Authors point-to-point responds reviewer comment #1 to egusphere-2025-2289

Please find the author's responses in black below the reviewer's comments in blue. Changes in the manuscript text are shown underlined.

First, we would like to thank reviewer #1 for their thoughtful and honest assessment of our work, which helped us to improve the manuscript, especially with respect to a better model evaluation. We have carefully considered all comments and have revised the manuscript accordingly. Reviewer #1 had two major and some minor comments, which we are addressing in the following. As some answers also match the raised points by reviewer #2, they might appear very detailed in some cases.

First Major Comment by reviewer #1: The setup of the model is quite concerning. The model reads the monthly output of NOx, OH, HO_2, and H_2O from CAM-chem, while organic peroxy radicals (RO2) were calculated from the most abundant VOCs, including methane, ethane, and propane. First, CAM-chem was driven by its dynamic core, and it might be nudged by other reanalysis such as MERRA-2 (Modern-Era Retrospective analysis for Research and Applications, Version 2). However, the meteorological fields in the authors' model were simulated by its own dynamic module, ICON. There is a mismatch between the meteorological fields driving the two models, which makes it unreasonable to directly match the chemical fields from CAM-chem to the ICON meteorology fields. Second, NOx, HO_2, OH, RO2, and VOCs are chemically linked. The way the authors calculated RO_2 from methane, ethane, and propane is physically unreasonable, as it breaks the mass conservation between these species. Overall, the authors' current approach of combining meteorology and chemical fields violates fundamental physical laws, including conservation of momentum and mass. The authors should adopt either a fully online or a fully offline approach, rather than the hybrid method they use now.

1. Use of CAM-chem fields and conservation of momentum/mass.

We acknowledge that the original text did not clearly convey how the CAM-chem output is used in PRIEST. In the present version of ICON-ART PRIEST: NOx, OH, HO_2, H_2O, RO_2 and VOCs from CAM-chem are not transported as prognostic tracers in ICON. They enter the PFAS chemistry only as prescribed background fields to compute reaction rates. The only substances that are actually transported and deposited by ICON-ART PRIEST are the PFCA tracers (PFOA, PFNA, 8:2-FTOH, etc.).

The CAM-chem-derived species have no associated continuity or momentum equation in ICON, so there is no second “dynamical core” transporting them.

Because of this, there is no overlapping of dynamical cores. ICON’s dynamical core transports only the meteorological state and the transported PFAS tracers. The CAM-chem fields are used diagnostically as space-time snapshots (monthly means), and do not evolve dynamically within ICON. Therefore, the conservation equations solved by ICON are not altered or duplicated, and momentum conservation is not violated. The CAM-chem fields enter as monthly means, which already filter out sub-monthly dynamic variability.

The original CAM-chem fields are 6-hourly and fully consistent with their own dynamics, but by the time they are monthly averaged, much of the dynamical information associated with advective transport and transient perturbations is removed. The ICON model thus treats them as slowly varying background fields rather than as dynamically active tracers. In this sense, they behave like climatological or reanalysis-based oxidant fields often used in offline chemistry calculations. This type of semi-offline coupling is standard practice in atmospheric modeling. Regional and global chemistry models (e.g. limited-area models driven by global CTMs) routinely use oxidants or other species from external models as time-varying boundary/initial or background fields without being considered as overlapping dynamical cores. We have now made this point more explicit in the revised text to avoid the impression that two independent dynamical systems are transporting the same tracers.

To make all this transparent, we have explicitly mentioned it in the description of the chemical setup in Sect. 2.2.1. We now explicitly state that:

- NOx, OH, HO_2, H_2O, RO_2, and VOCs from CAM-chem are used as prescribed monthly fields.
- Only PFAS species are transported by ICON-ART PRIEST.
- The CAM-chem fields have no momentum or transport equations in ICON and thus do not affect momentum conservation.

Further, in response to your comments, we have replaced the corresponding paragraph (L57 - 165). with: “In ICON-ART PRIEST, reactants from CAM-chem (NOx, OH, RO_2, HO_2, and H_2O) are not transported as prognostic tracers. They are ingested only as prescribed monthly-mean background fields to compute PFAS reaction rates. The only species that are prognostically transported and deposited by ICON-ART PRIEST are the PFCA tracers (e.g. PFOA, PFNA, 8:2-FTOH, 8:2-FTO, 8:2-FTI) and the associated mixed aerosols, together with the meteorological state. Consequently, the CAM-chem-derived species have no continuity or momentum equations in ICON; there is no second dynamical core, and the conservation

equations for mass and momentum solved by ICON remain unaltered. Because the CAM-chem fields are used in monthly-mean form, most sub-monthly dynamical variability associated with transport is already filtered out, so they act as slowly varying climatological oxidant fields, consistent with standard semi-offline couplings widely used in regional and global chemistry–transport modeling".

We hope this clarifies your concerns about fundamental physical conservation laws on our current setup.

2. The physically inconsistent treatment of RO_2 // RO_2 calculation and mass balance

Regarding the second part of your first major comment (RO_2 calculation), we agree that OH, NOx, HO_2, RO_2 and VOCs are chemically coupled in reality, and it is a pressing issue that should be addressed in the near future to improve the mass balance consistency.

In the current ICON-ART PRIEST version CH_4, C_2H_6, and C_3H_8, as well as OH, HO_2 and NOx, from CAM-chem are used as background concentrations to diagnose RO_2. These background species are not transported or chemically updated within ICON. Hence, as background fields, they do not directly affect the internal mass conservation of transported PFAS tracers in ICON-ART PRIEST.

To address this concern, we have: Clarified in the revised manuscript that RO_2, OH, HO_2 and NOx are treated as prescribed background fields in the current PRIEST version, and we openly discuss the associated limitation for chemical consistency (P10, L281 – L284):

"Then, calculated RO_2 from CAM-chem most abundant VOCs is prescribed as background fields. These field are neither transported nor chemically updated within ICON and thus do not enter the internal mass budget of the transported PFAS tracers, as for the rest of the background concentration reactants. Consequently, the approximate RO_2 diagnostic used here should not have a significant impact in the global mass conservation of PFCAs in PRIEST."

Our initial reasoning was that, since the VOCs and oxidants are not prognostic in ICON and only the PFAS species are transported and deposited, the global mass balance of PFAS would not be compromised by the approximate RO_2 calculation. However, we agree with you that from a chemical-mechanism point of view, using a simplified RO_2 diagnostic based on a subset of VOCs and prescribed OH/HO_2/NOx is not ideal and breaks, at least conceptually, the strict chemical linkage among these species.

(L284 – L286) “Nevertheless, from a chemical-mechanism perspective, diagnosing RO_2 from a limited VOC subset and prescribed OH/HO_2/NO_2/NO fields breaks the strict chemical coupling that would ideally link VOCs with these compounds.”

We also now explicitly state that RO_2 will be calculated interactively within an extended chemical mechanism in a future version of ICON-ART PRIEST, so that RO_2 production and loss are treated consistently with the VOC and oxidant fields. This will remove the current diagnostic approximation and ensure a fully self-consistent photochemical system: “(L287 – L289) The offline diagnose of RO_2 limitation is acknowledged in the current PRIEST version, and it will be calculated following a fully online interactive approach in a future release. This will be achieved by incorporating the calculation into the gas-phase reaction mechanism (Sect.2.2.1), so that RO_2 production and loss are fully consistent with the VOCs and oxidant fields.

We also note, as pointed out by the additional reviewer (published by our editor, Dr. Hoffmann), that while the semi-offline treatment of non-PFAS reactants introduces errors due to the mismatch between CAM-chem chemistry and ICON dynamics, these errors are expected to be significantly smaller than the PFAS-specific uncertainties at this stage. We agree with this assessment and have strengthened the uncertainty and sensitivity analysis accordingly.

Point 3 in additional reviewer comments: “While I agree with Referee 1 that the treatment of non-PFAS reactants as semi-offline provided from a different model will introduce errors based on the mismatch of dynamics and chemistry, I believe these errors will be significantly smaller than the PFAS-specific uncertainties of the model. This echoes the point of both Referee 1 and Referee 2 that uncertainties and sensitivities are an important aspect of this stage of modeling and should be explored.”

Second major comment: Further analysis is required to better understand the model performance. Figures D1 and D2 demonstrate that the model cannot capture the variability of surface concentrations of PFNA and PFOA, and the simulation results appear overly consistent. I think this is reasonable, as it could represent an initial step for this type of modeling. The coarse resolution could be a potential explanation for the discrepancy, however, I believe that more effort is needed to identify the sources of uncertainty. For example, the meteorological fields should be examined before validating PFCA. In addition, emissions could also be a potential source of uncertainty, and sensitivity tests would be necessary to assess their contribution. All these analyses would be helpful for both the authors and the readers in understanding the underlying issues with the model system.

