Lagrangian Inversion of VCP Tracers in the U.S.
during the 2021 Southwest Urban NOx and VOC Experiment (SUNVEx) and the RECAP campaign

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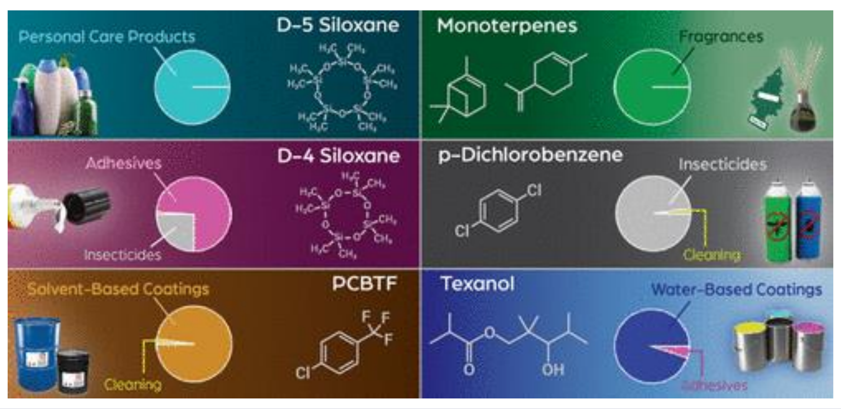
1. Introduction

i) Long-lived Volatile Chemical Product (VCP) Tracers:



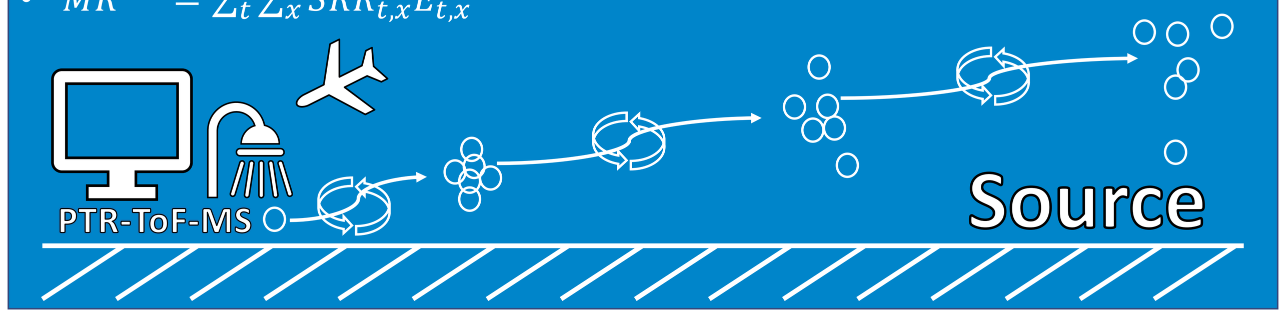
Emerging source of VOC emissions from human activity that increasingly impacts air quality on a local-, to regional scale (McDonald et al., 2018).

Fig. 1: Chemical formula of VCP tracers and associated sources (Fig from Gkatzelis et al.; 2021).

ii) Lagrangian Inversion:

FLEXPART-WRF: Source-Receptor Relationship (a.k.a., Footprint) [s m-3 kg -1]

- Estimate role of Emissions (E) on an observation (MR^{est})
- $MR^{est} = \sum_t \sum_x SRR_{t,x} E_{t,x}$



2. Methodology

i) 3D-VAR optimization using FLEXPART-WRF

- $MR^{est}_{i,j} = \sum_t \sum_x SRR_{i,j,t,x} E_{t,x}$,
  i, time of observation; j, chemical compound observed;
  t, x, time and location of back-trajectories (up to 12 hours before observation)
- $E_{t,x} = D_{t,x} E'_x$,
  where: $E'_x = \sum_t E_{t,x}$ and $D_{t,x} = \frac{E_{t,x}}{E'_x}$
  and $D_{t,x}$ is the diel evolution for each grid cell.

