Volcanic Plume Aging During Passive Degassing and Low Eruptive Events of Etna and Stromboli Volcanoes

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Abstract Volcanic gases and aerosols emissions from passive degassing or low eruptive events are now included in most climate models despite large uncertainties still exist about their injection height and their temporal and spatial variability. The aim of this study is to quantify the evolution of the gas and aerosols inside volcanic plumes with high kilometric-resolution simulations. With online chemistry and aerosols, these simulations are carried out together with in situ measurements of aerosol and gas-phase properties to assess the impact of Etna and Stromboli volcanic plumes produced by passive degassing and regular Strombolian activity, respectively. Comparison between simulation and observations show that the simulation reproduces the main characteristics of the volcanic plume evolution and confirms that volcanic plumes produced by passive degassing or low eruptive events have a strong impact on cloud condensation nuclei (CCN) formation increasing the number of CCN by a factor of 5. It was also shown that depending on the plume location, the aerosols will act as CCN at different distance from the vent. In the marine atmospheric boundary layer, the aerosols will act as CCN at proximity to the vent (less than 50 km) because of strong condensation sink inhibiting nucleation. In comparison, in the free troposphere, aerosols will act as CCN far from the vent, at more than 200 km. To the best of our knowledge, this study using in situ measurements as well as subkilometric simulations is unique.

1. Introduction

Active volcanoes are one of the most dangerous natural hazard on Earth (e.g., Loughlin et al., 2015). In addition to lava flows and volcanic bombs, volcanoes can emit large amounts of volatile species in the atmosphere, from both eruptive or passive degassing events (Mather, 2015; Oppenheimer et al., 2014). Volcanic plumes are composed of several gaseous species (water vapor [H2O], sulfur dioxide [SO2], carbon dioxide [CO2], hydrogen sulfide [H2S], hydrogen chloride [HCl], ...) and aerosols (Allard et al., 2000). Since sulfur dioxide is one of the main precursor gases for new particle formation (Kerminen et al., 2018; Kulmala et al., 2000; Weber et al., 1995, 1999), volcanic plumes are also considered as an important source of nanometric-sized particles (Boulon et al., 2011; Sahyoun et al., 2019). They can additionally contain primary aerosols whose emission mechanism is not yet well understood (Mather et al., 2006; Roberts et al., 2018).

Depending on their injection height in the atmosphere, these volcanic gases and aerosols can have different impacts. For strong eruptive events, volcanic plumes can reach stratospheric levels where aerosols scatter and absorb solar radiation on large scales, inducing a net global cooling via the direct aerosol effect (Robock, 2000; Stenchikov et al., 1998). It was shown that large volcanic plumes can cause a decrease of the mean global surface temperature by tenth of degree over several years following eruptions (Robock & Oppenheimer, 2003, and reference therein). For low eruptive or passive degassing events, volcanic plumes are mostly confined in the troposphere, and their impacts on aerosol properties and on the regional radiation budget are still largely unknown (Mather, 2015; Sellitto et al., 2017). Depending on their size and chemical composition, these aerosols can modify the regional radiation budget by scattering and absorbing solar radiation and therefore have an impact on local meteorology (Mather, 2015) and climate (Haywood & Boucher, 2000). They can also interact with meteorological processes as they can act as a cloud condensation nuclei
(CCN) (Mather, 2015) or Ice Nuclei (Hoyle et al., 2011) and therefore modify the local radiative budget via the indirect aerosol effect. Deposition of acidic gases and aerosols can also affect terrestrial and aquatic environments (Delmelle, 2003). Volcanic emissions are also known to cause significant impacts on air traffic transport and can additionally cause damage to the airframe and/or engine components (Schmidt et al., 2014). Finally, nanometric size aerosols are dangerous for human health, as they can penetrate deep into the lungs and even into the bloodstream (U.S. Environmental Protection Agency; https://www.epa.gov). It is therefore essential to understand the evolution of gases and aerosols in the volcanic plume in order to better predict and therefore anticipate the associated risks.

The high spatial and temporal variability of the tropospheric volcanic plumes and the extreme condition encountered within the plumes (high temperatures, high gas-phase concentrations, …) make in situ observations difficult. Recent satellite-based observations open a new era in the observation of volcanic plumes (Queier et al., 2019; Theys et al., 2019), where chemical constituents, especially SO$_2$, can be measured thanks to passive ultraviolet, infrared, and microwave sensors on the satellites (see review of Carn et al., 2016). However, the SO$_2$ concentration is only measured by satellites once a day (mostly polar orbiting satellites) making the study of the evolution of volcanic plumes complicated.

At present, research efforts were mainly focused on the impact of large explosive volcanic eruptions on climate through numerical global simulations. They are summarized in the Intergovernmental Panel of Climate Change (2014) reports. In these studies, climatic impacts of volcanic eruptions are simulated through the formation of sulfuric acid aerosols from sulfur dioxide oxidation. These impacts are (1) an enhancement of the aerosol optical depth modifying the scattering radiation effect (Berthet et al., 2017; Kravitz et al., 2011; Khodri et al., 2017; Randles et al., 2013; Voldoire et al., 2013) and (2) an increase in the concentration of cloud droplets of small radius and hence cloud reflectivity (Quaas & Boucher, 2005). Despite the fact that they concern between 30% and 70% of the total SO$_2$ annual emissions (Halmer et al., 2002; Mather et al., 2003), only a few recent studies exist on the impact of volcanic plumes resulting from passive degassing or low-intensity eruptive events on the radiative budget on global scale (Mather, 2015; Schmidt et al., 2012).

Studying these volcanic plumes requires solving the atmospheric structures present in the free troposphere (FT) and in the atmospheric boundary layer, not achievable by current climate models that parametrized the boundary layer subgrid processes. Thanks to the increase of computational resources, regional modeling studies at high kilometric resolution with dynamic, chemistry, and aerosol interactions are possible, even if simulation length has to be limited to few days and on regional domains. To the best of our knowledge, no studies exist on modeling tropospheric volcanic aerosols aging at the kilometer resolution. In this context, this article aims to increase our knowledge on our ability to understand the main processes taking place within volcanic plumes and their potential impacts with kilometer-resolution simulations.

