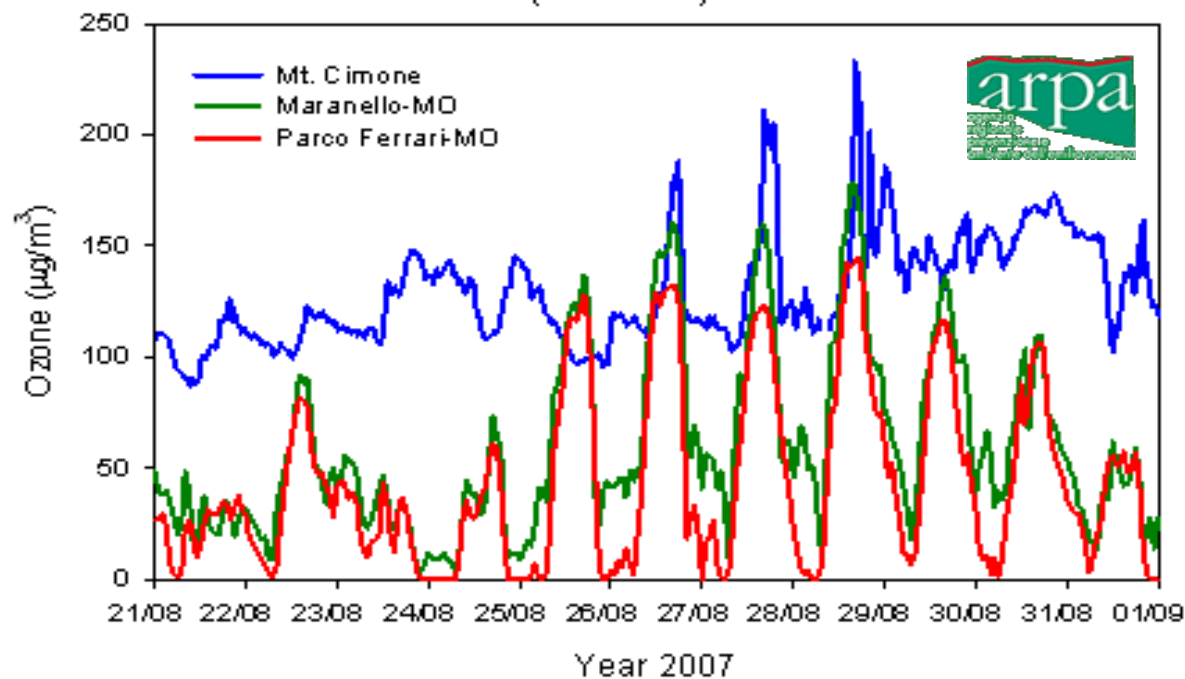
- ❑ Data identified as affected by STT showed higher residuals for O₃.
- ❑ With respect to the remaining data, STT-affected periods showed a 4.2 ± 1.7 ppb (mean $\pm 1 \sigma$) increase in O₃.
- ❑ O₃ increase maximised in DJF and minimised in JJA.
- ❑ Clear impacts also on CO, CO₂ and CH₄

Tropospheric ozone: transport of polluted air mass

Geopotential height (expressed in meters, coloured scale) and wind vectors at 800 hPa, deduced by BOLAM analysis on 26 August 2007 12:00 UTC (A) 29 August 2007 12:00 UTC (B).