Temporal inversion model:

- Assume that only the area sector affects VCP emissions:
  $D_{t,x} \equiv D'_t$, so that $MR^{est}_{i,j} = \sum_t \sum_x M_{i,j,t,x} D'_t$,
  with $M_{i,j,t,x} = SRR_{i,j,t,x} E'_x$

Spatial inversion model:

- Assume temporal profile mixed for each location in the emission inventory:
  $MR^{est}_{i,j} = \sum_t \sum_x M'_{i,j,t,x} E'_x$,
  with $M_{i,j,t,x} = SRR_{i,j,t,x} D_{t,x}$

3D-VAR optimization and cost function:

- Assume Lognormal distribution of measurements and emissions and minimize cost-function with respect to the median of these distribution using the 3D-VAR framework (Brioude et al., 2011).

ii) Emissions Inventory (FIVE-VCP)

Fuel-based Inventory of Vehicle Emissions with VPCs (Coggon et al., 2021).

Compoumd	Maximum
D5-Siloxane	8.3e-1
D4-Siloxane	4.5e-1
PDCBZ	8.4e-1
PCBTF	2.3

Tab. 1: Normalization factors [(mol km-2 h-1] for average emissions map of the NEI (Fig. 2).

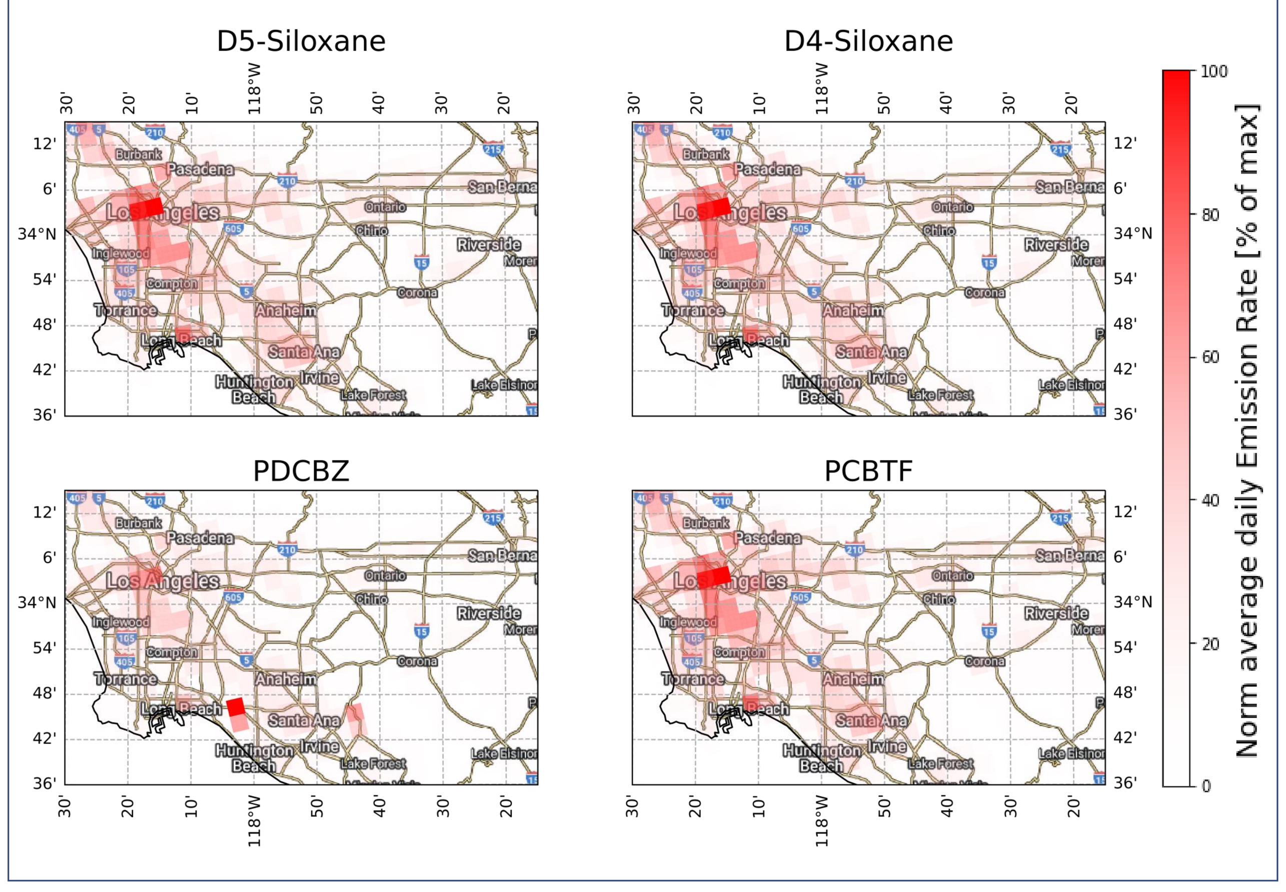


Fig. 2: Average weekday emissions map (July 2021) of the selected VCP tracers under consideration, normalized to the maximum average weekday emission (found in Tab. 1). The maps show emissions distributions for D5-Siloxane (top left), D4-Siloxane (top right), PDCBZ (bottom left), and PCBTF (bottom right).

iii) VCP data selection

- Continuous ground-site measurements at Clark County (July 2021, Las Vegas, NV) and Pasadena (August 2021, Los Angeles, CA) from the Southwest Urban NOx and VOC Experiment (SUNVEx).
  Data selected from PBL height comparison between model and stationary Lidar measurements.
