Collection of observational ozone data over the global oceans & polar regions to assess chemistry and temporal evolution:

Efforts of the TOAR-II Oceans Working Group

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1. Introduction

Constraints from ozone (O_3) observations over the oceans are needed in addition to those from terrestrial regions to fully understand global tropospheric chemistry and its interactions with the Earth system and climate. The TOAR-1 was a great initiative addressing the global tropospheric ozone issues but could not include ozone over the oceans and polar regions as specific target of their assessment. In the Phase-II, i.e., TOAR-II, we aim for this. Here we present the observational data set specifically collected for this purpose. The activity is also regarded as an extension of previous works (e.g., Lelieveld et al., 2004, Kanaya et al., 2019), where the used datasets were smaller.

The main scientific goals are to characterize

1) O_3 spatial distribution, seasonal and geographical variability, long-term trends;
2) O_3 production-loss processes, budget (halogens, NOx, ship emissions, etc..); and
3) State of representation of O_3 in remote regions in global and regional models.

Summary

◆ TOAR-II will include "Oceans" as an Assessment paper, examining the spatio-temporal variability of ozone primarily in the atmospheric boundary layer over the global oceans and polar regions, based on our new observational data collection from Ship/buoys, Aircraft, Ozonesondes, and Coastal/polar sites.

◆ Multi-model mean (6 members) well reproduced the observed seasonality in several oceanic regions, successfully assessing the state of representation of ozone in remote regions.

◆A significant long-term increasing trend was identified with the combined ship/buoy and coastal site data, over the tropical Atlantic region.

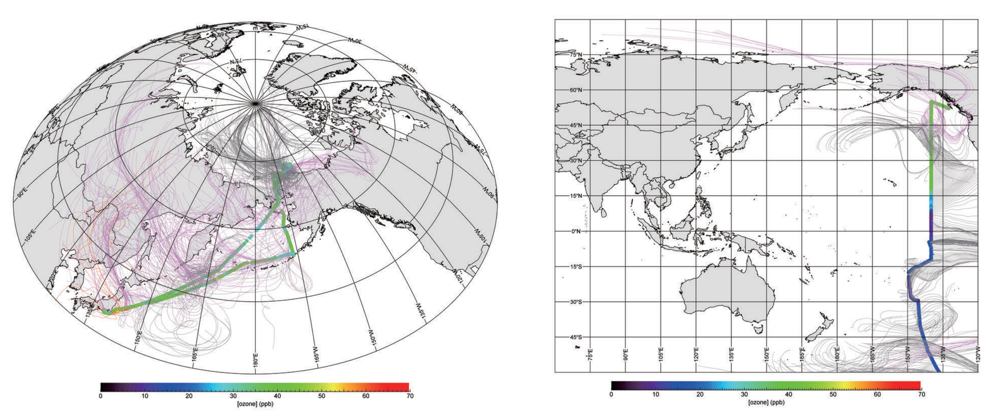
◆Strong photochemical destruction was suggested from daytime O_3 minima over the tropical Pacific and Indian Oceans. We found that the negative correlation between IO and O_3 could be influenced by the interplay of atmospheric transport and chemistry, as well as reactive iodine initiation mechanisms.

2. Observational data collection & processing

We created five csv files, incorporating observed ozone data from 1) ship/buoys, 2) aircraft, 3) ozonesondes, 4) coastal sites, and 5) polar stations, respectively. Most of the monitoring data are from reliable instruments (e.g., Model 49i from Thermo Fisher, and Model 205 from 2B tech) calibrated periodically.