This study focuses on the evolution of sulfur dioxide and aerosol size distribution in the Etna and Stromboli volcanic plumes during two cases study periods in June 2016. Note that Etna and Stromboli volcanoes are two of the most active volcanoes in Europe. At that time, Etna was in passive degassing phase, whereas Stromboli was in a normal phase of strombolian activity corresponding to a low-intensity eruptive event. The main objectives of this paper are (1) to reproduce the observed spatial and temporal evolution of the volcanic plumes produced by Etna and Stromboli volcanoes using kilometer-resolution simulations, (2) to quantify the processes involved in the aerosol size distribution evolution inside the volcanic plumes, and (3) to quantify the ability of the aerosols contained in the volcanic plumes to act as CCN.

This paper is divided into five sections: Section 2 presents the campaign and the data available. The modeling framework is described in section 3. Section 4 presents the structure of the simulated volcanic plumes and their evaluation with the available data. Aging of the volcanic plumes and their effects on CCN are presented in section 5. Finally, the discussion and conclusions are given in section 6.

2. STRAP Campaign Around Etna and Stromboli, 15 and 16 June 2016

In order to understand the processes involved in the atmospheric volcanic emission rates and in the composition of the gas and particles mixture erupted from the vent, two STRAP campaigns were conducted (the acronym STRAP means “Synergie Transdisciplinaire pour répondre aux Aléas liés aux Panaches volcaniques” in french and can be translated in english to “Transdisciplinary collaboration to investigate volcano plumes risks”). One of them was made around Piton de la Fournaise, in La Réunion (Tulet et al., 2017) and another around Etna and Stromboli volcanoes, in Italy (Sahyoun et al., 2019; this study).
Figure 1. Track of the four SAFIRE-ATR42 flights: ETNA15 corresponds to 15 June 2016 flight around Etna (diamonds), ETNA16 to 16 June 2016 flight around Etna (dots), STRO15 to 15 June 2016 flight around Stromboli (squares), and STRO16 to 16 June 2016 flight around Stromboli (triangles). SO2 concentration measured airborne are in colors (ppb). Black lines correspond to the location of the two nested domains at 500 m horizontal resolution (section 3).

This study focuses on the latter campaign during which Etna volcano was in a phase of passive degassing and Stromboli volcano in a normal phase of strombolian activity, which are typical intereruptive conditions for both volcanoes. During those days, the volcanic plumes height remained below 4 km above the sea level, in the marine atmospheric boundary layer (MABL) for the Stromboli plumes and in the FT for the Etna plumes.

These two volcanoes are monitored throughout the year by the Istituto di Geofisica e Vulcanologia in Italy, providing access to daily emissions data of the main emitted gases: H2O, CO2, and SO2. In addition to this permanent observation, four flights were conducted during the STRAP campaign, using the French research aircraft SAFIRE-ATR42 equipped with a range of instrumentation for the study of aerosols and gas-phase properties (the acronym SAFIRE means “Service des Avions Franais Instrumentés pour la Recherche en Environnement” in french and can be translated in english to “the French facility for airborne research”). Full details of all instruments installed on the aircraft are provided by Sahyoun et al. (2019); however, for the purpose of this work, we will provide a short overview of the instruments that are used in this study. The flight trajectory and the measured SO2 concentration are presented in Figure 1. Two flights were located around Etna and two others around Stromboli. Flight tracks involved first doing a vertical sounding to locate the height of the volcanic plume, this was then followed by a number of transects crossing over the plume for distances up to 100 km. Further transects involved flying along the center of the plume.

The main data sets related to the gases and aerosols properties used in this work are listed in Table 1. The SO2 concentration is measured by ultraviolet fluorescence SO2 analyzer (Teledyne API). The number of aerosols are given by two condensation particle counters (CPCs): One measures aerosol concentration of particles with a cutoff diameter higher than 2.5 nm (Kupc et al., 2013) and another with cutoff diameter higher than 10 nm (Weigel et al., 2009). The size distribution is given by a custom-made airborne Scanning Mobility Particle Sizer spectrometer (SMPS) from 20 to 390 nm having more than 100 channels and by a GRIMM Optical Particle Counter from 0.25 to 2.5 μm having 30 channels. It should be noted that the aerosol inlet...
Table 1
Data Available Around Etna and Stromboli Volcanic Plumes During 15 and 16 June 2016 (Dp Are for Particle Diameter)

| Data                                      | Instrument | Location | Sampling period | Unit      |
|-------------------------------------------|------------|----------|-----------------|-----------|
| Emissions mass rate (H₂O, CO₂, SO₂)      | Analyzer   | Vent     | Daily           | kg s⁻¹    |
| SO₂ concentration                         | Analyzer   | Flights  | 1 s             | ppb       |
| Particle number concentration (Dp > 2.5 nm)| CPC        | Flights  | 1 s             | cm⁻³      |
| Particle number concentration (Dp > 10 nm)| CPC        | Flights  | 1 s             | cm⁻³      |
| Aerosol size distribution (100 channels from Dp = 20 nm to 1 μm)| SMPS      | Flights  | 84 s            | cm⁻³      |
| Aerosol size distribution (30 channels from Dp = 0.25 to 32 μm)| OPC       | Flights  | 6 s             | cm⁻³      |

installed on the aircraft has 50% sampling efficiency for 5 μm aerosol particles (Freney et al., 2014), so it is unlikely that particles much larger than this size were sampled.

3. Modeling Framework

The Mesoscale Non-Hydrostatic model (Meso-NH; Lac et al., 2018) is used to simulate the atmospheric processes involved in the Etna and Stromboli volcanic plumes evolution. Thanks to its fully coupled framework (small-scale dynamic, online chemistry and aerosols, radiative transfer, …), Meso-NH is able to represent atmospheric motions from the vent of the volcanoes up to hundreds of kilometers away from it and is able to simulate the atmospheric processes implicated in the volcanic plume evolution (Lac et al., 2018). Furthermore, Meso-NH has been successfully used to study volcanic plumes transport over South West Indian Ocean (Tulet & Villeneuve, 2011) and La Reunion Island (Durand et al., 2014).