- Airborne data collected during the experiment aimed at Re-Evaluating the Chemistry of Air Pollutants in CAlifornia (RECAP-CA; June 2021, Los Angeles, CA).
  Data selected from water vapor mixing ratio comparison between model and measurements. ($\rho \geq 0.6$)

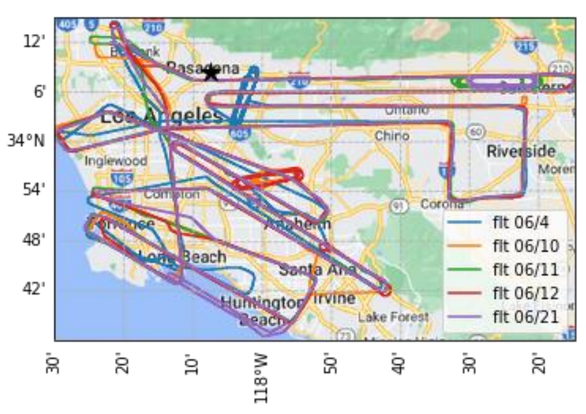


Fig. 3: Flight tracks of a selection of flights (different colored lines) performed in the framework of RECAP-CA in June of 2020. The selection of flights is based on the ability of WRF to reproduce the features in the water vapor mixing ratio profile. At the Pasadena ground site (black marker), a PTR-TOF-MS instrument was deployed during August 2021 in the framework of the SUNVEx campaign.

3. Model configuration

i) Weather Research Forcasting model (WRF)

12 configurations of WRF were tested with variation in horizontal resolution, boundary layer scheme and initial/boundary conditions.

- Initial and boundary conditions: High-Resolution Rapid Refresh (HRRR) model covering the CONtiguous United States (CONUS; 3 km resolution)
- Boundary layer scheme: MYNN-EDMF
- Horizontal resolution: 4 km x 4 km
- Validation: Mobile Doppler Lidar to probe performance in the LA basin

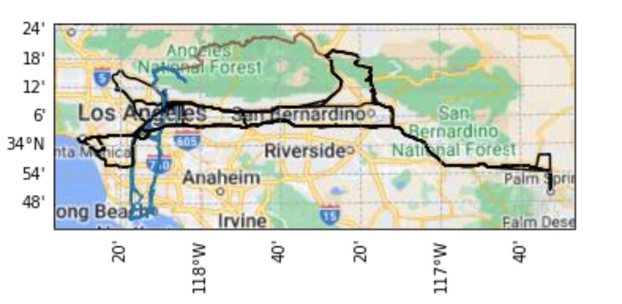


Fig. 4: Tracks of the mobile Doppler Lidar of which vertical profiles of windspeed were used to evaluate performance of the different WRF configurations. Data from the SUNVEx (LA, August 2021) campaign. Blue, brown and black tracks were driven to focus on the coastal, mountain and average model performance.

