**General Comments:** Review of "Balloon Observations Suggesting Sea Salt Injection into the Stratosphere from Hunga Tonga-Hunga Ha'apai" by Vernier et al. for publication in Atmospheric Chemistry and Physics.

The paper presents data from a balloon campaign in Brazil in August 2022, about 7 months following the eruption of the Hunga volcano in the south Pacific. Plume material from the eruption is observed in the balloon dataset consistent with ground-based lidar and satellite observations. Number concentrations and scattering ratios are observed on three flights, while separately filters are collected on a single flight. The high altitude volcanic plume is observed on all 4 flights. Some heterogeneity in the plume characteristics is noted, but in the main the plume is observed at the same altitude (roughly 17 - 27 km). Filter samples are captured on August 22, 2022 on a flight that tops out at ~21km altitude, well into the main part of the plume as observed on previous days. Controls on the filters allow analysis over three distinct altitude ranges. Filters are recovered and subjected to offline analysis including ion chromatography. The main result articulated in the paper is that there is compelling evidence for marine aerosol in the body of the volcanic plume. This is plausible because of the large amount of sea water that was lifted to the lower stratosphere by the eruption.

This is a challenging manuscript to evaluate, and I don't find it suitable in its present form but I think it can be improved.

First, a lot of the microphysical information about the POPC and COBALD measurements is buried in supplemental material, but this seems pretty important to interpretation of the later chemical results.

In Section S2 the POPC extinction is computed for different assumptions of the particle properties, with best agreement between the balloon observations and SAGE III/ISS obtained by assuming the refractive index of sea salt. This anticipates the later conclusion of the paper. The improved consistency between POPC and COBALD measurements is interesting, but I'm unclear on whether this is related simply to the change in refractive index assumed or also to a size correction (does the size distribution assumed in the calculation change from the first to second to third row in Figure S2?).

**Authors:**
We thank the reviewer for the constructive assessment of our work. We agree that the microphysical constraints provided by POPC and COBALD are important to the chemical interpretation. As per your suggestion, we will integrate the microphysical analysis into the main body of the manuscript to provide a more cohesive narrative.

### 1. *POPC Methodology and Refractive Index (RI).*

**R2 Comment: "**Line 246-247 and section S1 discuss that a size correction is needed for the POPC measurements, although it is not explained how this is done (there is a reference to a manuscript in preparation)."

"I'm unclear on how the size thresholds for the POPC measurements are supposed to be determined, though as Figure S1 shows I can understand that a given amount of material would have a different scattering depending on its composition."

**Authors:** Indeed, both the size correction and the extinction retrievals from the size distribution are critical steps in deriving extinction and backscatter coefficients from POPC data. Both steps are fundamentally dependent on the aerosol refractive index n. Specifically**:**

- The real part of the RI (n) is the primary driver here, as PSL, sea salt, and sulfate have negligible absorption components at these wavelengths.
- We will clarify that the RI is applied to both the size correction and the optical calculations used to generate Figure S2.
- The improved consistency between POPC and COBALD is primarily driven by this RI shift (moving from n=1.43 for sulfate to n=1.55 for sea salt), which better aligns the in situ data with SAGE III/ISS.

**Manuscript Revision:** We will move these methodological details from the Supplement to Section 2.2 prior to showing results from POPC.

### 2. *Technical Corrections (Tables and Calibration)*

**R2 Comment: "**There is also a reference in the S2 text to Table 3 that should be I think to Table S1."

**Authors:** The reviewer is correct. This was a typographical error. The reference will be corrected to Table S1. Additionally, we will add a text to the Supplement clarifying that the POPC size thresholds are determined using a 6-point calibration with known PSL sizes (0.3 to 10 µm), with the remaining 24 channels interpolated from these digital cutpoints. The size cutoff is shown in Figure R0 along the theoretical scattering efficiency values for PSL.