We fully agree that a more systematic assessment of uncertainties and sensitivities is important at this early stage of PFAS modeling. Following your suggestion, we conducted a new suite of eleven additional simulations (each 2 years long, with the first year used as spin-up) designed to separate the influence of emissions, oxidant fields, and internal variability. This is described in the new section 4.5. Sensitivity and uncertainty tests (P23, L511):

(L512 – L523) "To evaluate the sensitivity and uncertainty associated with two of the most important oxidants (reactants) and the emission inventory, we conducted eleven additional simulations (each two years long, with the first year used as spin-up). These experiments were designed to separate the influence of oxidant fields, emissions, and internal variability. The experiments were divided into two groups as follows:

- Group 1 (Control + oxidant sensitivity):
    - Control experiment using the POPE "Best Guess" emission scenario.
    - Four oxidant sensitivity experiments, where OH and RO_2 concentrations are scaled (X0 and X10) to explore the sensitivity of PFCA formation to these reactants.
- Group 2 (emission uncertainty and initialization):

Six emission-uncertainty experiments, using the Upper Bound (UB) and Lower Bound (LB) POPE emission scenarios, each initialized at three different times (one month before, at, and one month after 2006-01-01) to sample internal variability associated with different initial conditions."

(L524 – L529) "To systematically interpret the results of these simulations, four distinct statistical analyses were applied: (1) Relative Mean Difference (RMD) to quantify percentage changes in PFCA concentrations relative to the Control; (2) Statistical Significance Testing (ANOVA for oxidant sensitivity and Paired Permutation Tests for emission uncertainty) to assess the robustness of spatial differences; (3) Linearity Analysis to determine if PFCA production responds proportionally to changes in radical concentrations; and (4) Signal-to-Noise Ratio (SNR) analysis to distinguish the emission signal from the model's internal chaotic variability."

(L530 – L532) "First, the RMDs of annual mean PFOA and PFNA concentrations were calculated for both groups relative to the Control experiment. For the second group, RMDs were also computed between simulations with different initialization days (Appendix Tables E1–E5 and Figs. E1–E4)."

This analysis shows that POPE emission uncertainties (UB vs. LB) lead to substantially larger changes in PFOA/PFNA than the differences caused by varying

the initialization date, indicating that emission uncertainty is a primary driver of PFAS spread in our system.

We also added ANOVA and paired permutation tests to the manuscript:

- An ANOVA was conducted to test differences in the means between Group 2 experiments (UB/LB) and Control.
- Additionally, because the experiments share a common emission origin within each scenario, we applied a paired permutation test to assess the significance of differences in spatial patterns.
- The tables with these statistical results are now included as Tables E2–E5 in the revised manuscript.

(L533 – L551) "In addition, an analysis of variance (ANOVA) was applied to the group one experiments, whereas a Paired Permutation Test (PPT) was used for the second group because the experiments in principle share a common emission origin. Together, these tests were used to assess the statistical significance of differences in spatial patterns (Table E2 - E5).

The analysis demonstrates that uncertainties in POPE emissions (UB vs. LB) lead to substantially larger variations in PFOA and PFNA concentrations compared to differences arising from varying initialization dates. This indicates that emission uncertainty is a primary driver of PFCAs dispersion within the model system (Figure E3 and E4).

RMD analysis for the first group of simulations shows that variations on OH and RO_2 radicals have an impact on PFOA production. However, for PFNA that influence can be seen only with respect to OH, whereas sensitivity to RO_2 is negligible (Figures E1 and E2). These findings are also supported by table E1, which presents ANOVA test results obtaining that mean production levels differs significantly with varying OH and RO_2 concentrations. Despite, a noticeable exception is the relationship between PFNA and RO2, which yielded a p-value of 0.97, exceeding the significance threshold of 0.05, even when RMD does not differ a lot in matters of percentage.

Table E1. Relative mean differences and ANOVA test for OH and RO_2 sensitivity experiments.

Compound	Experiment	RMD (%)	ANOVA (f,p)
PFOA	RO2_0	-0.38	79.53, 1.91E-29
PFOA	RO2_10	0.97	
PFOA	OH_0	-0.0025	10.54, 2.71e-05
PFOA	OH_10	0.67	
PFNA	RO2_0	-0.033	0.031, 0.97
PFNA	RO2_10	0.0024	
PFNA	OH_0	-0.18	33.99, 2.25e-15
PFNA	OH_10	0.99	

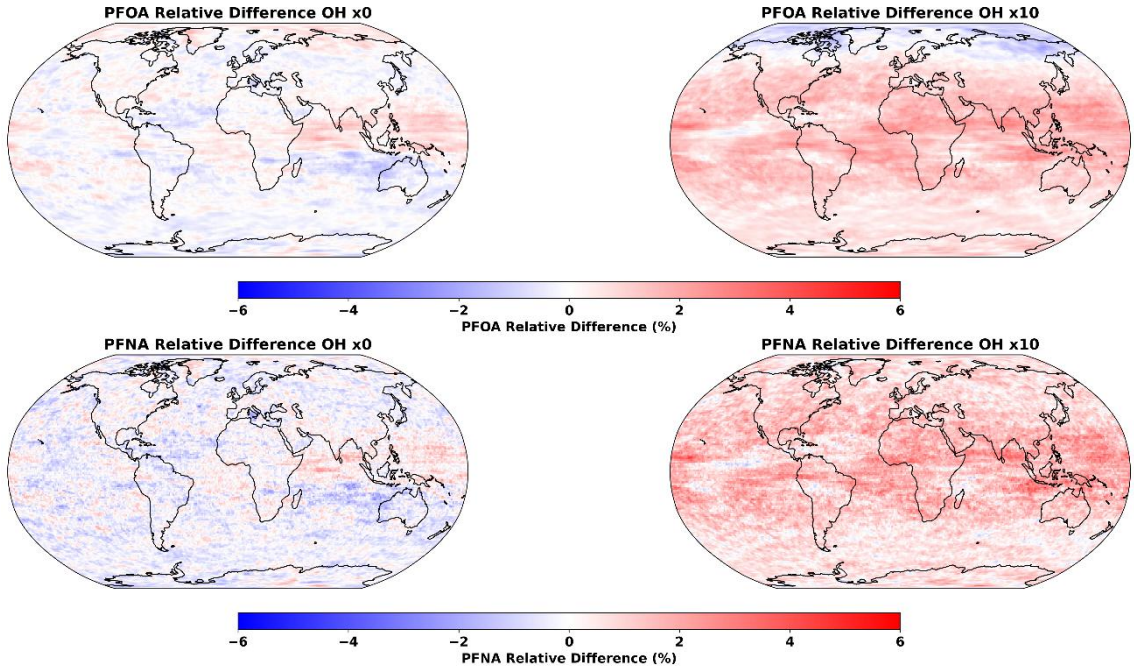


Figure E1. Relative Mean Differences (%) in annual mean atmospheric concentrations of PFOA (top) and PFNA (bottom). Panels show sensitivity experiments for OH x0 (left) and OH x10 (right) relative to the control simulation.

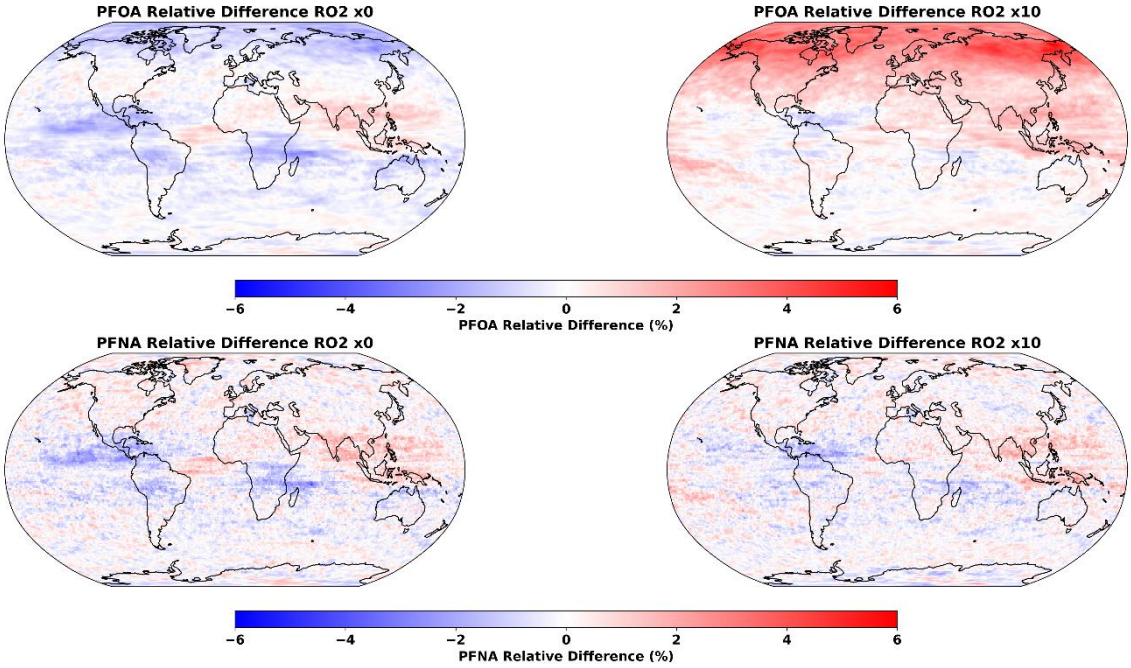


Figure E2. Relative Mean Differences (%) in annual mean atmospheric concentrations of PFOA (top) and PFNA (bottom). Panels show sensitivity experiments for RO_2 x0 (left) and RO_2 x10 (right) relative to the control simulation.

