

Discussion comment on Renard et al. AMT-2015-2012 "LOAC: a small aerosol optical counter/sizer"

### Introduction

The small size and mass of the LOAC instrument, as well as its wide detection range for the particle size distribution and potential to distinguish particle nature makes it a highly attractive instrument for volcanology applications. Measurements of the volcanic aerosol emission are challenging due to the difficult-to-access terrain, and can be hazardous during eruptions. The lightweight LOAC offers both possibility for ground-based deployment at the volcano summit, and balloon-based launches through the volcano plume to quantify the aerosol emission. There is strong interest to measure volcanic aerosol sources due to their impacts on climate and atmospheric chemistry, and on air quality and health.

There exists a primary volcanic aerosol emission even during passive (ash-poor) volcanic degassing, and that is the focus of study here undertaken at Mt Etna during passive degassing (no eruption of lava/ash, but a gas flux equating to  $\text{SO}_2 \sim 2000$  tonnes/day). Evidence for a primary aerosol emission from volcanoes such as Mt Etna includes time-averaged sampling at the crater-rim (filter-pack sulfate, cascade impactor) and sun-photometers operated close to source. This primary emission is observed to be multi-modal and is believed to arise from high-temperature near-vent plume processing (e.g. generating sulfate-precursor  $\text{SO}_3$ ). However, the actual aerosol emission (particle number and size-distribution) is still not sufficiently quantified for initialisation of atmospheric models, which leads to uncertainties in models of volcanic plume atmospheric impacts, e.g. in how reactions on the surface area of the (poorly constrained) emitted volcanic aerosol catalyse the conversion of volcanic HBr into reactive bromine, BrO. The original research goal of my study was to better quantify the Mt Etna aerosol emission e.g. in terms of lognormal distributions as needed for initialisation of atmospheric chemistry models (whilst measuring aerosol relative to plume tracer  $\text{SO}_2$  enables the results to be combined with reported  $\text{SO}_2$  flux observations to yield volcanic aerosol fluxes). Upon starting to analyse the data I developed a second research goal which is better understand the LOAC instrument functioning in volcanic plume conditions.

### Method (in brief)

A field experiment was conducted at Mt Etna volcano (Sicily, Italy, 3.3 km asl) in 1-4 October 2013 where a hand-held version of the LOAC instrument was deployed to measure in-situ aerosol alongside  $\text{SO}_2$  mixing ratio measured by in-situ Multi-Gas electrochemical sensor (for details see Roberts et al. 2012). The measured  $\text{SO}_2$  acts largely as a plume tracer on the time/spatial scales of the field experiment. The measurements sampled plume already cooled to ambient temperature, and likely sampled the plume edge rather than centre. The unusual strong northerly winds on 02 October 2013 enabled measurements across a range of plume conditions. The emissions were first measured at the summit, sampling at the crater-rim of the three main active craters (Voragine, North-East Crater, and Buocca-Nova, hereafter VOR, NEC, BNC) with highly concentrated conditions

at SO<sub>2</sub> up to ~30 ppmv. The plume was then sampled on the volcano flank (hereafter: flank) a few hundred meters downwind (SO<sub>2</sub> ~ 3 ppmv, with concentrations decreasing further during descent from the summit by foot). An even more dilute grounding plume (hereafter: vweak) was then sampled at ~1.5 km downwind (SO<sub>2</sub> ~ 0.3 ppmv) that corresponds to a few minutes of wind-advection.

## Results

The Mt Etna SO<sub>2</sub> and aerosol observations on 01 October are shown in Figure 1, where aerosol volume density has been calculated directly from the LOAC instrument for total particles (volume density for particle subsets below a threshold is also shown). The time-series show the measurement at crater-rim (VOR, NEC, BNC), on the flank and in the dilute weak plume further downwind. High SO<sub>2</sub> mixing ratio and aerosol volume density are observed at the three craters sampled in turn, and then progressively decreasing aerosol and SO<sub>2</sub> in the more dilute flank and vweak plumes. Temporal (co-varying) fluctuations in SO<sub>2</sub> and aerosol are also seen due to local turbulence/wind-fields changing the in-situ plume exposure. There are also some periods of very high aerosol that are not correlated to SO<sub>2</sub> and can be attributed to episodes of resuspended dust (that mostly occurred whilst walking on the terrain). The further analysis below selects time-periods minimally affected by these dust events.

A closer analysis of the time-series of number density in each size-bin also highlights non-linearities in the aerosol measurement with respect to the SO<sub>2</sub> time-series, Figure 2. For example, as progressively more dilute plume is sampled across the time-series the number density of large particles decreases as expected, but the number of small particles actually increases. Figures 3-4 and Figures 5-6 further show the time-series as progressively more dilute plume is sampled in the selected Flank and vweak time-periods. These non-linearities can be more clearly seen by plotting aerosol number versus SO<sub>2</sub> for each size bin. This is shown in Figure 7 for the flank and Figure 8 for the weak plume, and in Figure 9 for the weak and flank plume time-periods combined. The negative correlation between aerosol and SO<sub>2</sub> is less severe in the more dilute plume, with all size bins exhibiting positive correlation to SO<sub>2</sub> in the weakest plume. However, even the positive correlation is not always linear: the gradient often becomes steeper in stronger plume.