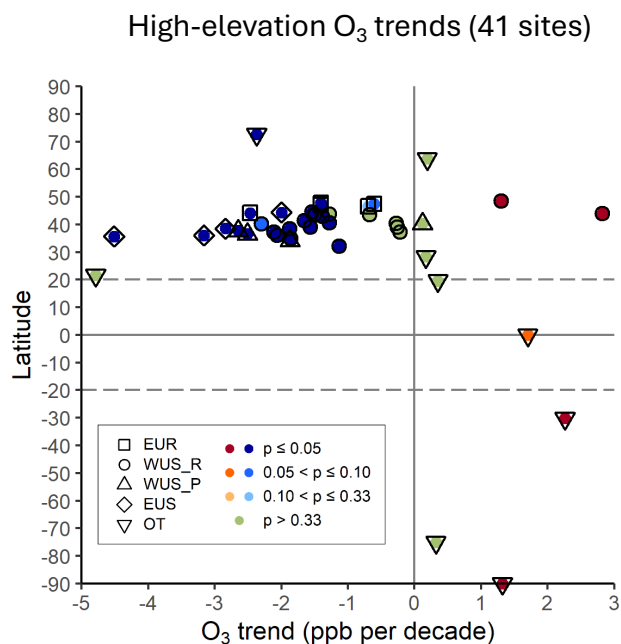


Modena (Po basin) surface ozone



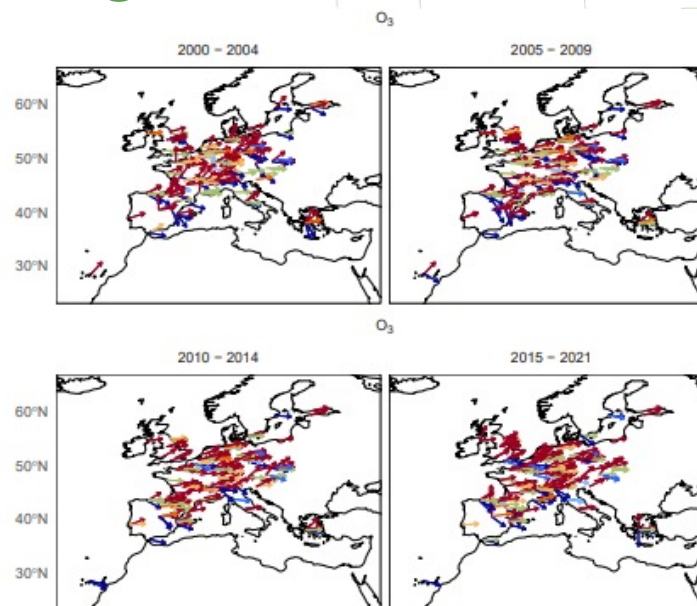
Atmos. Chem. Phys., 9, 4615–4618, 2009
www.atmos-chem-phys.net/9/4615/2009/
© Author(s) 2009. This work is distributed under
the Creative Commons Attribution 3.0 License.

Tropospheric ozone: a look to long-term trends

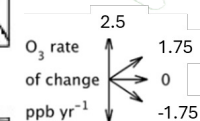


- 41 high-elevation (700 – 3900 m a.s.l.) sites
- Trends calculated on monthly anomalies
- >50 % on hourly data availability for each month
- quantile regression on the 50th quantile
- Generally decreasing trends in the middle northern latitudes

Putero et al. (2023). <https://doi.org/10.5194/acp-23-15693-2023>



Urban O₃ trends (144 sites) – 50th quantile



- 144 urban European sites
- Trends calculated on monthly anomalies
- >90 % on hourly data availability for each month
- Piecewise quantile regression on 0.5 – 0.95 quantiles (to identify breakpoints)
- Slowing in the increase of high European O₃, more site with upward trend in 2015-2021 than 2000 – 2004.
- Majority of trends positive and of high certainty ($p \leq 0.05$) in Europe across the 20-year period.

Bates et al. (2025). <https://doi.org/10.5194/egusphere-2024-3743>

Tropospheric ozone (references)