As expected, RMD values for PFOA Lower Bound (LB) and Upper Bound (UB) relative to the control experiment are larger between different emission scenarios, ranging from 41 to 62 % (Table E2). The PPT supports this result, showing significant statistical differences with a P-Value substantially lower than 0.05. These changes are also evident in Figures E3 and E4, where global RMD values range from +13 to +150 % (UB) and −15 to −75 % (LB) relative to the control experiment. For PFNA, these values are larger than for PFOA, with about +50 to +105 % (UB) and -70 to -80 % (LB). Additionally, the PPT shows that means for all experiments differ significantly for both pollutants, with p-values below 1.0E-4 and Observed Differences (OD) between 40 and 60 mol/mol."

Table E2. PFOA Relative mean differences and Paired Permutation Test for LB and UB against Control sensitivity experiments.

Compound	Experiment	RMD (%)	Pair. permut. test (D0,permut)
PFOA	LB_0	52.30	49.9, <1.0e-4
PFOA	UB_0	52.30	49.9, <1.0e-4
PFOA	LB_P1	-55.64	53.1, <1.0e-4
PFOA	UB_P1	41.63	-39.7, <1.0e-4
PFOA	LB_M1	-49.10	46.8, <1.0e-4
PFOA	UB_M1	62.50	-59.6, <1.0e-4

Table E3. PFNA Relative mean differences and Paired Permutation Test for LB and UB against Control sensitivity experiments

Compound	Experiment	RMD (%)	Pair. permut. test (OD,permut)
PFNA	LB_0	-76.16	50.91, <1.0e-4
PFNA	UB_0	75.54	-50.91, <1.0e-4
PFNA	LB_P1	-77.77	51.94, <1.0e-4
PFNA	UB_P1	63.61	-43.43, <1.0e-4
PFNA	LB_M1	-74.51	49.99, <1.0e-4
PFNA	UB_M1	87.59	-58.24, <1.0e-4

Table E4. PFOA relative mean differences and Paired Permutation Test for LB and UB in their different corresponding initialization period

Compound	Experiment	RMD (%)	Pair. permut. test (OD,permut)
PFOA	UB_0 vs UB_P1	-7.00	10.17, <1.0e-4
PFOA	UB_0 vs UB_M1	6.70	-9.73, <1.0e-4
PFOA	UB_M1 vs UB_P1	-12.84	19.90, <1.0e-4
PFOA	LB_0 vs LB_P1	-7.00	-39.7, <1.0e-4
PFOA	LB_0 vs LB_M1	6.70	46.8, <1.0e-4
PFOA	LB_M1 vs LB_P1	12.84	-59.6, <1.0e-4

Table E5. PFNA relative mean differences and Paired Permutation Test for LB and UB in their different corresponding initialization period.

Compound	Experiment	RMD (%)	Pair. permut. test (OD,permut)
PFNA	UB_0 vs UB_P1	-6.42	75.70, <1.0e-4
PFNA	UB_0 vs UB_M1	6.22	-73.31, <1.0e-4
PFNA	UB_M1 vs UB_P1	-11.90	14.90, <1.0e-4
PFNA	LB_0 vs LB_P1	-6.42	10.28, <1.0e-4
PFNA	LB_0 vs LB_M1	6.22	-99.55, <1.0e-4
PFNA	LB_M1 vs LB_P1	-11.90	20.24, <1.0e-4

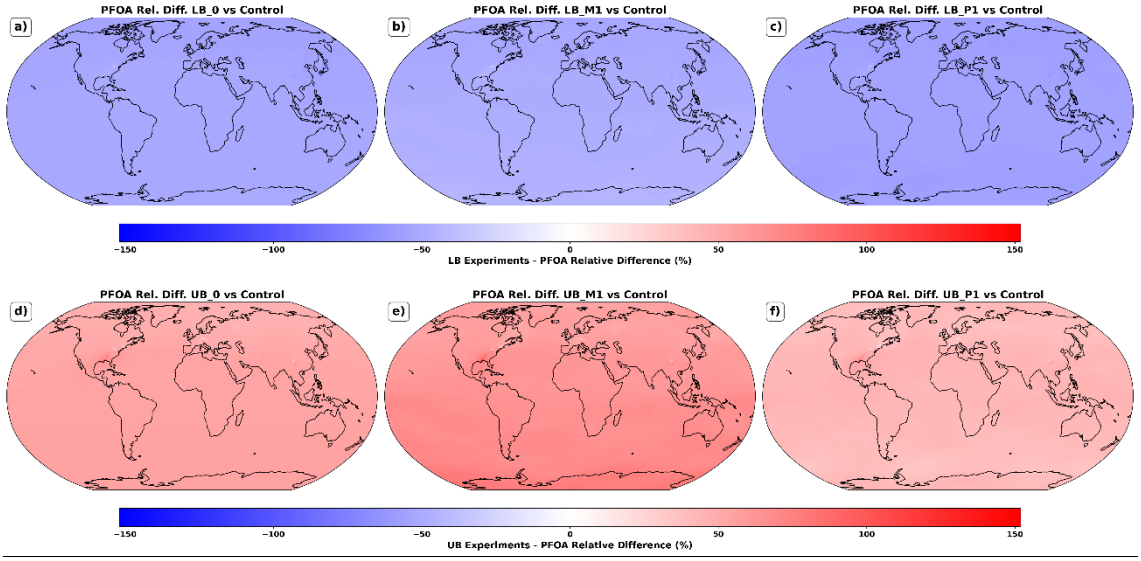


Figure E3. Relative mean differences PFOA from different initialization times. a) LB 0 vs Control, b) LB M1 vs Control, c) LB P1 vs Control, d) UB 0 vs Control, e) UB M1 vs Control, f) UB P1 vs Control.

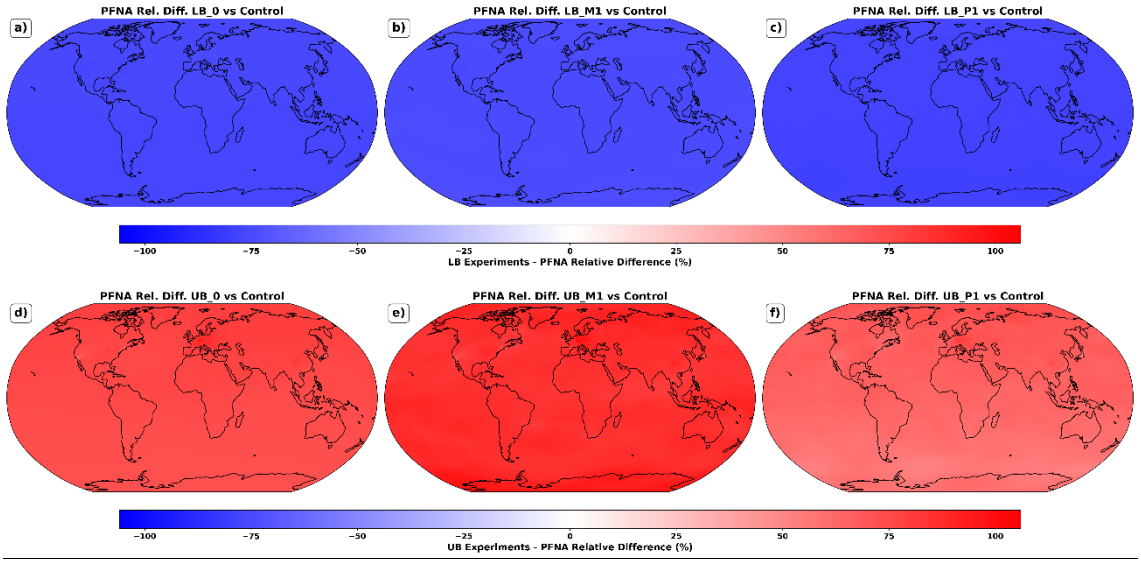


Figure E4. Relative mean differences PFNA from different initialization times. a) LB 0 vs Control, b) LB M1 vs Control, c) LB P1 vs Control, d) UB 0 vs Control, e) UB M1 vs Control, f) UB P1 vs Control.

We examined whether PFOA/PFNA production scales linearly with available OH and RO_2, or whether competing loss pathways saturate the PFAS yield. The analysis shows that PFOA production is strongly and approximately linearly sensitive to OH, while PFNA exhibits a much weaker response to OH changes. PFNA also shows only a very small sensitivity to RO_2 variations, suggesting that for increased RO_2 concentrations, other chemical pathways (e.g. RO_2/OH + NO, RO_2/OH + RO_2) consume RO_2 without producing PFCA, leading to a saturation effect.

The corresponding diagnostics are now presented in Fig. E5. A new couple of paragraphs explaining results were added in the new chapter 4.5.

