

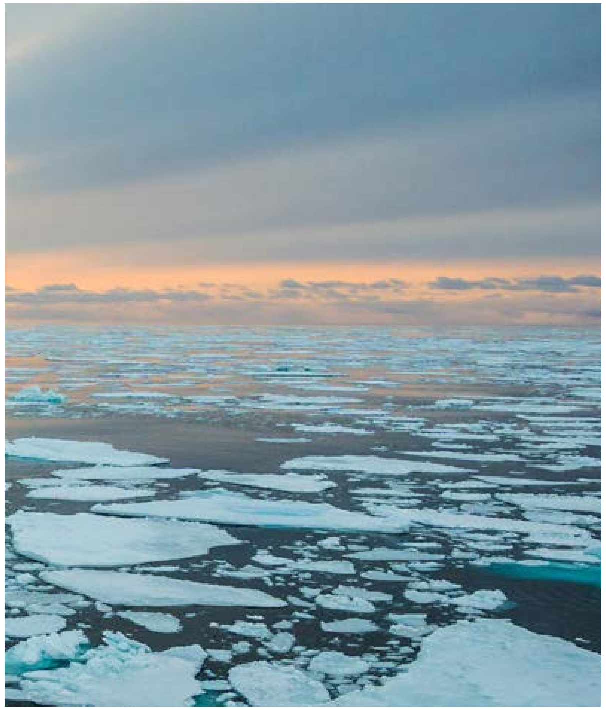


Defining environmental parameter domains for secondary organic aerosol formation

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UNIVERSITY OF CALIFORNIA UCRIVERSIDE

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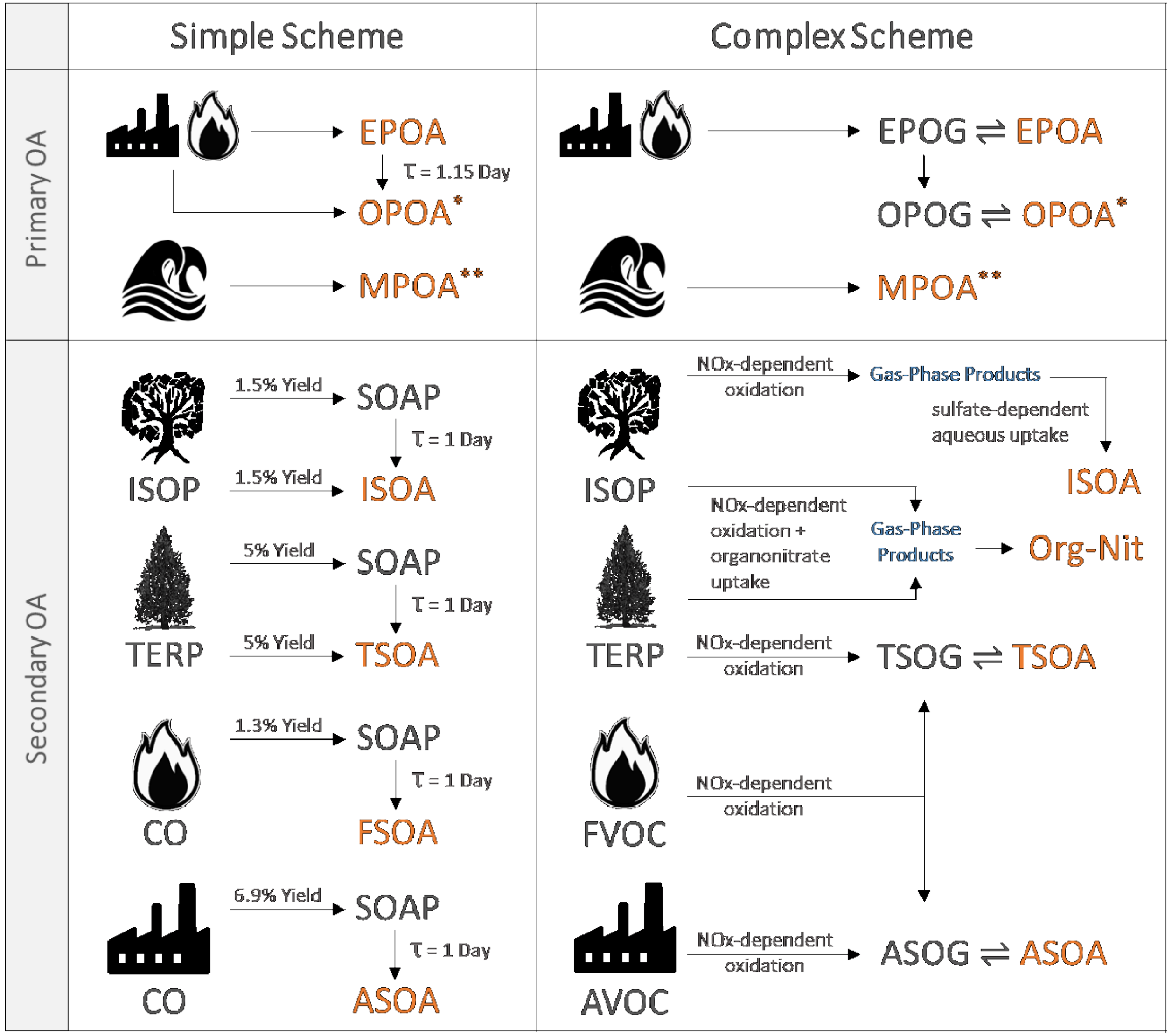
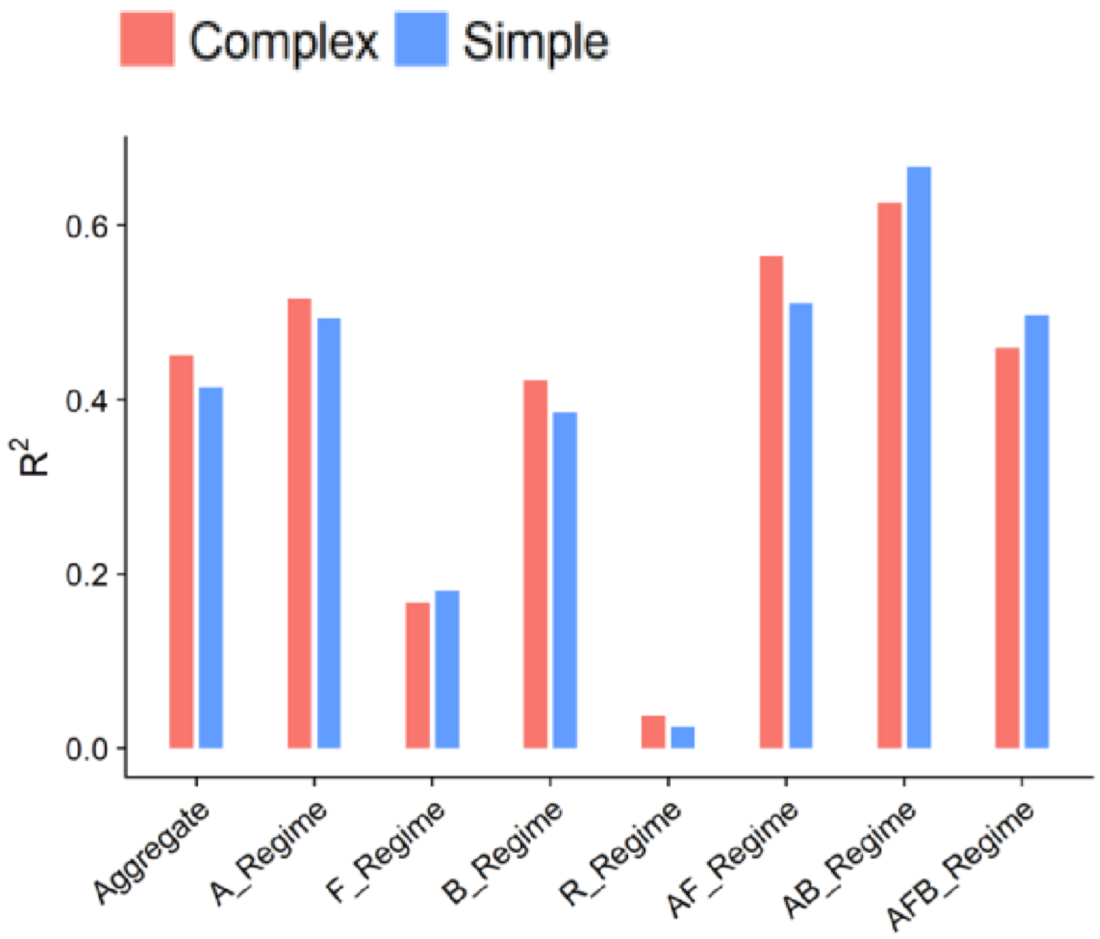
SOA represents a particularly difficulty problem for atmospheric modelers, in part due to the complexity of its formation and fate

A variety of modeling schemes have been developed, with a **wide range of complexity** to balance computational efficiency with mechanistic fidelity



Pai et al., 2019

However, increased OA mechanism complexity within models has **not** always translated to increased model performance against observations



Pai et al., 2019

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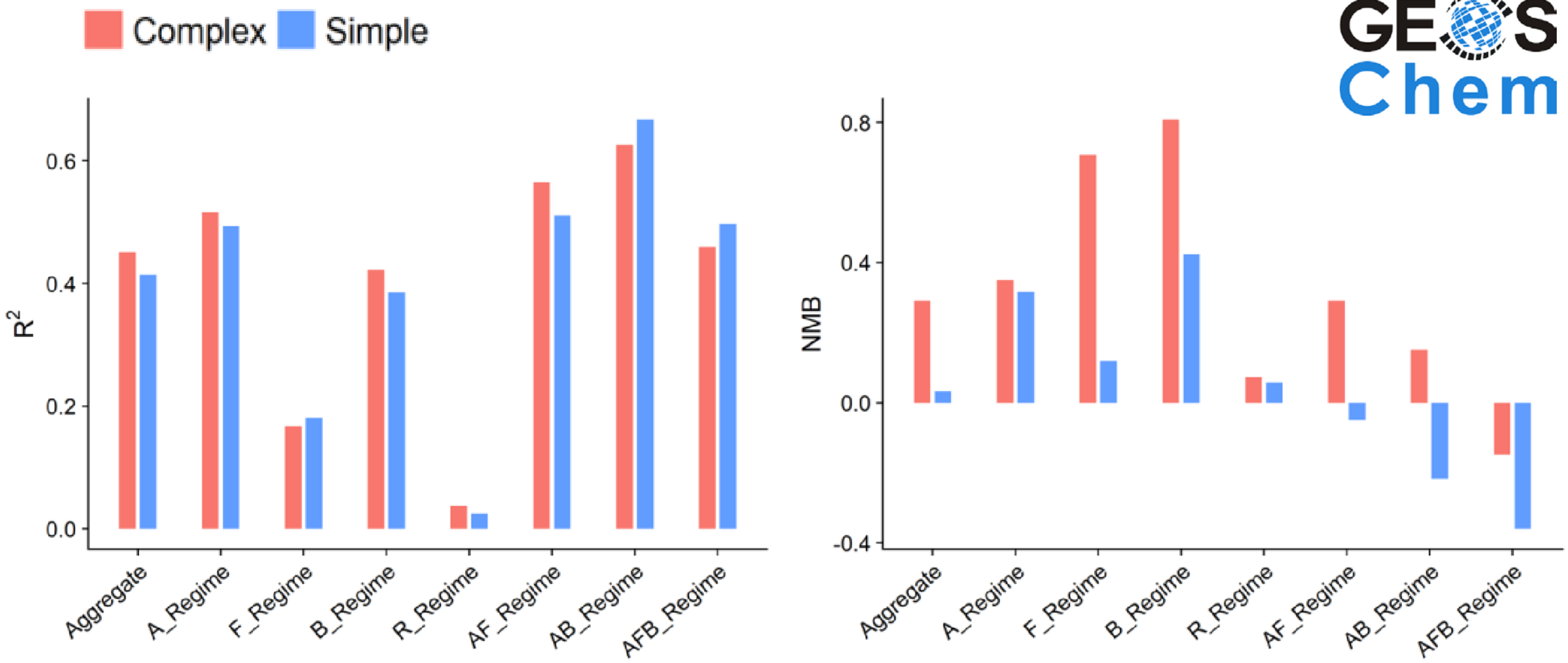
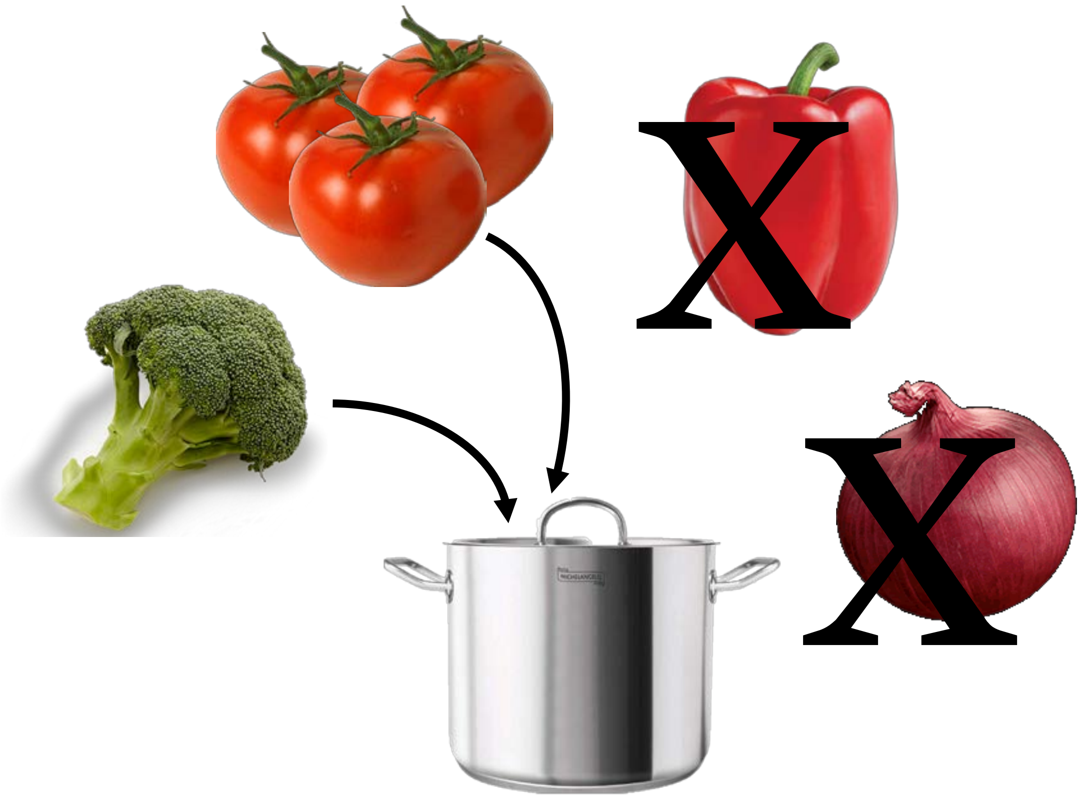


Pai et al., 2019

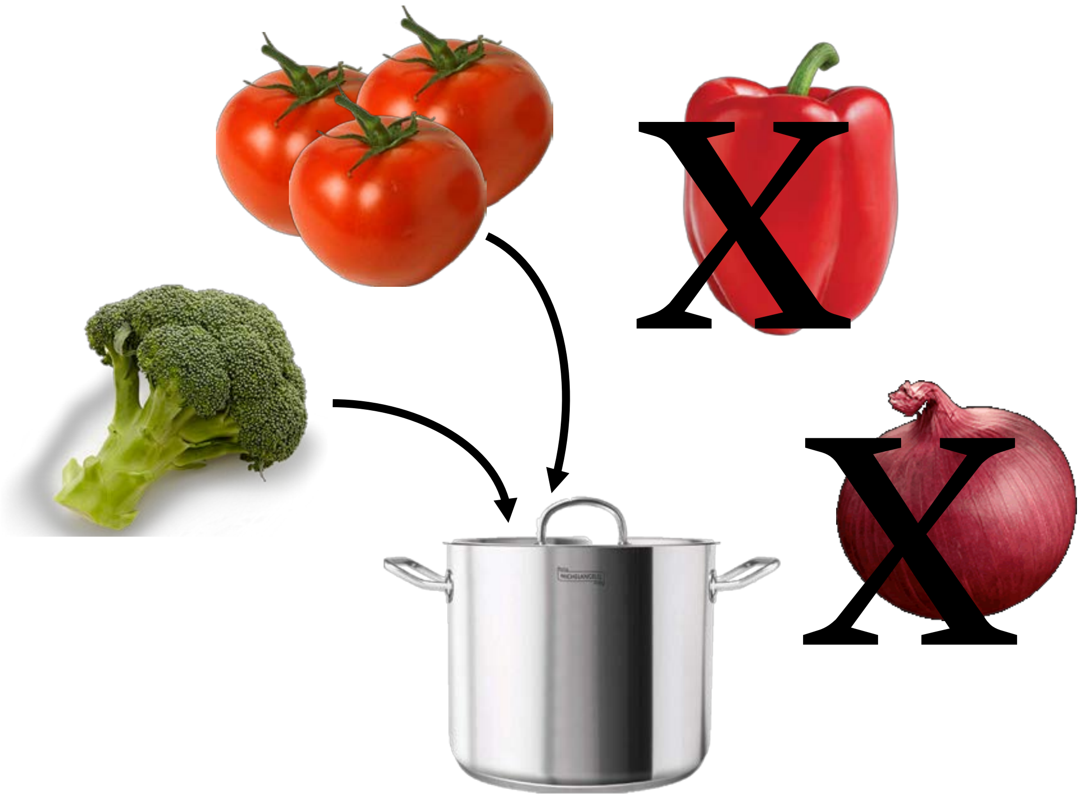
If the final result is not coming out as expected, what are the possible explanations?

?

Source of discrepancies can come from issues with **available ingredients**

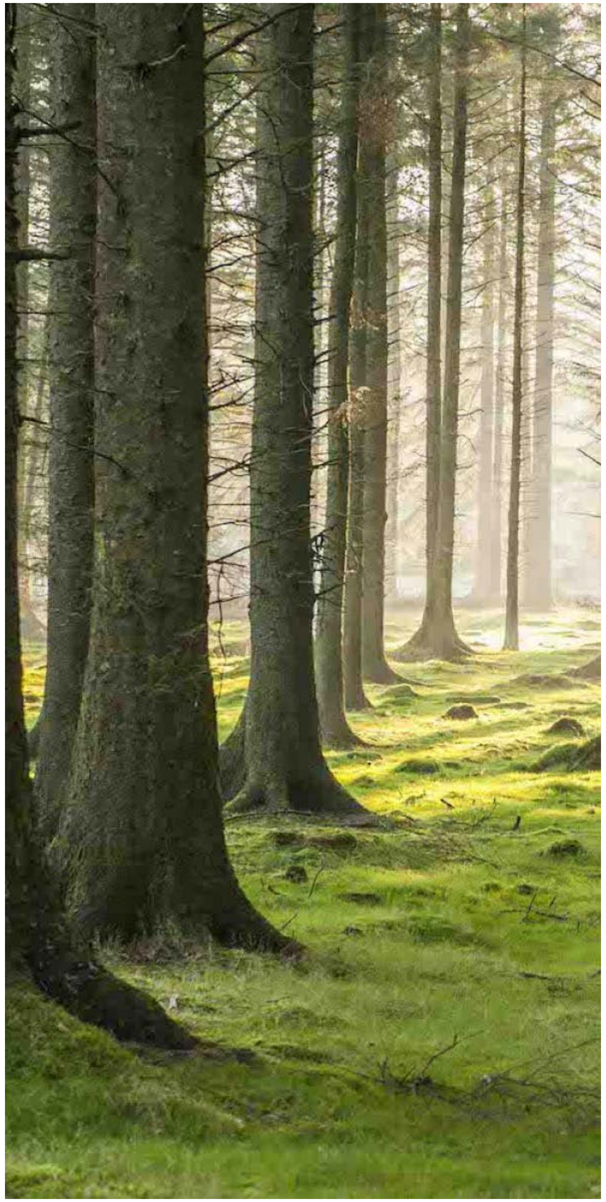


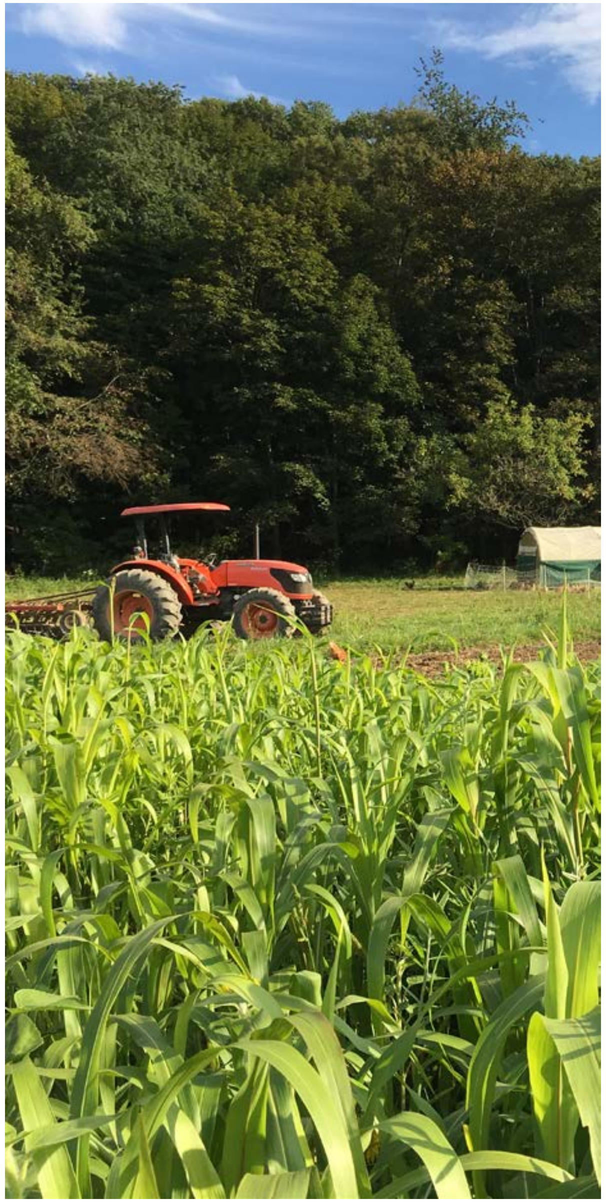
Source of discrepancies can come from issues with **available ingredients,**
as well as their **processing**



And what about the rest of the **kitchen**?