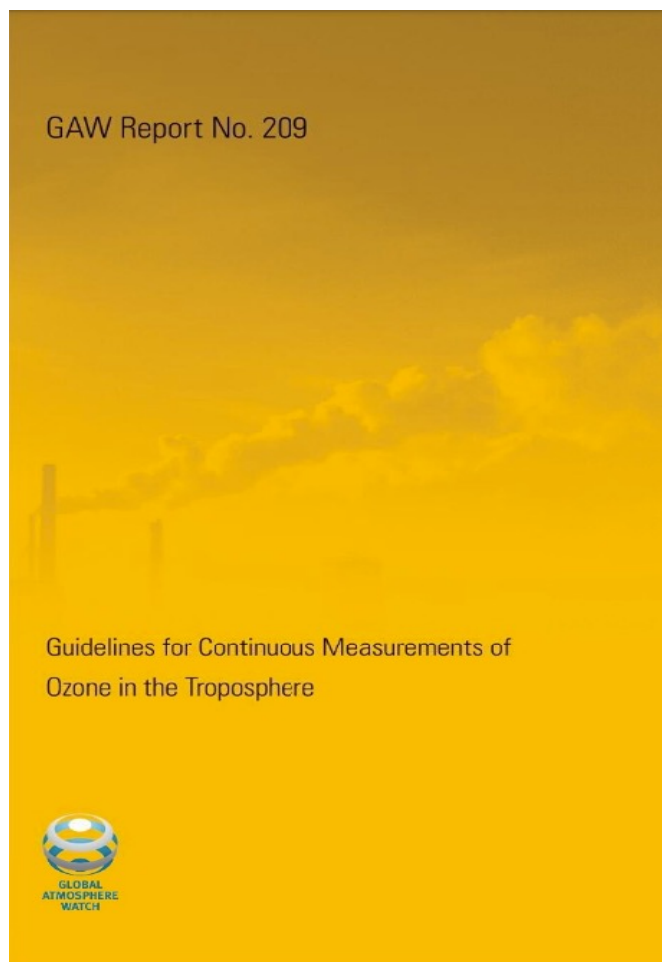


TABLE OF CONTENTS

1. INTRODUCTION	1
2. HOW TO USE THESE GUIDELINES	4
3. DATA QUALITY OBJECTIVES FOR TROPOSPHERIC OZONE MEASUREMENTS	5
3.1 Units, quantities and measurands	5
3.2 DQOs for key GAW goals	6
3.3 DQOs for model assimilation and validation	7
3.4 Completeness, comparability, compatibility and representativeness	7
3.5 Recommendations for metadata inclusion	8
4. PRIMARY OZONE REFERENCE AND THE WORLD CALIBRATION CENTRE FOR SURFACE OZONE	9
4.1 Introduction	9
4.2 Primary ozone standard	10
4.3 World Calibration Centre for Surface Ozone (WCC-Empa)	12
5. SELECTION OF MEASUREMENT TECHNIQUES FOR MEASURING TROPOSPHERIC OZONE AT GAW STATIONS	13
6. ULTRAVIOLET ABSORPTION TECHNIQUE FOR MEASURING TROPOSPHERIC OZONE	14
6.1 Theory	14
6.2 Limitations of ultraviolet monitors for measuring ozone in ambient air	14
6.3 Water vapour correction to ambient ozone mole fraction measurements	18
7. GAW STATION OZONE MEASUREMENT SETUP	19
7.1 Facility requirements	19
7.2 Personnel requirements	19
7.3 Occupational health and safety	19
7.4 Instrumentation requirements	20
7.5 Air inlet and sample lines	20
7.6 Associated key measurements	21
7.7 Environmental issues that affect GAW stations and ozone observations	22
8. GAW STATION OPERATING GUIDELINES FOR QUALITY OZONE OBSERVATIONS	23
8.1 System records	23
8.2 Regular quality control and instrument maintenance checks	23
8.3 Cleaning ozone instrumentation and inlet lines and testing	24
8.4 Data acquisition and initial data processing	25
8.5 Use of the slope and intercept settings in the ozone analyser	26
8.6 Making zero and span measurements and filter checks along with ambient ozone observations	26
8.7 Calibrating the station surface ozone analyser(s) with the station calibrator	27
9. QUALITY ASSURANCE AND QUALITY CONTROL	30
9.1 Introduction	30
9.2 Calibration	30
9.3 Evaluation of overall measurement uncertainties	31
9.4 Example of a systematic uncertainty analysis	32

<https://library.wmo.int/viewer/49557/?offset=#page=1&viewer=picture&o=bookmarks&n=0&q=>

Tropospheric ozone (references)



arXiv > stat > arXiv:2304.14236

Statistics > Applications

[Submitted on 27 Apr 2023]

Guidance note on best statistical practices for TOAR analyses

Kai-Lan Chang, Martin G. Schultz, Gerbrand Koren, Niklas Selke

The aim of this guidance note is to provide recommendations on best statistical practices and to ensure consistent communication of statistical analysis and associated uncertainty across TOAR publications. The scope includes approaches for reporting trends, a discussion of strengths and weaknesses of commonly used techniques, and calibrated language for the communication of uncertainty. The focus of this guidance note is placed on trend analysis, which is expected to be the main statistical topic of interest across many TOAR-II focus working groups, but some of the recommendations and principles provided below are also valid for other applications. Recommendations are highlighted and numbered from R1 to R9.

Subjects: [Applications \(stat.AP\)](#), [Methodology \(stat.ME\)](#)
 Cite as: [arXiv:2304.14236 \[stat.AP\]](#)
 (or [arXiv:2304.14236v1 \[stat.AP\]](#) for this version)
<https://doi.org/10.48550/arXiv.2304.14236>

Submission history

From: Kai-Lan Chang [[view email](#)]
 [v1] Thu, 27 Apr 2023 14:54:31 UTC (11,273 KB)

Table 1: A brief comparison of statistical capabilities of three commonly applied techniques.

	GLS	Sen-Theil	Quantile regression ¹
	Mean	Median	Percentile/Quantile
Inference statistics of a trend			
Robust to small sample size		✓	*2
Robust to outliers		✓	✓
Makes use of all available information	✓		✓
Inference with non-normal distribution on residuals		✓	✓
Unique solution	✓		
Adjustment for non-IID residuals (e.g. incorporation of autocorrelation)	✓		✓
Incorporation of covariates	✓		✓
Extend to piecewise trends	✓		✓
Extend to adaptive nonlinear trends	*3		*3
Extend to extreme percentile estimate			✓ ²

¹ Least absolute deviations method (median regression) can be considered to be a special case of quantile regression, so it is not listed independently.

² For quantile regression, the median estimate is robust to the small sample size problem, but a larger sample size is required for extreme percentile estimates (depending on applications, Das et al., 2019). See Table 2 for TOAR-specific recommendations.

³ These extensions can be made via the class of standard or quantile generalized additive models.