(L558 – L567) “Additionally we checked for the direct response from PFOA and PFNA production to OH and RO_2 radical concentrations in the model, we performed a linearity analysis test. This sensitivity test estimates whether production responds linearly or nonlinearly to changes in OH and RO_2 concentrations. The test considers three possible cases based on the three experiments—radical (OH or RO_2) x0, x10, and control, as follows: Perfect linearity occurs when the three experiments are perfectly aligned in a straight line, meaning that PFOA and PFNA production is directly proportional to the increase of OH and RO_2. Saturation takes place when the slope between the Control experiment and radical x10 is smaller than the slope between radical x0 and Control, meaning that production of PFCAs is limited by availability of precursor concentrations rather than by radical concentrations. Finally, Acceleration appear when the slope between Control and radical x10 is larger than the slope between radical x0 and Control, which means that high concentrations of radicals drive more efficient chemical pathways that produce PFCAs instead of other loss pathways.”

(L568 – L574) “Figure E5, shows the annual mean burden of radicals (OH and RO_2) on the X-axis and the annual mean of PFCAs (PFOA and PFNA) production on the Y-axis. Panels a and d present PFNA annual mean burden against OH and RO_2 radical annual mean burden. Both panels indicate that radicals do not highly influence the PFNA production, instead, that radicals are driving other chemical pathways. In this particular case, even when linearity analysis shows Saturation, OH seems to contribute less than RO_2 to the mean annual burden of PFNA production. For PFOA, also the contribution of RO_2 shows a stronger saturation meaning that RO_2 is mostly used on other intermediate reactions than on the PFOA production. Besides, for OH, PFOA is showing a slight Acceleration pattern indicating exponential response of PFOA formation to the radical.”

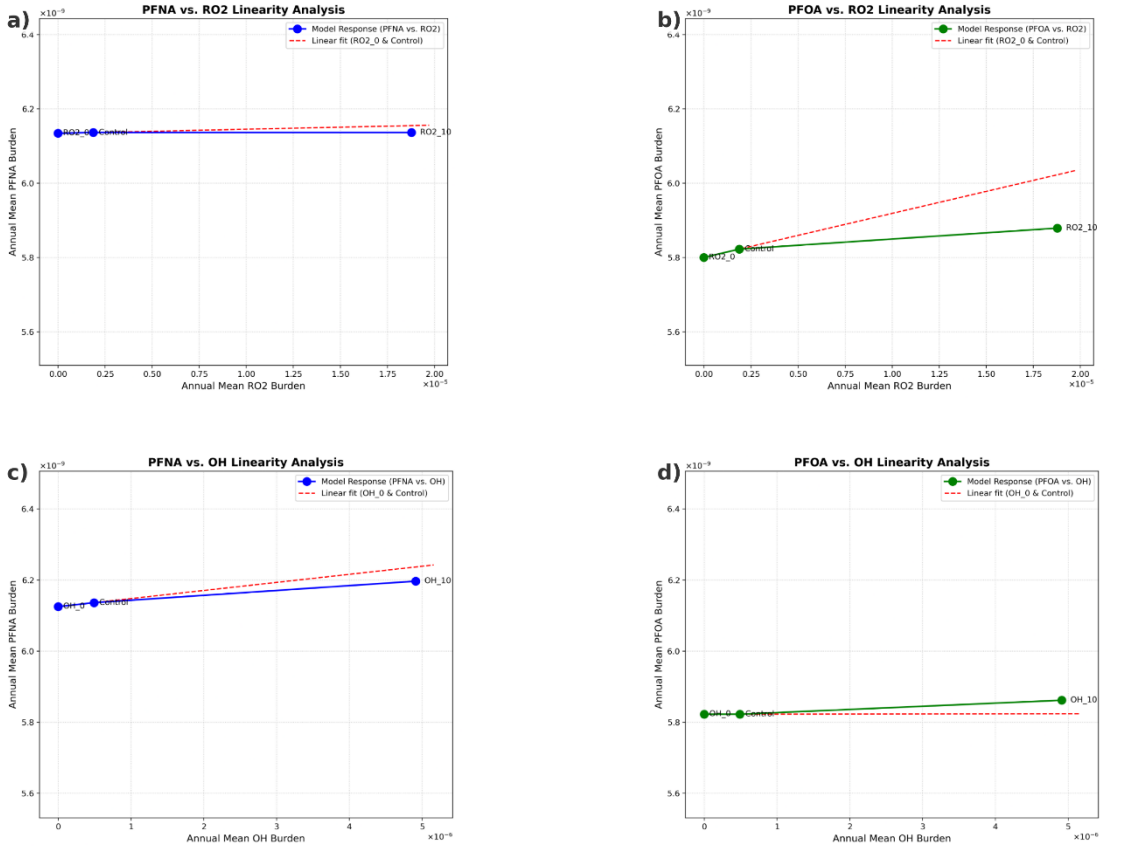


Figure E5. Linearity analysis of global annual mean burdens of PFNA and PFOA. Panels (a–b) show the response to RO_2 and (c–d) to OH. The model response (solid line) is compared against a linear fit (dashed red line) across three points: radical removal (x0), base case (control), and a ten-fold increase (x10). The deviation of the solid line from the dashed line represents the non-linear chemical feedback of the system.

Besides these analyses, we also performed a signal-to-noise ratio (SNR) analysis:

To quantify the relative importance of emissions ("signal") versus internal variability from different initialization times ("noise"), we computed the Signal-to-Noise ratio for Group 2. The resulting maps (Fig. E6) show a strong signal, i.e. emissions clearly dominate over internal variability in determining the simulated PFCA fields. This supports the interpretation that uncertainties in emissions are a key limitation of current PFAS modeling, consistent with your comment and Dr. Hoffmann's posted assessment. An additional set of four paragraphs were also added to chapter 4.5 to incorporate detailed results and analysis to the manuscript.

(L575 – L580) "Another useful tool to estimate the sensitivity and internal uncertainty is the Signal to Noise Analysis. First, sensitivity to emissions is quantified obtaining the mean of all the respecting LB an UB experiments. The Control experiment represent its own mean, as there is only one Control simulation. The range of the uncertainty due to emissions (signal) is obtained by subtracting the LB mean from the UB mean. Figure E6b displays uncertainty due to emission differences. Higher values indicate regions with the strongest emission influence,

mainly located over Eastern North America, Central Europe, and Eastern China, as well as downwind regions."

(L581 – L585) "Secondly, noise is obtained by calculating the standard deviation across all the experiments at all initialization times. This represents the internal variability (or internal noise) of the model; a metric of expected variability caused by the model's chaotic dynamics. Figure E6c depicts regions over the world where changes in the model's chaotic dynamics are most relevant; these areas are consistent with regions where the system is naturally more chaotic, such as the tropics, particularly over the open tropical oceans."

(L586 – L593) "Finally, the Signal to Noise Ratio (SNR) is calculated by dividing the emission uncertainty (signal) by the internal variability (noise). Figure E6a presents the spatial distribution of this ratio, revealing that the signal strongly dominates the noise across the entire globe. As indicated by the map's uniform dark green color and the legend, 100% of the surface area presents an SNR greater than 2, categorized as a "Strong Signal" where emissions dominate over initialization. This is further supported by the SNR statistics located into the box at the upper right of the map, showing a high global mean SNR of 18.66 and a median of 19.05. These values confirm that the variability driven by the different emission scenarios is significantly larger than the model's internal chaotic variability, ensuring that the detected emission impacts are robust and clearly distinguishable from background noise."