The problem of **“atmospherically relevant”**



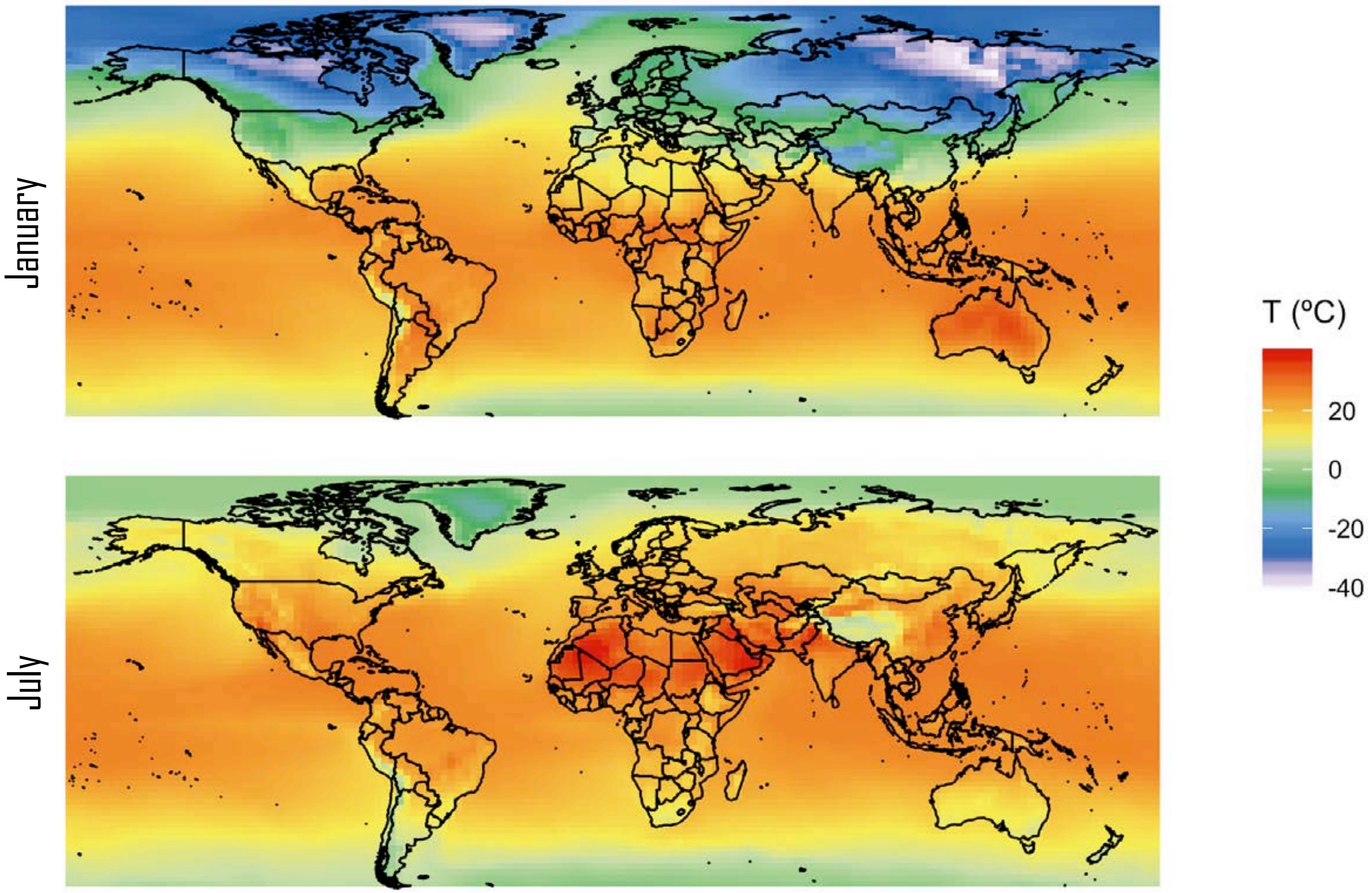


Project questions:

- What are the globally modeled **spatiotemporal patterns of atmospheric parameters** relevant to SOA formation?
- How do their distributions **vary across domains** relevant to human health and policy?
- How do the ranges of these distributions compare to those of **chamber studies** used to derive SOA yields?

Temperature and humidity together represent key ambient conditions relevant to SOA chemistry and partitioning

Mean monthly surface temperature (2013)



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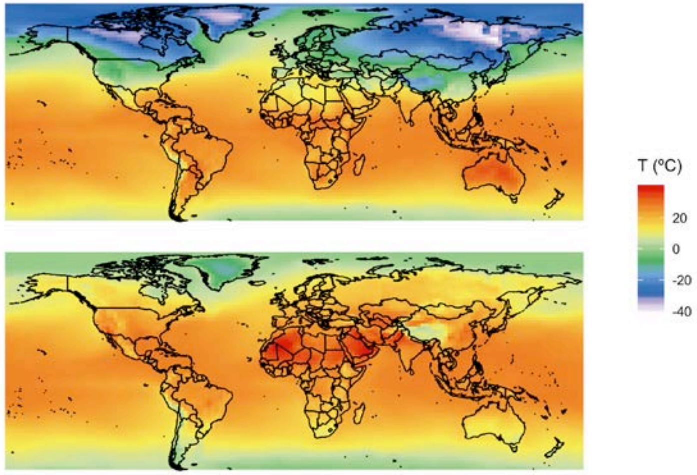

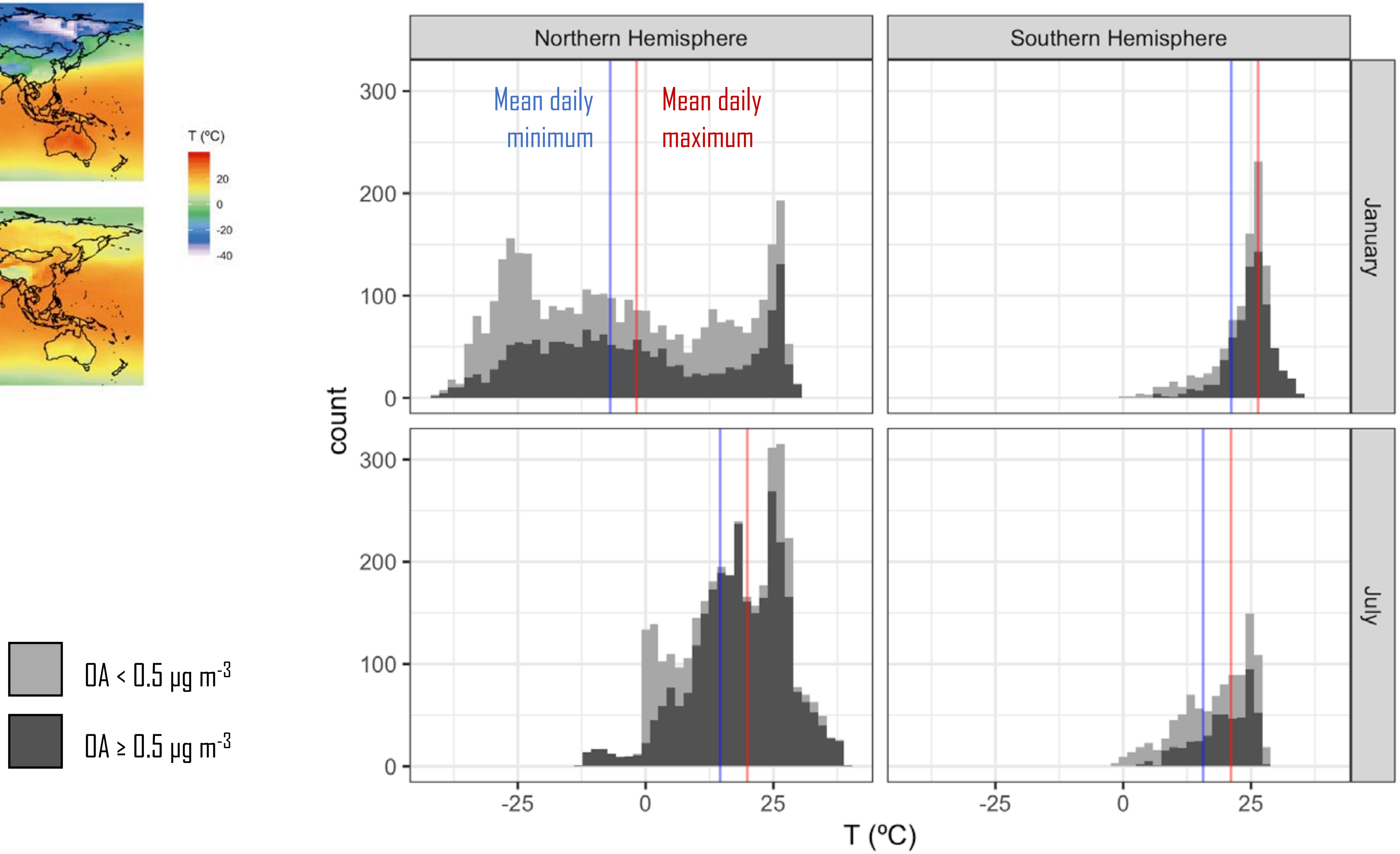

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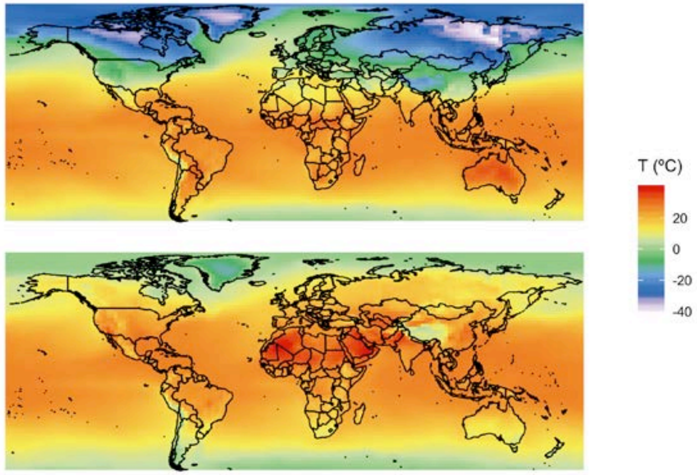

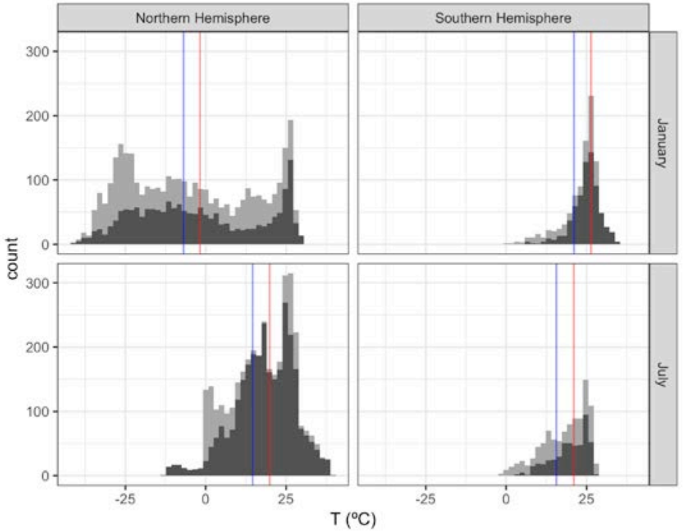

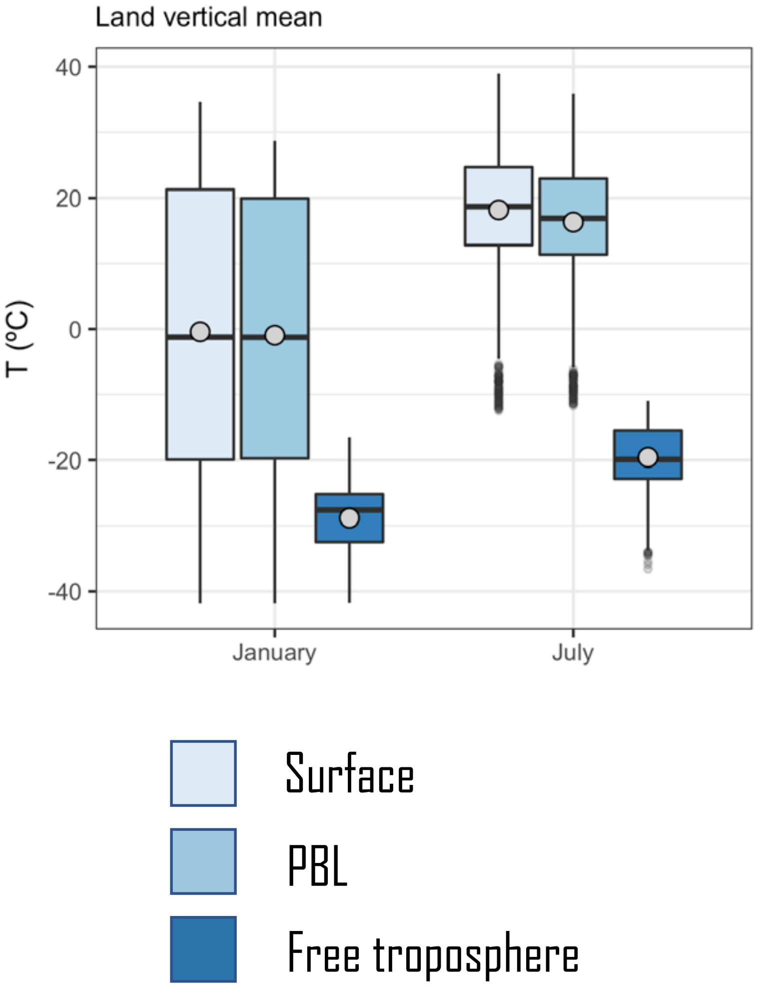

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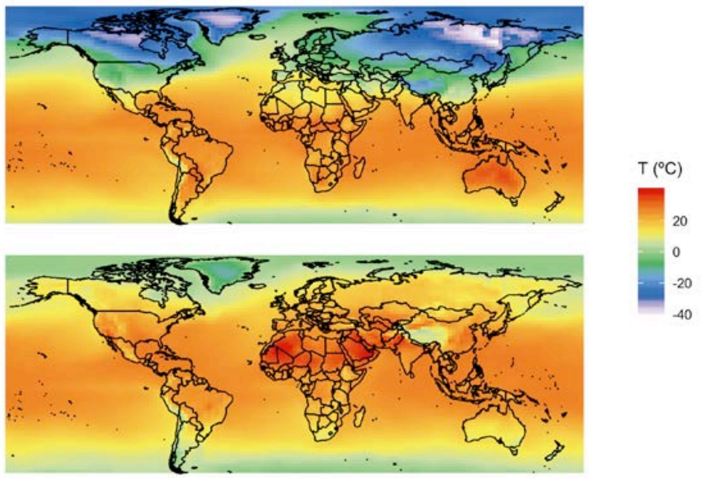
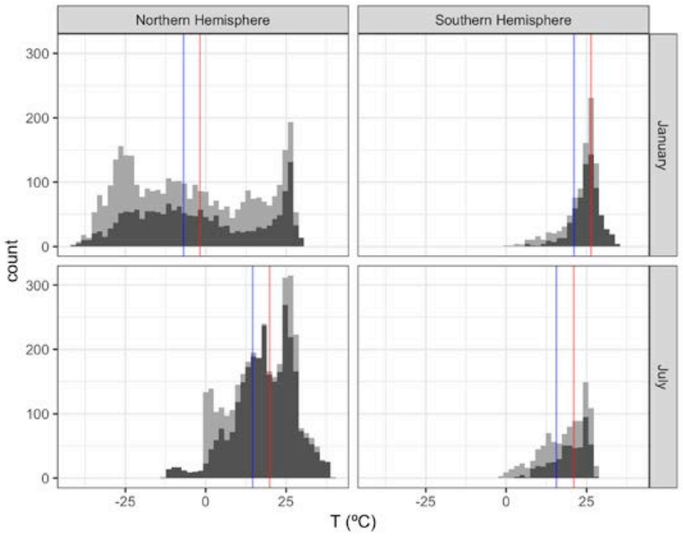
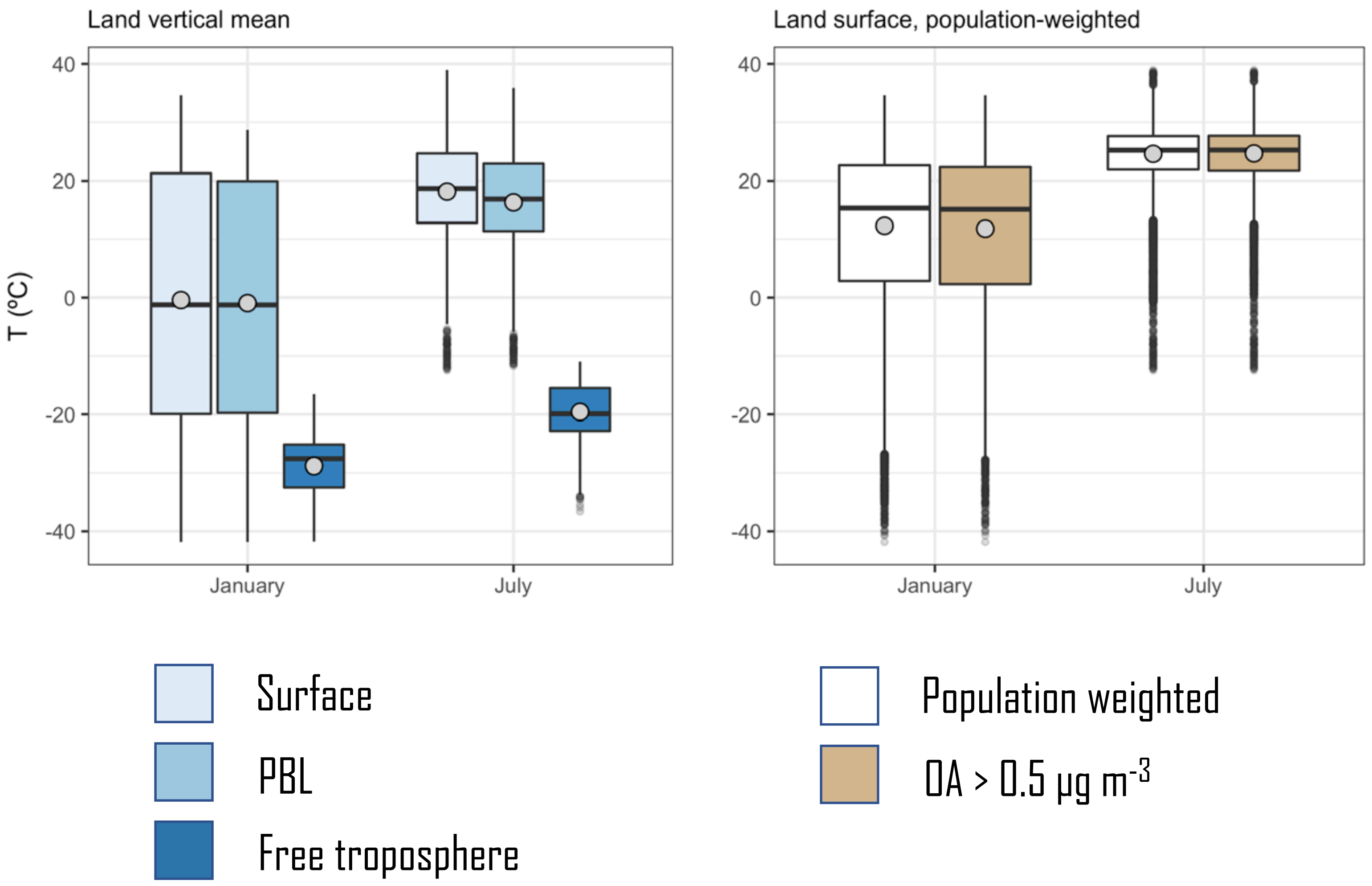
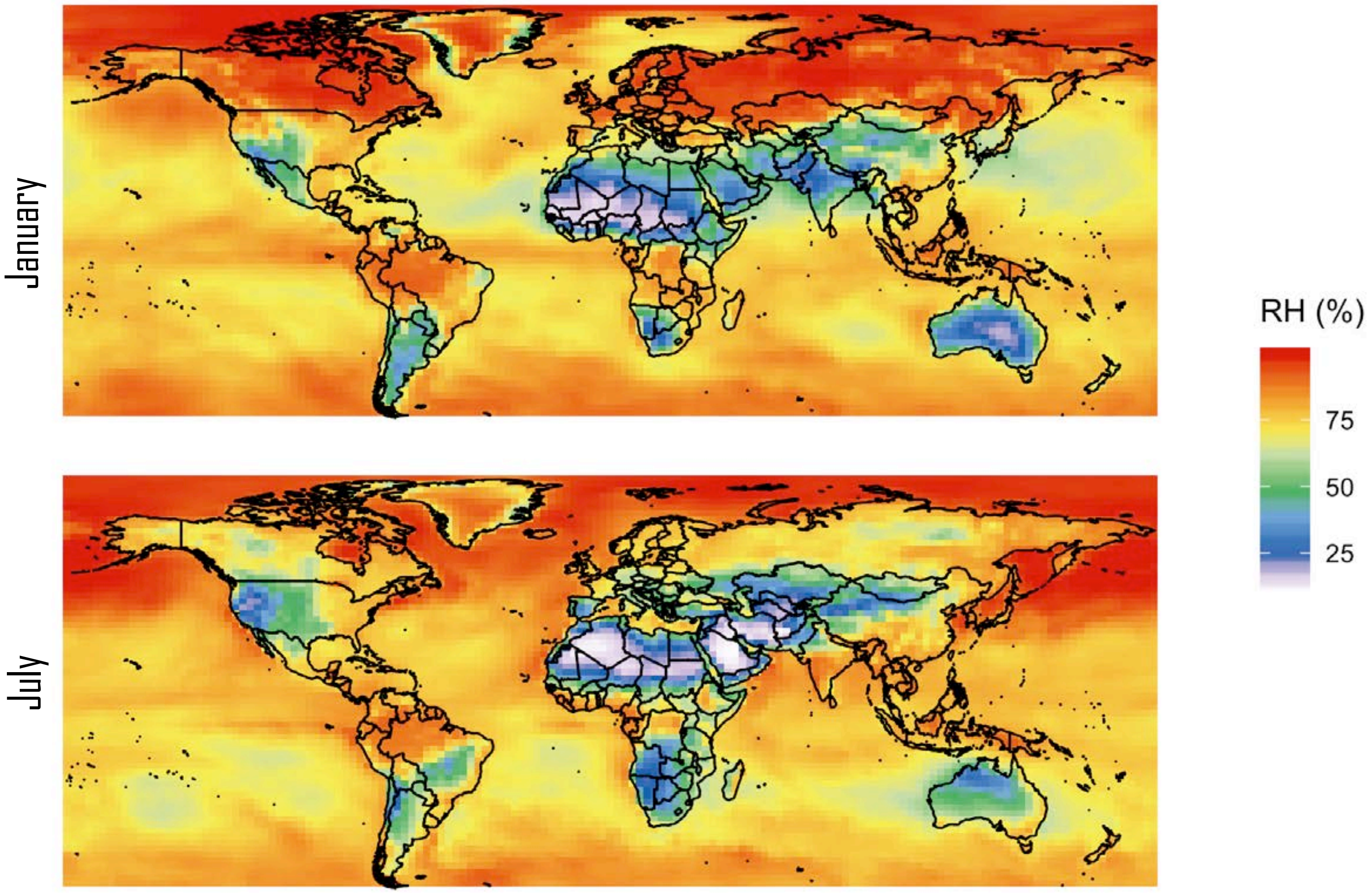






Temperature and humidity together represent key ambient conditions relevant to SOA chemistry and partitioning

Mean monthly surface humidity (2013)



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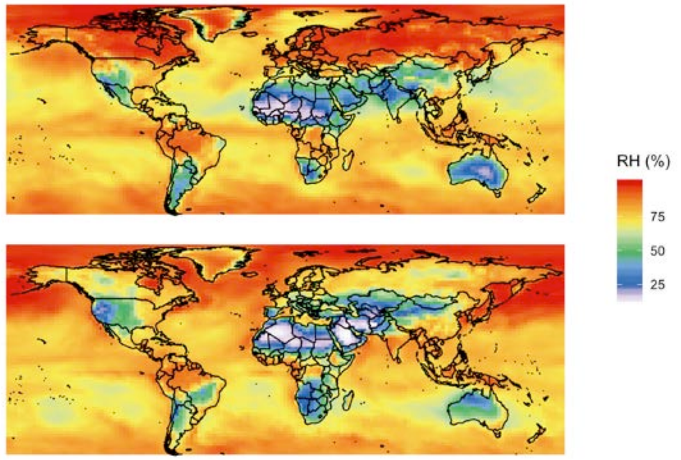