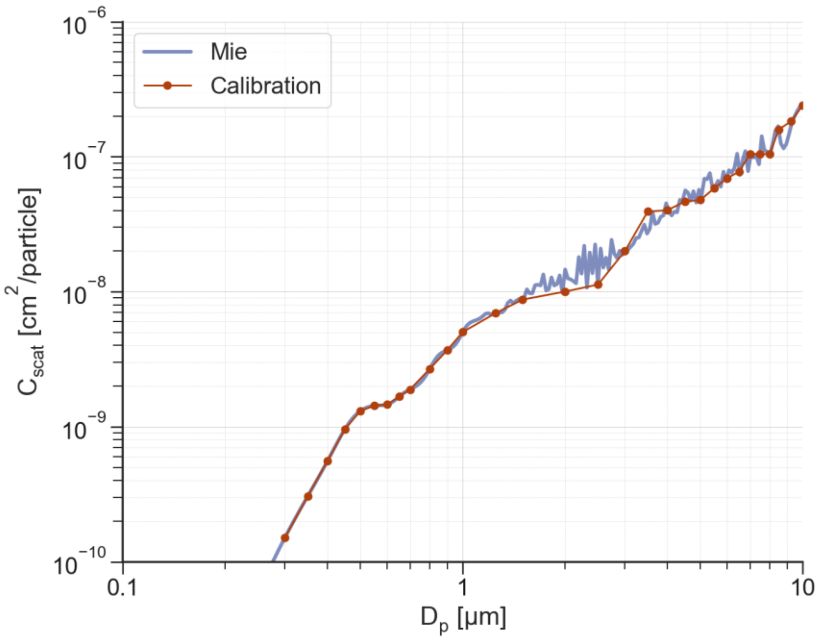


Figure R0. Size thresholds of the POPC along the scattering efficiency curve of PSL.

A technical paper describing in details the POPC is in preparation and should be submitted to AMT within the next few weeks.

### *3. Particle Size Distribution (PSD) and Effective Radius*

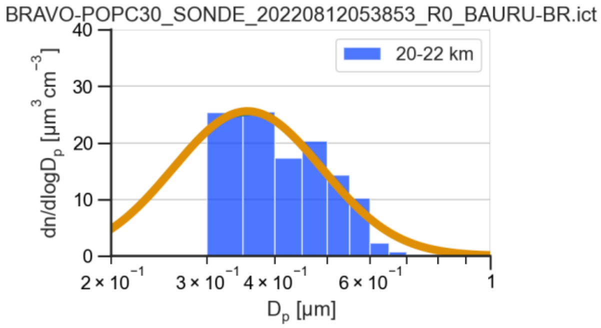
**R2 Comment:** “Finally, the particle size distribution in Figure S3 needs more information provided with it. Since you show the equation, what are the final parameters for the curve fit in S3?”

**Authors:** To resolve any ambiguity, the explicit log-normal fit parameters for the uncorrected size distribution shown in **Figure S3** are as follows:

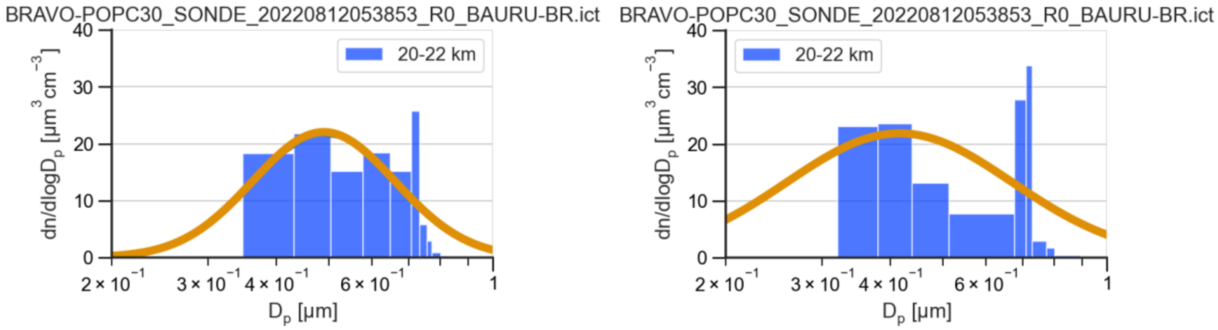
Total Number Concentration (cm$^{-3}$) = 8.79

Geometric Median Diameter (nm)=356.30

Sigma= 1.37



No correction



Sulfate correction

Sea Salt correction

Figure R1. Log-normal fits for the different corrected size distribution using Fig. S1

We also plan to add the following paragraph in section 2.2 that will explain how the correction is done.