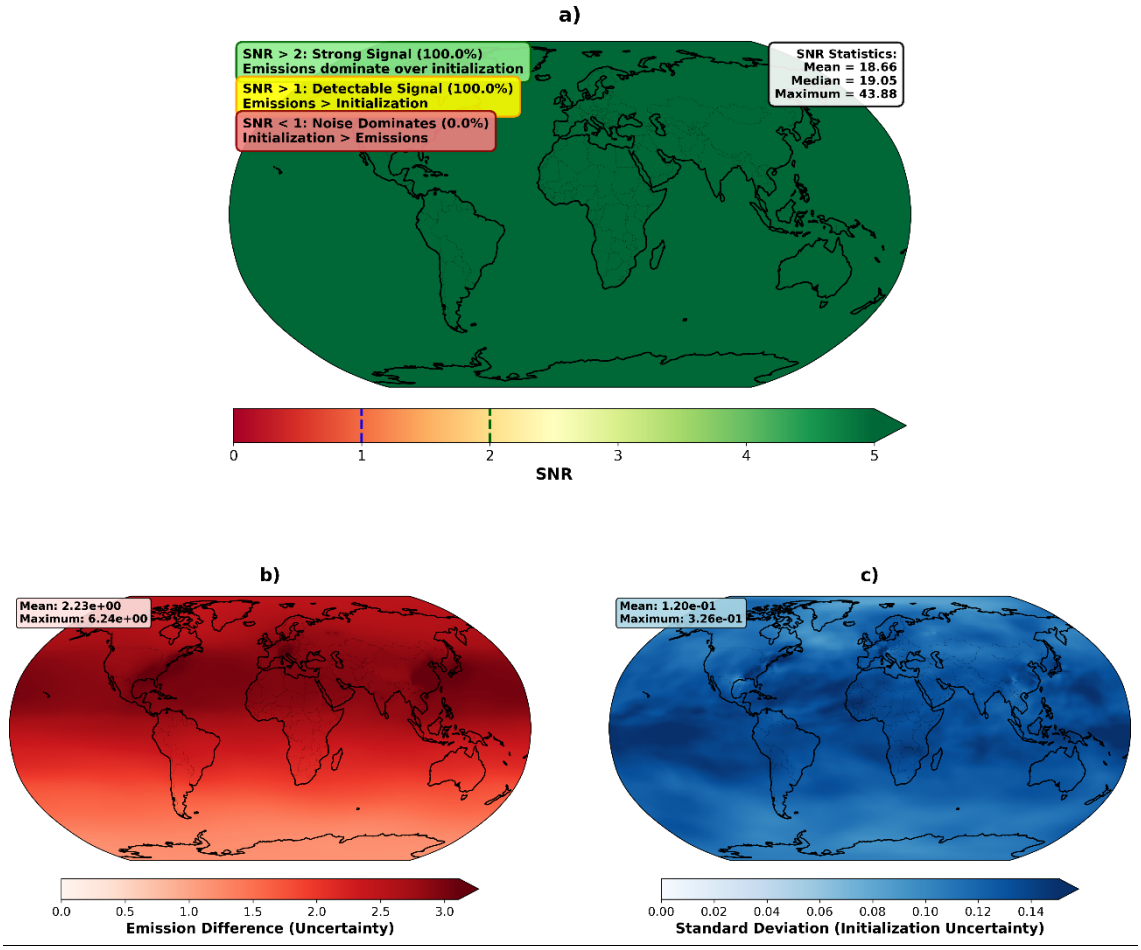


Figure E6. Signal to noise ratio analysis, emissions vs initialization time A) Signal to Noise Ratio (SNR): Emission sensitivity vs initialization uncertainty. B) Signal: Emission sensitivity, absolute value from differences of all UB initializations and LB initializations. C) Noise: Internal variability, standard deviation from all the initializations.

These new analyses directly respond to your request to better identify the main sources of uncertainty and to clarify whether discrepancies in surface concentrations and deposition patterns are dominated by model physics, oxidant fields, or emissions. We have added a new subsection in the Discussion summarizing these findings and explicitly stating that, at this stage, uncertainties in emissions and in oxidant fields are larger than those introduced by the semi-offline coupling.

Specific Comments by reviewer #1

We are very thankful reviewer #1 pointed out some specific parts in our manuscript which should be corrected and/or improved. We also appreciate and agree with your comments addressed these individually as follows.

Abstract: “ICON-ART PRIEST” should be written out in full the first time it appears.

In the abstract it is now read as:

(L1 – L3) “This study presents the ICON-ART (ICOsahedral Non-hydrostatic model framework with Aerosol and Reactive Tracers) PRIEST (PFCA Reactions In Earth System Transport) model extension, developed to simulate the transport and transformation of Per- and Polyfluorinated Substances (PFAS) in the atmosphere.”

Lines 60–73: This paragraph is confusing. It is unclear whether it refers to updates or to the previous version of the ICON-ART PRIEST model. The authors seem to describe ICON-ART PRIEST as a new model, but placing this paragraph here is confusing. The updates should instead be mentioned after line 76.

The paragraph was restructured to:

(L61 – L76) “To address these complex interactions, we developed PRIEST, an extension to the ART component implemented in the ICON model framework. ICON-ART PRIEST introduces aqueous-phase chemistry to simulate the adsorption and partial dissolution of gaseous-phase compounds in atmospheric water droplets (following Henry's Law). These compounds are redistributed as aerosols, leading to subsequent wet deposition. This extension improves the representation of PFCA precursors' transformation, transport, and scavenging within the atmosphere respecting previous modeling efforts. ICON-ART PRIEST also improves the spatial resolution to approximately 105 km^2, finer than previous global efforts using 4 x 5 degrees. We integrate an up-to-date, temporally and spatially resolved emission model (POPE) which includes PFCAs and precursors considering different compartments including industrial production, consumer product usage and disposal, and airport firefighting exercises. Additionally, POPE accounts for emissions to water bodies and incorporates air-water partitioning. Previous studies have emphasized the importance of atmospheric precursors in establishing the global burden of these compounds (Wallington et al., 2006; Yarwood et al., 2007; Thackray et al., 2020). In this regard, emissions of 8:2 fluorotelomer olefin (8:2 FTO) and 8:2 fluorotelomer iodide (8:2 FTI) are derived from 8:2 fluorotelomer alcohol (8:2 FTOH) emissions according to the criteria established by Thackray et al. (2020). Specifically, 48 % of the total emissions are attributed to 8:2 FTOH, an equal fraction to 8:2 FTO, and 4 % to 8:2 FTI, based on Wang et al. (2014); Prevedouros et al. (2006). Emissions are also included for PFOA and PFNA (the primary PFCA products) instead of only for the precursor compounds (Wallington et al., 2006), which allows us to calculate the total burden of these compounds from emissions and releases.”

(L77 – L79) “PRIEST’s gas-phase reaction mechanism is based on Thackray et al. (2020) but is further extended with 22 aqueous-phase reactions (Table B3), and adopts a fully online-coupled approach that simultaneously resolves meteorology and global-scale chemistry.”

(L80 – L82) “Through the evaluation of ICON-ART PRIEST, we examine how the simulations adjust with observed atmospheric concentrations and wet deposition patterns across different regions, helping identify potential sources of uncertainty and areas for future improvement.”

Section 2.2.1: As I mentioned in my major comments, this monthly OH estimation may be inappropriate, given the connections between OH and other species.

We appreciate you raising this important point regarding the consistency of OH estimation. We acknowledge that using monthly fields with a superimposed diurnal cycle simplifies the complex, instantaneous coupling between OH and other species (such as NOx and VOCs). However, we believe this approach is appropriate for the specific objective of this study because of two main reasons.

Starting by the timescales of PFCA precursors lifetime, such as 8:2 FTOH, 8:2 FTO, and 8:2 FTI on the order of weeks (approximately 10 – 30 days). They "integrate" exposure to OH over long periods, so their global burden and transport are determined by that integrated oxidative capacity of the atmosphere during that period, rather than instantaneous fluctuations in local chemistry. Therefore, the average oxidative capacity matters more than the exact instantaneous correlation between OH and other reactants at a specific second.

On the other hand, the implemented OH scaling method based on incoming solar radiation, improved the OH estimation preventing the recurrent night oxidation of precursors, which would be not physically consistent.

We recognize that simple monthly means represent a limitation in our modeling approach. Our method of scaling monthly OH fields by real-time solar radiation specifically addresses this by imposing a realistic diurnal cycle, ensuring that oxidation only occurs when photochemistry is active. Section 2.2.1 has been updated to explicitly acknowledge this limitation and justify why it remains valid for simulating long-lived PFCA precursors.

(L151 – L156) “While we acknowledge that this offline approach simplifies the instantaneous covariance between OH and short-lived drivers like NOx, it provides a computationally efficient approximation of the atmosphere’s oxidative capacity. Given that PFCA precursors (e.g., 8:2 FTOH, 8:2 FTO, and 8:2 FTI) have atmospheric lifetimes on the order of weeks (Young and Mabury, 2010; Thackray et al., 2020; Wallington et al., 2006), their transport is driven by integrated OH exposure rather than rapid chemical fluctuations. Therefore, scaling monthly climatological fields by instantaneous solar radiation preserves the necessary diurnal bounds without requiring mandatorily a fully coupled online chemistry scheme.”

Line 240: The data link is not available.

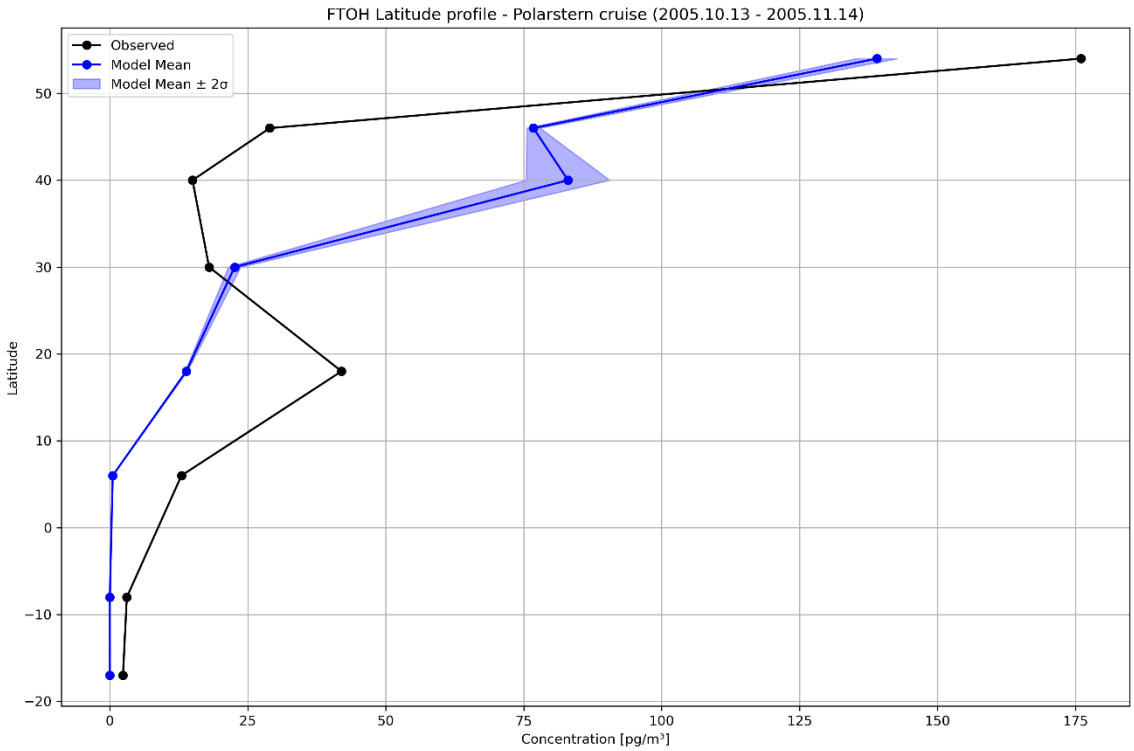
We appreciate you pointing out that the link was unavailable during the review period. However, we have double-checked the CAM-Chem data link, and it is now working properly. The last access date has been updated in the text.