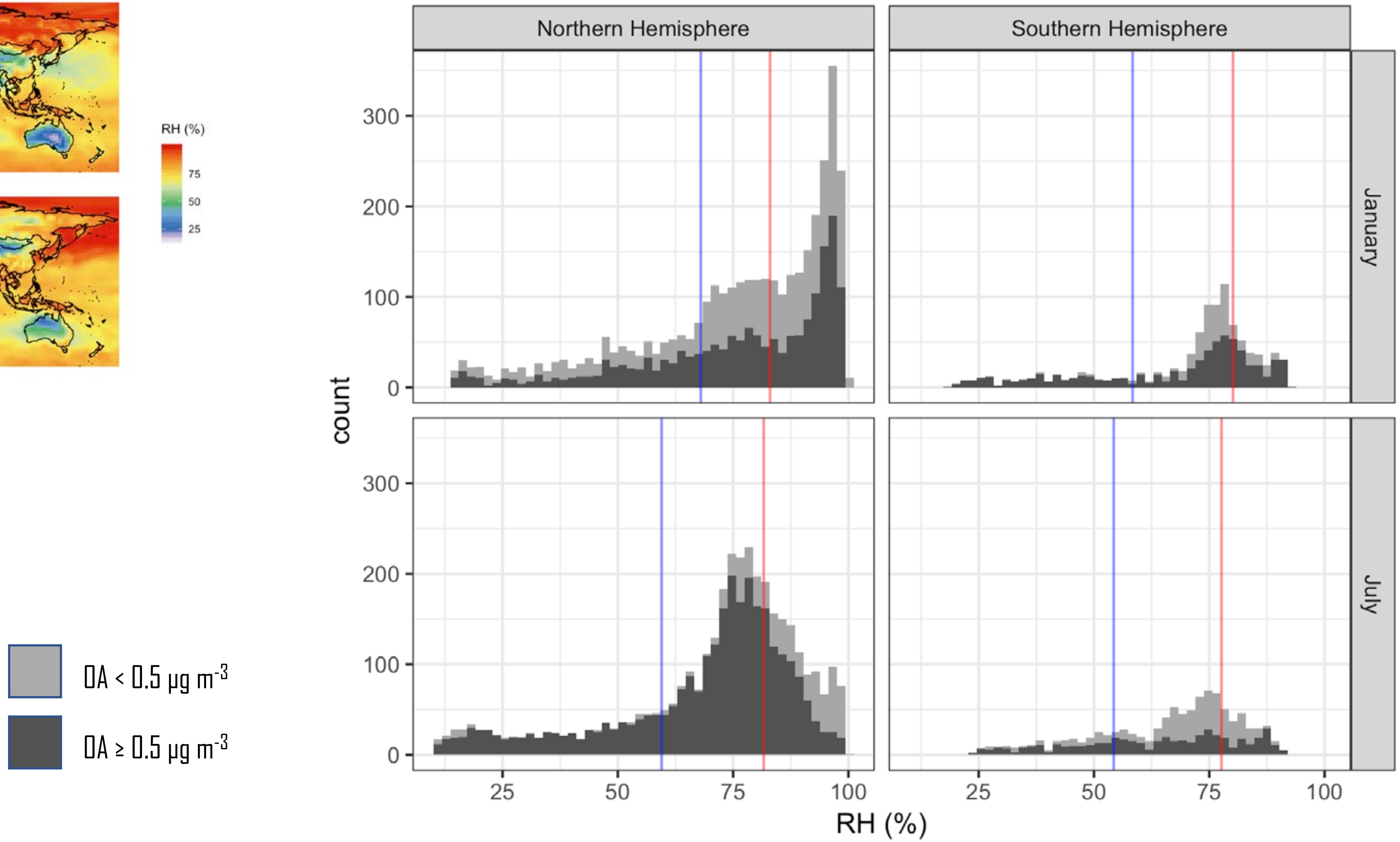

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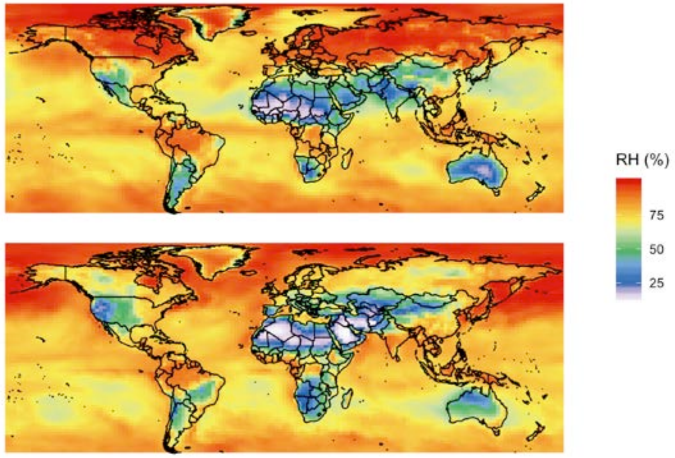
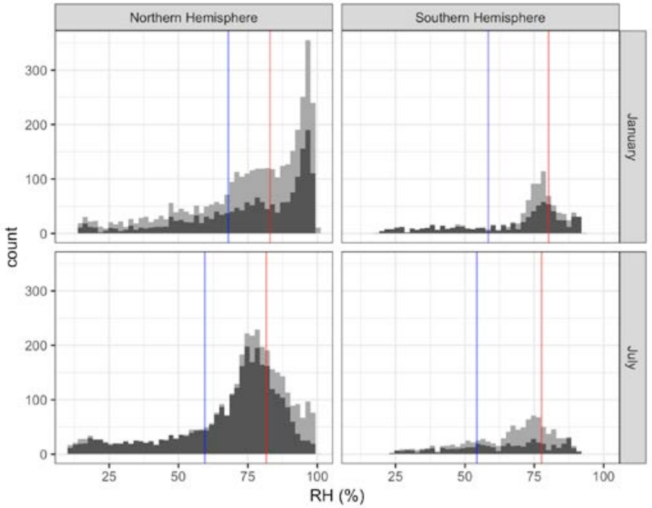
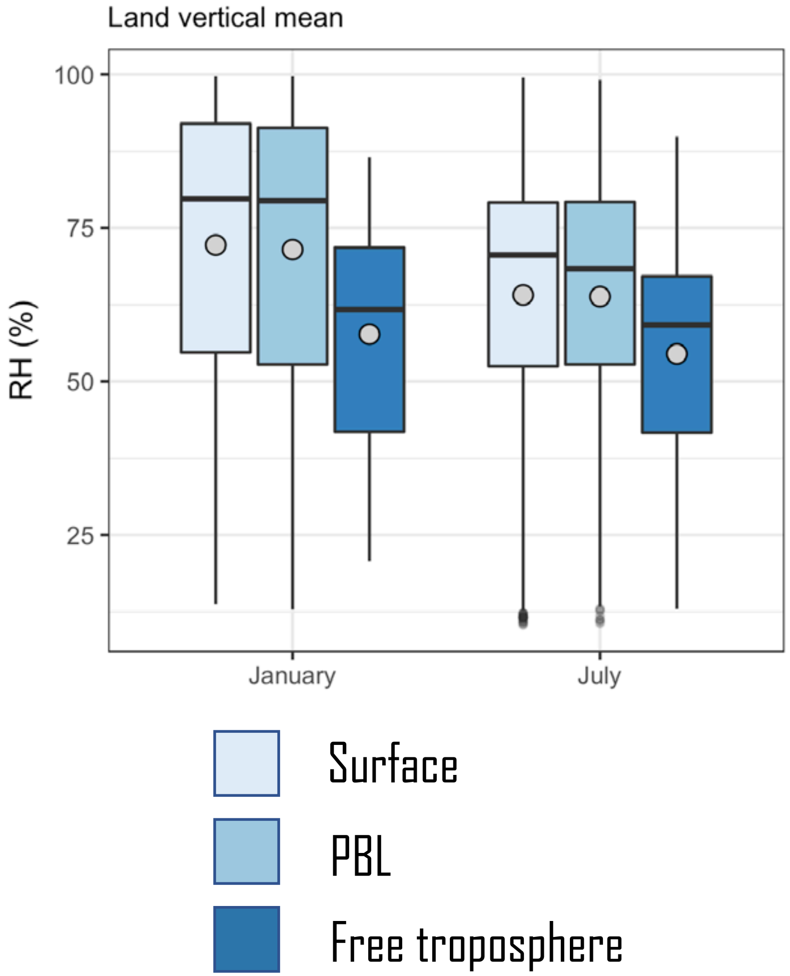
Mean monthly surface humidity (2013)







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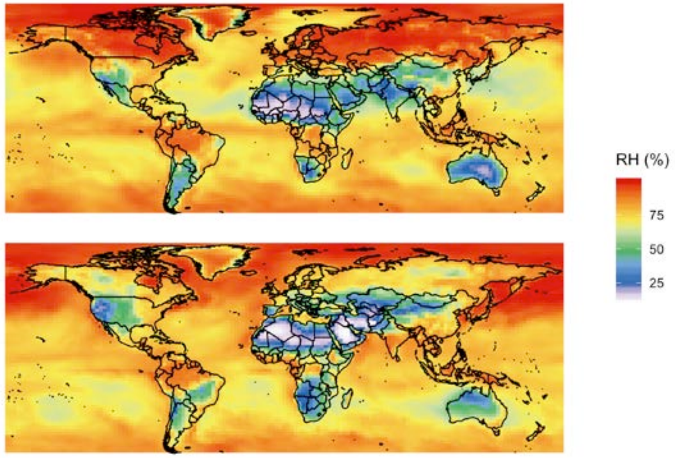
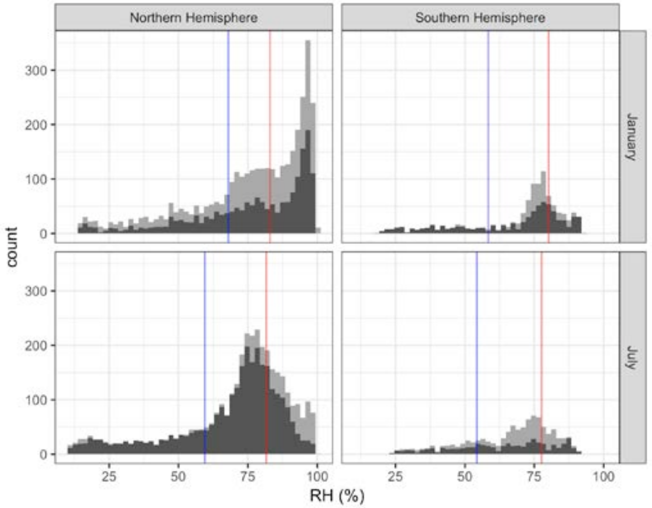
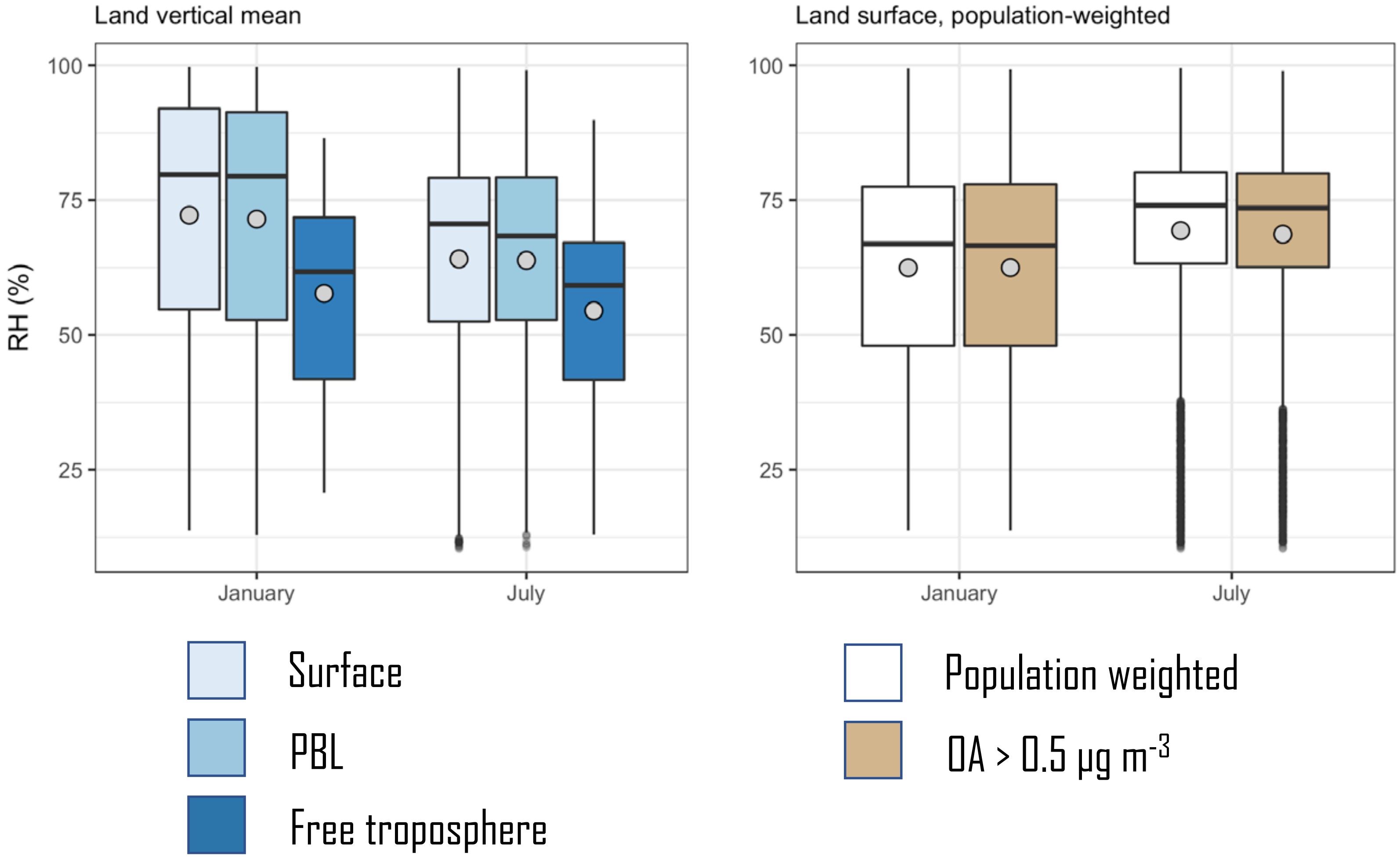
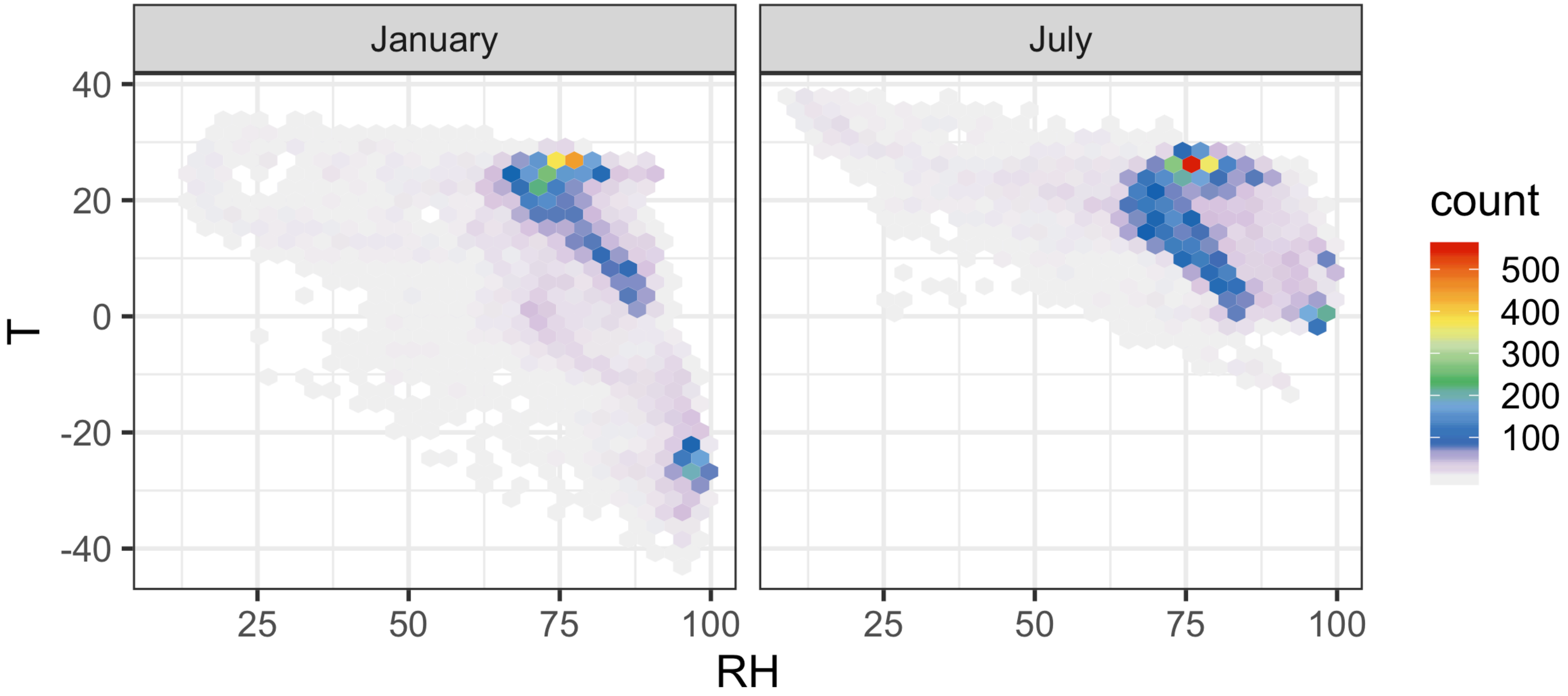


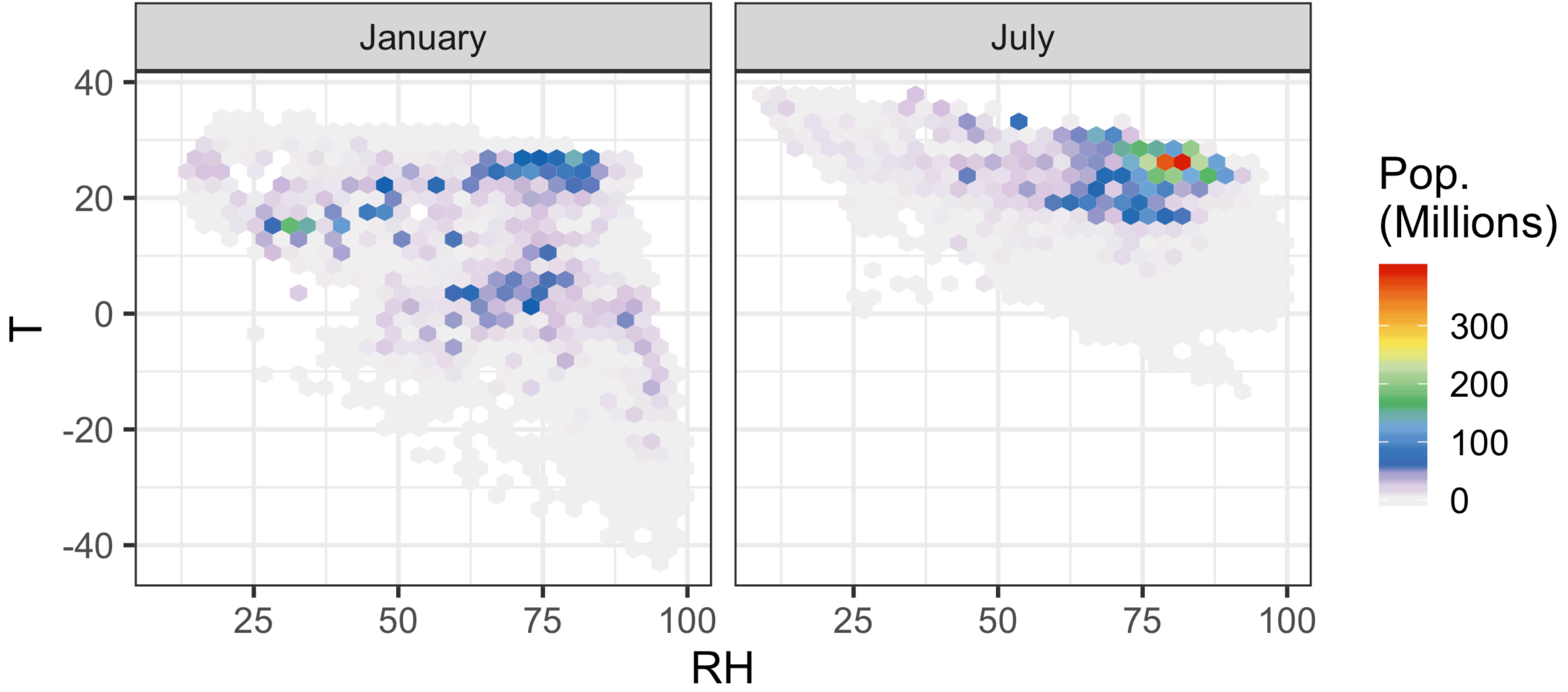




Together, **distributions of temperature and humidity** levels provide a snapshot of representative conditions at the surface

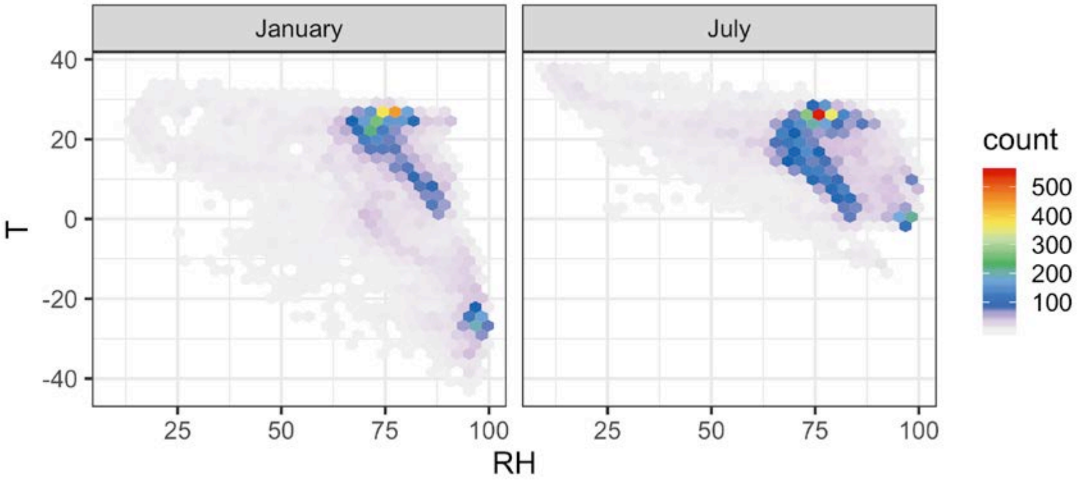


Summing **population counts** instead of grid cells highlights patterns for the areas where people tend to live

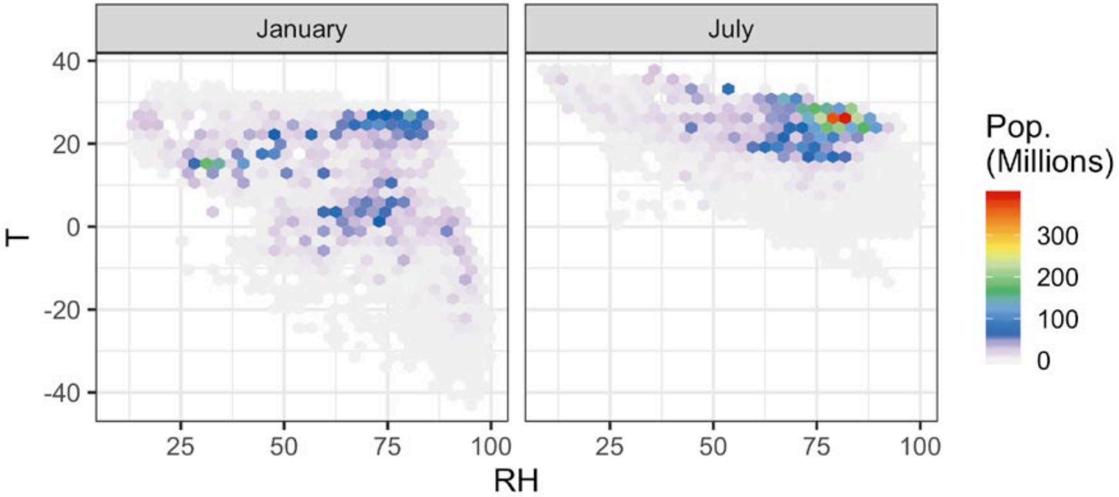


How do these representative conditions compare to the conditions used for **SOA chamber studies**?