The grid configuration, physical parameterization, and dynamical, aerosol, and chemical schemes and also the surface fluxes and emissions used in this study are described in the following sections.

3.1. Grid Configuration

The horizontal grid configuration contains three domains in two-way interactions: one domain at 2 km horizontal resolution and two others at 500 m horizontal resolution zoomed on both volcanoes (Etna and Stromboli; Figure 1). The vertical grid is common to both domains and has 70 stretched levels. The first level is at 10 m above the surface. The top of the domain reaches 22 km with a maximum vertical grid spacing of 1 km. The two nested domains at 500 m horizontal resolution and the 10 m vertical grid spacing above the surface are used to better represent the boundary layer processes around the volcano vents and hence the injection height of the volcanic plumes. The orography used is based on Shuttle Radar Topography Mission database at 250 m (Farr et al., 2007) (https://www2.jpl.nasa.gov/srtm/).

3.2. Physical Parametrization and Dynamic

The radiative scheme used in this study is the one used at the European Centre for Medium-Range Weather Forecasts (Gregory et al., 2010) including the Rapid Radiative Transfer Model parameterization for longwave radiation (Mlawer et al., 1997). The microphysics scheme is a single-moment bulk mixed-phase scheme that predicts the mixing ratio of five microphysical species: cloud water, rain, cloud ice, snow, and graupel (Pinty & Jabouille, 1998). A shallow convection parameterization based on mass-flux calculations (Bechtold et al., 2001) is used in the large domain. The turbulence parameterization is based on a 1.5-order closure (Cuxart et al., 2000). To have more mixing and diffusion of scalar variables in the boundary layer, the three-dimensional mixing length of Deardorff (1980) is used. Associated with an explicit Runge-Kutta temporal scheme, momentum variables are advected with a fifth-order weighted essentially nonoscillatory scheme (Lunet et al., 2017). Scalar and other meteorological variables (including chemistry and aerosol variables) are advected with a monotonic Piecewise Parabolic Method to ensure positive values (Colella & Woodward, 1984) with forward-in-time temporal scheme (Lunet et al., 2017). The dynamical time step is 4 s in the host domain and 2 s in the nested domains.

The initial and boundary conditions for meteorology are provided by the European Centre for Medium-Range Weather Forecasts operational high-resolution analysis with a horizontal and temporal resolution of 0.125° (≈13 km) and 6 hr, respectively.
3.3. Aerosol Scheme

The ORganic Inorganic Lognormal Aerosol Model (ORILAM; Tulet, 2005) is used to simulate aerosol processes, such as nucleation, coagulation, condensation, dry deposition, and sedimentation. Since anticyclonic and rainless conditions were present on the days of this study, no wet deposition scheme is activated. ORILAM is based on the modal aerosol dynamics modeling representing the aerosol size distribution as an assemblage of two distinct populations of aerosols called modes (Whitby & McMurry, 1997). As described in Schumann (2012), one mode combines nucleation and Aitken modes into a single Aitken mode (ait hereafter). This mode represents particles with diameters lower than 50 nm. The other mode is the accumulation mode (acc hereafter) and represents aerosols with diameters between 50 and 300 nm. No third mode is available in ORILAM; therefore, no coarse mode is used in this study. Based on calculations combining SMPS and Optical Particle Counter measurements made in the aircraft (not shown here), the errors due to the absence of a coarse mode are estimated on average to (i) less than 0.6% for the total aerosol number and (ii) less than 10% for the condensation processes. An error on the intermodal coagulation processes is also expected but is difficult to evaluate precisely. Including a coarse mode in ORILAM will be performed as part of future studies. The size distribution of the two modes is modeled by a lognormal distribution function defined by a particle number concentration ($N$), a median diameter ($D_p$), and a standard deviation ($\sigma_p$).

New homogeneous binary nucleation parametrization of Maattanen et al. (2018) has been implemented in Meso-NH and is used in this study. This parametrization is valid for a large range of sulfuric acid concentrations, ideal for studying volcanic plumes. Following a sensitivity study not shown here, the median diameter and standard deviation of the aerosol size distribution of the nucleated particle is taken to be 25 nm and 1.2, respectively. The condensation parametrization is treated following Binkowski (2003) and is adapted for the sixth moment. Sedimentation, dry deposition, and coagulation parameterizations used in this study are based on the initial work of Tulet (2005).

Initial parameters for the two lognormal modes ($N$, $D_p$, and $\sigma_p$) are obtained from SMPS measurements acquired during research flights. The initial parameters for the two modes are obtained when flights are outside the volcanic plumes (considered as background distributions) and are equal to $D_p = 40$ nm and $\sigma_p = 1.2$ for the mode ait and to $D_p = 60$ nm and $\sigma_p = 1.8$ for the mode acc. In this study and for numerical stability constraint, the geometric standard deviation of the two modes are kept constant during the simulation.

The initial and boundary conditions for aerosols concentration are taken from Model for OZone And Related chemical Tracers, Version 4 (MOZART-4) (Emmons et al., 2010) driven by meteorology from NCEP/NCAR reanalysis meteorological fields with a horizontal and temporal resolution of 0.5° ($\approx$ 50 km) and 6 hr, respectively. In the two days of simulation, meteorological conditions bring dust aerosols from north Africa. Although they can have effect on the condensation sink and therefore indirectly on the nucleation processes, they are only imposed as background aerosols initialized by MOZART-4. Their emissions are not taken into account explicitly.