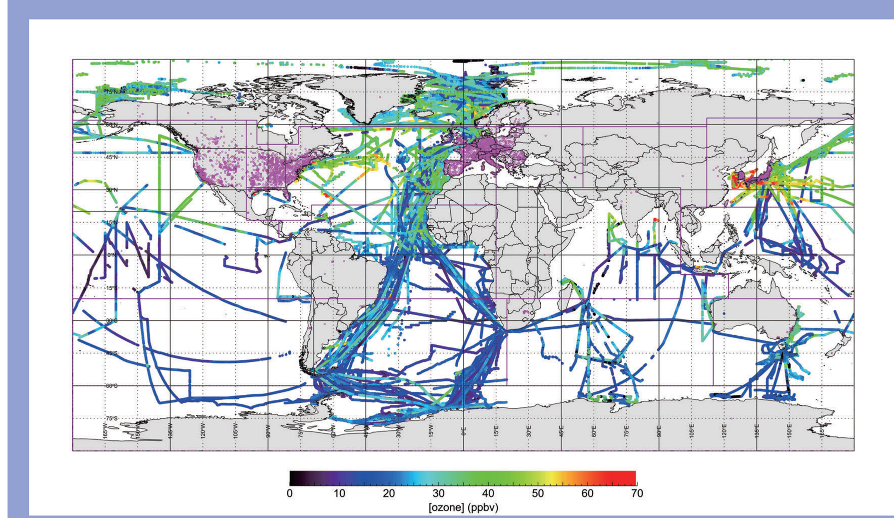
Type	Main Source	features	filename
1) **Ship/buoy**	Original	76 cruises/buoy operation, 210781 h data 1977-2022	toar2_oceans_ship_buoy_data_v0_95.csv
2) **Airborne**	NASA-GTE, FAAM, NSF & NOAA campaigns (up to 5000 m)	47 missions 424005 data points 1987-2020	toar2_oceans_airborne_data_5000m_v0_92r_new.csv
3) **Ozone sonde**	Mainly from HEGIFTOM homogenized (up to 5000 m)	29 sites/dataset, 666470 data points 1967-2022	toar2_oceans_ozonesondedata_v0_94.csv
4) **Coastal sites**	TOAR-II DB etc	21 sites, 3650252 h data (1957-1959) 1973-2022	toar2_oceans_coastalsites_v0_94.zip
5) **Polar sites**	TOAR-II DB etc	17 sites, 3362716 h data 1973-2023	toar2_oceans_polarsites_v0_90.zip

Co-located pollution tracer observations (CO, NOx, or CN) were available for only a small fraction of the data; therefore, we relied on backward trajectories (HYSPLIT) to select purely marine air masses without pollutions. Cases were selected when air masses traveled over unpolluted marine or polar regions for 72 or more hours prior to the observations. The free troposphere (>2500m) over land was also considered unpolluted.



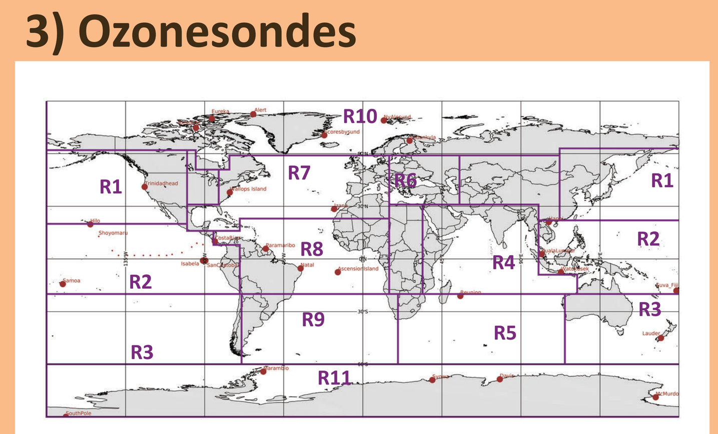
Statistical analyses were performed after dividing the data per platform into 11 regions, R1-3: North, Tropical, and South Pacific, R4-5: Tropical and Southern Indian Ocean, R6: Eastern Mediterranean (mostly no data), R7-9: North, Tropical, and South Atlantic, R10: Arctic, and R11: Southern Ocean, to study the distribution and variability, temporal trends.