Guidance note on best statistical practices for TOAR analyses

Kai-Lan Chang¹, Martin G. Schultz², Gerbrand Koren³, and Niklas Selke²

¹Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder and NOAA Chemical Sciences Laboratory, Boulder, CO, USA
²Jülich Supercomputing Centre, Forschungszentrum Jülich, Germany
³Copernicus Institute of Sustainable Development, Utrecht University, Utrecht, the Netherlands

This document has been produced based on discussions in the statistics focus working group of the TOAR-II initiative, and approved by the TOAR-II Steering Committee April 26, 2023

The aim of this guidance note is to provide recommendations on best statistical practices and to ensure consistent communication of statistical analysis and associated uncertainty across TOAR publications. The scope includes approaches for reporting trends, a discussion of strengths and weaknesses of commonly used techniques, and calibrated language for the communication of uncertainty. The focus of this guidance note is placed on trend analysis, which is expected to be the main statistical topic of interest across many TOAR-II focus working groups, but some of the recommendations and principles provided below are also valid for other applications. Recommendations are highlighted and numbered from R1 to R9.

1 Definition of trend analysis

The purpose of trend analysis can be defined as

detecting and attributing the change and its uncertainty of the statistical properties in a time series of a predefined variable.

where the statistical properties represent how we define and express the trend (e.g. mean, median or extreme percentile changes). Each component of this definition will be discussed through relevant topics and recommendations as follows: Section 2 clarifies the distinct roles of linear and nonlinear techniques in trend quantification. Section 3 compares the commonly adopted statistical properties in trend assessment. Section 4 discusses data preparation for time series analysis. Section 5 identifies the fundamental factors affecting uncertainty quantification associated with the trend estimate. Section 6 demonstrates how the reliability of trend assessment can be determined through the relationship between quantified trend and uncertainty. Section 7 discusses the change point detection of trends. Section 8 provides additional resources.

This guidance note aims to provide recommendations of tropospheric ozone trend analysis from a practical aspect, without discussing technical details, although we do provide some R and Python code for quantile regression in the Annex E. Practitioners (referring to authors of publications written in the context of the TOAR activity) who are interested in the fundamental theory of trend analysis (e.g. the statistical relationship between the sample size, magnitude of trend and uncertainty) are referred to various textbooks (Chandler and Scott, 2011; Von Storch and Zwiers, 2001; Wilks, 2011) and articles (Chang et al., 2021; Weatherhead et al., 1998).

2 Quantitative versus qualitative summary of the trend

R1: Practitioners are recommended to provide quantitative trends and should avoid drawing conclusions when the magnitude of trends and associated uncertainties are not explicitly quantified.

Trend detection techniques can be generally classified as linear or nonlinear methods. By using a large number of parameters and numerical optimization, nonlinear methods offer a great deal of flexibility in modeling the nonlinear pattern of a time series. However, the result is often too complex mathematically to quantitatively provide a simple trend value and an uncertainty value. Unless there is a clear understanding of (non-linear) processes driving the trend, quantitative non-linear trend analysis poses the risk of overfitting.

arXiv:2304.14236v1 [stat.AP] 27 Apr 2023

Tropospheric ozone (references)



Atmospheric Measurement Techniques

ARTICLES & PREPRINTS ▾ SUBMISSION POLICIES ▾ PEER REVIEW ▾ EDITORIAL BOARD ABOUT ▾ EGU PUBLICATIONS ↗

Special issue

Articles / Special issue

Search

Tropospheric Ozone Assessment Report Phase II (TOAR-II) Community Special Issue (ACP/AMT/BG/GMD inter-journal SI)

Editor(s): AMT co-editors: Steffen Beirle, Diego Loyola, and Troy Thornberry | Co-organizers: Owen R. Cooper and Martin G. Schultz
Special issue jointly organized between Atmospheric Chemistry and Physics, Atmospheric Measurement Techniques, Biogeosciences, and Geoscientific Model Development

The Tropospheric Ozone Assessment Report (TOAR-II) is an official activity of the International Global Atmospheric Chemistry Project (IGAC) (<https://igacproject.org/activities/TOAR/TOAR-II>). The goal of TOAR-II is to build on the success of TOAR-I (2014–2019) and produce an updated assessment of tropospheric ozone's global distribution and trends from the surface to the tropopause. This effort includes an analysis of the impacts of ozone on human health, crop and ecosystem productivity, and climate.

Tropospheric ozone (references)