The POPC size thresholds, initially determined during instrument calibration using Polystyrene Latex (PSL) spheres, are corrected for the target aerosol species using the theoretical scattering efficiency curves provided in Figure S1. To derive a corrected size for a specific composition (e.g., sea salt or sulfate), we identify the scattering efficiency value corresponding to a given PSL-calibrated threshold. A horizontal line is then drawn from this value to intersect the scattering efficiency curve of the target species. The diameter at this intersection point is then defined as the corrected size threshold for that species.”

**R2 Comment:** By a little guesswork I computed a number median diameter D_pg = 0.36 microns and width sigma_g = 1.25 that gave me a curve like Figure S3. From these parameters I infer an effective radius of 0.2 microns, which is half the value quoted from Selitto et al. 2024 on line 598 of 0.4 microns. I’m not sure where the discrepancy is, or if my guessed parameters are wrong, but this seems important to be explicit about. In short, please better integrate the microphysical measurements into the main body of the text.

**Authors:** We agree with the reviewer that the microphysical measurements are important to the interpretation of our chemical results. As suggested, we will be integrating these microphysical measurements directly into the main body of the text.

Regarding the discrepancy in the effective radius $r_{eff}$ noted by the reviewer:

a) **Verifying the effective radius calculation:** The reviewer's "guesswork" calculation of $r_{eff}$ ~ 0.2 µm is actually quite close to our refined analysis. The figure below extracted from a recent work by *Souza et al. (2025, in revision)*, which utilizes the same balloon dataset, shows ($r_{eff}$) profiles for the August 12 flight with values near 280 nm (0.28 µm). This calculation specifically accounts for the size correction applied to the POPC data based on the presence of sea salt, which significantly shifts the interpreted particle size compared to standard PSL.

b) **Comparison with satellite estimates (Boone et al., 2024):** While our $r_{eff}$ is lower than the 0.4 µm quoted from *Selitto et al. (2024)*, it remains consistent with other satellite-derived estimates. In the revised manuscript, we will add the following statement to address this:

> *"Relative to SAGE III/ISS, the peak $r_{eff}$ observed by the POPC is lower by ~30%, but still falls within the lower range of estimates from Boone et al. (2024), who found a $r_{eff}$ between 280–400 nm assuming a lognormal distribution with ACE-FTS and SAGE III/ISS. The fact that POPC counting efficiency is approximately 50% for $r > 150$ nm may also explain some of the discrepancies with SAGE III/ISS (Souza et al. 2025, in revision)."*

c) **Integrating microphysics in the main manuscript:** To improve the integration of microphysical analysis in the manuscript, we will make the following revisions:

1. Include the POPC size correction methodology in the main text to clarify how optical properties are derived from particle size measurements.

2. Add a direct comparison of scattering ratios between COBALD and POPC, as suggested by Reviewer 1.

3. Clarify the limitations of refractive index assumptions when deriving optical properties from POPC data. Since sea salt and sulfate aerosols have similar refractive indices, we cannot definitively distinguish between these components based solely on optical measurements. This ambiguity will be explicitly addressed in the discussion.