1) Ship/buoys



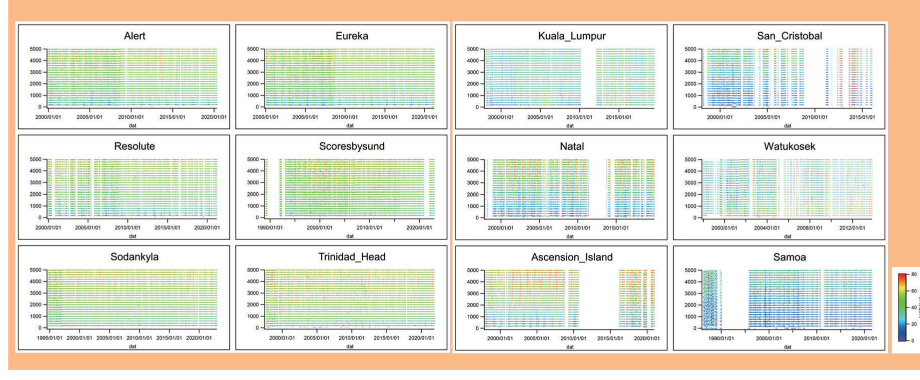
Hourly data from 63 research cruises/data sets from 1977 to 2022 are included. Based on 1-min data, where available, periods affected by ship plumes were removed, as identified by abrupt reductions in O_3 levels with NO titration. Fltering was not applied to the 15 O-Buoy data over the Arctic region, where similar O_3 level reductions could occur naturally, with the polar sunrise chemistry. Otherwise we relied on their own pre-screening.

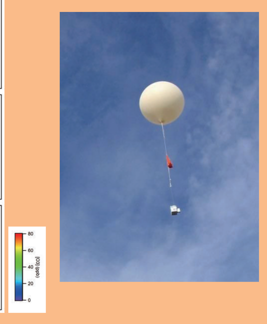
3) Ozonesondes



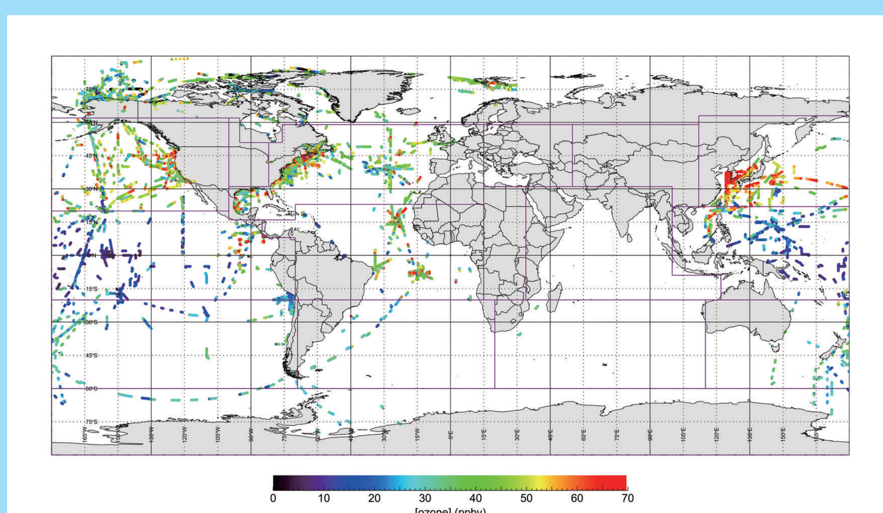
Ozonesonde data (1967-2022) covered the altitude range of 0-5000 m but only one data set per each 200-m layer (with the highest altitude of the layer) was stored, to reduce the volume. Of the 29 data sets, 24 are those homogenized in the HEGIFTOM* WG of TOAR-II, while the other 3 and 2 are from WOUDC data sites and campaigns.