Grid cell count



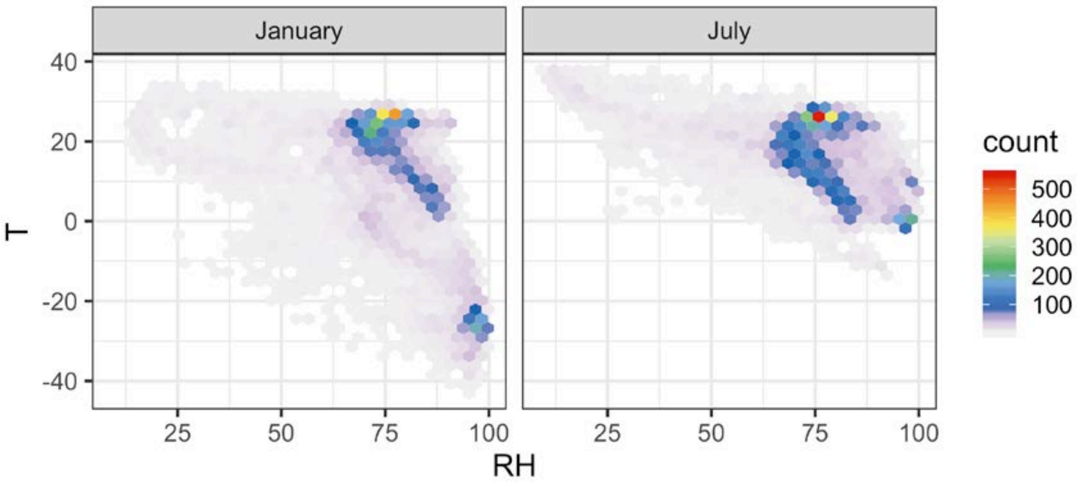
Grid cell population count



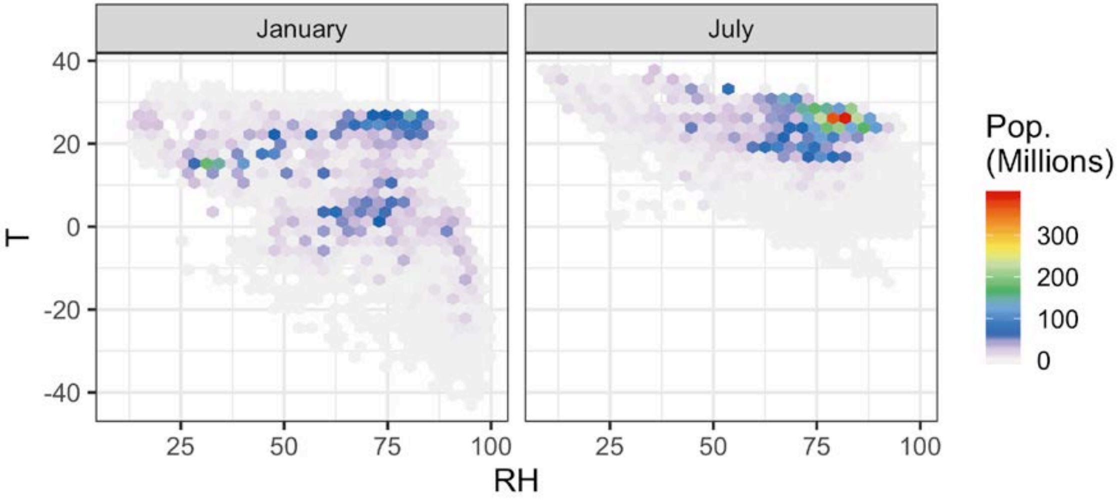
- 123 SOA published chamber studies (including 1259 listed experiments) reviewed for species and conditions used
- Of those, 48 studies reported both temperature and humidity data
- Precursor species in all studies binned and tallied by temperature and humidity

How do these representative conditions compare to the conditions used for **SOA chamber studies**?

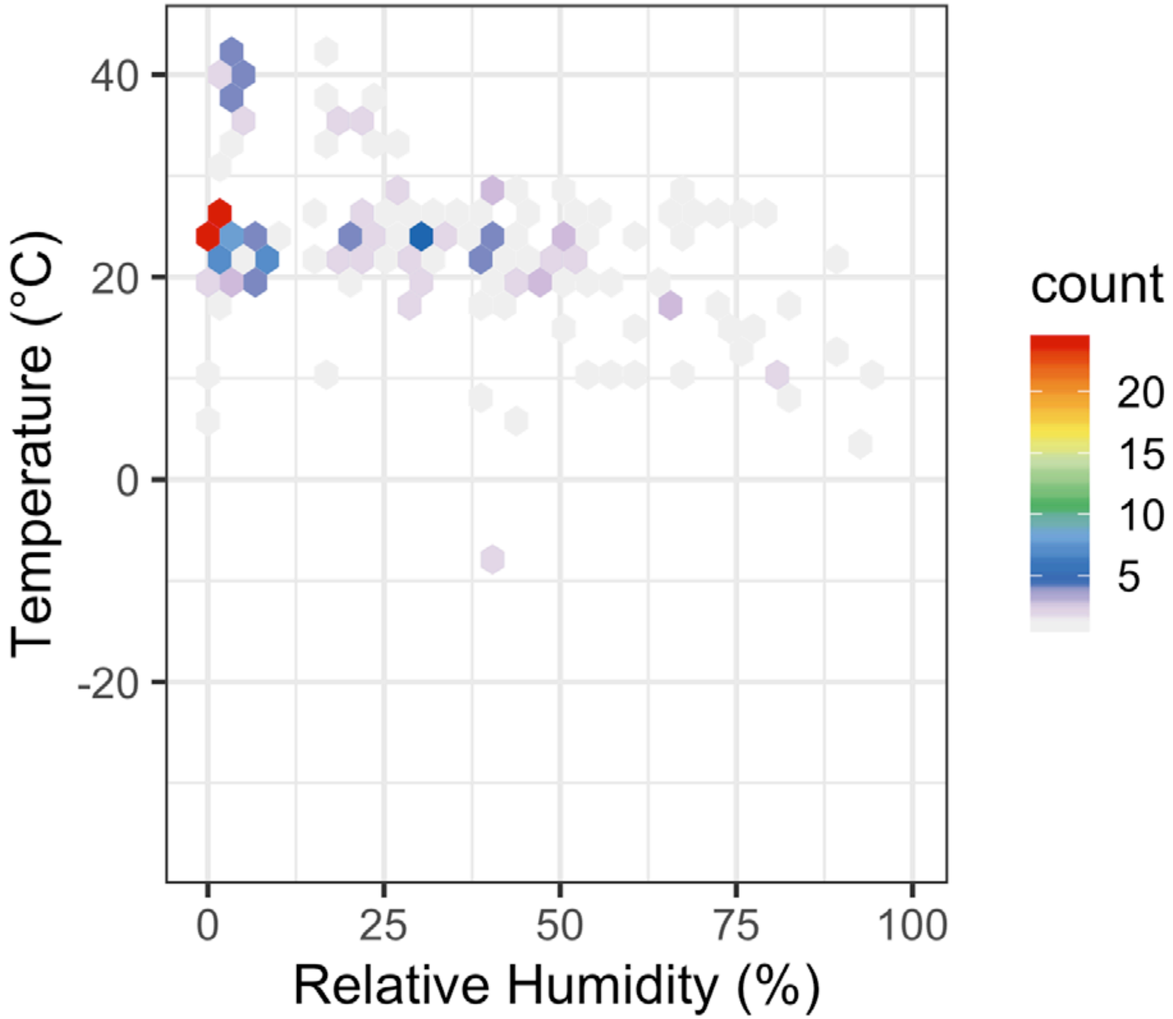
Grid cell count



Grid cell population count

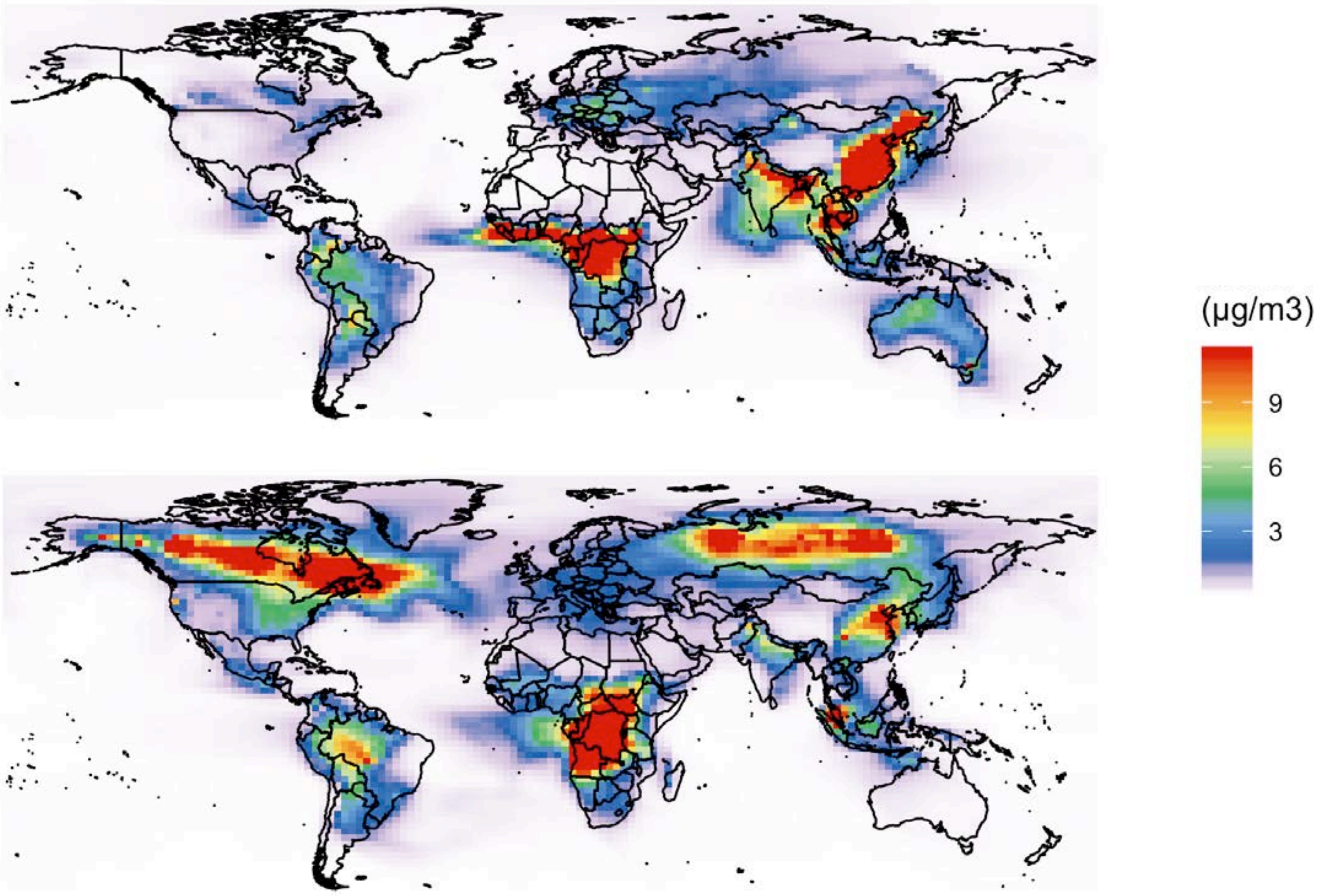


Study count by species



Mass loading represents another key factor of SOA formation that can be compared for modeled atmospheric relevance

Mean monthly surface OA (2013)



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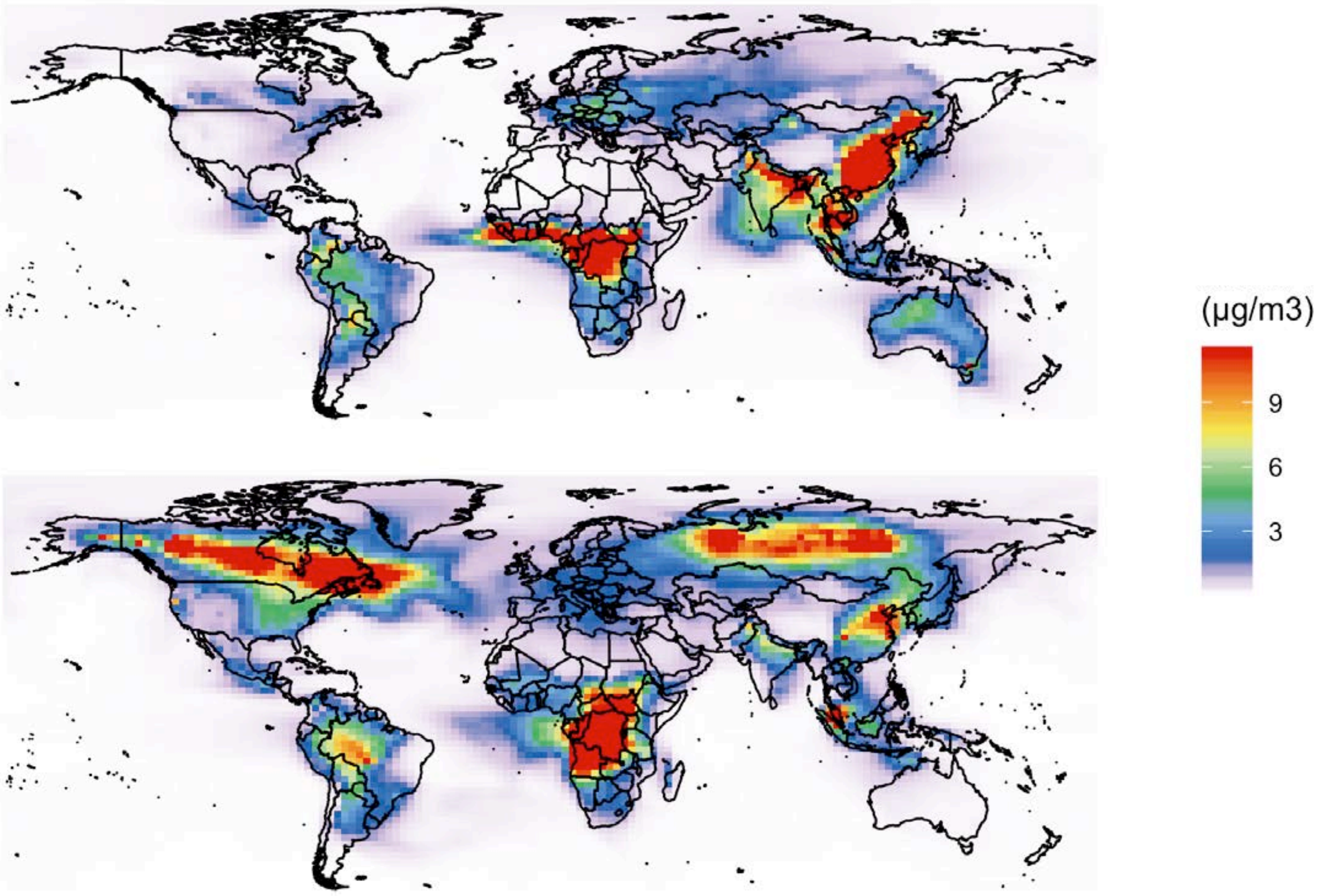
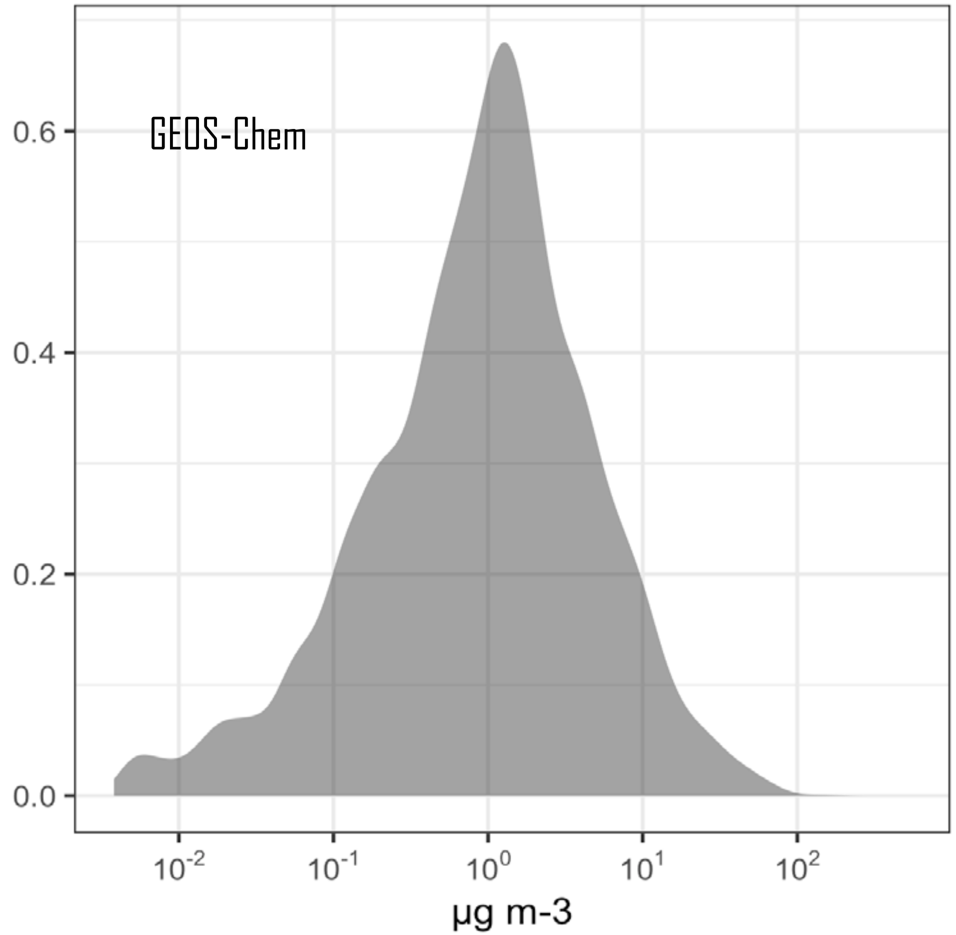


Frequency density of chamber mass loading vs. GEOS-Chem OA (population > 0)



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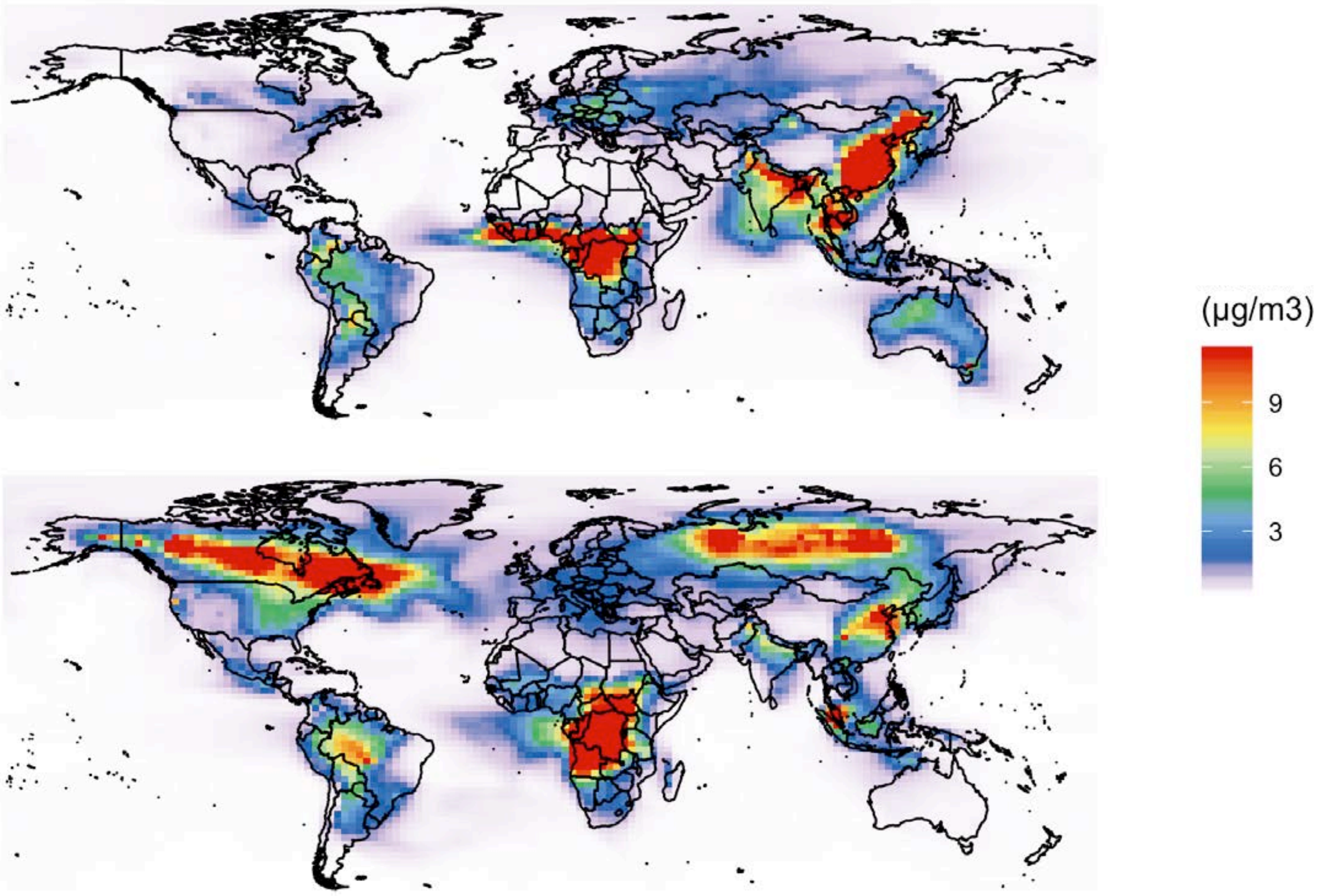