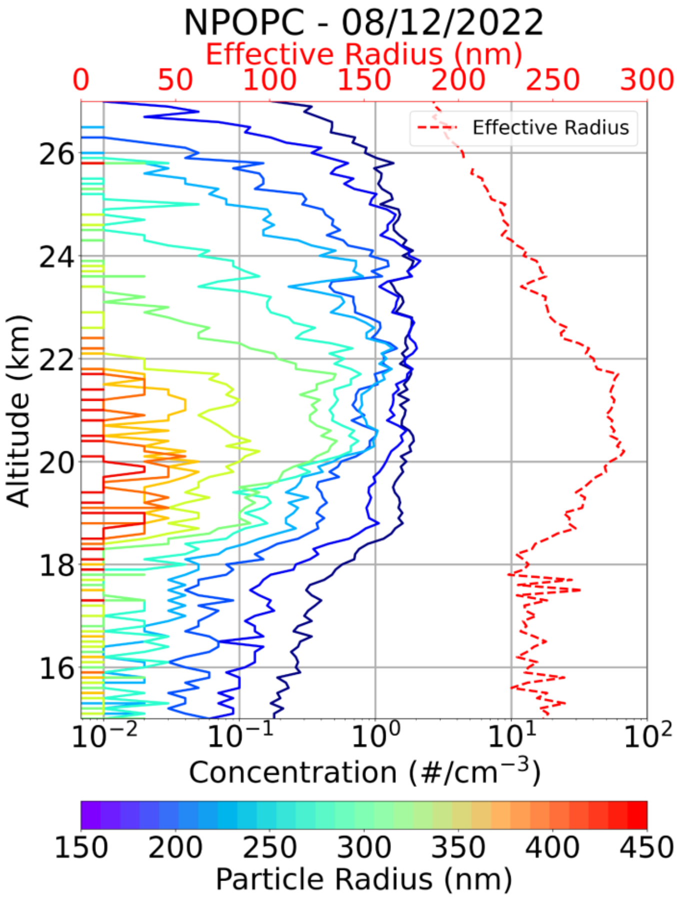


Figure R2. Extracted from Souza et al. (2025, in revision). It shows the vertical profile of particle and effective radius from the POPC flights on 8/12/2022

Souza, G., Vernier, J., Quintão, D., Biazon, B., Lopes, F., dos Santos, J., Pandit, A., Das, R., Liu, H., Knepp, T., Vernier, H., & Landulfo, E. (2025). *Sedimentation and growth of volcanic aerosols within the Hunga plume: Insights from unique tropical in situ and satellite measurements*. https://doi.org/10.22541/essoar.174241613.36494891/v1

https://essopenarchive.org/doi/full/10.22541/essoar.174241613.36494891/v1?__cf_chl_tk=.g0bdF74jG3W.FVwL2TsXlhu06fUe2ni_DpVnygczUI-1776868906-1.0.1.1-p4T4T8DRHkx2aPjKy5iYVOwycK1.uVY_.g.Ay6gds9U

**R2 Comment:** “Second, to the main conclusion of the paper, let me just start with the fact that there are a whole lot of hypotheses advanced for the plume composition from a single profile. I appreciate that the authors are not over-selling the result in the abstract, but the implications seem to be that there is almost no extant sulfate aerosol in the observed plume and that the composition seems to be dominated by marine aerosol and sulfate coated ash. This has profound implications for the modeling and remote sensing of the volcanic plume.

To confounding factors there is only a single sentence on the sample handling, lines 298-299, and a hint in section S3 of losses on the filters. I am unsure if there is any possibility for sulfate to have evaporated or otherwise been lost on the filters. Further explanation is needed. And to bring it full circle, can the microphysical properties be better integrated with this compositional analysis to strengthen the conclusion?"

**Authors:** We sincerely thank Reviewer 2 for their thoughtful and constructive critique of our manuscript. Their comments have helped us refine our interpretation and presentation of the data. Below, we address each concern in detail, incorporating revisions to the manuscript that strengthen our conclusions while acknowledging the limitations of a single-profile study.

**1. Addressing the Concern About "A Whole Lot of Hypotheses from a Single Profile."**

**Reviewer's Concern:**
***"There are a whole lot of hypotheses advanced for the plume composition from a single profile."***

**Authors:**
We acknowledge that our study is based on a single vertical profile of the HTHH plume. However, we emphasize that our conclusions are not drawn from this profile alone but are supported by:

- Inconsistency with the POPC/SAGE/COBALD comparison since the refractive index of sea salt and sulfate is similar.
- Consistency with established literature on volcanic plume chemistry (e.g., chloride depletion, gypsum formation, and ammonia neutralization).
- Stoichiometric and optical constraints that collectively paint a self-consistent picture**.**

**Key Revisions in the Manuscript:**

a) We will soften the language in the abstract and conclusion to avoid overstatement. For example:

*"Our measurements suggest that the plume composition includes significant contributions from marine aerosols and sulfate-coated ash, with soluble sulfate concentrations lower than typical for volcanic layers."*

b) We will add a paragraph in the Discussion (Section 4.1) to explicitly acknowledge the limitations of a single profile and the need for further validation, stating:

*"While our data provides compelling evidence for marine aerosol dominance and sulfate depletion in the sampled plume, we acknowledge that a single vertical profile cannot capture the full spatial or temporal variability of the HTHH plume. Future studies with additional in situ measurements (e.g., size-resolved aerosol composition, sulfate speciation) are needed to validate these interpretations and explore their global extent."*