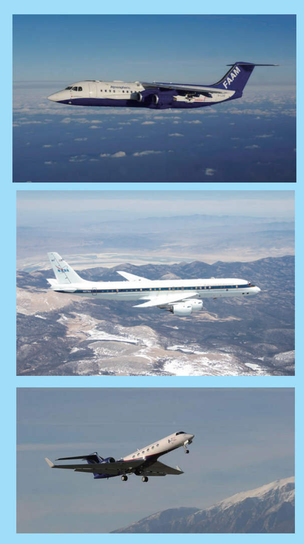
*https://hegiftom.meteo.be/datasets/ozonesondes





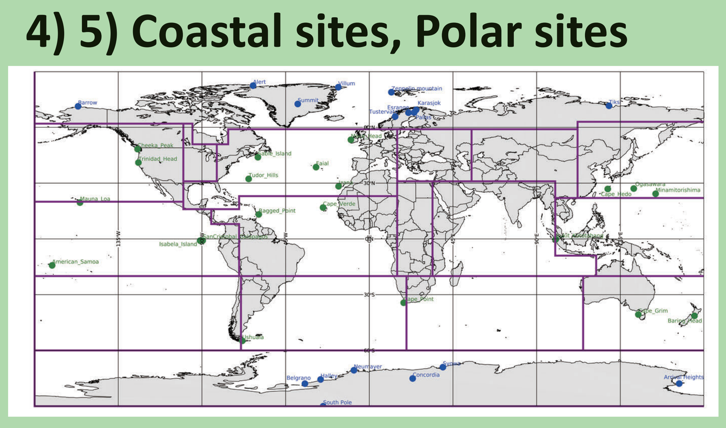
2) Aircraft

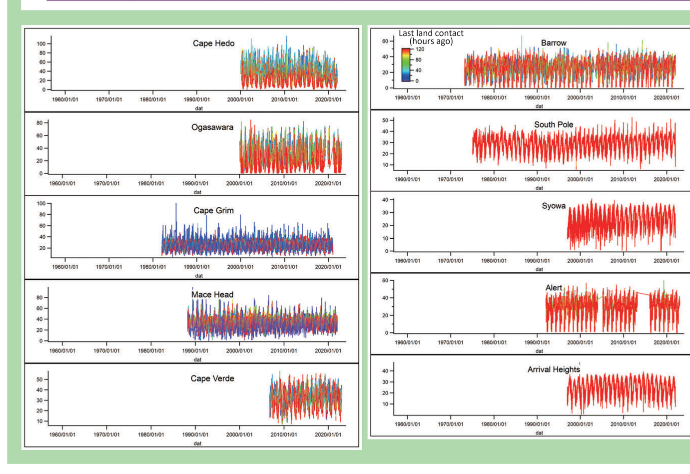




Data from 47 aircraft missions (1987-2020) in the altitude range 0-5000 m with time steps of 10-90 s are stored. They consist of 21 NASA Global Tropospheric Experiment (GTE) and follow-on missions, 6 FAAM Airborne Laboratory missions, and 20 missions from NOAA and NSF aircraft observations.