An update on low-cost sensors for the measurement of atmospheric composition

December 2020

Edited by Richard E. Peltier

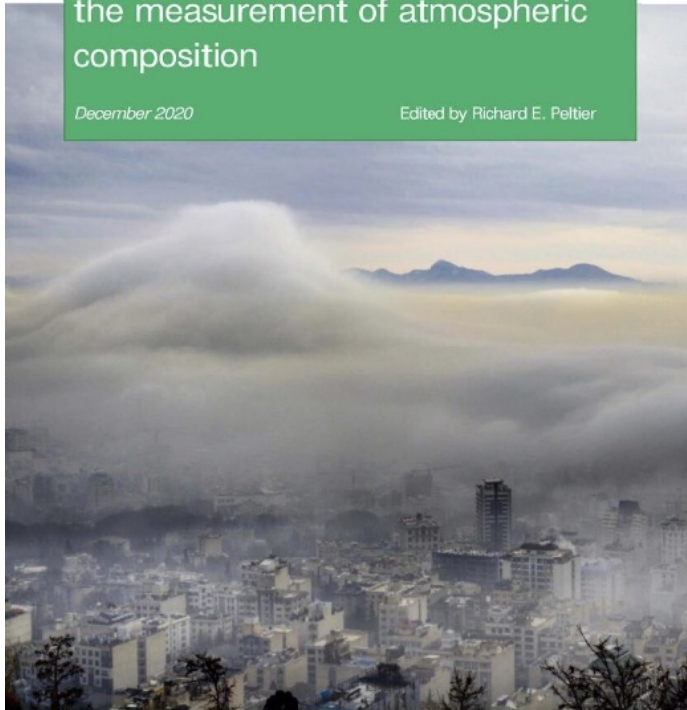


Table of Contents

List of Authors.....	5
Executive Summary.....	6
Resumé analytique.....	9
Resumen	13
PE3HOME	17
执行摘要	21
موجز تنفيذي	23
Objectives of this document.....	26
Introduction	27
Current and future applications	30
Main Components and Principles	37
An Example of Low-Cost Sensor Costs	40
Calibration and Quality Assurance/Quality Control of LCSs.....	42
Quality Assurance and Calibration	42
Quality Control of Sensors and Sensor Networks	46
Evaluation activities	49
Performance evaluation programmes.....	49
Generalizations Across Specific Atmospheric Components.....	52
Particulate Matter	52
Ozone	52
Carbon Monoxide	53
Sulfur Dioxide.....	53
Hydrogen Sulphide and VOC sensors	53
Greenhouse Gases: Carbon Dioxide and Methane.....	53
Low-cost sensor Applications	54
Supplemental Ambient Use Applications.....	54
Other Applications.....	55
Sensor Characterization	60
Characterization of Gas phase Sensors	60
Electrochemical (EC) sensors	60
Metal oxide semiconductor (MOS) sensors.....	61
Photoionization detector (PID) sensors.....	61
Non-dispersive infrared (NDIR) sensors	61
Characterization of PM Sensors	62
Sensor Characterization in Stationary Long-Term Deployment	63
Sensor Characterization in Mobile Applications	64
Sensor Characterization in Exposure Applications	65
Sensor Characterization in Source Applications	65
Communicating LCS to Society	66
Potential for using LCS to increase awareness and understanding of air pollution	68
Considerations for communicating LCS data to different audiences.....	69
Framework for best practice use in communicating data from LCS.....	70



<https://library.wmo.int/records/item/37465-an-update-on-low-cost-sensors-for-the-measurement-of-atmospheric-composition?offset=29>

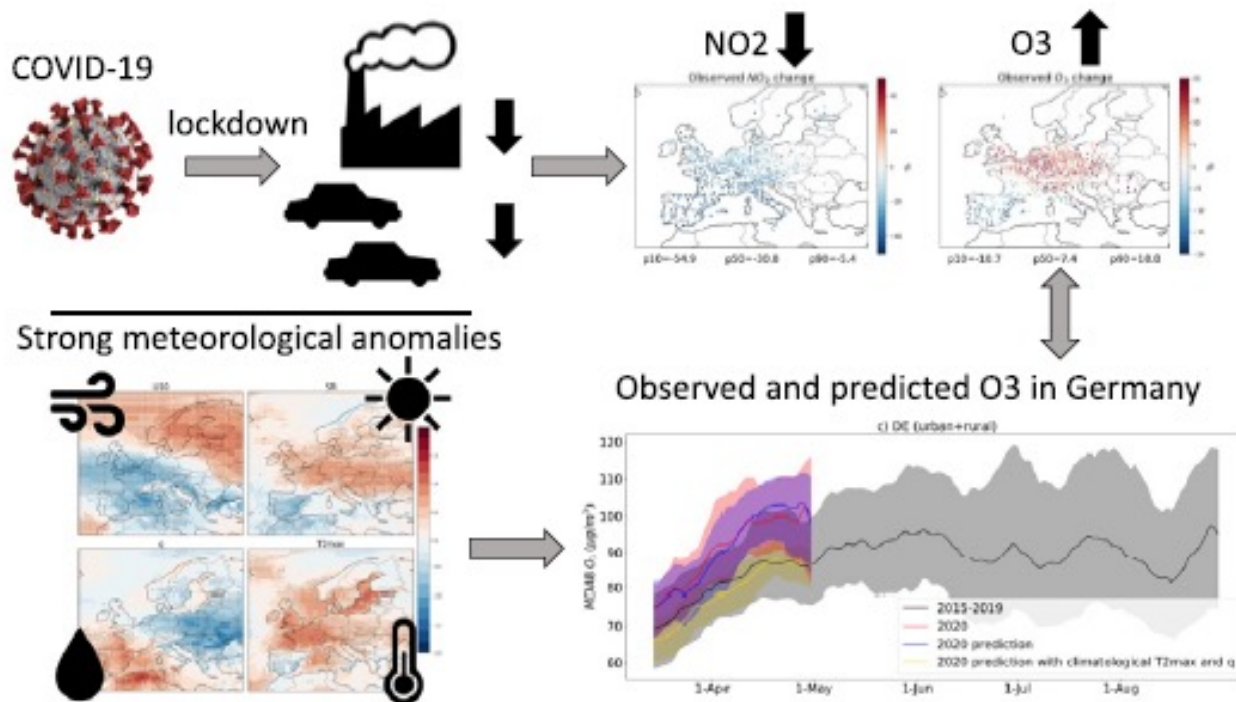


THANKS!