(L250 – L252) "For this purpose, data from the Community Atmospheric Model with Chemistry (CAM-chem) was obtained (https://rda.ucar.edu/datasets/ds313.7, accessed: December 12th, 2025) (Lamarque et al., 2012; Tilmes et al.,2015; Emmons et al., 2020)."

Figure 6: Error bars are necessary to better understand the zonal variability.

We thank you for this helpful suggestion. We agree that visualizing the variability is crucial for interpreting the zonal mean results.

To address this, we have updated Figure 6 to include a shaded blue area surrounding the model mean line. This shaded region represents two standard deviations (2σ) of the model data over the sampling period. We believe this addition effectively illustrates the meridional variability and model uncertainty.



The caption was modified to:

Figure 6. 8:2 FTOH latitudinal profile of atmospheric concentrations [pg/m^3]. Observed data (black) vs. Model (blue line). The shaded blue area indicates the model variability, defined as ± 2 standard deviations calculated over the sampling period.

Once again, we thank you sincerely for your insightful comments. They have helped us to clarify the physical consistency of our setup, to better articulate the limitations of the current semi-offline approach, and to substantially strengthen the uncertainty and sensitivity analysis in the revised manuscript.

Kind regards,

Hiram Meza

on behalf of all co-authors.

Authors point-to-point responds reviewer comment #2 to egusphere-2025-2289

Please find the author's responses in black below the reviewer's comments in blue. Changes in the manuscript text are shown underlined.

First, we want to thank reviewer #2 very much for the thoughtful and honest assessment of our work, and for recognizing both the importance of the PFAS problem and the challenge of evaluating a model-development paper at this early stage.

Reviewer #2 main concerns: "That it is apparent from Figures D1 and D2 that the model is not capable of reproducing the observed spatial variability of PFAO and PFNA. Given the simplified mechanism, uncertainties in global emission inventories, potential mismatches between chemical fields introduced by the use of the CAM-chem model for initialization of atmospheric oxidants, as well as limited observations for model validation, it is unclear what causes these mismatches and what steps could be undertaken to improve simulations. Given that this is a model development paper, I am not sure how to properly weigh these against each other or to suggest a more in-depth study to investigate the sources of uncertainty in model results."

Regarding the mismatch between simulated and observed spatial variability of PFOA and PFNA, we now make much clearer that several factors contribute: (i) large uncertainties in global PFAS emissions, (ii) the simplified PFAS mechanism, (iii) the semi-offline use of CAM-chem oxidant fields, and (iv) limited observations.

To address this, we have added a new set of short ensemble simulations in which we vary POPE emissions (Upper/Lower Bound and Best Guess), oxidant fields (scaling OH and RO_2), and initialization dates. From these, we compute relative differences, ANOVA and permutation tests, and a Signal-to-Noise ratio. The results (now summarized in a new appendix) show that uncertainties in emissions and oxidants clearly dominate over internal model variability, which directly answers your concern about what drives the mismatches and where improvements should focus. A detailed description and analysis can be found in our answer to reviewer #1 as most of the raised concerns by reviewer #2 overlap.

We also have expanded the manuscript by adding a new subsection (L511) 4.5 Sensitivity and uncertainty tests. There, the new suit of eleven simulations and multiple diagnostics (RMD, ANOVA, paired permutation tests, linearity, and signal-to-noise analysis) and results are described.

In line with reviewer #1's comment, we also clarify the treatment of CAM-chem oxidants: NOx, OH, HO_2, RO_2, H_2O and VOCs from CAM-chem are used as prescribed monthly-mean background fields only; they are not transported by ICON, and only PFAS species are prognostic tracers. This avoids overlapping dynamical cores and ensures that conservation in ICON applies to the transported PFAS tracers. At the same time, we explicitly discuss the limitations of this semi-offline setup and outline a planned future version with a more interactive treatment of RO_2 and oxidant chemistry.

Specific comments by reviewer #2

In line with Reviewer 1's comment, the authors should explore ways to minimize the identified mismatch.

We completely agree with your comment. In the revised manuscript we now quantify and rank key uncertainty sources to directly inform them. The new experiment design explicitly separates (a) oxidant sensitivity from (b) emission uncertainty and (c) internal variability. This has been attended following the first reviewer recommendation and described in the point-by-point section dedicated to his first mayor concerns.

Whenever possible Figures should communicate uncertainties/ variation in the data beyond bar-plots (especially if n=2, which would merit just plotting point data). For higher n, boxplots or distribution plots would be appropriate

We agree and have revised the visualization strategy accordingly. In the revised manuscript we prioritize showing distributions (or individual points) rather than only aggregated bars where sample sizes are small (Figures 2 – 4). Following the same principle, we replaced any bar-only plots with (i) point plots when n≈2, and (ii) box-style summaries when n is larger, and ensure captions specify what is shown (median, whiskers, n). Also, for the latitudinal profile we now include variability around the mean: Figure 6 has been updated to include a shaded envelope representing ±2σ around the model mean, improving interpretability of meridional variability and uncertainty.

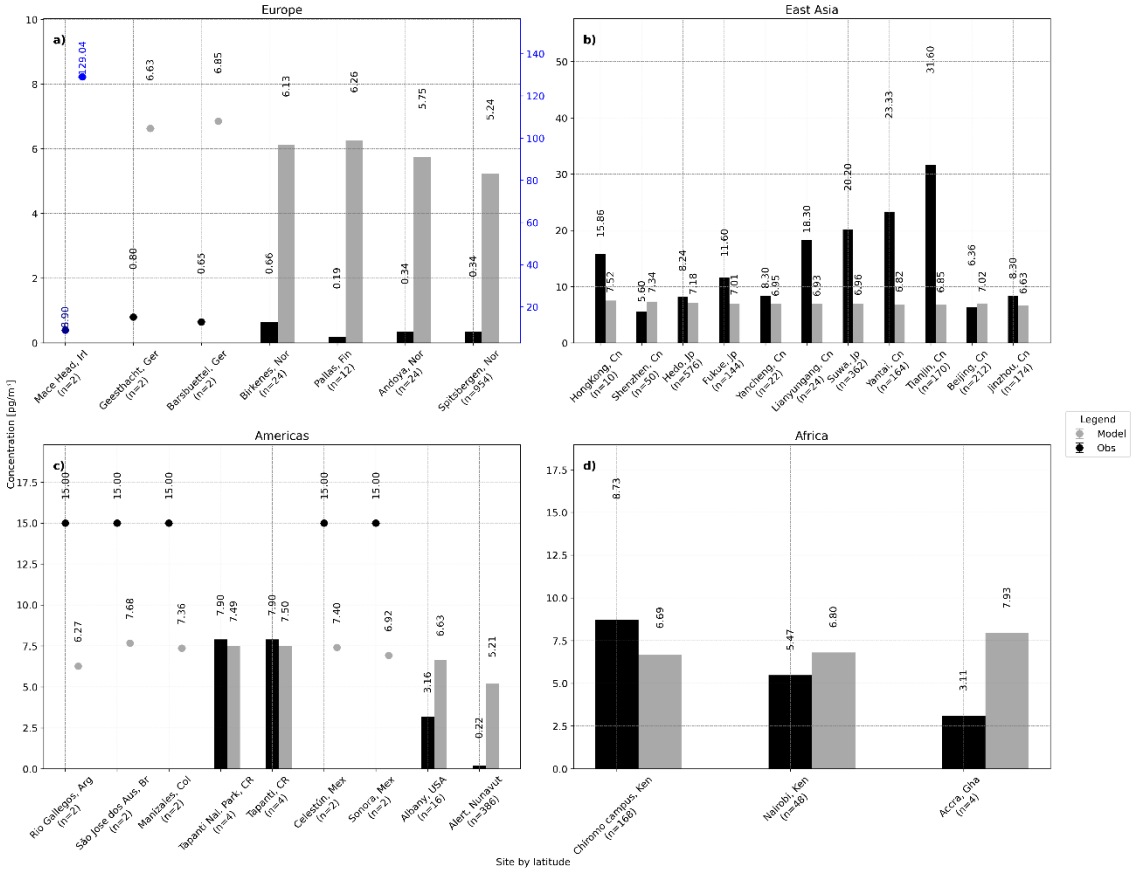


Figure 2. Observed and simulated atmospheric PFOA concentrations [pg/m3] in a) Europe, b) East Asia, c) Americas and d) Africa. Observed (black), modeled (gray) and number of observations (down the site name). Panel (a) includes a secondary right-hand axis (blue) for the Mace Head site, due to its large magnitude values.