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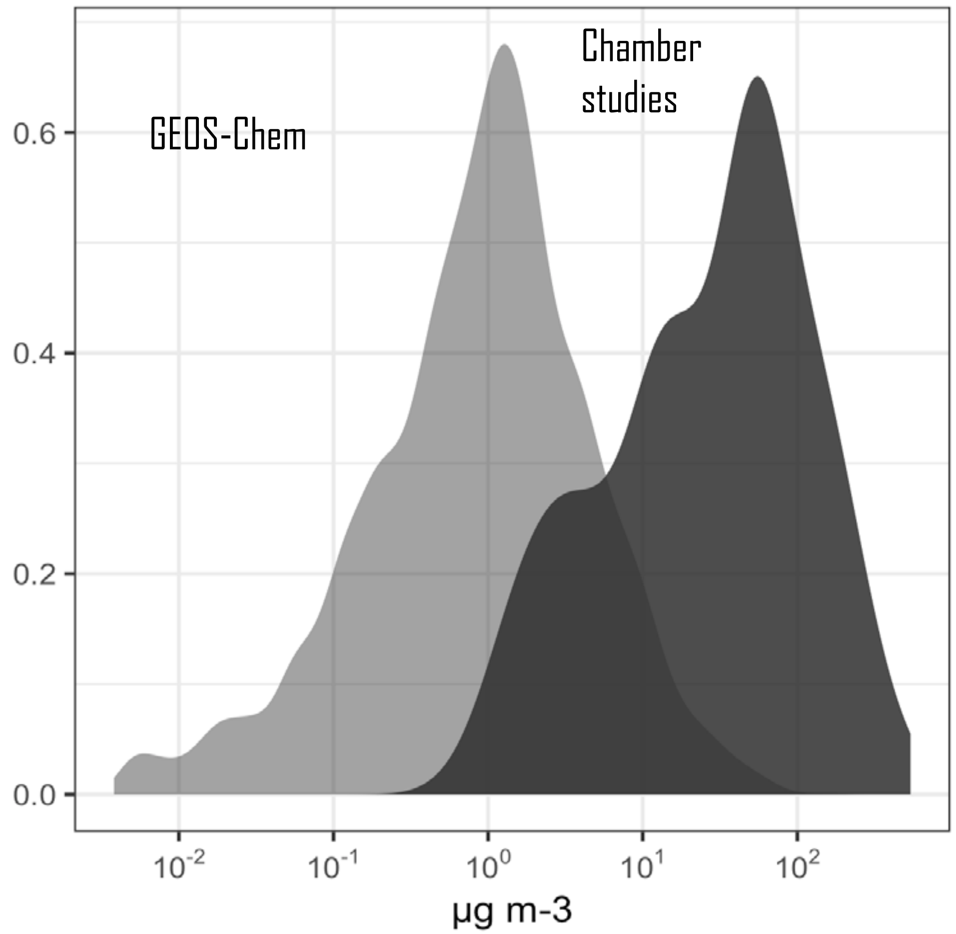
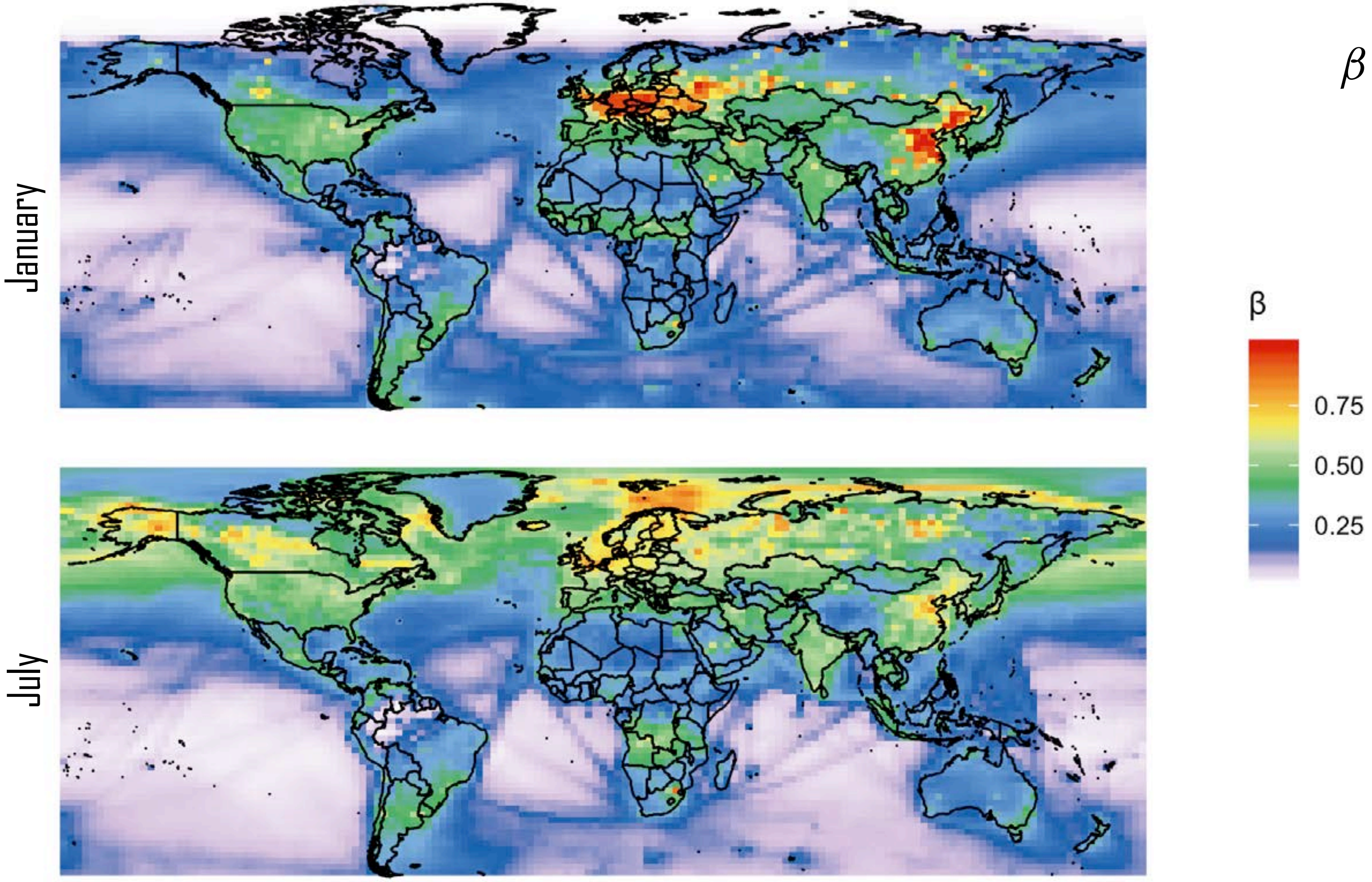


The modeled **NO branching ratio** varies strongly by season, location, and time of day

Mean monthly surface β (2013)

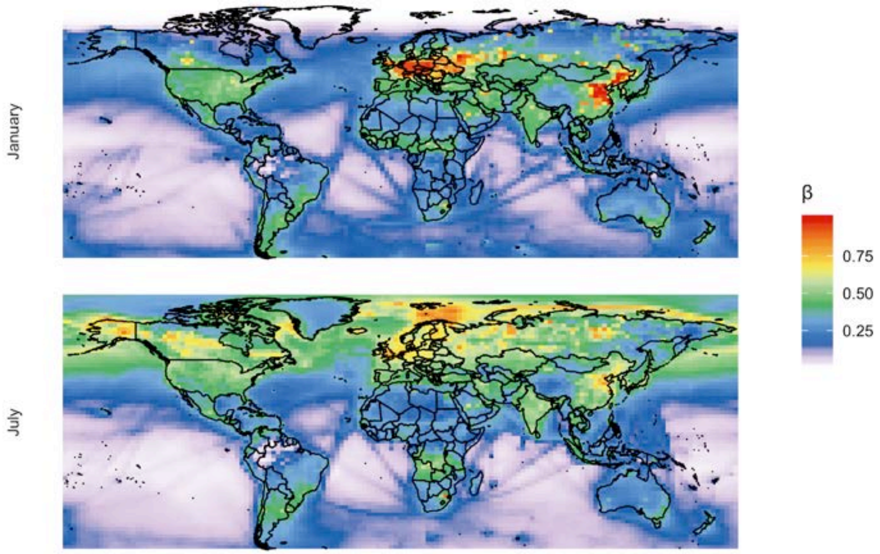


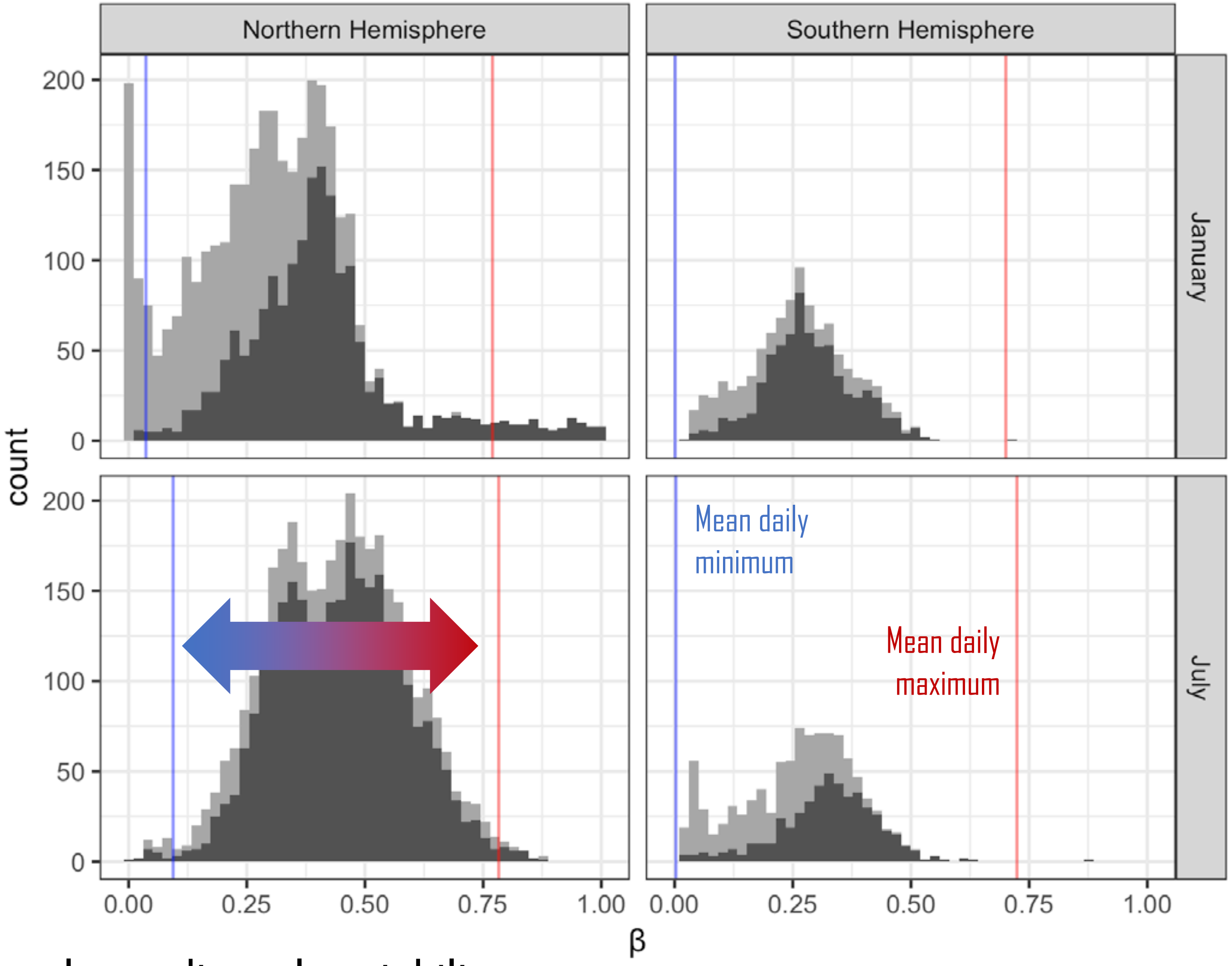
$$\beta = \frac{k_{RO_2+NO}[NO]}{k_{RO_2+NO}[NO] + k_{RO_2+HO_2}[HO_2]}$$

Pye et al., 2010

The modeled **NO branching ratio** varies strongly by season, location, and time of day

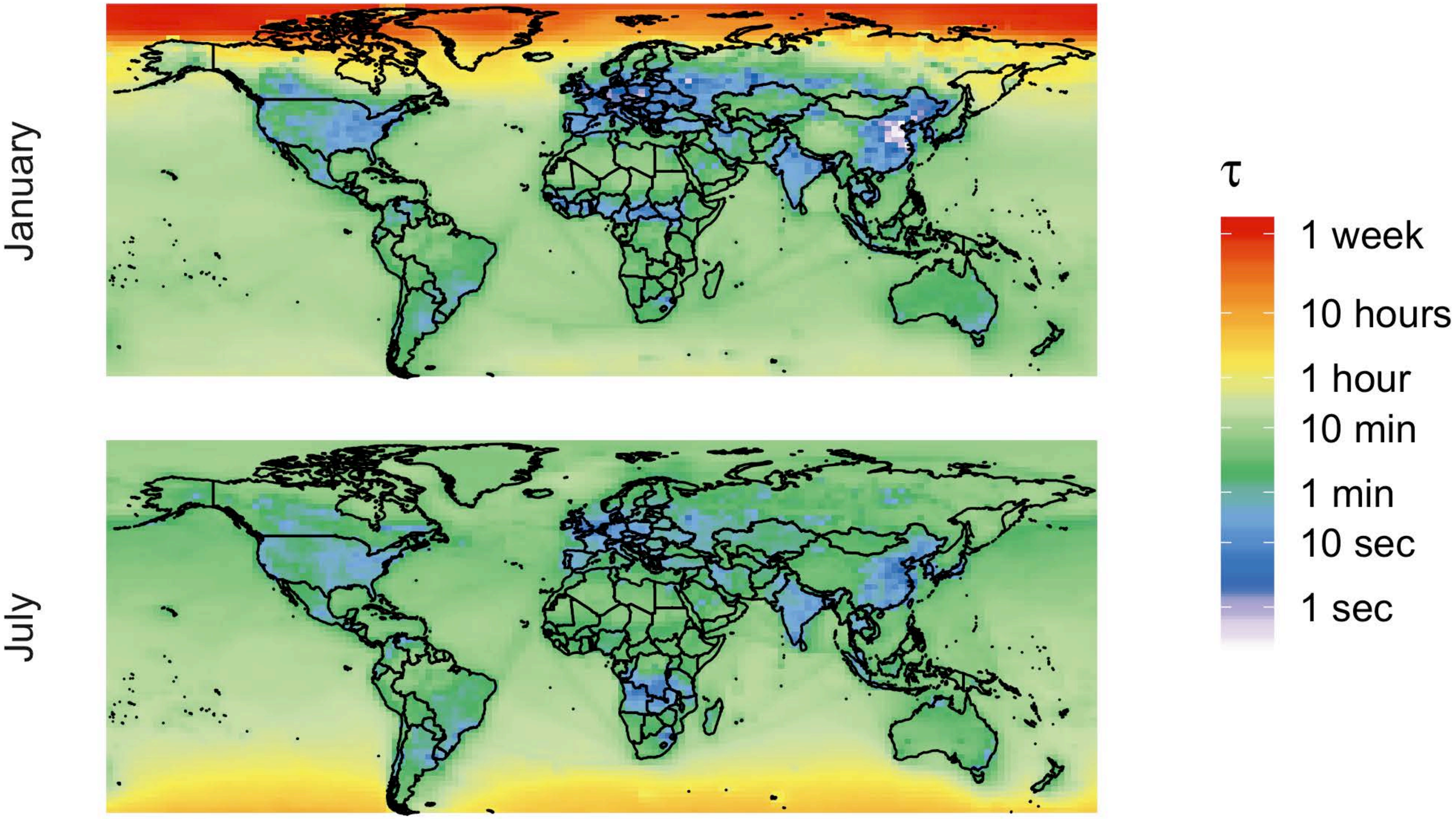
Mean monthly surface β (2013)





large diurnal variability

Spatial patterns of mean **RO_2 chemical lifetime** tend to vary inversely with branching ratio



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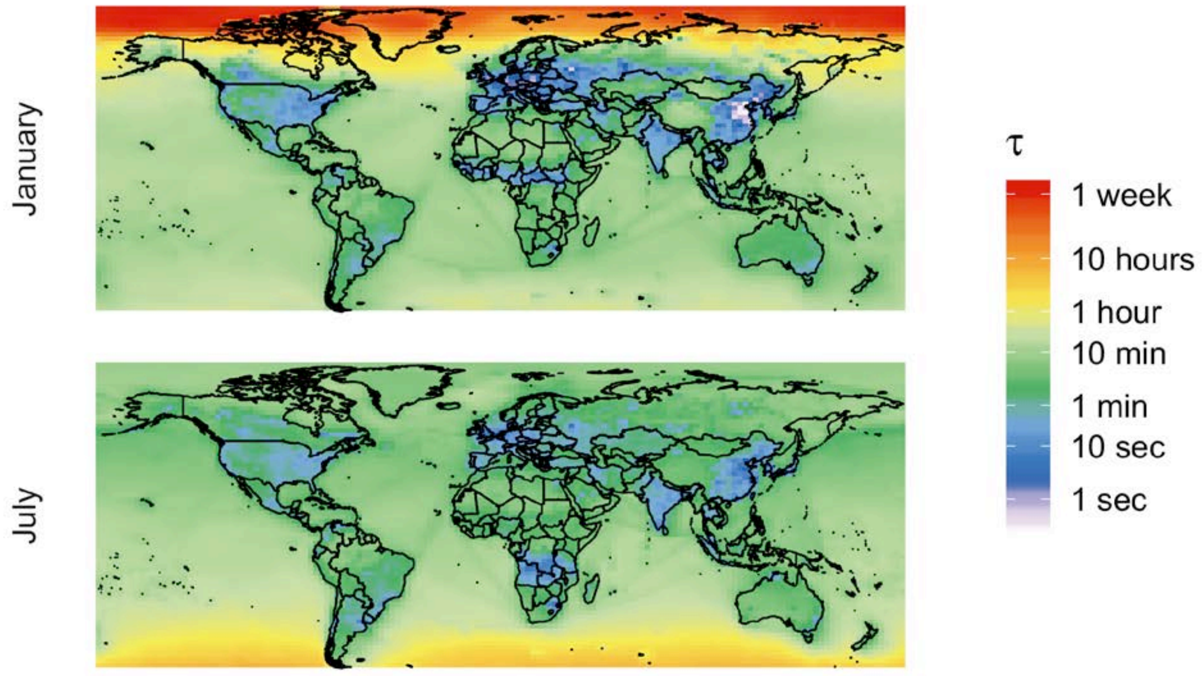
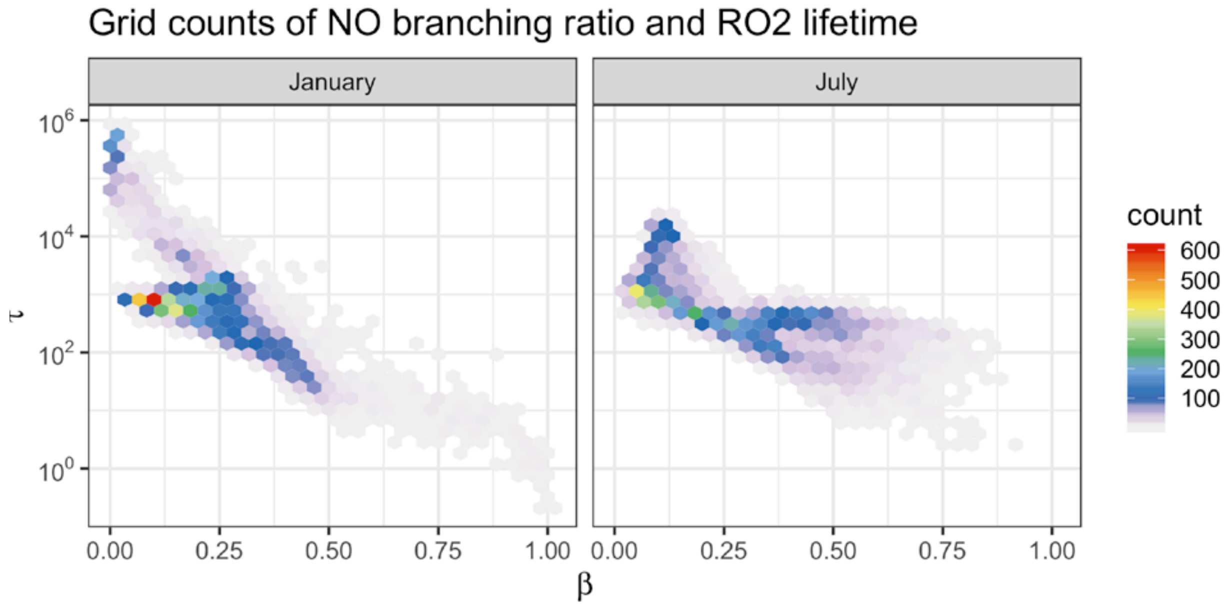
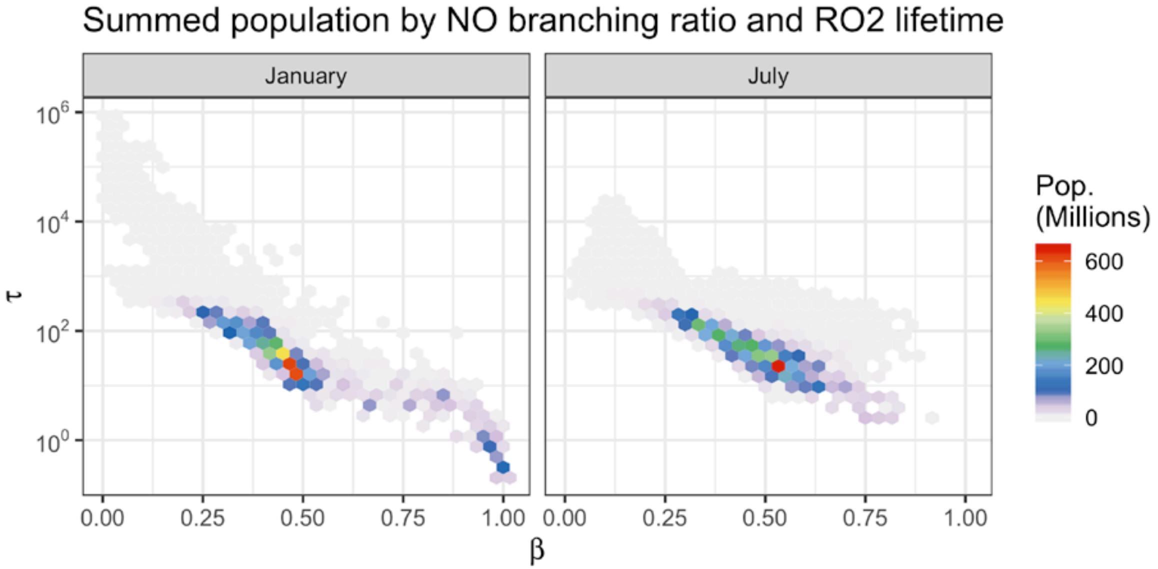
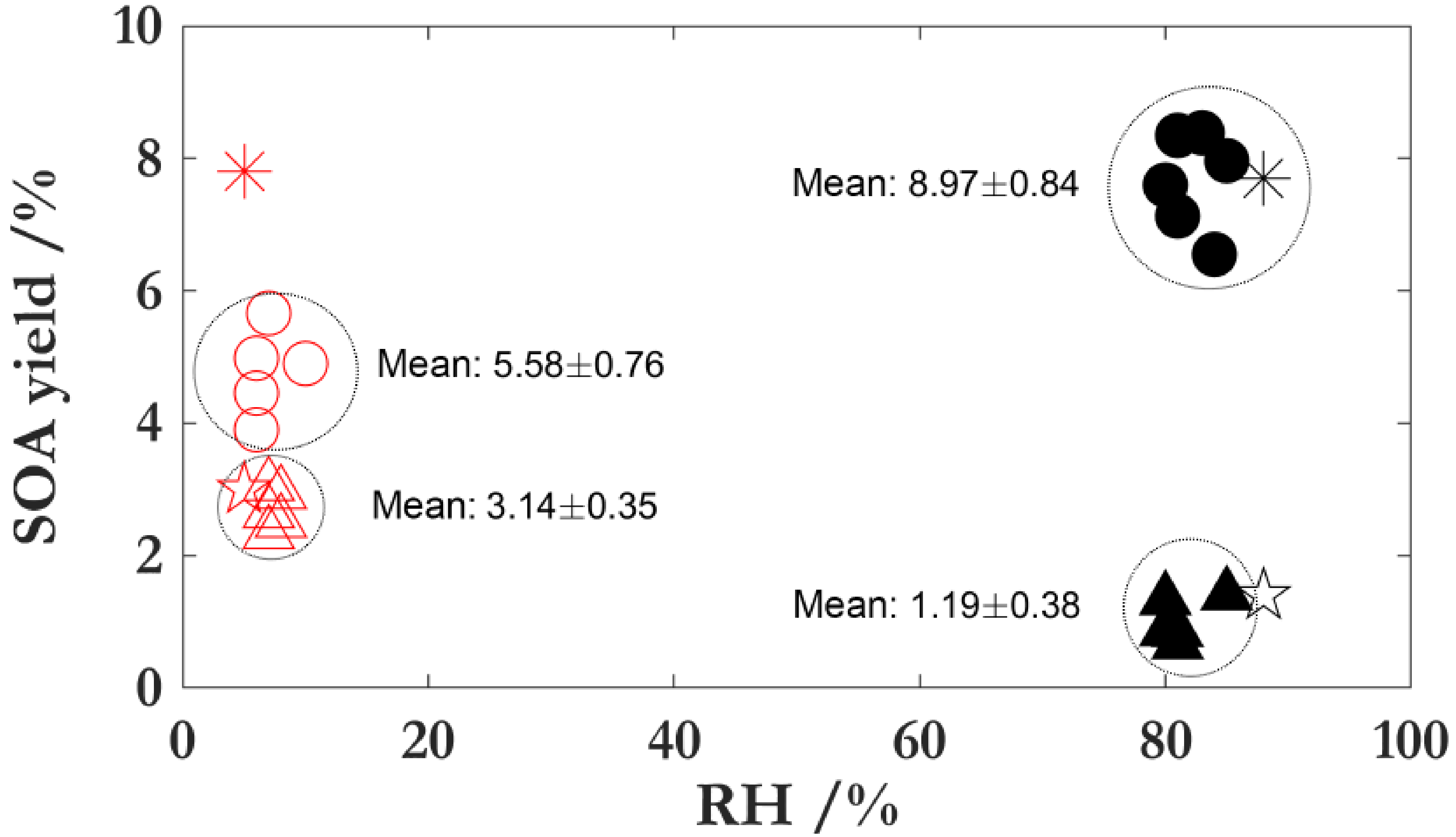