3.4. Gas Chemistry

The gas-phase chemical mechanism used in this study is an updated version of the original Regional Lumped Atmospheric Chemical Scheme (Crassier et al., 2000). Four prognostic gaseous species are added for the purposes of the aqueous chemistry application (ammonia, sulfuric acid, hydroxyl radical, and formic acid), leading to 41 prognostic species in the gas phase (Leriche et al., 2013). In this configuration, sulfuric acid ($H_2SO_4$) available for nucleation and/or condensation on existing particles is directly formed by reaction between the hydroxyl radical (OH) and $SO_2$ and is therefore highly dependent on sunrise. The photolytic rates are calculated using the Tropospheric Ultraviolet and Visible radiation model (Madronich & Flocke, 1999). The Version 5.3 has been implemented recently in Meso-NH and is used in this study. The chemistry time step is equal to 1 s for both domains.

As for aerosols, the initial and boundary conditions for gaseous chemical species are taken from the same MOZART-4 data.

3.5. Surface Fluxes and Emissions

The surface-atmosphere interactions are grouped on a surface modeling platform called SurfEx (Surface Externalisée in French; Voldoire et al., 2017). The SurfEx platform used in this study includes the Interaction Soil-Biosphere-Atmosphere model (Noilhan & Planton, 1989), a land surface model to represent
biosphere fluxes, the Town Energy Balance model (Masson, 2000), to represent town fluxes, and the Coupled Ocean-Atmosphere Response Experiment parameterization of sea surface fluxes (Fairall et al., 2003). A sensible heat flux of 1,000 W m$^{-2}$ is imposed at the volcano's vents to better represent the injection height of the two volcanic plumes in comparison with observations.

Surface emissions of aerosol and chemical compounds are taken from the Emissions of atmospheric Compounds Compilation of Ancillary Data (http://eccad.aeris-data.fr/), which compiles the main emissions data sets available for the community. Anthropogenic emissions are provided by the monthly MACCity emissions data set (MACC/CityZEN EU projects) (Lamarque et al., 2010) with a horizontal grid resolution of 0.5° ($\approx$50 km). To represent biomass burning emissions, the monthly Global Fire Emissions Database, Version 3 (van der Werf et al., 2010) database was used with a horizontal resolution of 0.5° ($\approx$50 km). The biogenic emissions are modeled by Model of Emissions of Gases and Aerosols from Nature (Guenther et al., 2012) and was recently implemented in Interaction Soil-Biosphere-Atmosphere. In addition to these emissions, SO$_2$ and latent heat flux emissions are imposed at the volcano's vent based on daily SO$_2$ emissions: 2,160 to 3,283 kt day$^{-1}$ for Etna and 172 to 345 kt day$^{-1}$ for Stromboli, for 15 to 16 June 2016, respectively. At that time, there are no SO$_2$ emissions measurements at higher frequency.

4. Description and Evaluation of the Simulation With Available Observations
4.1. Volcanic Plumes Structure

The spatial distribution of the simulated volcanic plumes and the aircraft flights position are shown in Figure 2. The volcanic plumes locations are represented by the simulated SO$_2$ (isoline at 4 ppb) at a representative time of the flights, that is 15 June 2016 at 15 UTC for ETNA15 and STRO15 flights and 16 June 2016 at 8 UTC for ETNA16 and STRO16 flights.

Due to a rotation of the prevailing wind from East to the Northeast during these two days, volcanic plumes present different structures. For 15 June at 15 UTC (Figure 2a), Etna and Stromboli plumes are well separated. Etna plume is advected to the Southeast of the vent in the FT, while Stromboli plume is advected in both East and West directions due to vertical wind shear and is located in the MABL. Due to the turbulent mixing of the MABL, simulated SO$_2$ is more diluted in Stromboli plume than in the Etna plume. For 16 June at 8 UTC (Figure 2b), a part of the Etna and Stromboli plumes are mixed above the Stromboli volcano close to the emission; Etna plume propagates to the Northeast. When subsiding, the plume transport rotates in the direction of the Stromboli, which is advected to the Northwest. Both plumes are located in the MABL inducing a strong dispersion of the simulated SO$_2$. The simulated SO$_2$ is colocated with the position of the four flights (white dots in Figure 2) in terms of horizontal and vertical positions. Evaluation of the simulated chemical and aerosols fields in the aircraft will be made in the next sections.
Among the four flights, ETNA15 and STRO16 flights covered the longest distances (more than 200 km from the volcanoes vent) and are interesting for studying volcanic plumes aging processes. For this reason, the remaining discussion will focus on these two flights.

4.2. Sulfur Dioxide Concentration

For 15 June 2016 at 15 UTC (Figures 3a and 3c), vertical oscillations on simulated SO\(_2\) of Etna plume are visible close to the vent. This is a result of the presence of orographic waves reinforced by a stable atmospheric boundary layer at that time. Despite these orographic waves, the Etna plume, injected at 4 km, is advected to more than 200 km to the Southeast of the vent, at approximately 3,300 m above sea level (a.s.l.; in the FT). The width and thickness of the plume are approximately equal to 2 km and 500 m, respectively. SO\(_2\) concentration decreases from approximately 210 ppb close to the vent, which is on the same order of magnitude as that observed by Roberts et al. (2018) during another passive degassing events of Etna on October 2013, to roughly 10 ppb at 150 km, corresponding approximately to an horizontal loss rate of about 1.3 ppb km\(^{-1}\).

For 16 June 2016 at 8 UTC (Figures 3b and 3d), Stromboli plume is located in the MABL and is advected to the Northwest at a constant height (\(\approx 150\) m a.s.l.). Simulated SO\(_2\) varies from 200 ppb close to the vent to 10 ppb at 75 km, corresponding to an horizontal loss rate of 2.5 ppb km\(^{-1}\). Note that this loss rate is more important than Etna plume because of the turbulent mixing in the MABL and the water vapor content which is more important in the MABL (10 g kg\(^{-1}\)) than in the FT (4 g kg\(^{-1}\)).