4) 5) Coastal sites, Polar sites

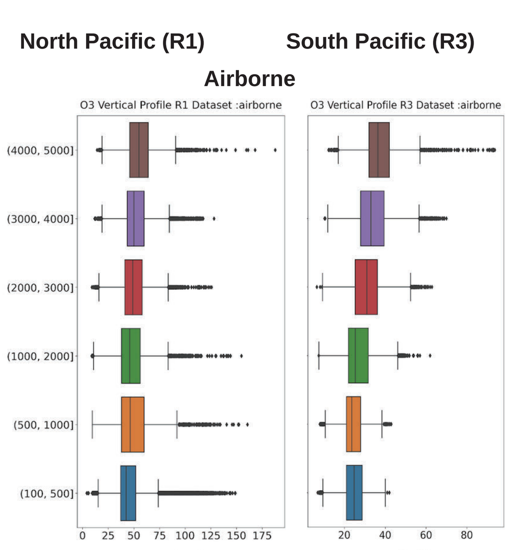


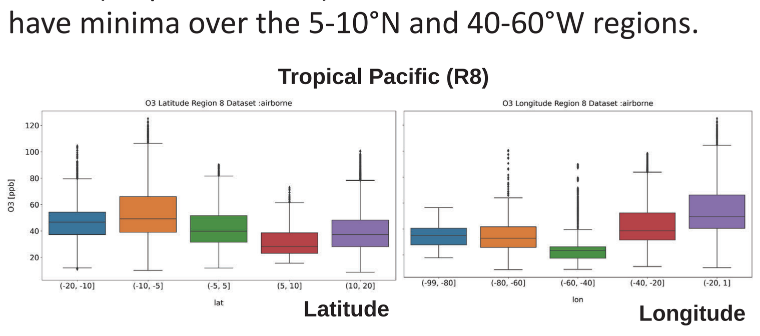


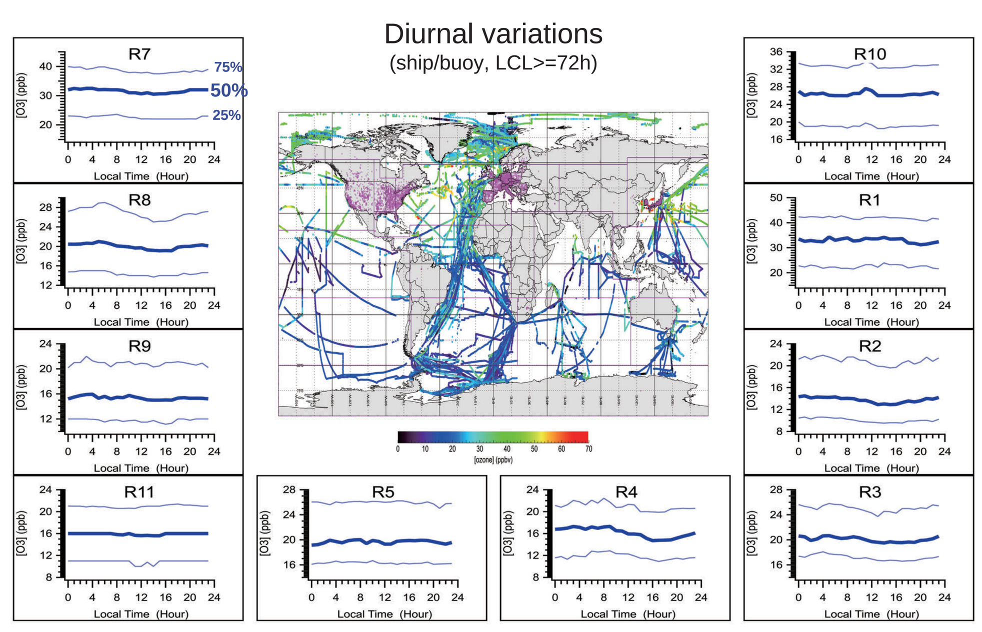
We considered 21 non-polar coastal sites including 16 from the TOAR-II database, 2 from EANET, 1 from CSIRO, and 2 from campaigns, and 17 stations from polar regions, including 15 from TOAR-II, 1 from EBAS (Alert), and 1 from INTA (Belgrano station). All data are hourly.

3. Geographical distributions & Temporal variability

Vertical profiles of airborne data for the North and South Pacific (R1 and R3) both indicated that ozone levels tend to increase with the altitude. Latitudinal/longitudinal cross sections of airborne data for R8 (Tropical Atlantic) showed that the O_3 levels have minima over the 5-10°N and 40-60°W regions.