Summary

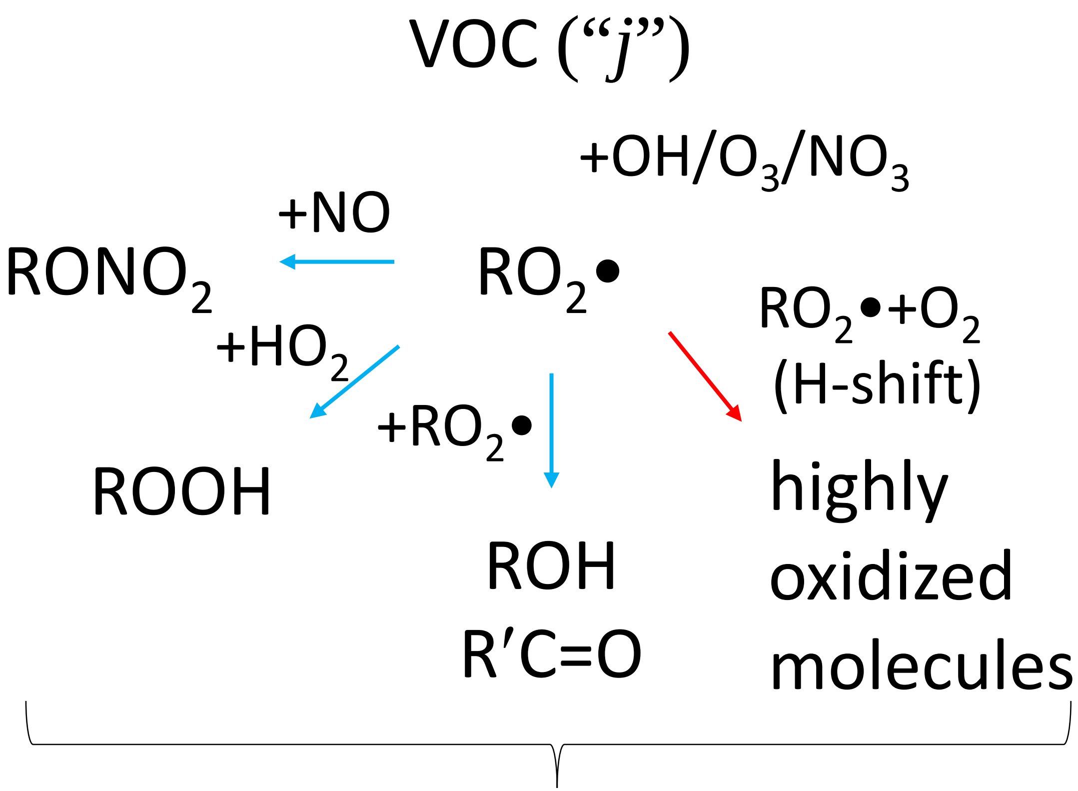
- Ranges of key parameters for SOA formation within models can be defined for domains of interest
- The spatiotemporal patterns of these parameters can help highlight areas and conditions in particular need of additional study
- Ongoing work will explore some of these uncertain areas, both in the real-world chamber and in the modeled “kitchen”



Maximum yields of SOA from toluene and isoprene under dry (red color) and humid (black color) conditions (◦: toluene-NO2- hv; △: isoprene-NO2-hv; ⋆: isoprene-O3; ∗: isoprene-H2O2-hv).

Jia and Xu, 2018

a) Gas-Phase Reactivity



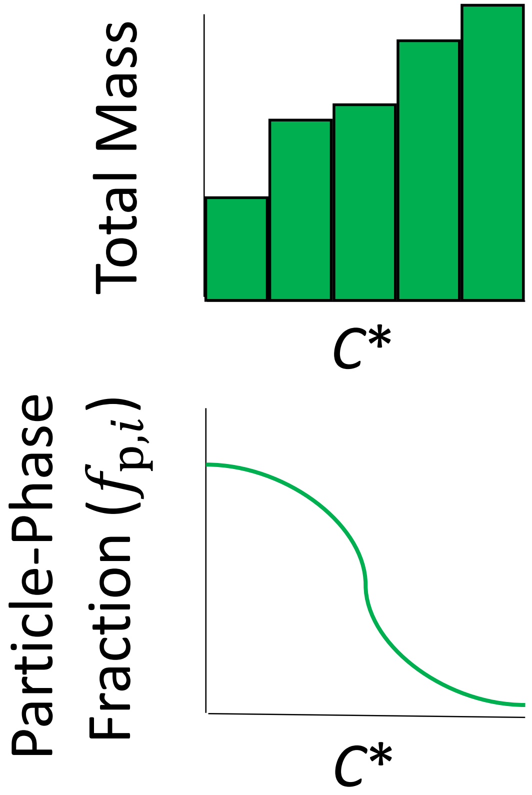
Relevant Equations and Parameters:

$$\Delta \mathrm{VOC}_{j,\mathrm{NO}} = \beta\ \Delta \mathrm{VOC}_j$$

$$\Delta \mathrm{VOC}_{j,\mathrm{HO2}} = (1-\beta)\ \Delta \mathrm{VOC}_j$$

$$\beta = \frac{k_{\mathrm{RO2+NO}}[\mathrm{NO}]}{k_{\mathrm{RO2+NO}}[\mathrm{NO}] + k_{\mathrm{RO2+HO2}}[\mathrm{HO_2}]}$$

b) Gas-Particle Partitioning

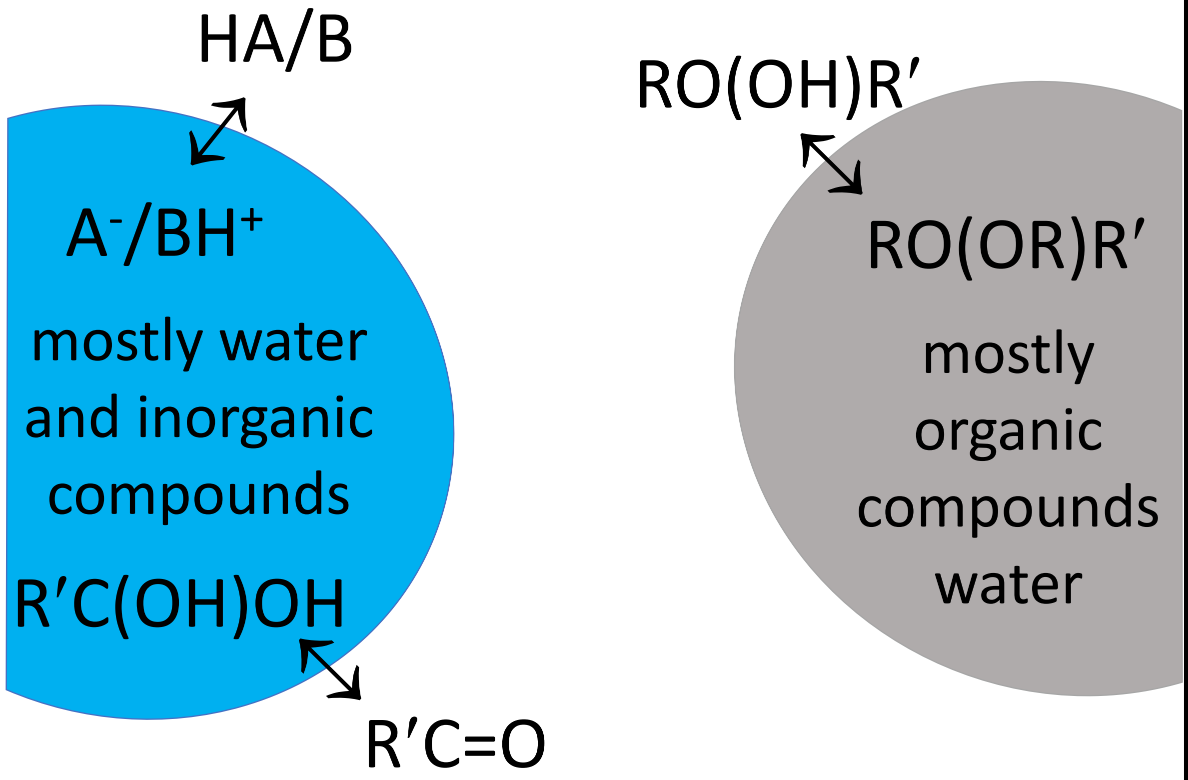


Relevant Equations and Parameters:

$$K_{p,i} = \frac{1}{C^*} = \frac{RT}{10^6 \overline{MW} \zeta_i p^\circ_{L,i}}$$ (RH, *T*, OA composition)

$$f_{p,i} = \frac{1}{1 + C_i^*/m_{OA}}$$ (RH, *T*, OA mass, m_{OA})

c) Multiphase Chemistry



Relevant Equations and Parameters:

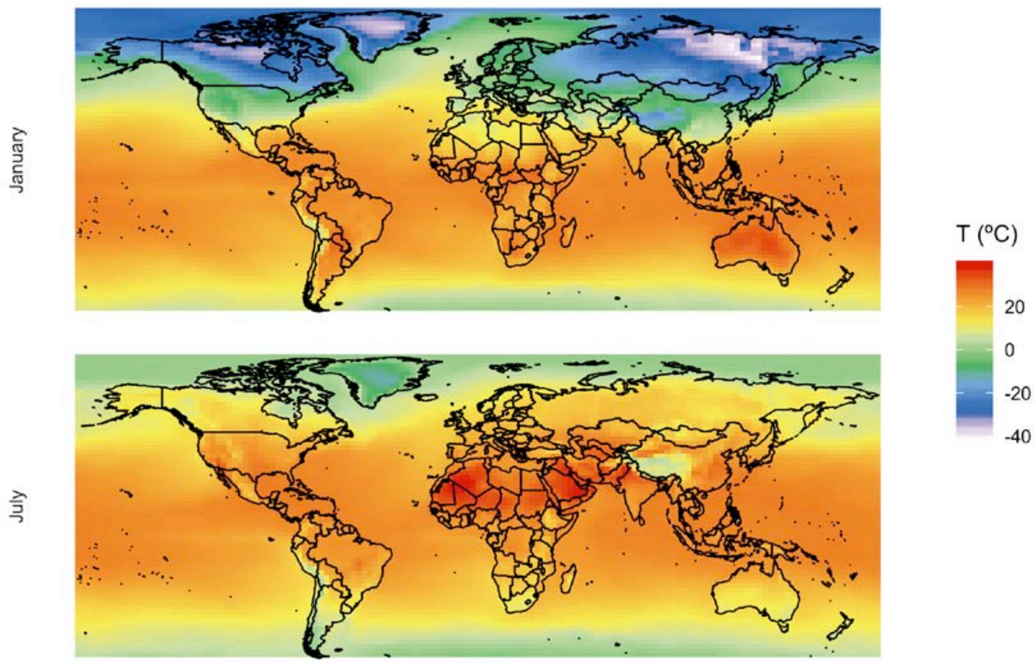
$$C^*_{\mathrm{HA,eff}} = C^*_{\mathrm{HA}} * \frac{\{\mathrm{H}^+\}}{\{\mathrm{H}^+\} + K_\mathrm{a}}$$ (RH, T, pH)

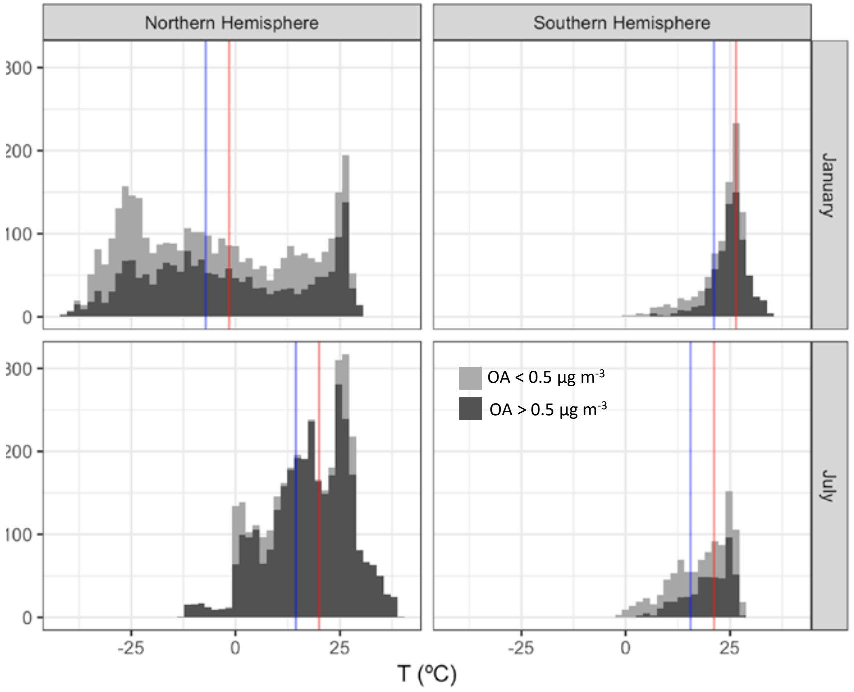
$$C^*_{\mathrm{aq},i} = \frac{f_{\mathrm{gas},i}\, m_{\mathrm{aq}}}{f_{\mathrm{aq},i}}$$

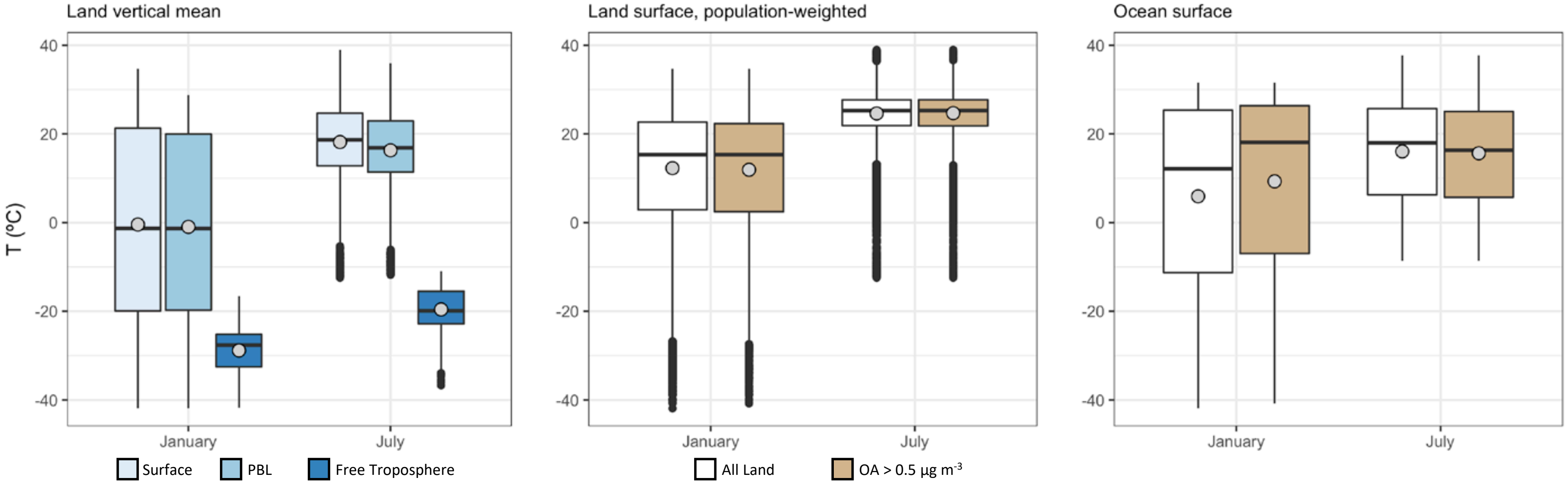
$$f_{\mathrm{aq},i} = \frac{\mathrm{LWC}/C^*_{\mathrm{aq},i}}{1 + \mathrm{LWC}/C^*_{\mathrm{aq},i}}$$

(RH, T, pH, mass of particle-phase water, m_{aq})