The observed SO\(_2\) (Figures 4a and 4b; red line) fall within the bounds of the simulated values (Figures 4a and 4b; gray lines) except at some points for ETNA15 flight where the observed SO\(_2\) concentrations have higher values than the simulated one. The temporal evolution of the observed SO\(_2\) presents a smoother variability than the simulated ones (e.g., at 15 UTC on 15 June). For both flights, the simulation reproduces the peak of SO\(_2\) concentration measured by the aircraft, indicating the correct position of the simulated plumes. For ETNA15 (Figure 4a), the three main SO\(_2\) peaks are located close to the volcanos vent (Figure 4e).
measured SO$_2$ concentration increases as the aircraft approaches the volcanic injection height. Close to the volcano vent at 14hr15 UTC, the observed concentration of SO$_2$ is approximately 35 ppb at 2,800 m a.s.l. and increased to 80 ppb at 15 UTC when the aircraft reaches more than 3,000 m a.s.l. These peaks are well reproduced by the simulation with concentrations ranging from 40 ppb at 14hr15 UTC to 90 ppb at 15 UTC (within 10% of the observations). For STRO16 flight (Figure 4b), two SO$_2$ peaks are simulated close to the volcanoes vent. First SO$_2$ peak, at 7hr30 UTC, is reproduced within 10% of the observed values (80 ppb). However, when the aircraft approaches the volcano vent for the second time, at 9 UTC, simulated SO$_2$ concentrations show a peak which is not measured by the aircraft: Either the volcano’s SO$_2$ emissions are lower at this time (difficult to verify this without high-frequency observations of the volcanic emissions) or the aircraft is measuring outside the plume or the mixing of the two plumes (Figure 2b) is not well positioned in the simulation. It was shown that the Stromboli volcano experiences a low-explosive event approximately every 10 min (Blackburn et al., 1976), and the SO$_2$ flux can vary by a factor of 4 between two explosions (Burton et al., 2009). Simulated SO$_2$ emissions do not vary a lot during these 2 days of simulations (2 to 4 kg s$^{-1}$) and can also be the origin of this difference.

### 4.3. Total Aerosol Number

For ETNA15 flight (Figure 4c), the observed number of aerosols is mainly composed of aerosols with diameters between 2.5 and 10 nm (in diameter), as described in Sahyoun et al. (2019). The simulation does not represent this particle size because, as explained in the section 3, the simulated aerosol distribution is defined by only two modes: Aitken and accumulation, and the median diameter of these modes is too coarse to represent particle sizes with diameters lower than 20 nm. Another mode, the nucleation mode, would be needed to be able to properly represent these particles. Despite this numerical limitation, the number of simulated aerosols is comparable to that observed by the CPC (>10 nm) (blue line in Figure 4c) and the SMPS (green line in Figure 4c) which are well represented by the two simulated modes. The number of simulated (black line in Figure 4c) and observed (green and blue lines; Figure 4c) aerosols with diameter higher than 10 nm is present in less than 8% of differences. The maximum simulated and observed aerosol concentrations of aerosol with diameter higher than 10 nm is around 50,000 cm$^{-3}$. With the exception of a short period at 15 UTC when no observations data are available, the peaks in number aerosols concentration (Figure 4c) are well correlated with peaks in SO$_2$ concentrations (Figure 4a) for both observations and simulation.
Figure 5. In (a) and (b), the aerosol number size distribution \( \frac{dN}{d\ln(D_p)} \) [cm\(^{-3}\)] observed by the SMPS onboard the aircraft and simulated for the ETNA15 and STRO16 flights, respectively. Temporal evolution of the aerosol number size distribution \( \frac{dN}{d\ln(D_p)} \) [cm\(^{-3}\)] observed by the SMPS for both the (c) ETNA15 and (d) STRO16 flights and the difference between observations and simulations for (e) ETNA15 and (f) STRO16 flights in percent. Thick black lines in (c) and (d) represent the isovalue \( 10^3 \) and \( 10^4 \) [cm\(^{-3}\)]. Lowest panels show the temporal evolution of the distance of the aircraft from the vent (black line) and the altitude of the flights (gray dashed line) for both (g) ETNA15 and (h) STRO16 flights.

Unlike ETNA15, the number of aerosols observed in STRO16 is mainly composed of aerosols with diameters greater than 10 nm, which is comparable with the number of simulated aerosols. This is explained by the higher condensation sink in the MABL than in the FT (supporting information Figure S1), which tends to inhibit nucleation and confirms through simulations the hypothesis proposed by Sahyoun et al. (2019). The maximum aerosol concentration are localized close to the vent (Figure 4d), where SO\(_2\) concentrations are highest (Figure 4b): Whether at 7 UTC or 8hr50 UTC, aerosol concentrations exceed 20,000 cm\(^{-3}\). Variations in the number of observed aerosols are related to the aircraft’s sinuous trajectory, which had the objective of detecting the plume’s boundaries. This variability makes it difficult for the model to accurately simulate aerosol number concentration. At about 8hr40 UTC, an increase in the number of aerosols is observed but not simulated: This is explained by the fact that in the simulation, the aircraft is outside the plume (SO\(_2\) concentration < 4 ppb; Figure 4a). Near the volcano’s vent at 8hr50 UTC, the CPCs show a high concentration of particles despite low concentrations of SO\(_2\) being observed. As mentioned earlier, it can come from a change in the volcano regime or from a smoothing of the SO\(_2\) data by the instrumental time averaging.

Note that total simulated aerosol number is very sensitive to new particle formation from nucleation processes that can vary by a few orders of magnitude with respect to the nucleation parameterization (Maattanen et al., 2018). This can also explain discrepancies between simulation and observation.

### 4.4. Aerosol Size Distribution

Figure 5a and 5b show the observed and simulated distributions at all aircraft positions, the cutoff diameters of the observations is equal to 18 nm. Two modes are clearly visible in the observations (black line) and are
Figure 6. Spatial distribution of the simulated median diameter (nm; colors) at 15 UTC on 15 June 2016 at 3.3 km above sea level for mode ait (a) and mode acc (b). Black contours in (a) correspond to isoline $5 \times 10^5$ cm$^{-3}$ s$^{-1}$ for the nucleation rate and gray contours in (a) and (b) to aerosols number in per cubic centimeters. In (c), the evolution of the aerosol size distribution extracted along the volcanic plume (black squares on (b)), colors correspond to the distance from the vent in kilometers.

well reproduced by the simulation (green line) with mean diameters around 25 nm for mode ait and 80 nm for mode acc for ETNA15 flight. Due to condensation in the MABL, the aerosols on STRO16 flight are larger with median diameters equal to 30 and 90 nm, for modes ait and acc, respectively.