IR0000032 – ITINERIS, Italian Integrated Environmental Research Infrastructure
(D.D. n. 130/2022 - CUP B53C22002150006) Funded by EU - Next Generation
Mission 4 "Education and Research" - Component 2: "From research to business"
3.1: "Fund for the realisation of an integrated system of research and innovation infrastructures"



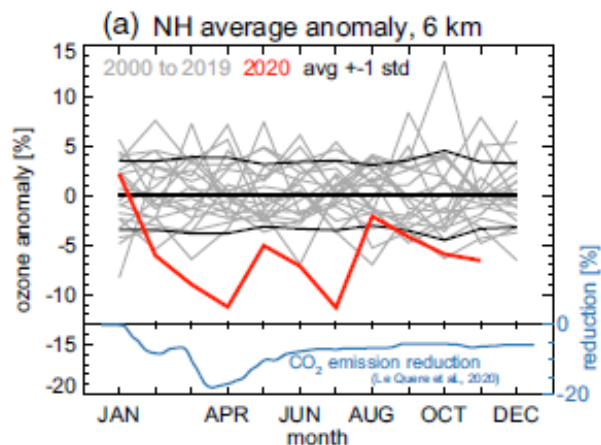
Fingerprints of the COVID-19 economic downturn



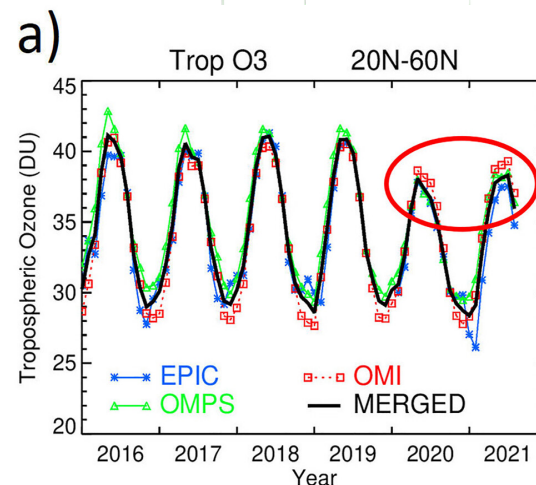
- At the begin, most of these works focused on high-emission sources or urban environments
- Varying O₃ behavior as a function of the reduction in the emissions, mainly dependent on whether the photochemical O₃ formation in the considered regions was NO_x- or VOC-limited

Ordóñez C. et al., 2020 Early spring near-surface ozone in Europe during the COVID-19 shutdown: Meteorological effects outweigh emission changes *Sci. Total Environ.* **747** 141322. <https://doi.org/10.1016/j.scitotenv.2020.141322>

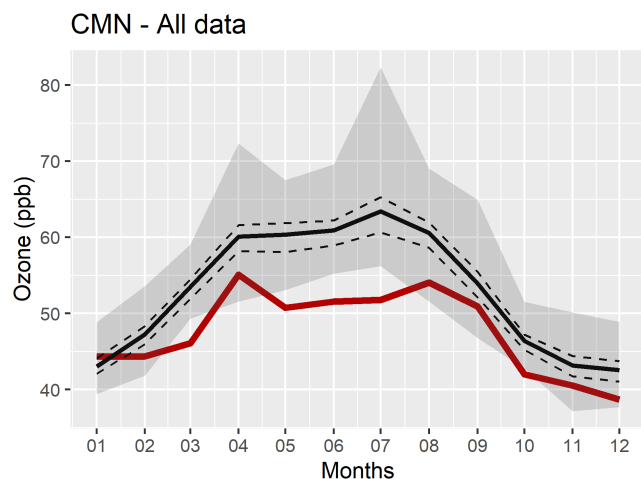
Fingerprints of the COVID-19 economic downturn