ii) FLEXPART-WRF

- Turbulent parameterization: TKE-driven (Verreyken et al., 2019)
- Horizontal resolution:
  - 4.0 km x 4.0 km for optimization temporal profiles
  - 1.3 km x 1.3 km for optimization of spatial distributions
- Lifetime: 12 hours
- Back-trajectories generated:
  - Hourly (ground site)
  - Every 40s (airborne)

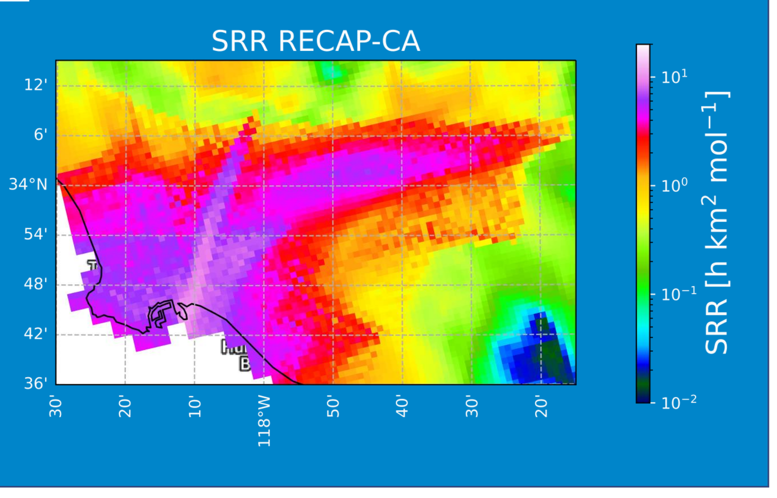


Fig. 5: Total footprint [h km2 mol-1] of the selected flights for the spatial inversion using the RECAP-CA flights taking place on 4, 10, 11, 12, and 21 of June 2021. Measurements were found to be most sensitive to emissions occurring in urban regions and over the harbor.