The evolution of these size distributions is illustrated as a function of time for observations (Figure 5c and 5d) and differences between observation and simulation (Figures 5e and 5f). It should be noted that the time resolution of the SMPS is 84 s and that of the simulation is 4 s for the hosted domain and 2 s for the nested domains. Time interpolation of simulated distributions is therefore necessary to compute differences between observations and simulations, this interpolation smoothes high-simulated aerosol concentrations of mode ait (red lines in Figures 5a and 5b). For ETNA15 and STRO16 flights, the observed distributions show high aerosol number concentration of mode ait near the vent (black curve; Figures 5c and 5d). Values exceed $10^4$ cm$^{-3}$. Around these points, the differences between observed and simulated aerosol number concentrations are important, more than 150%. This is mainly due to the temporal interpolation of the simulated distribution smoothing high concentrations. For ETNA15, there is a high concentration of aerosol far from the vent at about 14hr45 UTC, which is present in both the observations and simulations. At that moment, the aircraft turns around the volcanic plume (Figure 1) and most certainly passes inside the plume. Close to the vent of Stromboli, observation show also higher concentration of aerosols than simulation. This overestimation can be due to the volcanic emissions evolution, which is not taken into account in the simulation. With regard to STRO16 flight, there is an area with high aerosol number concentrations of mode ait (also visible in Figure 4d), at about 8hr40 UTC and 40 km from the vent, which is not reproduced by the simulation and which is most certainly due to the fact that the simulated aircraft is not exactly in the plume at this time. Between 50 and 300 nm, the simulated aerosol number concentration underestimates by 6% and 16% the observed aerosol number concentration for ETNA15 (Figure 5e) and STRO16 (Figure 5f) flights, respectively.

Despite differences in the number of aerosols observed and simulated, the simulation reproduces the temporal variability of SO$_2$ and aerosol size distributions, making the study on the aging of these two plumes valuable.
5. Volcanic Plumes Aging

The following section is interested in characterizing the differences in aging between a volcanic plume located in the FT (Etna volcano; ETNA15 flight) and one located in the MABL (Stromboli volcano; STRO16 flight).

5.1. FT: Etna

The impact of the volcanic plume on the spatial distribution of the simulated median diameter for modes ait and acc is clearly noticeable (Figures 6a and 6b). For mode ait, the median diameter is the smallest around 25 nm near the vent (Figures 6a and 6c), where the maximum nucleation rate is detected (black curve on Figure 6a). Along the volcanic plume, the aerosols of mode ait grow by coagulation and condensation until they reach a distribution with a median diameter around 35 nm (Figures 6a, 6c, and S2). The maximum number of aerosols is observed within the plume with concentrations above 20,000 cm$^{-3}$. Due to nucleation, the median diameter of mode ait is two times smaller in the plume than outside. However, for mode acc, aerosols are larger in the plume than outside. Close to the volcano vent (approximately 70 km), coagulation processes remain dominate as long as nucleation is significant. Then it is the condensation process that mainly increases the median diameter of the mode acc (Figures S1 and S2) from 60 nm to more than 90 nm away from the vent. Unlike mode ait, the number of aerosols in mode acc does not change along the track, mainly because condensation process, which is the dominant process implicated in the variation of the distribution of mode acc, have no impact on aerosol number.

5.2. MABL: Stromboli

As in Figure 6, Figure 7 shows evolution of the aerosol parameters and size distributions in the Stromboli volcanic plume localized in the MABL (STRO16 flight).

Condensation process which is effective up to 100 km from the vent causes the rapid growth of the median diameter of modes ait and acc (Figure S4). For mode ait, the median diameter doubles over 100 km, from 30 nm near the vent to more than 60 nm at 100 km from it (Figure 7a). For mode acc, the median diameter increases from 60 nm close to the vent to more than 90 nm at 100 km from it. For both ait and acc modes, the
aerosols generated by the plume are larger than those present in the surrounding environment. In this volcanic plume, nucleation processes are only present in the vicinity of the vent creating high aerosol number concentration of mode ait (25,000 cm$^{-3}$) in the first 20 km from the vent (Figures 7c and S3). Aerosol number concentration decreases along the volcanic plume due to intramodal coagulation passing from 25,000 and 3,500 cm$^{-3}$ close to the vent to less than 5,000 and 2,900 cm$^{-3}$ at more than 50 km from it, for mode ait and acc, respectively (Figure S3).

### 5.3. Impact on CNN

The impact of these two volcanic plumes on cloud microphysics is estimated through a calculation on condensation nuclei based on the work of Abdul-Razzak et al. (1998) and Abdul-Razzak and Ghan (2000). From the particle size distributions extracted along the two plumes (black squares in Figures 6c and 7c) and the gas-phase composition of the volcanic plumes (Figures S5 and S6), it is possible to calculate a number of aerosols acting as condensation nuclei for a given supersaturation, corresponding to $S_{\text{max}}$ in Abdul-Razzak and Ghan (2000). Three supersaturations (0.1%, 0.3%, and 0.5%) are chosen because they represent meteorological conditions present in fog and maritime cumulus that can be encountered in the Mediterranean sea, close to Etna and Stromboli volcanoes (Seinfeld, 2006). The evolution of CNN in both plumes (ETNA15 and STRO16) at these three supersaturations are shown in Figure 8.