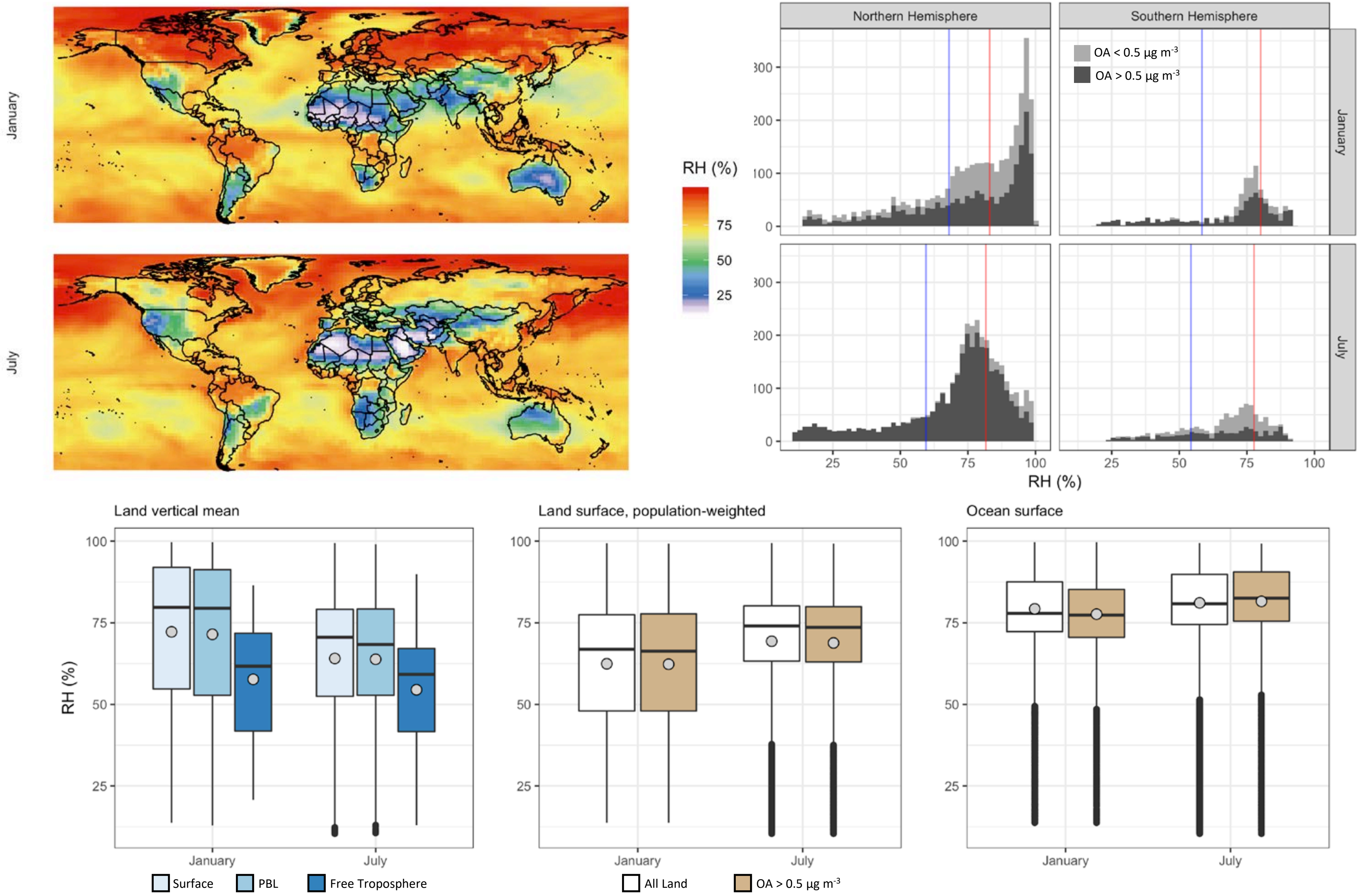
Temperature



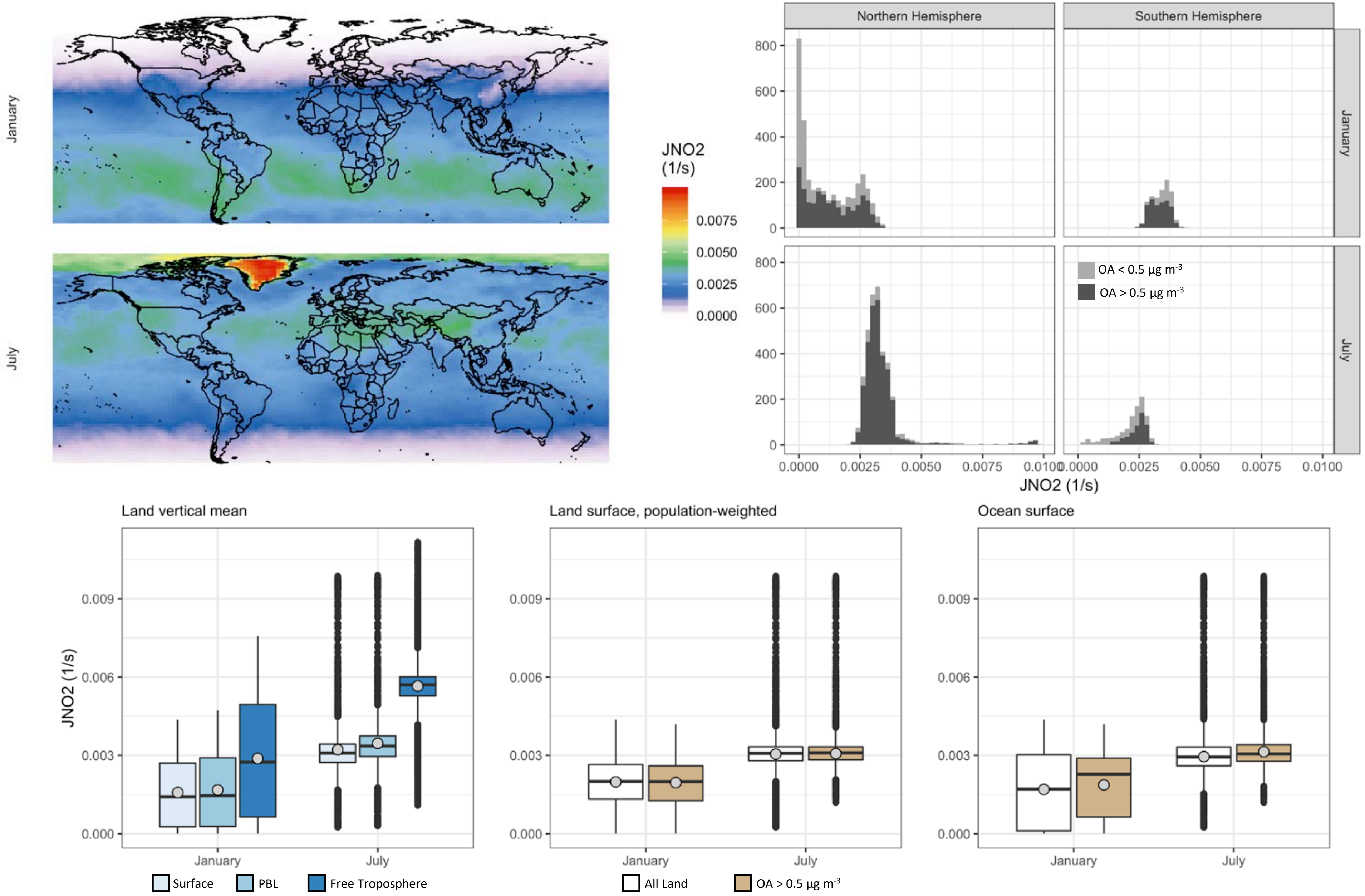




Relative Humidity

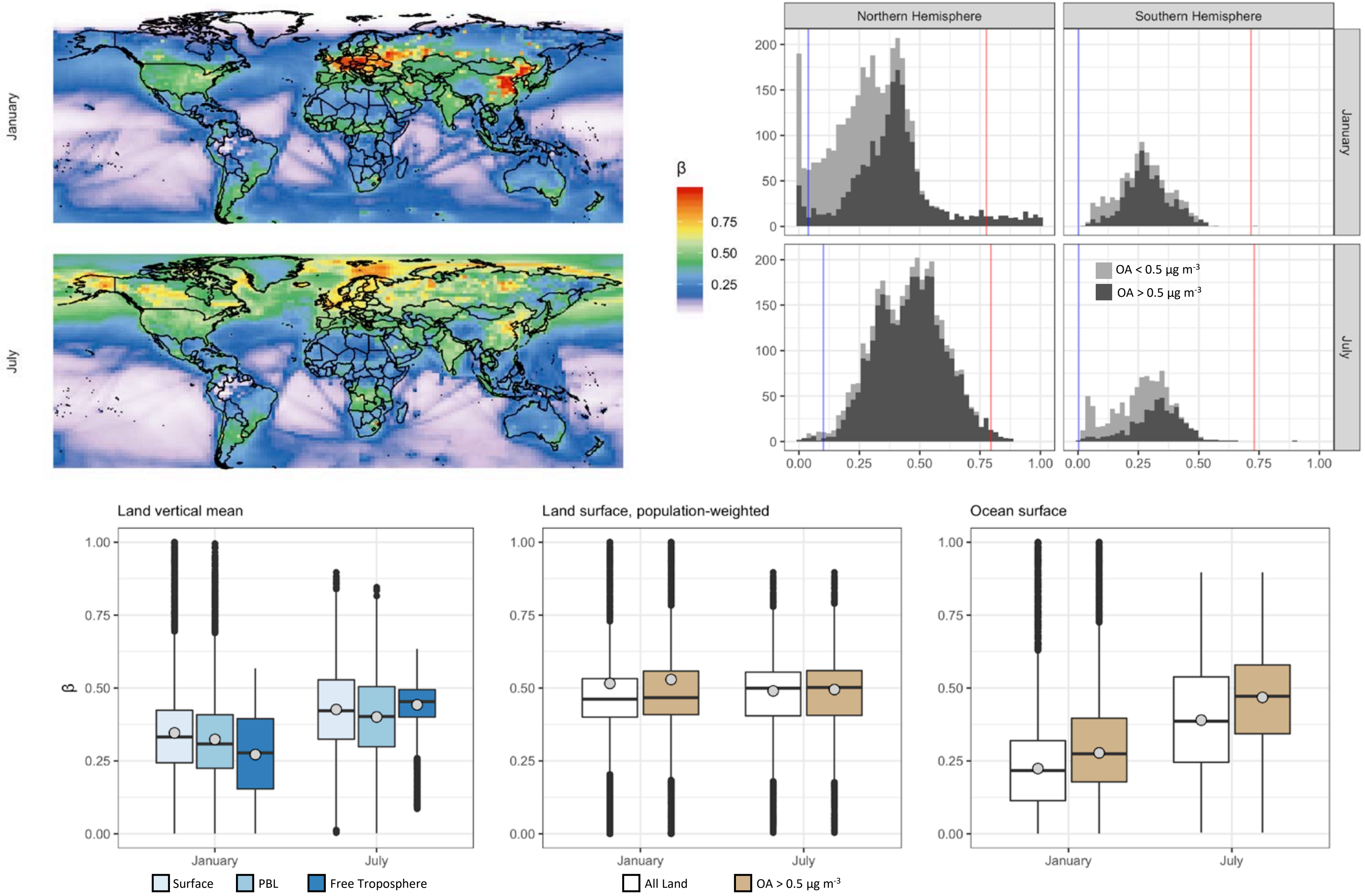


JNO_2

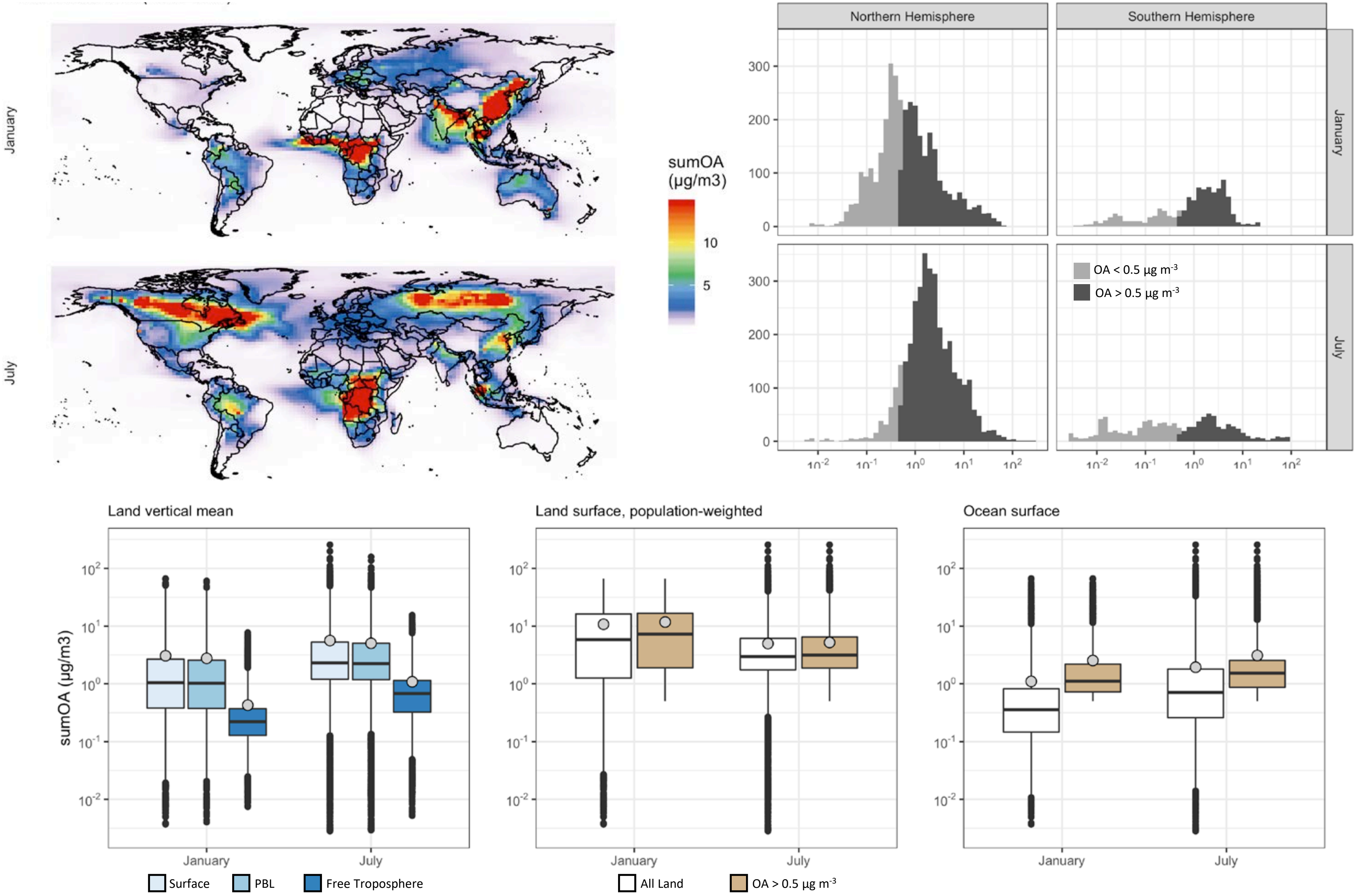


January
July
JNO2 (1/s)
0.0075
0.0050
0.0025
0.0000
Northern Hemisphere
Southern Hemisphere
January
July
800
600
400
200
0
OA < 0.5 µg m-3
OA > 0.5 µg m-3
0.0000
0.0025
0.0050
0.0075
0.0100
JNO2 (1/s)
Land vertical mean
Land surface, population-weighted
Ocean surface
JNO2 (1/s)
0.009
0.006
0.003
0.000
January
July
Surface
PBL
Free Troposphere
All Land
OA > 0.5 µg m-3