### 2. Clarifying the Claim of "Almost No Extant Sulfate Aerosol."

**Reviewer's Concern:**
***"The implications seem to be that there is almost no extant sulfate aerosol in the observed plume."***

**Authors:**
We appreciate the reviewer's caution regarding this interpretation. Our IC measurements indeed show low soluble sulfate concentrations, but we do not claim that sulfate is absent. Instead, we propose that sulfate may be present in insoluble forms (e.g., $CaSO_4$) or coarse particles not fully captured by IC. This interpretation is supported by:

- **Stoichiometric Evidence:**
  The $Na^+$:$Cl^-$ ratios (0.98 at Position 2, 1.23 at Position 3, 0.76 at Position 4) and $Ca^{2+}$:$SO_4^{2-}$ ratios (up to 81.4 at Position 4) indicate chloride depletion and sulfate consumption via gypsum formation, respectively. These ratios are consistent with established mechanisms in volcanic plumes (Mather et al., 2003; Ayris & Delmelle, 2012).

- **ACE-FTS Discrepancy:**
  We will explicitly address the apparent discrepancy between IC and ACE-FTS in the revised manuscript (Section 4.7):

*"While our IC data suggests low soluble sulfate concentrations, ACE-FTS observations indicate persistent sulfate signatures at similar altitudes. This discrepancy may reflect the presence of insoluble sulfate phases (e.g.,* $CaSO_4$*) or coarse particles not fully extracted during filter analysis. Thus, the IC and satellite observations are not contradictory but reflect differences in measurement sensitivity and phase detection."*

### 3. Addressing Sample Handling and Potential Sulfate Loss

**Reviewer's Concern:**
*"To confounding factors, there is only a single sentence on the sample handling, lines 298-299, and a hint in section S3 of losses on the filters. I am unsure if there is any possibility for sulfate to have evaporated or otherwise been lost on the filters. Further explanation is needed."*

**Authors:**
We will expand our description of sample handling in the revised manuscript (Section 2.3) to address this concern by adding the following:

> "Filters were handled with sterilized instruments in a Laminar air flow chamber to minimize contamination. After recovery, the sampler was immediately transferred to a dry-ice container to limit volatilization and post-collection chemical reactions. Using sterile instruments, filters were then placed in sterile glass Petri dishes, sealed with aluminum foil, and maintained under cold-chain conditions until extraction and analysis. Regarding pressure conditions, the filters were not maintained at stratospheric pressure after sampling. As is standard practice in balloon-borne aerosol collection, the sampled particles equilibrate during descent within the closed sampler housing. No active gas purging was applied post-collection.
>
> While volatile sulfuric acid ($H_2SO_4$) can evaporate from filters, we argue that because of the stratospheric seawater injection during the eruption, the sulfur in the HTHH plume existed in a chemically stabilized form due to reactions with the injected seawater. The formation of sodium sulfate ($Na_2SO_4$), a non-volatile salt, is supported by our stoichiometric data ($Na^+$:$SO_4^{2-}$ molar ratios of ~2:1 at Position 3) and aligns with established literature on submarine eruptions (Colombier et al., 2023). Thus, sulfate loss due to volatilization is unlikely to fully explain the observed low soluble sulfate concentrations."

### 4. Integrating Microphysical Properties with Compositional Analysis

**Reviewer's Concern:**
*"Can the microphysical properties be better integrated with this compositional analysis to strengthen the conclusion?"*

**Authors:** We will add a new subsection (Section 3.3.1: "Integration of Microphysics and Composition") to explicitly link the microphysical and chemical datasets. E.g.:

> *"To 'bring it full circle,' we integrate the microphysical properties of the aerosols (POPC/COBALD) with their chemical composition (IC). The refractive Index needed to correct the size of the POPC data and derived optical properties to be compared with SAGE and COBALD suggest either the dominance or mixture of sea salt and sulfate. This optical constraint, combined with the $Na^+$:$Cl^-$ ratios and $Ca^{2+}$:$SO_4^{2-}$ ratios from IC, provides a self-consistent picture of a plume dominated by marine aerosol that may include sulfate-coated ash as observed in previous volcanic plumes (Vernier et al., 2013). The presence of a sulfate absorption signature is confirmed by ACE-FTS but cannot be quantified."*

## Minor comments:

**R2**: Line 79: suggest "…sulfate aerosols and caused…" as more correct

**Authors:** We thank the reviewer for this helpful suggestion. The sentence has been revised accordingly to improve clarity and grammatical correctness.