4. Results

4.1 Temporal inversion results

i) Normalized temporal profile for VCP tracers

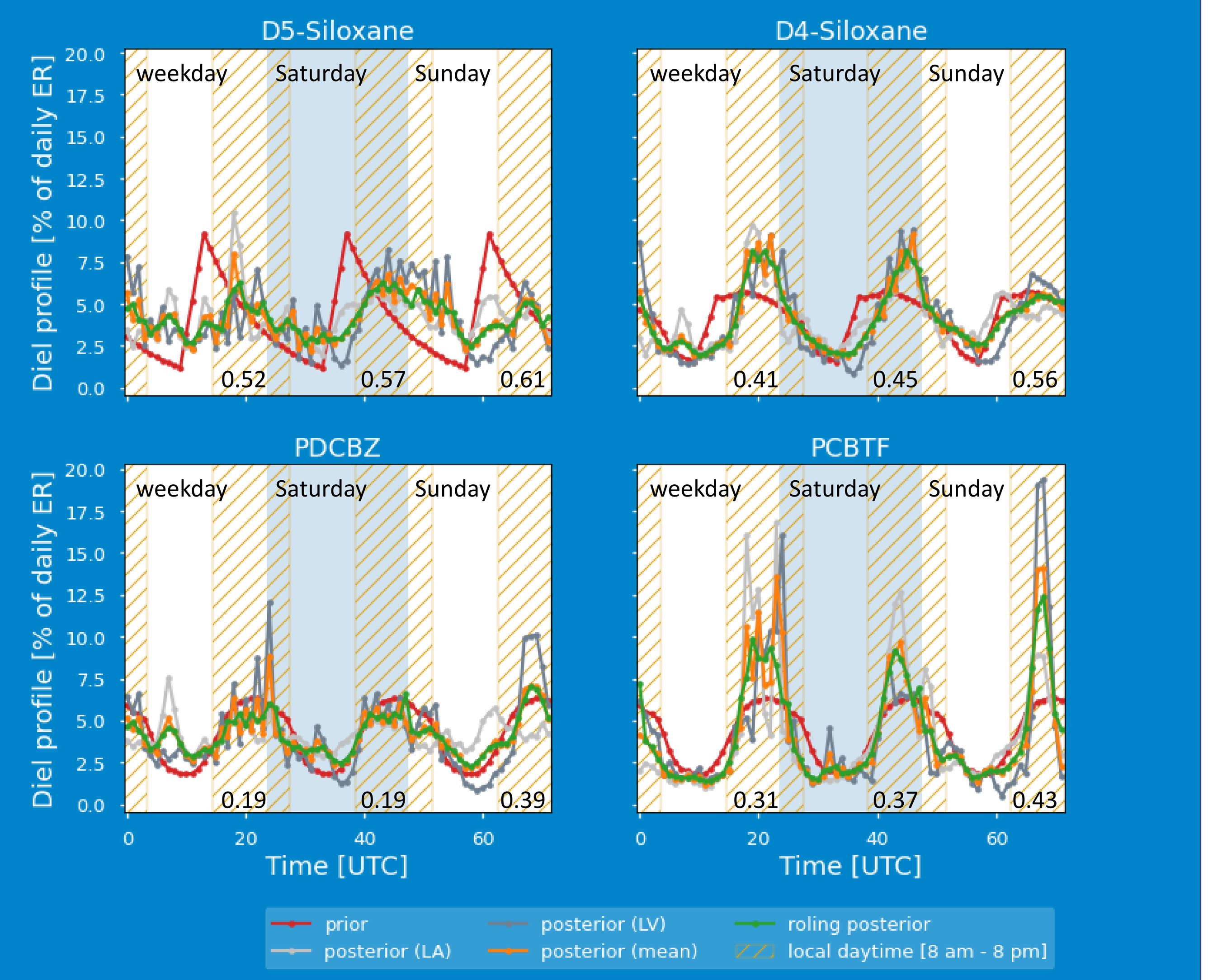


Fig. 6: Normalized diel profiles for the different VCP tracers at different stages of the inversion. In red the diel profile observed for the area source of the prior, in gray the posterior normalized profiles for the LA (light) and LV (dark) and the average posterior (orange). In green the 3-hour rolling average diel profile. The yellow hatched line represents local daytime (8 am to 8 pm). The number on the bottom right of each day is the surface of the inversion result used to normalize the diel profile (scaling factor).