Steinbrecht et al. (2021). <https://doi.org/10.1029/2020GL091987>



Ziemke et al. (2022). <https://doi.org/10.1029/2022GL098712>

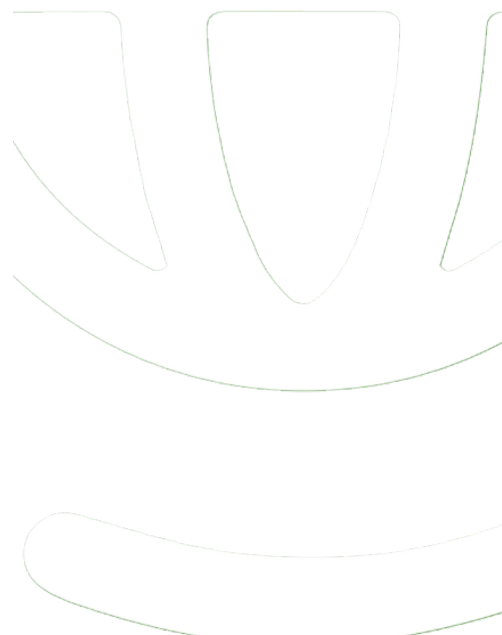
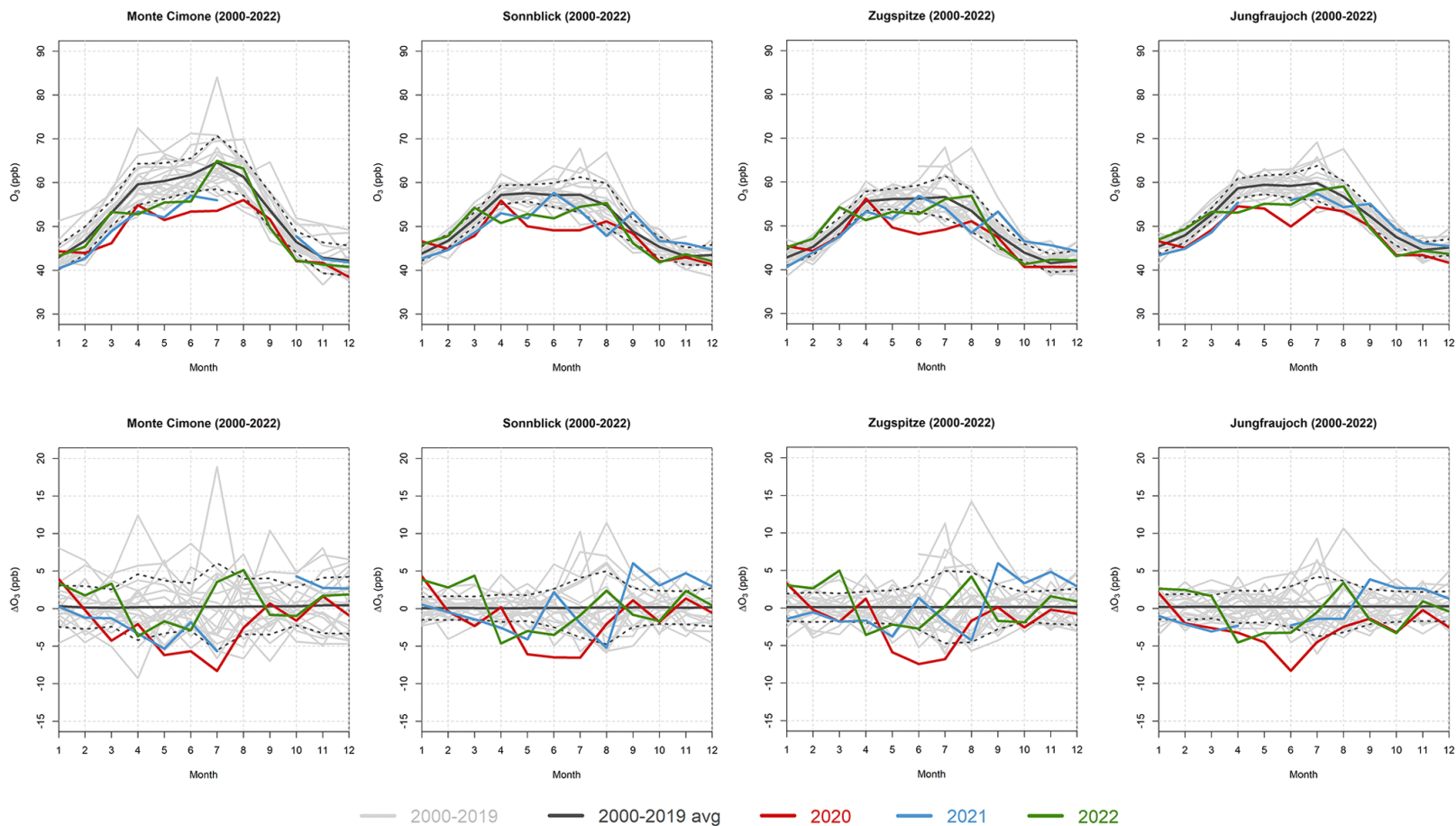


Free-troposphere: consistent reduction of O₃ in 2020-2021 as seen, e.g., by

- ground-based remote sensing (Steinbrecht et al., 2021)
- in-situ mountain top observations (Cristofanelli et al., 2021)
- satellite measurements of tropospheric column O₃ (Ziemke et al., 2022)