Revised text (Line 79):
"The abundant water vapor accelerated the transformation of $SO_2$ into sulfate aerosols and caused the plume to descend to 24–26 km within three weeks due to radiative cooling (Sellitto et al., 2022; Legras et al., 2022)."

**R2:** Line 154: "lower" should be "larger", shouldn't it? Entirely different meaning.

**Authors:**
We thank the reviewer for carefully noting this wording. The term "lower" is used intentionally here to indicate that the HTHH eruption produced a smaller stratospheric aerosol optical depth (sSAOD) compared to moderate eruptions, despite the injection of water vapor. To avoid any ambiguity, we will revise the sentence for clarity.

Revised text (Line 154):
"Despite injecting a relatively modest amount of $SO_2$ (~0.42 Tg) (Carn et al., 2022), it produced a significantly larger sSAOD than moderate eruptions observed since the late 2000s (Fig. 1b)."

**R2:** Line 201: Figure 2 shows zonal mean CALIOP products, right? I don't think this is stated explicitly, so I was confused when later you said data didn't cover Brazil.

**Authors:** We thank the reviewer for pointing out this lack of clarity. Figure 2 indeed shows zonal-mean CALIOP scattering ratio cross-sections, which were not explicitly stated in the original text. We will revise the manuscript to clarify this. The revised text will read:

"*Although the CALIOP data are averaged zonally, measurements within the South Atlantic Anomaly (SAA) region, particularly over Brazil, are excluded due to instrumental noise. As a result, the zonal means shown in Fig. 2 do not include data from this region, which prevents a direct comparison with the ground-based lidar observations at Bauru.*"

**R2:** Line 269: What is "Orbitrap"?

**Authors**: We thank the reviewer for pointing out the lack of definition. We will clarify the term "Orbitrap" in the revised manuscript, which will now read as:
"*The CHEM filter sampler is a sampling device that captures aerosol particles on filters for offline chemical analysis. It has previously been used to study organic aerosols from the troposphere to the stratosphere using high-resolution Orbitrap mass spectrometry (a Fourier-*

*transform mass analyzer capable of molecular-level chemical characterization) through offline analysis (Benoit et al., 2023, 2024)."*

**R2:** Line 299: What does "positioned into a dry to minimize" mean? I feel like some words are missing here.

**Authors:** We thank the reviewer for noting this lack of clarity. The sentence will be revised to correct the wording and explicitly describe the post-recovery handling procedure. It will now read as:
*"The extended sampling time maximized aerosol collection, allowing additional mass to be collected. The internal temperature of the sampler airflow ranged between 17 and 35 °C during the flight (Fig. 4c) and remained below 36 °C up to recovery. Immediately after recovery, the samplers were sealed in dry, airtight containers to minimize aerosol loss and chemical reactions."*

**R2:** Line 390: Please put altitudes on panels for Figure 5.

**Authors:** We thank the reviewer for this helpful suggestion. The altitudes corresponding to each sampling position will be added directly to the panels in Figure 5 of the revised manuscript for improved clarity.

**R2**: Line 402: I think you mean 18 - 21 km altitude here.

**Authors:** We thank the reviewer for catching this typo. It now reads *"Sodium ($Na^+$) and chloride ($Cl^-$) exhibited pronounced enhancements at Pos 4 (18–21.6 km), reaching concentrations of 1.21 ± 0.07 $\mu g\ m^{-3}$ and 2.47 ± 0.68 $\mu g\ m^{-3}$, respectively."*

**R2**: Line 430: Should be Table 6 and not Table 4.

**Authors:** We thank the reviewer for noting this error. The table reference has been corrected.

**R2**: Line 458: You mean "for >0.01 um" and not "ford"?

**Authors:** We thank the reviewer for catching this typographical error. The text has been corrected.

**R2:** Line 461: What is "oonic"?

**Authors:** We thank the reviewer for identifying this typographical error. The term "oonic" has been corrected to "ionic."