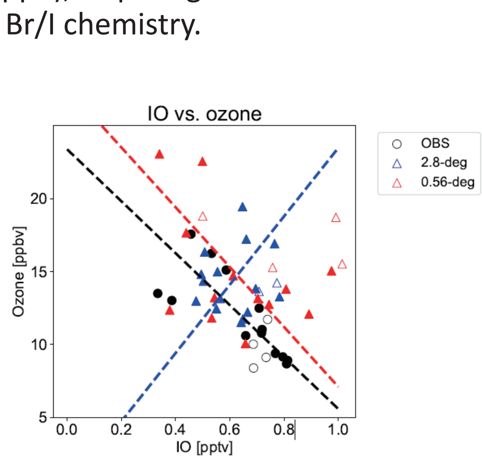






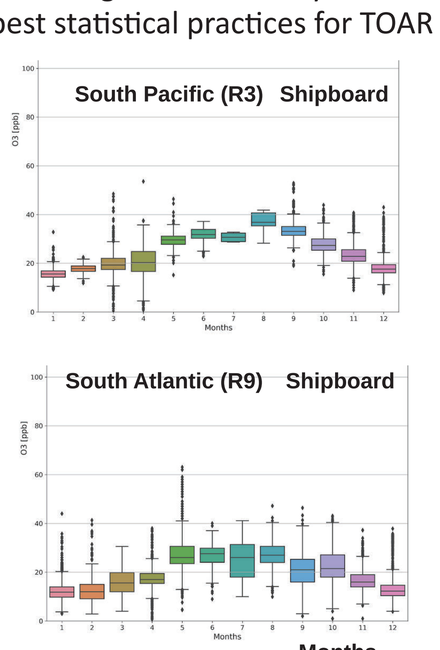
In the diurnal variation, all regions basically showed flat or patterns with daytime minima, representing photochemical destruction, as expected over the clean oceanic regions. In the R2, tropical Pacific, the hourly medians showed a diurnal pattern with an amplitude of 1.6 ppb (12% of the 24-h median of 13.8 ppb), requiring more O_3 destruction than predicted by the CHASER model with Br/I chemistry.

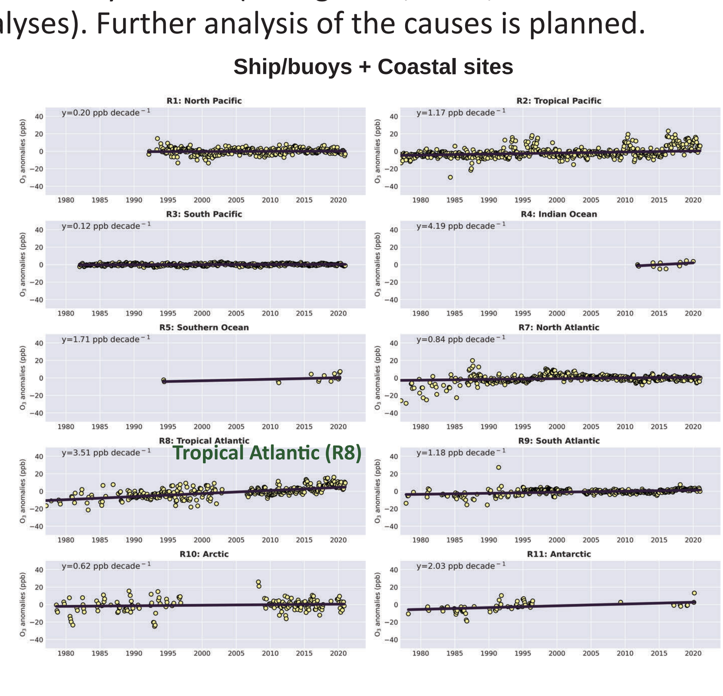
Previously we found a negative correlation between observed IO and O_3 that persisted down to low O_3 levels (<10 ppb) over the tropical Pacific, which remained unexplained by the 2.8° resolution CHASER model simulation, suggesting that O_3-independent initiation of reactive iodine species may have continued to destroy O_3 at such low levels (Takashima et al., 2022). Sekiya et al. (2020; submitted) found that a model with a higher resolution (0.56°) could partially resolve such a discrepancy, representing an interplay between chemistry and transport, while the O_3-independent initiation process would remain important.