Figure 8 shows that the aerosols present in the Etna and Stromboli plumes will act differently on the formation of CCN. As expected, the aerosols acting as CCN are always higher in the case of a volcanic plume (plain vs. dots lines in Figures 8a and 8b). The volcanic plumes lead to an increase in the number of potentially activable aerosols as CCN as it is mentioned in literature (Mather et al., 2003).
Table 2
Critical Diameter [nm] for the Three Supersaturation Considered (0.1%, 0.3%, and 0.5%) for Modes Ait and Acc

| Mode | ETNA15        | STRO16       |
|------|---------------|--------------|
|      | Ait           | Acc          | Ait           | Acc          |
| Critical diameter (0.1%) [nm] | 110.6         | 119.4        | 100.4         | 104.2        |
| Critical diameter (0.3%) [nm] | 53.2          | 57.4         | 48.4          | 49.8         |
| Critical diameter (0.5%) [nm] | 38.4          | 40.6         | 34.8          | 35.6         |

For the Etna volcanic plume (ETNA15; Figure 8a), a supersaturation of 0.5% must be achieved to see an effect on CCN formation. For this supersaturation, the number of activated aerosols increases with distance, with numbers going from 2,000 cm\(^{-3}\) near the vent to 8,000 cm\(^{-3}\) at approximately 200 km. This increase in the number of CCNs is mainly due to the growth of mode ait (Figures 6c and 8c). At more than 100 km from the vent, the aerosols have reached a diameter large enough to approach the critical radius (Table 2) and can thus be activated (Figure 8c). Near emission, less than 5% of the aerosols of mode ait are activated, while in the distance, more than 30% are activated. Mode acc does not vary a lot along the volcanic plumes and remains around the value near the vent corresponding to the background value. The further away from the plume, the larger the aerosols in mode acc have grown and the more they become but their number decreases, so that the number of activable aerosols in mode acc is relatively constant when moving away from the vent. The further away from the plume, the larger the aerosols in mode acc have grown and the more they become but their number decreases (Figure 6c). The number of activable aerosols in mode acc is therefore relatively constant when moving away from the vent and corresponds approximately to the absolute background activable aerosol concentration (≈1,500 cm\(^{-3}\); Figure 8a). For the supersaturations 0.1% and 0.3%, the critical activation diameters are too large (110.6 and 53.2 nm, respectively; Table 2) compared to the maximum median diameter of mode ait (35 nm) making the effect of these volcanic plumes on CCN formation negligible at these supersaturations.

For Stromboli (STRO16) volcanic plume, the number of aerosols close to the vent that can act as CCN is greater than far from it. This is a result of the high condensation sink where the aerosols of the mode ait grow very quickly in the MABL (Figure 7c), which make them activable as CCN close to the vent (lower than 20 km). Effect of aerosols on CCN formation is visible for supersaturation of 0.3% and 0.5% with the number of CCN exceeding 12,000 and 6,000 cm\(^{-3}\), respectively. The number of activated aerosols for mode acc does not vary a lot along the volcanic plume and is equal to 1,000 cm\(^{-3}\) which make their impact on CCN formation insignificant in comparison to aerosols in mode ait.

6. Discussion and Conclusion

This work provides a detailed analysis of the formation and aging of Etna and Stromboli volcanic plumes using a combination of numerical simulations and in situ observations. To the best of our knowledge, the observations available from the STRAP campaign as well as the simulations carried out using a 3-D atmospheric model with online chemistry and aerosol at subkilometric resolution for studying volcanic plumes are unique. The evaluation of the simulation with available observations showed that the numerical simulation successfully reproduces the position and structure of the volcanic plumes with respect to SO\(_2\) concentration. However, for aerosol particles (median diameter and number concentration), it was difficult to compare the data with the model. This was mainly a result of high numbers of aerosols present with diameters smaller than what is used in the model (10 nm). For aerosols larger than 10 nm, the simulation reproduces the number and size of particles in the modes ait and acc, with differences lower than 10% and 5% on the aerosol number and median diameter, respectively.

The size distribution of aerosols between volcanic plumes located in the FT for Etna (ETNA15) and in the MABL for Stromboli (STRO16) does not evolve in the same way making their potential effect on climate and environment different. The median diameter of mode ait increases more than 5 times faster in the MABL (≈0.3 nm km\(^{-1}\)) than in the FT (≈0.05 nm km\(^{-1}\)). The subtle balance between condensation and nucleation processes is responsible of this difference. Once formed by the oxidation of sulfur dioxide, sulfuric acid which has a very low vapor pressure will condense onto preexisting particles or participate in nucleating new particles. These competitive processes between condensation on preexisting aerosols and nucleation are known.
(Binkowski & Shankar, 1995; Campbell et al., 2014; Middleton & Kiang, 1978) but rarely well represented in chemical transport models and to our knowledge never for volcanic plumes studies. It is complicated to represent it numerically because it is extremely sensitive to the chemical species concentration involved in the production of sulfuric acid (SO$_2$, O$_3$, OH, …), the aerosol size distribution, and the properties of the air mass. Based on sensitivity experiments with 0-D simulations using the same routines as the 3-D simulations (Text S1), the impact of the air masses characteristics and injection height on the evolution of the aerosol size distribution is assessed. The air temperature, the air density, the water vapor content, and the background aerosol concentration significantly affect the competition between condensation and nucleation and therefore the production of new aerosols: (i) the higher the temperature or the higher the background aerosol concentration, the higher the condensation sink and (ii) the higher the density or the higher the water vapor content, the higher the production of sulfuric acid. If the condensation sink is large enough, nucleation will be inhibited even if large quantities of sulfuric acid are present. In the present study, due to higher temperature (Figure S7) and aerosol numbers and diameters for the mode acc, the condensation sink (Figure S8) is higher in the MABL than in the FT which tends to inhibit nucleation and causes aerosols to grow more rapidly in the MABL than in the FT. In addition, unlike the FT, the median diameter of the mode ait in the MABL approaches or even exceeds the median diameter of the surrounding aerosols. For future global or regional scales simulations of volcanic plumes, the injection height of volcanic plumes has to be considered with attention. Errors on the position of volcanic plumes will influence a lot the evolution of aerosol distribution, in particular their size and number, which can have an impact on cloud microphysics, local meteorology, and climate.