Cristofanelli et al. (2021). <https://doi.org/10.1088/1748-9326/ac0b6a>

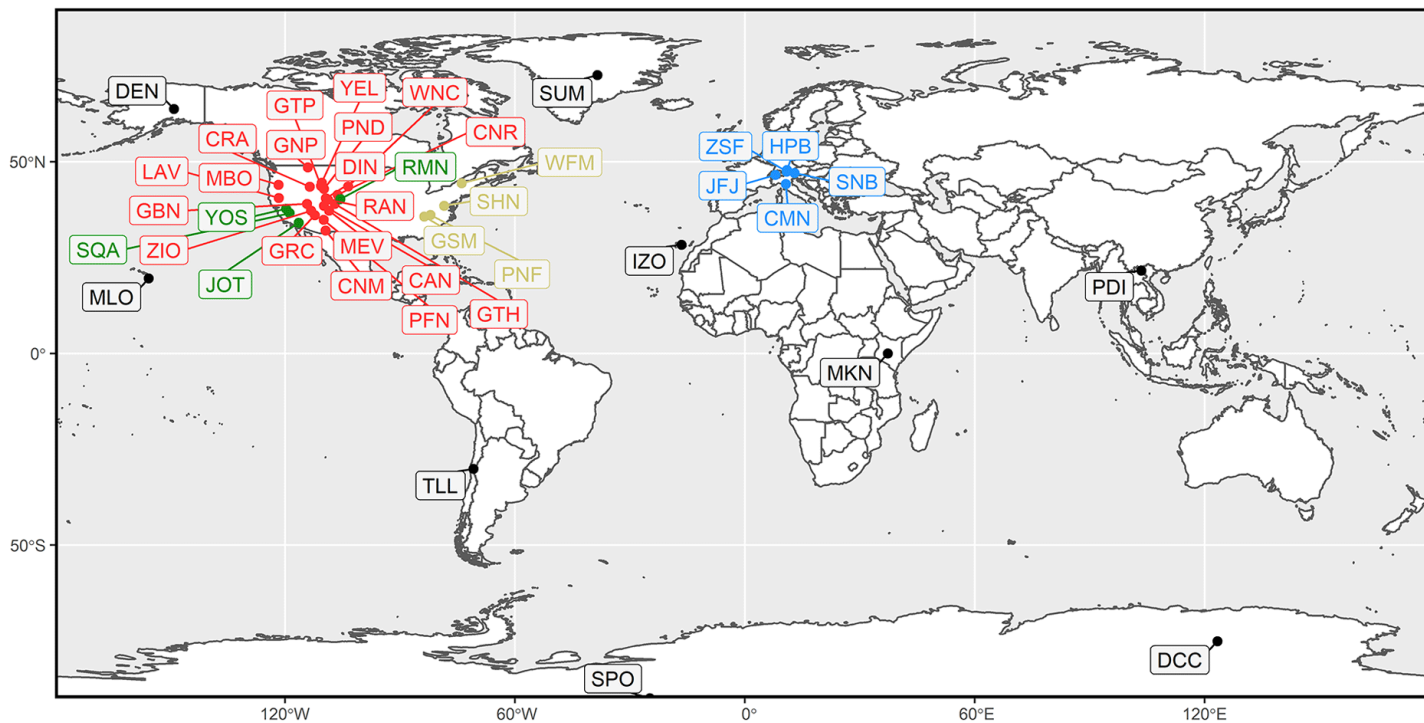
Fingerprints of the COVID-19 economic downturn



<https://doi.org/10.5194/acp-23-15693-2023>
 © Author(s) 2023. This work is distributed under the Creative Commons Attribution 4.0 License.

Research article |

Fingerprints of the COVID-19 economic downturn



41 high-elevation (700 – 3900 m a.s.l.) sites

- EUR
- EUS
- OT
- WUS_P
- WUS_R

Season	WUS_R	WUS_P	EUS	EUR	OT
MAM 2020	−3.1 ppb (−6 %)	−4.3 ppb (−9 %)	−2.5 ppb (−4 %)	−2.1 ppb (−3 %)	−2.1 ppb (−3 %)
JJA 2020	−2.3 ppb (−5 %)	−2.9 ppb (−4 %)	−5.6 ppb (−12 %)	−4.8 ppb (−8 %)	−1.5 ppb (−5 %)
MAM 2021	−0.9 ppb (−2 %)	0.4 ppb (3 %)	0.9 ppb (3 %)	−2.7 ppb (−4 %)	−1.3 ppb (−1 %)
JJA 2021	2.7 ppb (6 %)	1.2 ppb (3 %)	−3.8 ppb (−8 %)	−2.6 ppb (−5 %)	0.4 ppb (1 %)

<https://doi.org/10.5194/acp-23-15693-2023>
 © Author(s) 2023. This work is distributed under the Creative Commons Attribution 4.0 License.

Research article |