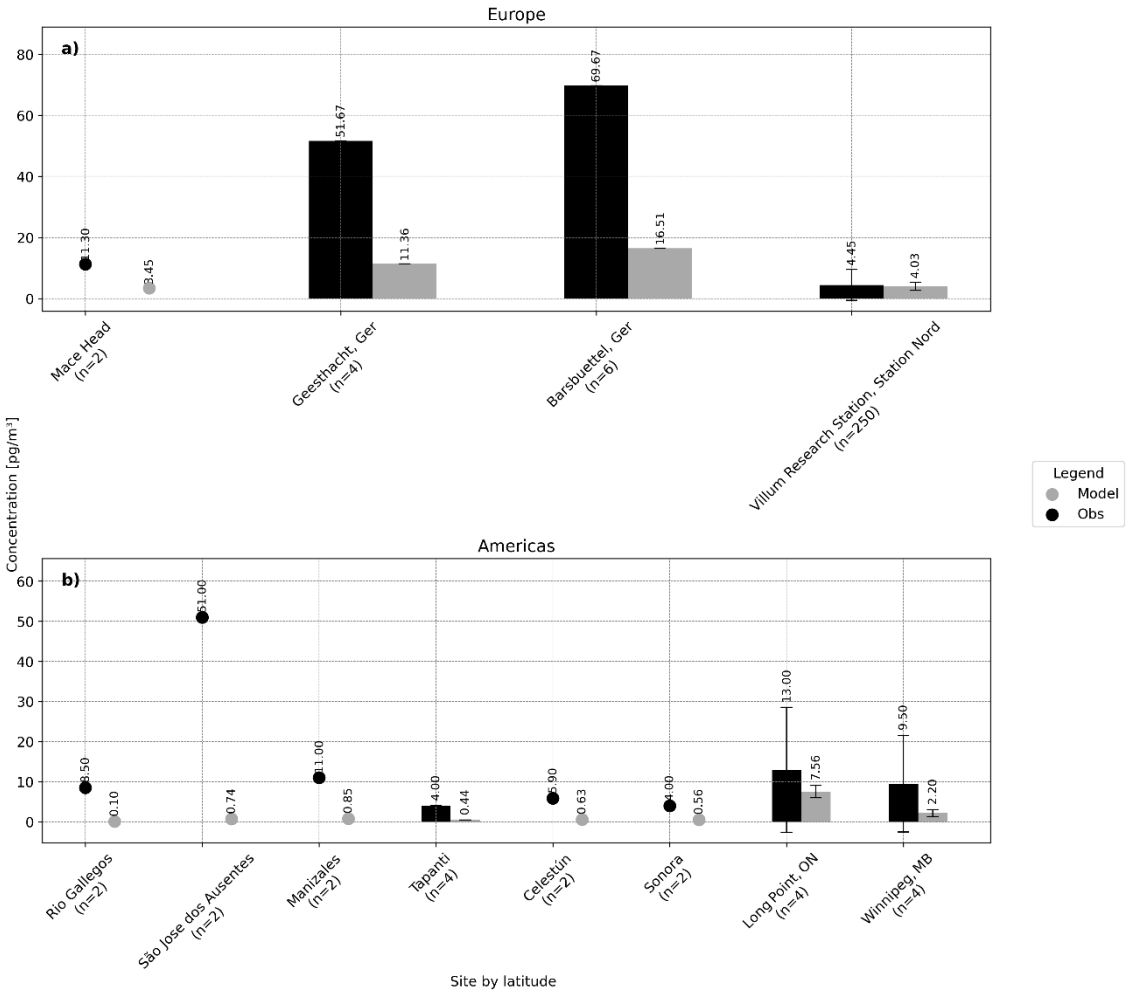


Figure 3. Observed and simulated atmospheric FTOH concentrations [pg/m3] in Europe and the Americas. Observed (black), modeled (gray) and number of observations.

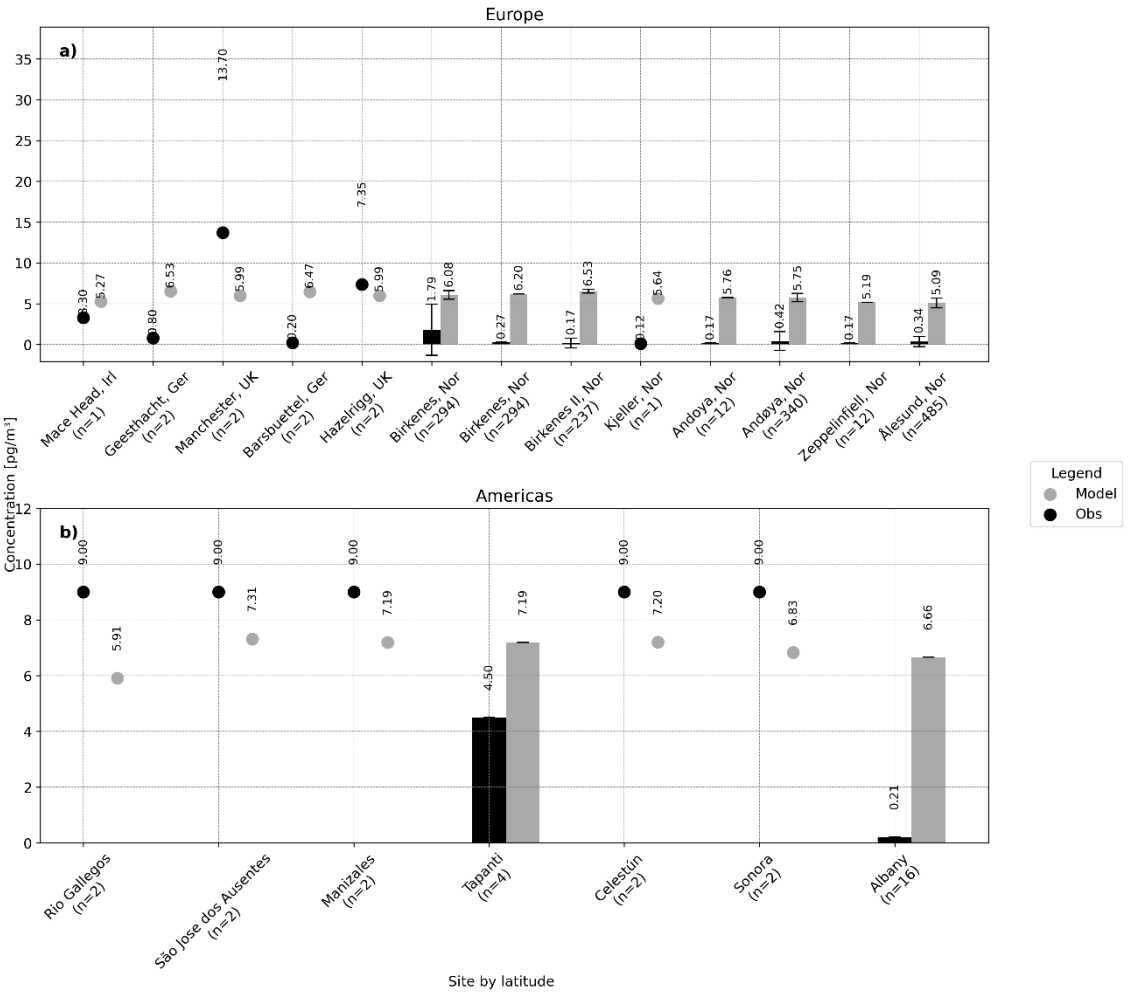


Figure 4. PFNA observed and simulated atmospheric concentrations [pg/m3] in Europe and the Americas. Observed (black), Modeled (gray). Number of observations next to site.

Figure 2: the different scales with change in color in Figure 2 are confusing and should be highlighted in caption (or otherwise changed)

We take your comment very thankfully and totally agree. In the revised manuscript we explicitly flag the scale change in the caption and adjust the figure presentation to remove ambiguity to:

"Figure 2. Observed and simulated atmospheric PFOA concentrations [pg/m^3] in a) Europe, b) East Asia, c) Americas and d) Africa. Observed (black), modeled (gray) and number of observations (down the site name). Panel (a) includes a secondary right-hand axis (blue) for the Mace Head site, due to its large magnitude values."

Code availability: It is inadvisable to solely rely on an institutional Git repository. The release should be tagged and submitted to an archive, such as zenodo to ensure preservation.

Thank you very much for this insightful recommendation in order to follow better practices in model development, we have now archived ICON-ART PRIEST v1.0 in Zenodo. Due to specific restrictions associated with the ICON-ART license, which is not fully public, the code is currently deposited in a private Zenodo record. The corresponding DOI is: https://doi.org/10.5281/zenodo.16615114.