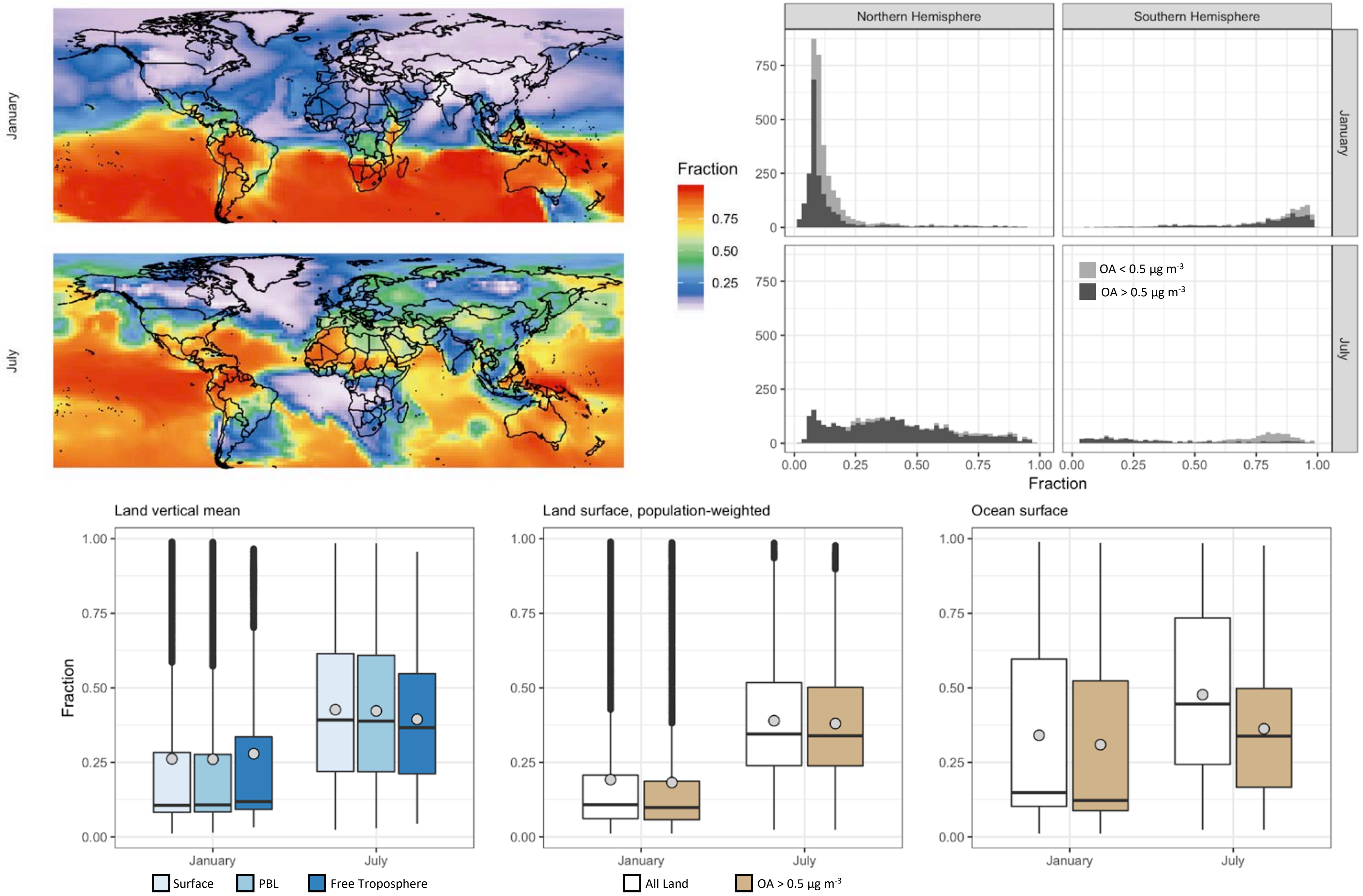
NO Branching Ratio



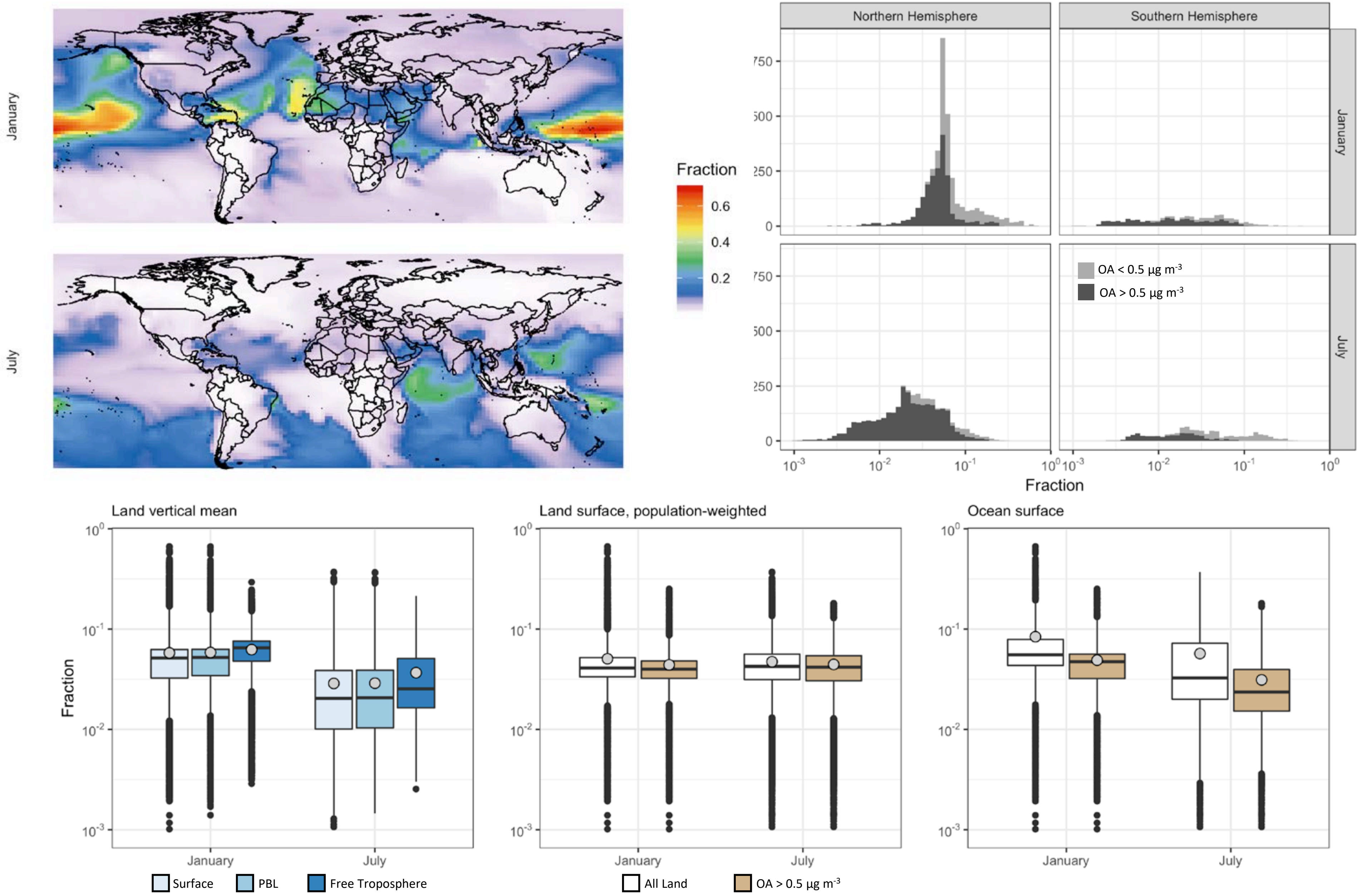
Total Organic Aerosol



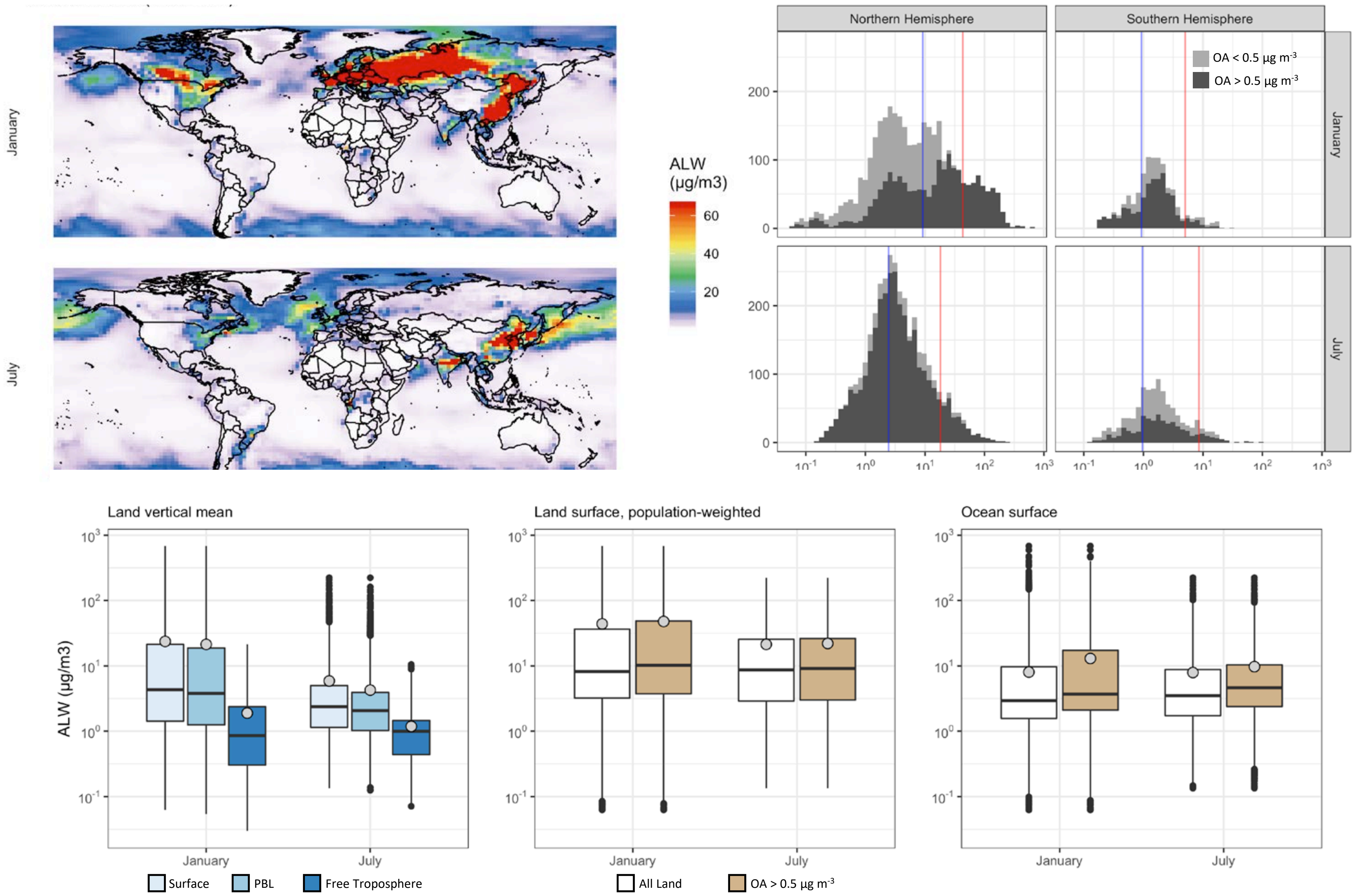
Isoprene/Terpene SOA vs. Total OA



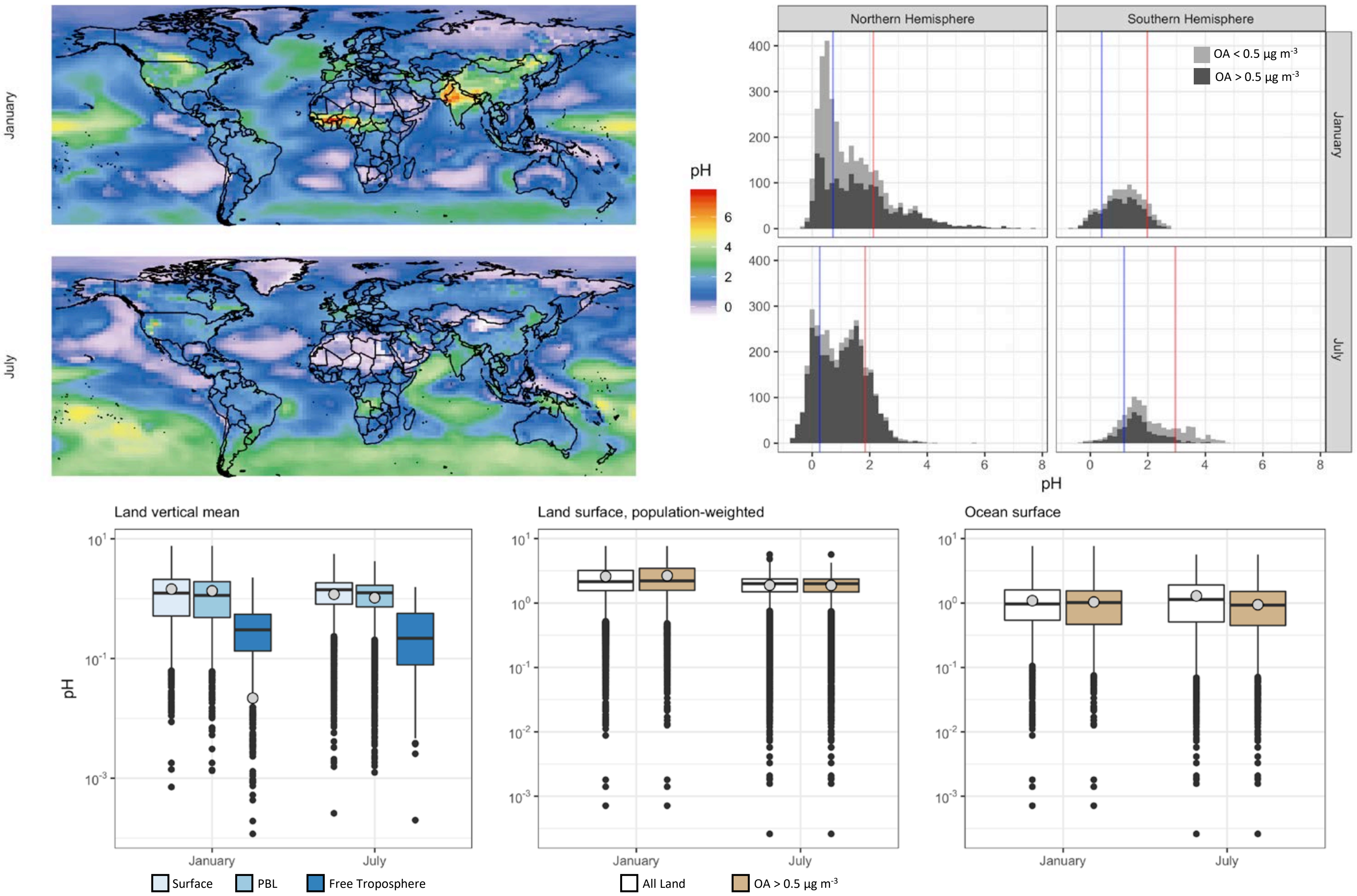
Aromatic SOA vs. Total OA



Aerosol Liquid Water

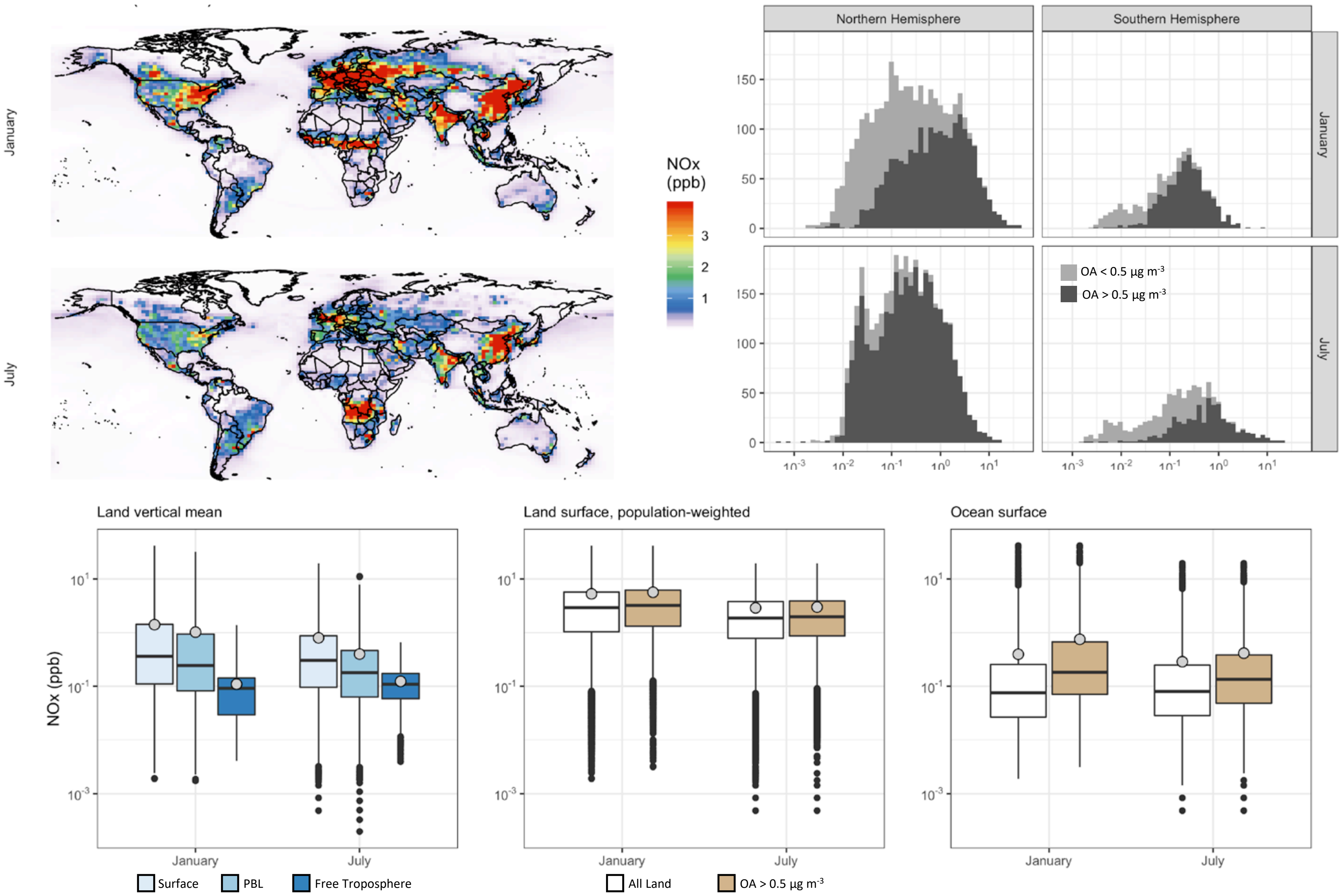


Aerosol pH



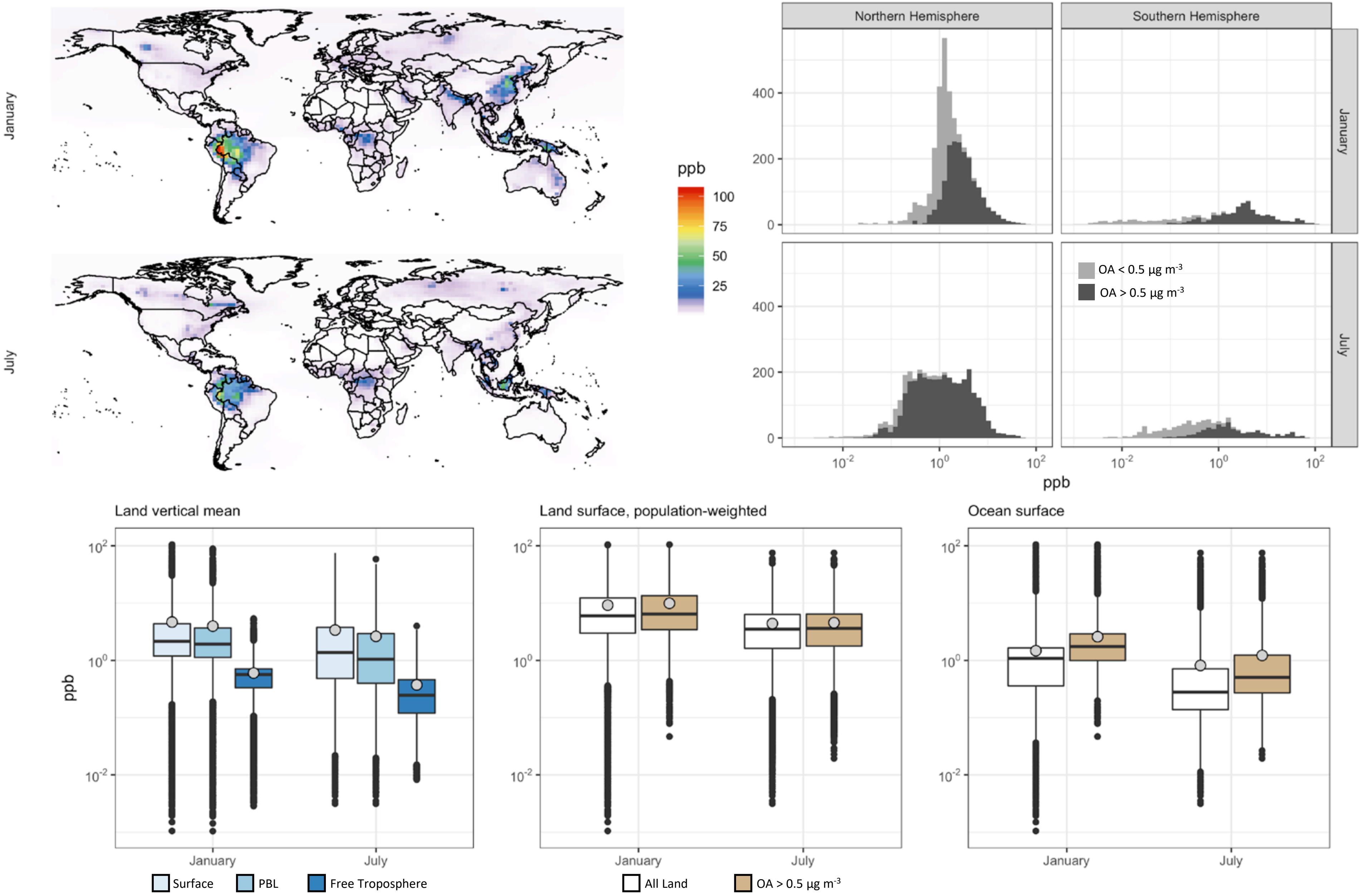
January
July
pH
6
4
2
0
Northern Hemisphere
Southern Hemisphere
OA < 0.5 µg m-3
OA > 0.5 µg m-3
400
300
200
100
0
0
2
4
6
8
pH
Land vertical mean
Land surface, population-weighted
Ocean surface
Surface
PBL
Free Troposphere
All Land
OA > 0.5 µg m-3

NOx



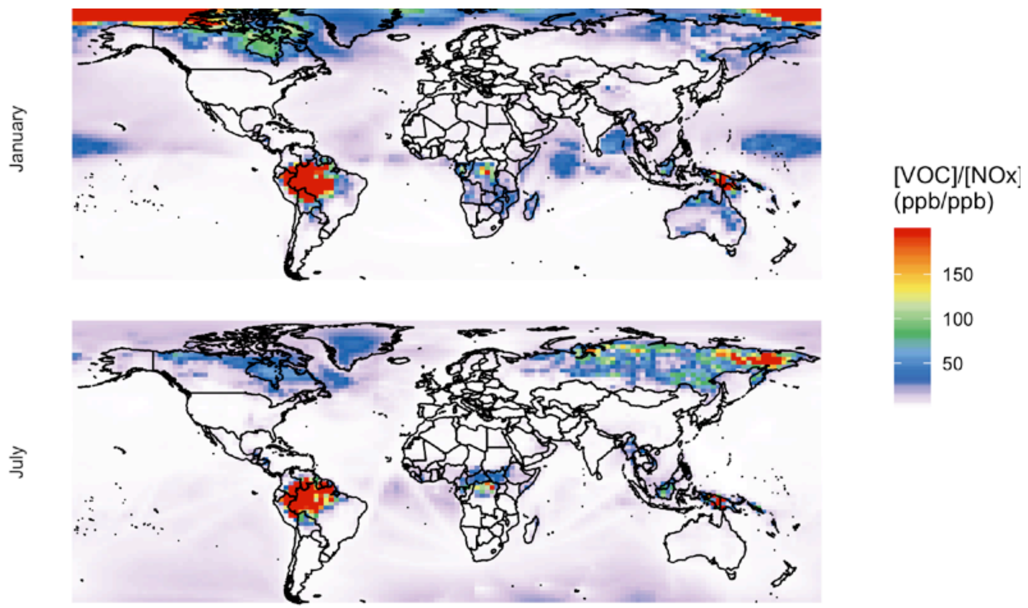
January
July
NOx (ppb)
3
2
1
Northern Hemisphere
Southern Hemisphere
150
100
50
0
OA < 0.5 μg m-3
OA > 0.5 μg m-3
10-3
10-2
10-1
100
101
Land vertical mean
Land surface, population-weighted
Ocean surface
NOx (ppb)
Surface
PBL
Free Troposphere
All Land
OA > 0.5 μg m-3

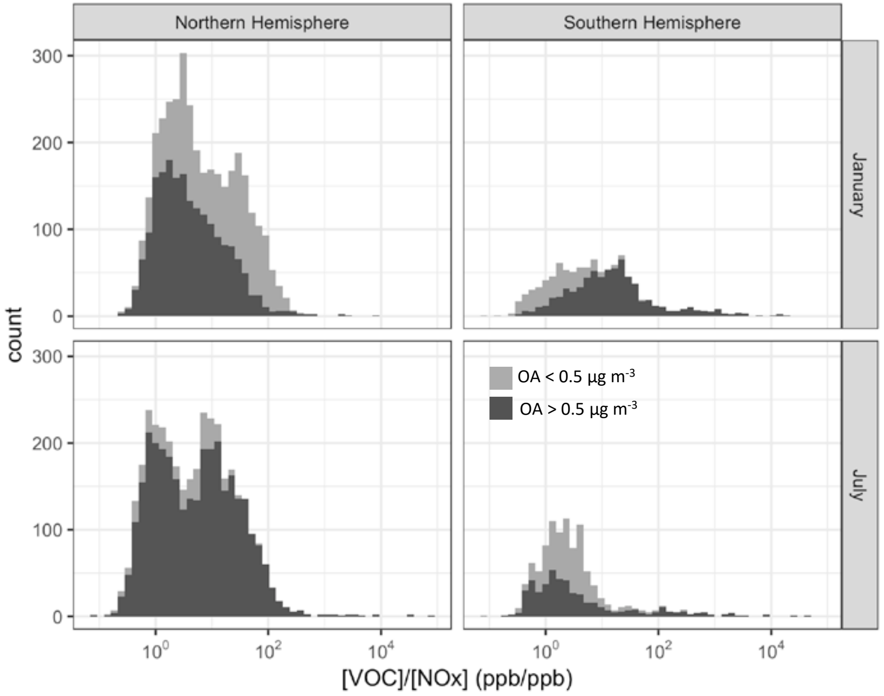
Summed VOCs

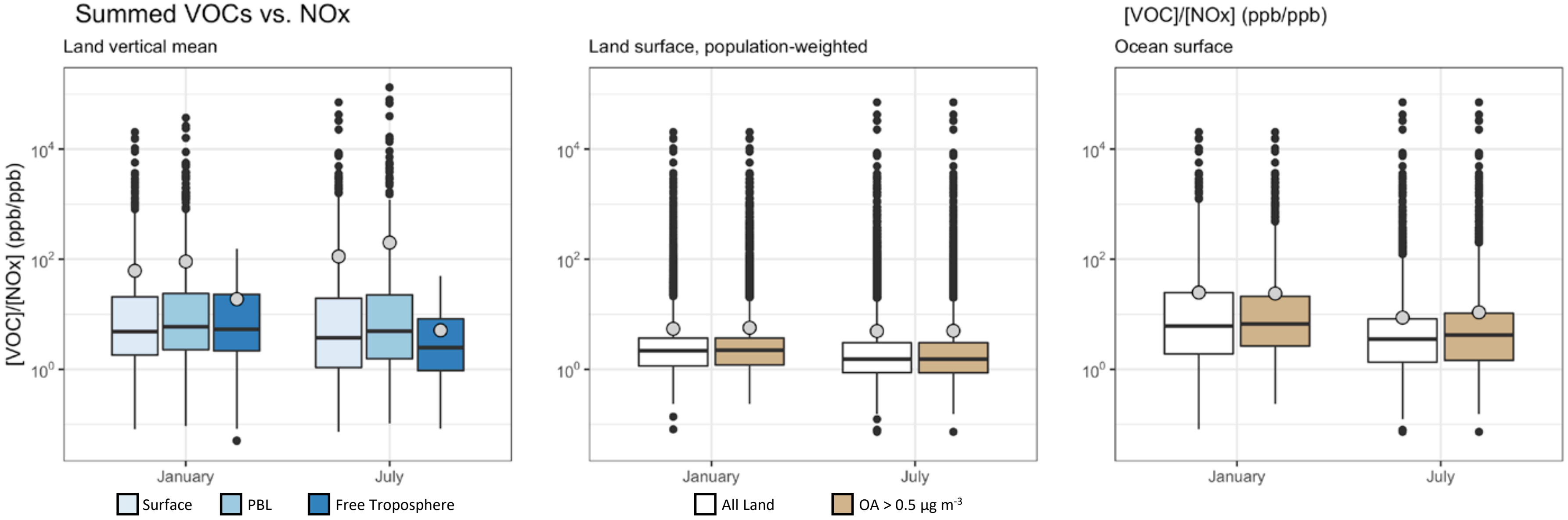


January
July
ppb
100
75
50
25
Northern Hemisphere
Southern Hemisphere
400
200
0
January
July
OA < 0.5 µg m-3
OA > 0.5 µg m-3
10-2
100
102
ppb
Land vertical mean
Land surface, population-weighted
Ocean surface
ppb
January
July
Surface
PBL
Free Troposphere
All Land
OA > 0.5 µg m-3

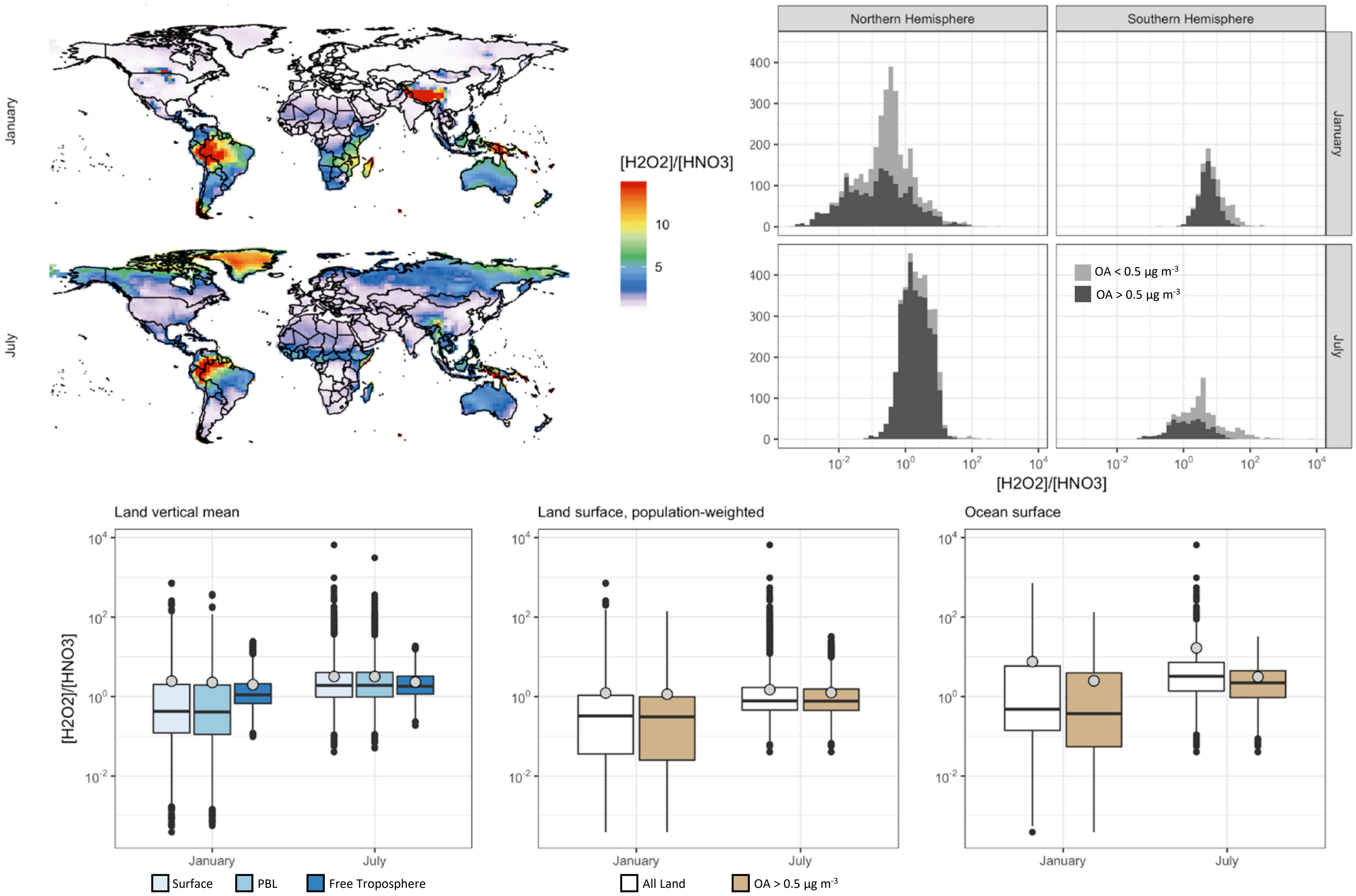
Summed VOCs vs. NOx





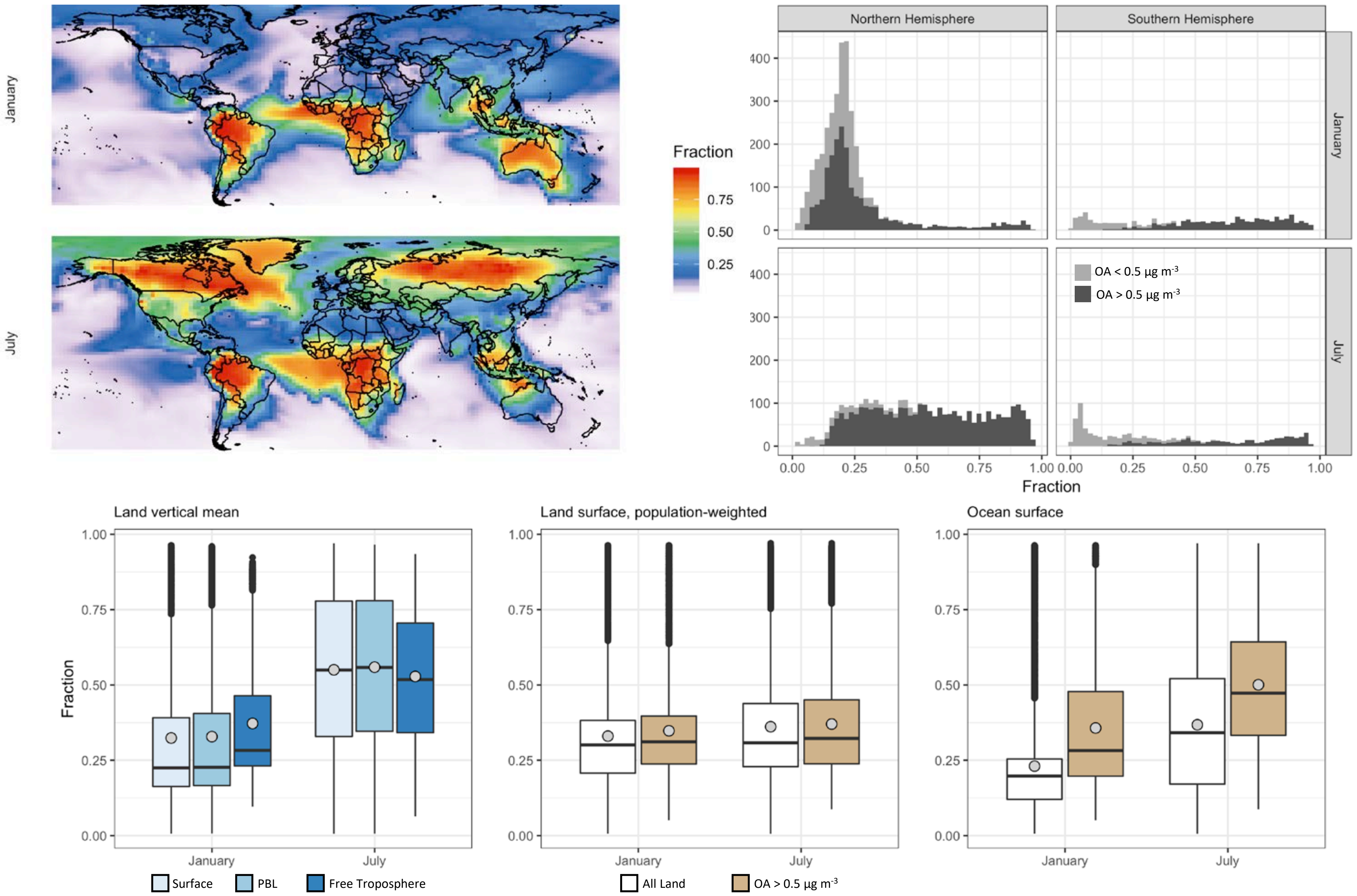


H_2O_2/HNO_3



January
July
[H2O2]/[HNO3]
10
5
Northern Hemisphere
Southern Hemisphere
400
300
200
100
0
January
July
OA < 0.5 µg m-3
OA > 0.5 µg m-3
10-2
10^0
10^2
10^4
[H2O2]/[HNO3]
Land vertical mean
Land surface, population-weighted
Ocean surface
[H2O2]/[HNO3]
January
July
Surface
PBL
Free Troposphere
All Land
OA > 0.5 µg m-3

OM/(OM+IM)



January
July
Fraction
0.75
0.50
0.25
Northern Hemisphere
Southern Hemisphere
400
300
200
100
0
January
July
OA < 0.5 µg m-3
OA > 0.5 µg m-3
0.00
0.25
0.50
0.75
1.00
Fraction
Land vertical mean
Land surface, population-weighted
Ocean surface
Fraction
January
July
Surface
PBL
Free Troposphere
All Land
OA > 0.5 µg m-3

RO2 Levels and ALW Frequencies