ii) Performance of new temporal profile

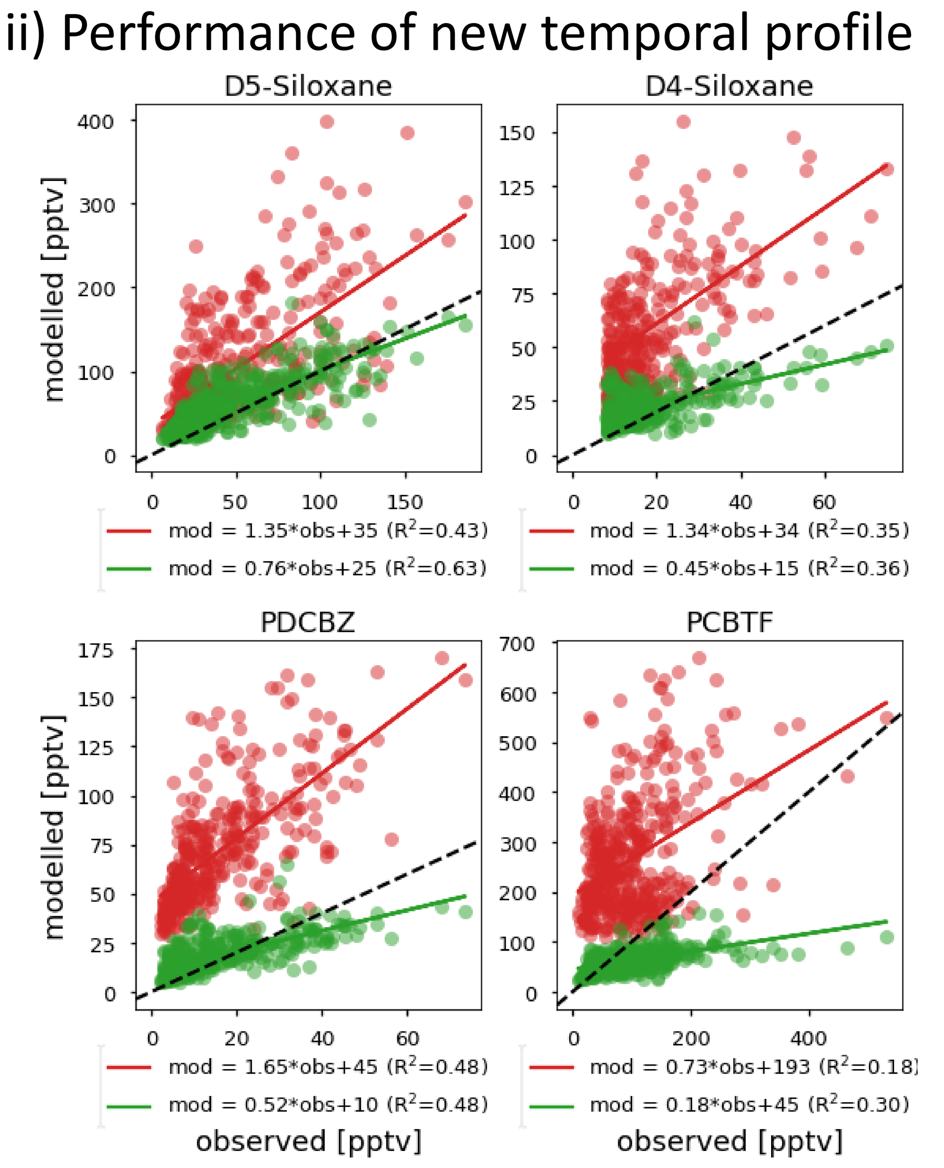


Fig. 7: Performance of the model to reproduce the mixing ratio [pptv] of the different VCP tracers using the emissions prior (red dots and line) and the rolling average posterior (green dots and line). The black dashed line is the 1:1 meridian. Model estimates of the mixing ratios on the y-axis and observations on the x-axis.

4.2 Spatial inversion results

i) BIAS of FIVE-VCP compared to inversion

Compound	Scaling FIVE-VCP
D5-Siloxane	0.66
D4-Siloxane	0.49
PDCBZ	0.13
PCBTF	1.35

The cost-function used for the optimization strongly penalizes emissions corrections above 100%. As such, enhancements in the posterior are limited to double the emissions in the prior.

Tab. 2: Scaling factor of the NEI to obtain the prior for the Lagrangian inversion. Scaling factor is defined by the median of the distribution by the ratio of the observed and modelled mixing ratio using the NEI and the FLEXPART-WRF footprints.