Independent of the location of the plume, median diameter of mode acc does not evolve enough to act significantly as CCN compared to a case where no plume is present. Strong differences on potentially activable CCN formation for both volcanic plumes are due to differences in the growth of mode ait between FT and MABL. In the FT, supersaturation of 0.5% has to be reached to activate aerosols as CCN. In that case, aerosols are mainly activated far from the vent, at more than 200 km from it: The median diameter of the mode ait grows sufficiently to reach critical diameter. In comparison, in the MABL close to the vent, at less than 20 km from it, median diameter of mode ait reaches critical diameter with supersaturation lower than in FT (0.3%). Our simulations illustrate that aerosols formed from volcanic plumes contribute to a fivefold increase in potential CCN number.

This result confirms that for both passive degassing or low-eruptive events in the FT, volcanic gases and aerosols have strong impacts on CCN concentration up to at least 200 km.

Potential impact of these kind of emissions on current climate models can be important as they affect the radiative via direct and/or indirect aerosols effect. Increases in this number of CCN will result in the increase in cloud droplet number and can therefore result in a higher surface cooling. However, to provide accurate guidance to climate modelers as in Fanourgakis et al. (2019), it is necessary to generalize these results by multiplying the simulated situations according to the intensity of degassing and weather conditions to obtain a statistical representation of the CCN formation on this kind of volcanoes. Furthermore, these kind of volcanic emissions are present throughout the year and will have a continuous impact on the radiative budget compared to less frequent explosive eruptions. It is therefore important to study volcanoes like Etna and Stromboli, which are strong gases emitters and therefore contribute, even during passive period of activity, to producing aerosols that may impact on atmospheric climate and pollution.

References

Abdul-Razzak, H., & Ghan, S. J. (2000). A parameterization of aerosol activation: 2. Multiple aerosol types. *Journal of Geophysical Research, 105*(D5), 6837–6844. https://doi.org/10.1029/1999JD901161

Abdul-Razzak, H., Ghan, S. J., & Rivera-Carpio, C. (1998). A parameterization of aerosol activation: 1. Single aerosol type. *Journal of Geophysical Research, 103*(D6), 6123–6131. https://doi.org/10.1029/97JD03735

Allard, P., Atulpa, A., Loyer, H., Carrot, F., Gaudry, A., Pinte, G., & Dongarr, G. (2000). Acid gas and metal emission rates during long-lived basalt degassing at Stromboli Volcano. *Geophysical Research Letters, 27*(8), 1207–1210. https://doi.org/10.1029/1999GL008413

Bechtold, P., Bazzle, E., Guichard, F., Mascart, P., & Richard, E. (2001). A mass-flux convection scheme for regional and global models. *Quarterly Journal of the Royal Meteorological Society, 127*(573), 869–886. https://doi.org/10.1002/qj.49712757309

Berthet, G., Igou, F., Catoire, V., Krasufof, G., Renard, J. B., Bourassa, A. E., & Guimbaud, C. (2017). Impact of a moderate volcanic eruption on chemistry in the lower stratosphere: Balloon-borne observations and model calculations. *Atmospheric Chemistry and Physics, 17*(3), 2229–2253. https://doi.org/10.5194/acp-17-2229-2017
Tulet, P., Di Muro, A., Colomb, A., Denjean, C., Duflot, V., Arellano, S., & Villeneuve, N. (2017). First results of the Piton de la Fournaise STRAP 2015 experiment: Multidisciplinary tracking of a volcanic gas and aerosol plume. *Atmospheric Chemistry and Physics, 17*(8), 5355–5378. https://doi.org/10.5194/acp-17-5355-2017

Tulet, P., & Villeneuve, N. (2011). Large scale modeling of the transport, chemical transformation and mass budget of the sulfur emitted during the April 2007 eruption of Piton de la Fournaise. *Atmospheric Chemistry and Physics, 11*(9), 4533–4546. https://doi.org/10.5194/acp-11-4533-2011

van der Werff, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., & van Leeuwen, T. T. (2010). Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997–2009). *Atmospheric Chemistry and Physics, 10*(23), 11,707–11,735. https://doi.org/10.5194/acp-10-11707-2010

Voldoire, A., Decharme, B., Pianezze, J., Lebeaupin Brossier, C., Sevault, F., Seyfried, L., & Riette, S. (2017). SURFEX v6.0 interface with OASIS3-MCT to couple atmosphere with hydrology, ocean, waves and sea-ice models, from coastal to global scales. *Geoscientific Model Development, 10*(11), 4207–4227. https://doi.org/10.5194/gmd-10-4207-2017

Voldoire, A., Sanchez-Gomez, E., Salas y Mélia, D., Decharme, B., Cassou, C., Sénési, S., & Chauvin, F. (2013). The CNRM-CM5.1 global climate model: Description and basic evaluation. *Climate Dynamics, 40*(9–10), 2091–2121. https://doi.org/10.1007/s00382-011-1259-y

Weber, R. J., McMurry, P. H., Eisele, F. L., & Tanner, D. J. (1995). Measurement of expected nucleation precursor species and 3500-nm diameter particles at Mauna Loa Observatory, Hawaii. *Journal of the Atmospheric Sciences, 52*(12), 2242–2257. https://doi.org/10.1175/1520-0469(1995)052<2242:MOENPS>2.0.CO;2

Weber, R. J., McMurry, P. H., Mauldin, R. L., Tanner, D. J., Eisele, F. L., Clarke, A. D., & Kapustin, V. N. (1999). New particle formation in the remote troposphere: A comparison of observations at various sites. *Geophysical Research Letters, 26*(3), 307–310. https://doi.org/10.1029/1998GL00308

Weigel, R., Hermann, M., Curtius, J., Voigt, C., Walter, S., Böttger, T., & Borrmann, S. (2009). Experimental characterization of the condensation particle counting system for high altitude aircraft-borne application. *Atmospheric Measurement Techniques, 2*(1), 243–258. https://doi.org/10.5194/amt-2-243-2009

Whitby, E. R., & McMurry, P. H. (1997). Modal aerosol dynamics modeling. *Aerosol Science and Technology, 27*(6), 673–688. https://doi.org/10.1080/02786829708965504