Seasonal patterns for ship/buoy data for the South Pacific and Atlantic (R3 and R9) similarly showed maxima in July/August , with R3 being 0-10 ppb higher for all months.

A statistically significant (p<0.01) long-term positive trend (+3.51 ppb/decade) was identified for the combined ship/buoy and coastal site data set for the Tropical Atlantic (R8), after removing the seasonality as recommended by TOAR-II (Chang et al., 2023; Guidance note on best statistical practices for TOAR analyses). Further analysis of the causes is planned.

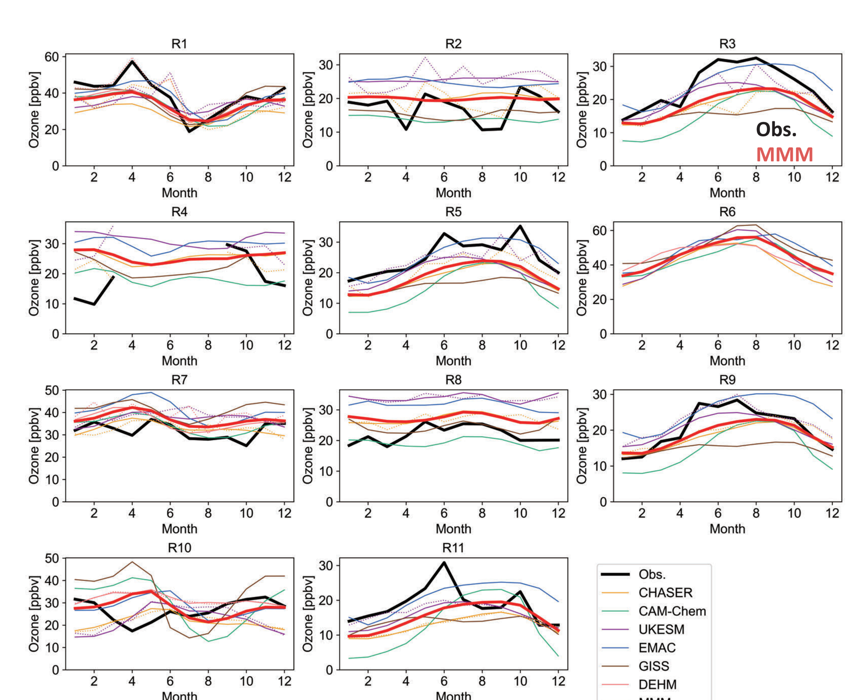


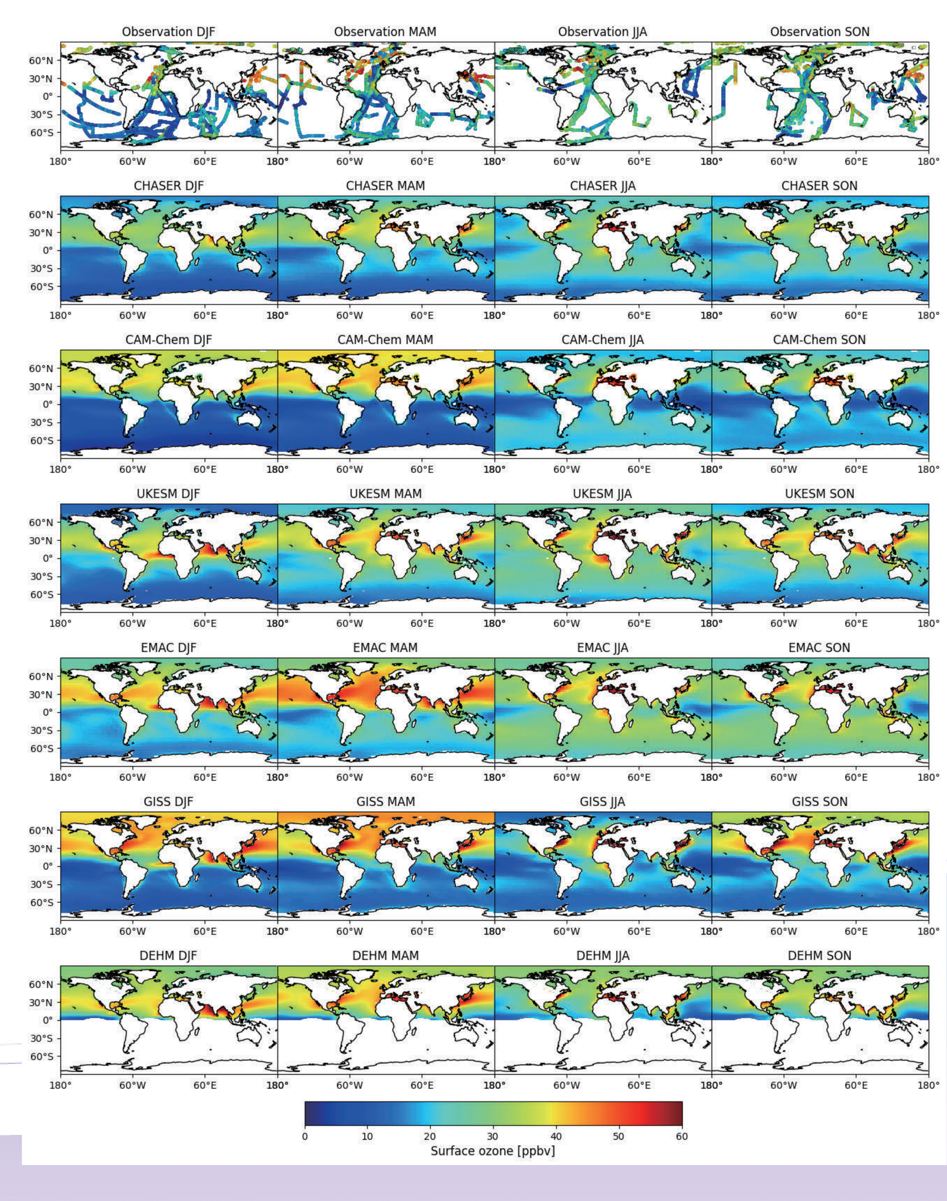


		Ship Buoys	Airborne < 1km	Ozonesondes <200m	Coastal Sites
R1:	North Pacific	2.48 (0.23)	-0.13 (0.95)	-2.44 (0.05)	0.17 (0.58)
R2:	Tropical Pacific	1.29 (0.62)	-1.92 (0.24)	-0.06 (0.85)	1.32 (<0.01)
R3:	South Pacific	1.94 (<0.01)	0.01 (0.99)	-	0.10 (0.15)
R4:	Indian Ocean	4.19 (0.35)	-	-	-
R5:	Southern Ocean	1.71 (0.74)	-	3.12 (<0.01)	-
R7:	North Atlantic	2.91 (<0.01)	-4.99 (0.30)	3.52 (<0.01)	0.20 (0.60)
R8:	Tropical Atlantic	2.67 (<0.01)	0.59 (0.93)	-0.14 (0.61)	3.24 (<0.01)
R9:	South Atlantic	3.60 (<0.01)	0.00 (1.00)	-	0.37 (0.42)
R10:	Arctic	0.62 (0.22)	-2.25 (0.62)	-1.91 (<0.01)	-
R11:	Antarctic	2.03 (0.14)	0.33 (0.94)	0.10 (0.90)	-
	Global	2.34	1.04		0.90

4. Modelling

Six models (CHASER, CAM-Chem, UKESM, EMAC, GISS and DEHM) have participated to evaluate the state of representation of ozone in the remote regions. First results show that the MMM (Multi-Model Mean) mostly reproduced well the seasonal variability of the ship/buoy based observations, for several regions. Further analyses, including those comparing the chemical production/loss terms, are planned.





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Acknowledgments

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