The section "Code Availability" has been updated accordingly:

(L716 – L722) "Code availability. The ICON-ART model is open source and accessible via the ICON model website: https://icon-model.org/ under a BSD 3-clause license. The simulations presented in this study are based on a code version closely aligned with ICON release 2025.04: ICON partnership (MPI-M; DWD; DKRZ; KIT; C2SM) (2025). ICON release 2025.04. WDCC at DKRZ. https://doi.org/10.35089/WDCC/IconRelease2025.04. (ICON partnership (MPI-M and DWD and DKRZ and KIT and C2SM), 2025). The model components of the PRIEST extension (v1.0) non-official version that was used to produce the results of this paper is available at https://doi.org/10.5281/zenodo.16615114 (Meza-Landero et al., 2025). Certain model components used in this work are not fully open-source, but can be provided upon reasonable request to the corresponding author."

Once again, we are grateful for your careful reading and suggestions, which have helped us sharpen the discussion of uncertainties and make the model's limitations and next steps much more transparent.

Warm regards,

Hiram Meza

on behalf of all co-authors.

Authors point-to-point responds Referee Comment #3 to egusphere-2025-2289

Please find the author's responses in black below the reviewer's comments in blue. Changes in the manuscript text are shown underlined.

Explicit inclusion of aqueous/aerosol chemistry is an important advancement for PFAS specifically. Multiple aerosol modes with different behaviors is likely a reasonable representation, though there is little literature constraint on the PFAS side of this process.

We are very thankful because of the post from the editor regarding a reviewer #3, and for the careful evaluation and for recognizing the importance of explicit aqueous/aerosol chemistry and multi-mode aerosol treatment for PFAS modeling. Your comments align very well with those of Referees 1 and 2 and have helped us sharpen the analysis.

While I agree with Referee 1 that the treatment of non-PFAS reactants as semi-offline provided from a different model will introduce errors based on the mismatch of dynamics and chemistry, I believe these errors will be significantly smaller than the PFAS-specific uncertainties of the model.

Semi-offline treatment of non-PFAS reactants We agree with your assessment that using semi-offline non-PFAS reactants (from CAM-chem) introduces uncertainties between dynamics and chemistry, but that these are likely smaller than the PFAS-specific uncertainties at this stage. In the revised manuscript we clarify that:

NOx, OH, HO_2, RO_2, H_2O and VOCs from CAM-chem are used as prescribed monthly background fields only. Solely PFAS species are prognostic tracers transported by ICON-ART PRIEST; CAM-chem fields are not transported and have no momentum equation in ICON.

In response to your comments, together with reviewer #1 comments, we have replaced the following paragraph (original manuscript):

(L151 – L154) "To reduce computational costs, reactants are not transported in ICON-ART PRIEST. Only the products of reactions and the mixed aerosols are advected and turbulently transported. This simplification is justified because the reactants are typically short-lived, exist at concentrations too low to affect the overall budget, or maintain stable concentrations due to their abundance. Additionally, these reactants have already been transported by their original calculation model (CAM-chem)."

By (reviewed manuscript):

(L157-L165) "In ICON-ART PRIEST, reactants from CAM-chem (NOx, OH, RO_2, HO_2, and H_2O) are not transported as prognostic tracers. They are ingested only as prescribed monthly-mean background fields to compute PFAS reaction rates. The only species that are prognostically transported and deposited by ICON-ART PRIEST are the PFCA tracers (e.g. PFOA, PFNA, 8:2-FTOH, 8:2-FTO, 8:2-FTI) and the associated mixed aerosols, together with the meteorological state. Consequently, the CAM-chem-derived species have no continuity or momentum equations in ICON; there is no second dynamical core, and the conservation equations for mass and momentum solved by ICON remain unaltered. Because the CAM-chem fields are used in monthly-mean form, most sub-monthly dynamical variability associated with transport is already filtered out, so they act as slowly varying climatological oxidant fields, consistent with standard semi-offline couplings widely used in regional and global chemistry–transport modeling."

To address concerns regarding the RO_2 calculation and mass balance, we agree that OH, NOx, HO_2, RO_2 and VOCs are chemically coupled in reality, and it is a pressing issue that should be addressed in the near future to improve the mass balance consistency.

In the current PRIEST version:

CH_4, C_2H_6, and C_3H_8, as well as OH, HO_2 and NOx, from CAM-chem are used as background concentrations to diagnose RO_2. These background species are not transported or chemically updated within ICON. Hence, as background fields, they do not directly affect the internal mass conservation of transported PFAS tracers in ICON-ART PRIEST.

This has been also clarified in the revised manuscript and limitations are also openly discussed.

(L281 – L284) "Then, calculated RO_2 from CAM-chem most abundant VOCs is prescribed as background fields. These fields are neither transported nor chemically updated within ICON and thus do not enter the internal mass budget of the transported PFAS tracers, as for the rest of the background concentration reactants. As a consequence, the approximate RO_2 diagnostic used here should not have a significant impact in the global mass conservation of PFCAs in PRIEST."

Our initial reasoning was that, since the VOCs and oxidants are not prognostic in ICON and only the PFAS species are transported and deposited, the global mass balance of PFAS would not be compromised by the approximate RO_2 calculation. However, we agree with you that from a chemical-mechanism point of view, using a simplified RO_2 diagnostic based on a subset of VOCs and prescribed OH/HO_2/NOx

is not ideal and breaks, at least conceptually, the strict chemical linkage among these species.

(L284 – L286) "Nevertheless, from a chemical-mechanism perspective, diagnosing RO_2 from a limited VOC subset and prescribed OH/HO_2/NO_2/NO fields breaks the strict chemical coupling that would ideally link VOCs with these compounds."

Outlined a concrete plan for improving RO_2 in a future PRIEST release.

We now explicitly state that RO_2 will be calculated interactively within an extended chemical mechanism in a future version of ICON-ART PRIEST, so that RO_2 production and loss are treated consistently with the VOC and oxidant fields. This will remove the current diagnostic approximation and ensure a fully self-consistent photochemical system.

(L287 – L289) "The offline diagnose of RO_2 limitation is acknowledged in the current PRIEST version, and it will be calculated following a fully online interactive approach in a future release. This will be achieved by incorporating the calculation into the gas-phase reaction mechanism (Sect.2.2.1), so that RO_2 production and loss are fully consistent with the VOCs and oxidant fields."

This echoes the point of both Referee 1 and Referee 2 that uncertainties and sensitivities are an important aspect of this stage of modeling and should be explored.

We also explicitly discuss this semi-offline choice as a current limitation and outline that a more interactive oxidant/RO_2 treatment is planned for future versions in the respective answer for RO_2 calculation in the second point of the first reviewer major concerns.

Uncertainties, sensitivities and variability In response to your and the other reviewers' requests, we have added a dedicated uncertainty and sensitivity analysis based on eleven additional simulations (short 2-year runs, first year as spin-up), this is described more precisely in the answer to the major concerns from the first reviewer and subsection "4.5 Sensitivity and uncertainty tests".

A striking difference between the model and observations (e.g. in Table 1) is in the degree of variability. The model is significantly less variable at a given site. Exploring how much of this can be explained by the use of monthly non-PFAS reactant concentrations, possible unresolved time/space-variability of emissions, or other reasons would be informative.

Regarding the reduced variability at a given site (Table 1), we now explicitly discuss that this is consistent with: the use of monthly oxidant fields, the model resolution, and unresolved sub-grid variability in emissions. We have added text to make this interpretation clear and to emphasize that resolving finer time/space variability in emissions and oxidants is an important avenue for future work: (L694 – L700) "The overestimation of atmospheric concentrations in remote areas indicates a need for improved modeling of transport and deposition processes. Such as incorporating in-cloud processes as ice nucleation and cloud condensation with mixed aerosols enriched with PFCAs. In contrast, underestimations in major urban centers indicate that the local emissions assumed by POPE may be too low, or that missing source categories and secondary formation processes are more significant than currently accounted for. Additional features, such as kinetics considering Secondary Inorganic Aerosol (SIA) formation, could also be beneficial to address both overestimation in low-emission areas and underestimation in densely populated or heavily industrialized locales."

(L707 – L709) "While the current ≈ 105 km^2 grid resolution is an improvement compared to previous global studies, higher spatial resolution is still needed. Local features and processes significantly affect PFCA concentrations in industrial and populated areas. A finer grid resolution would better capture local sources and weather patterns, in particular precipitation events."

I wonder if the PFCA model concentrations compared to observations are the total gas+particle phase? My inference is that they must be, but I think it's unclear in the manuscript.

The inference made by the reviewer is correct: the PFCA concentrations used for comparison with observations are total (gas + particle) phase. We now state this explicitly in the manuscript where the comparison is introduced: (L351 – L352) "For PFOA and PFNA, the modeled concentrations represent the total of gas and particle phases."

We thank you sincerely for your insightful comments. They have helped us to clarify the physical consistency of our setup, to better articulate the limitations of the current semi-offline approach, and to substantially strengthen the uncertainty and sensitivity analysis in the revised manuscript.

Kind regards,

Hiram Meza

on behalf of all co-authors.