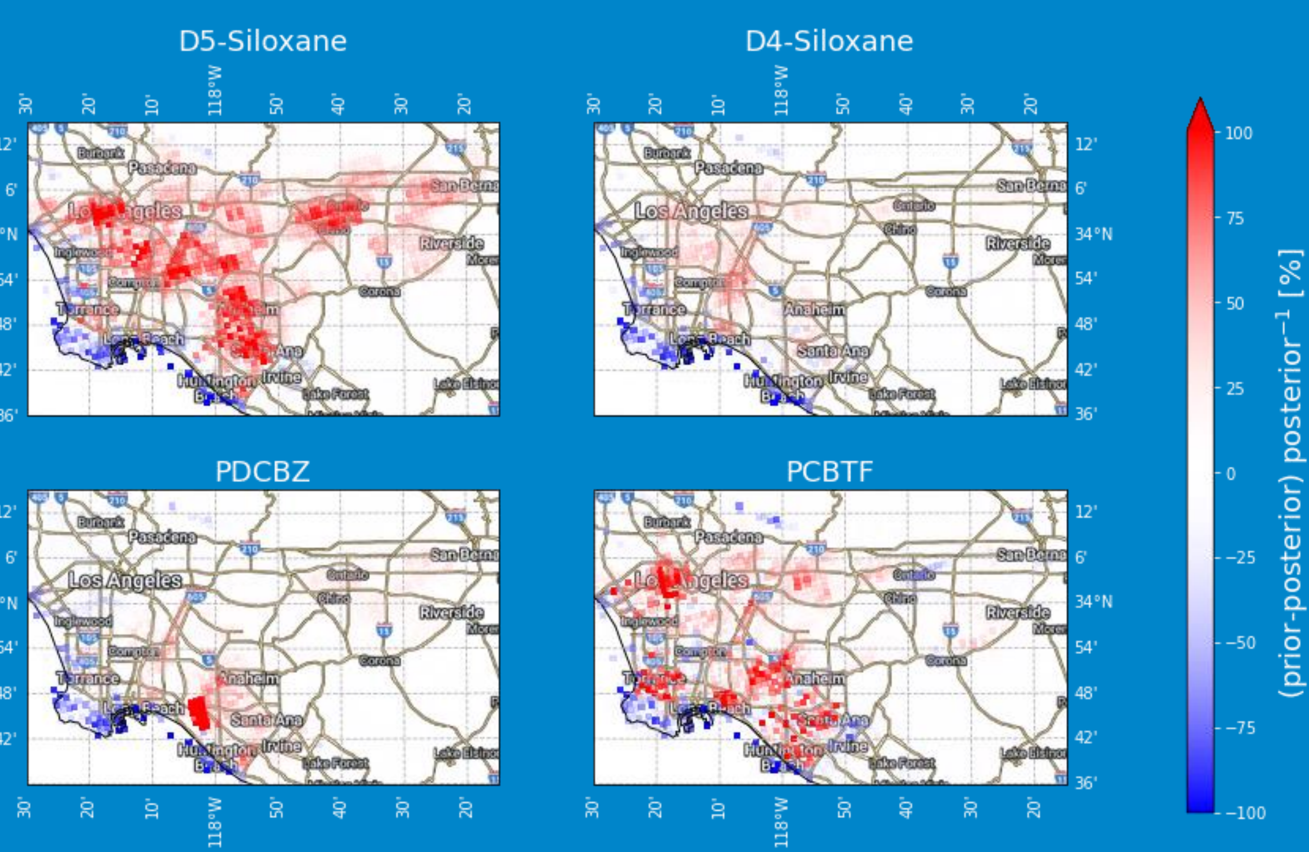


Fig. 8: Relative bias of the scaled national emissions inventory compared to the posterior obtained from the 3DVAR inversion for D5-Siloxane (top left), D4-Siloxane (top right), PDCBZ (bottom left), and PCBTF (bottom right).

ii) Performance of posterior

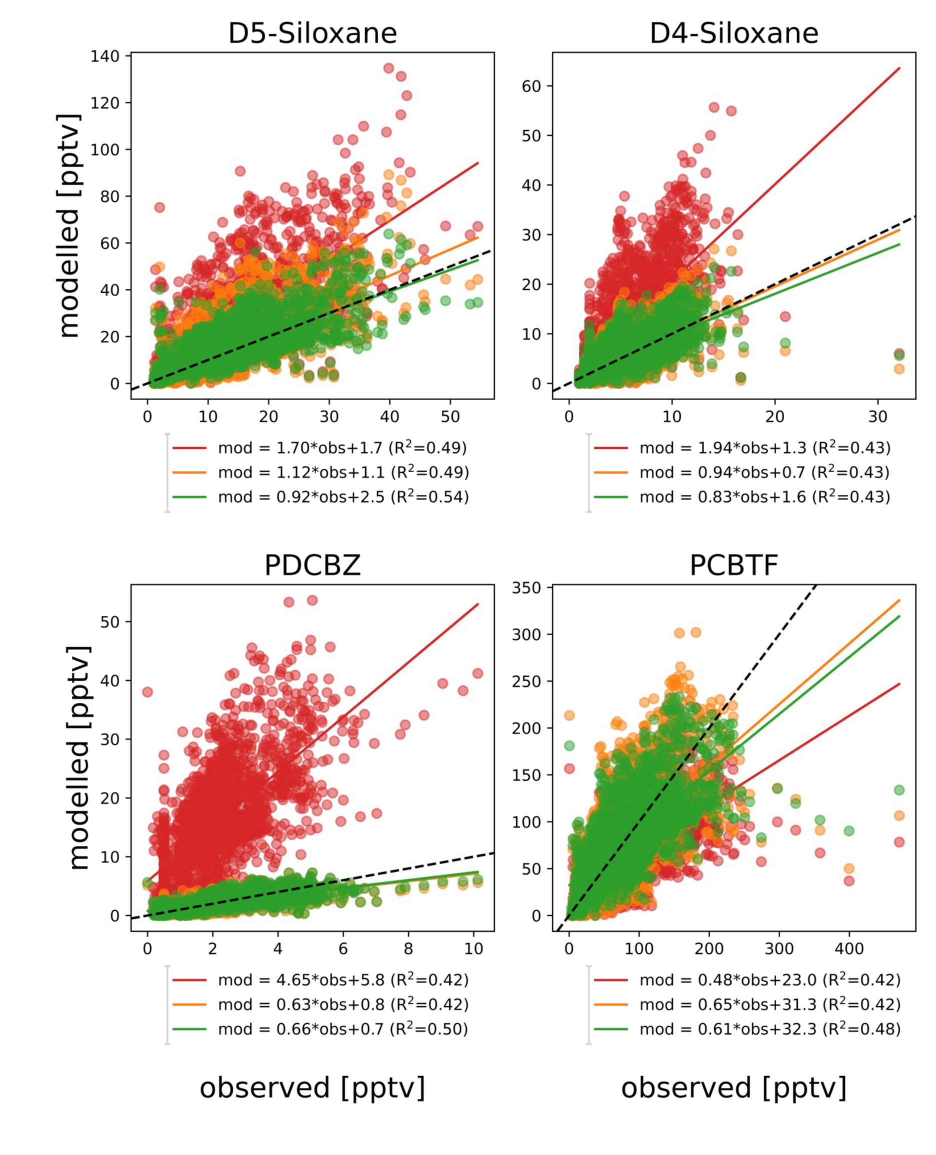


Fig. 9: Performance of the model to reproduce the mixing ratio [pptv] of the different VCP tracers using the NEI (red dots and line), a scaled EI that serves as prior for the inversion (orange dots and line) and the posterior (green dots and line). The black dashed line is the 1:1 meridian. Model estimates of the mixing ratios on the y-axis and observations on the x-axis.

5. Summary

Non-traditional anthropogenic volatile chemical products are an emerging source of petrochemical organic gasses in the atmosphere. Especially around large cities they have an increasing impact on air quality on local-, to regional scales. The emissions from these sources are highly uncertain. We present here the first top-down evaluation of VCP tracer emissions using an inversion framework with FLEXPART-WRF.

First, the temporal profile applied on the area source was optimized. Second, we focus on the spatial distribution of sources in the LA basin. The temporal inversion relies on continuous datasets obtained in LA and LV in the framework of SUNVEx while the spatial inversion leverages the high spatial coverage of flights performed in the framework of RECAP-CA.

Temporal optimization result:

- D5-Siloxane daytime maximum instead of morning peak
- D4-Siloxane and PCBTF stronger diel profile

Spatial optimization result:

- Urban emissions overestimated for all tracers
- Harbor/industrial emissions underestimated

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