To gain further insights, plots are now made of the aerosol size distribution. Aerosol concentration during the crater-rim observations can be extremely high, so might be an unusual case, therefore the analysis focuses mostly on the flank and vweak plume periods. In order to compare aerosol in plume of different strengths, the aerosol data is all normalised using co-measured SO<sub>2</sub> to SO<sub>2</sub> = 1 ppmv (i.e. actual observations are normalised downwards for flank but upwards for vweak plume). To keep track of the plume strength, the normalised aerosol size-distributions are also colour-coded according to the original SO<sub>2</sub> mixing ratio (a measure of plume strength). The normalised data is then converted into plots of dV/dlogD versus diameter to most easily see the size distributions, but trends in dV/dlogD for a given size-bin still reflect the number of particles observed in that bin (normalized for 1 ppmv SO<sub>2</sub>).

Figures 10 and 11 show the normalised distributions for flank and vweak plumes. For the Flank plume data (SO<sub>2</sub> around 3 ppmv) there is a strong effect of plume strength on the submicron

particles, with fewer particles observed in the strong plume. This holds also true up to ~2 microns. Conversely, more particles at ~4 microns are observed in the strong plume. For the VWeak plume, the small particle number is more stable with changing plume strength, although a small effect is still seen (slightly more small particles are observed as plume strength weakens from 0.6 to 0.4 ppmv SO<sub>2</sub>). A bigger effect is seen for particles at ~2 microns diameter where  $dV/d\log D$  is substantially greater in the stronger than in the weakest plume encountered.

Finally, Figure 12 shows the actual measurements (observed data, no normalisation) for the weak plume where SO<sub>2</sub> = 0.3-0.4 ppmv (28 observations in total), plotted as  $dV/d\log D$  and  $dN/d\log D$ . This weakest plume data indicates three volcanic modes may be present, confirming a multi-modal size distribution of the volcanic aerosol.

## Discussion

The data analysis shows correlations between SO<sub>2</sub> and aerosol volume, confirming the volcano as a primary source of aerosol at both sub-micron and supra-micron sizes. The LOAC shows good ability to identify multiple aerosol modes across sub- and supra-micron sizes, but also shows variations in the distribution that depend on plume strength, even for the weaker plume case.

Non-linearities are found in the correlations between aerosol number and SO<sub>2</sub>, and even anti-correlations in the data across the different size bins. It is difficult to find explanations for these non-linearities in terms of aerosol processes (or in terms of the SO<sub>2</sub> measurement given the non-linearities occur in different ways across the size-bins). Meteorology was also rather consistent during the experiment (with RH only significantly affected by the volcanic H<sub>2</sub>O emission in the strongest crater-rim plume, data not shown). Rather I suggest they can be mostly attributed to LOAC measurement error for these specific aerosol conditions.

I suggest the following processes might lead to under- and over-counting of submicron and supramicron particles by the LOAC in volcano plumes particularly at high plume strengths.

Specifically, for a large particle size-bin, Renard et al. already discussed that coincidence effects between particles can reduce the number of particles counted at that size. However, I hypothesize that the particle count at that size can also be over-counted if coincidence effects between two smaller sized particles add to produce a peak intensity corresponding to the large particle size bin. Given aerosol broadly follows a power-law type Junge distribution, even a low rate of coincidence (high counting efficiency) of particles at one size could cause a significant overcounting at larger particle size.

A significant cause of undercounting of small particles can also be due to their coincidence with larger particles. Depending on how the signal strengths combine, this could either lead to undercounting of the large particle, with an even larger particle being counted instead (see above) or simply might not affect the large particle count. However, in both cases it would cause undercounting of the small particle.

Thus, I hypothesize there can be sources of measurement bias which might cascade along the measured aerosol size distribution in volcanic plumes, or under other specific aerosol conditions particularly when many large particles are present.

### **Instrument Modelling**

To test the hypothesis I have developed a numerical model to simulate the LOAC measurement across the size distribution. Model inputs include the detection rate (40 kHz), a user-specified 'true' size distribution, peak intensity as a function of particle diameter (based on figure from Renard et al.), peak shape, and peak width as a function of particle diameter. Here I assume a simple triangular shape, with width that reaches a maximum of 500 micro-seconds for supra-micron particles, but decreases to a minimum of a few tens of micro-seconds for the sub-micron particles, however these parameters will be updated in future. Then the LOAC instrument detected signal is calculated as the sum of the signals from individual particle in the size distribution that are randomly distributed in the instrument air stream. Finally, the overall signal is analysed, above an assumed noise threshold (e.g. 1 mV). When the signal that has risen above the threshold crosses back below the threshold this is considered one particle with size corresponding to the overall maximum signal during the preceding period.

The model is still in development (with e.g. details on instrument noise to be added, peak widths to be updated), but as an example, Figure 13 illustrates  $dV/d\log D$  from a model run compared to an input size-distribution. The model predicts an over-counting of larger supra-micron particles and under-counting of small particles, consistent with the type of bias in the volcanic plume observations (Figures 10-11). This predicted bias also tends to be more severe at higher aerosol loadings and less severe at lower aerosol loadings (not shown). The model is not yet ready to be used as a predictive tool given various input parameters need first to be finalized. Nevertheless, the results suggest that future further development of instrument modelling across the size distribution might be an effective tool to correct for OPC instrument bias under volcanic plume conditions or in other specific cases where many large particles are present.

Figure 1

Overview of the SO<sub>2</sub> mixing ratio and LOAC volume density time-series. The three summit craters, and selected flank and weak plume time-periods are labelled.

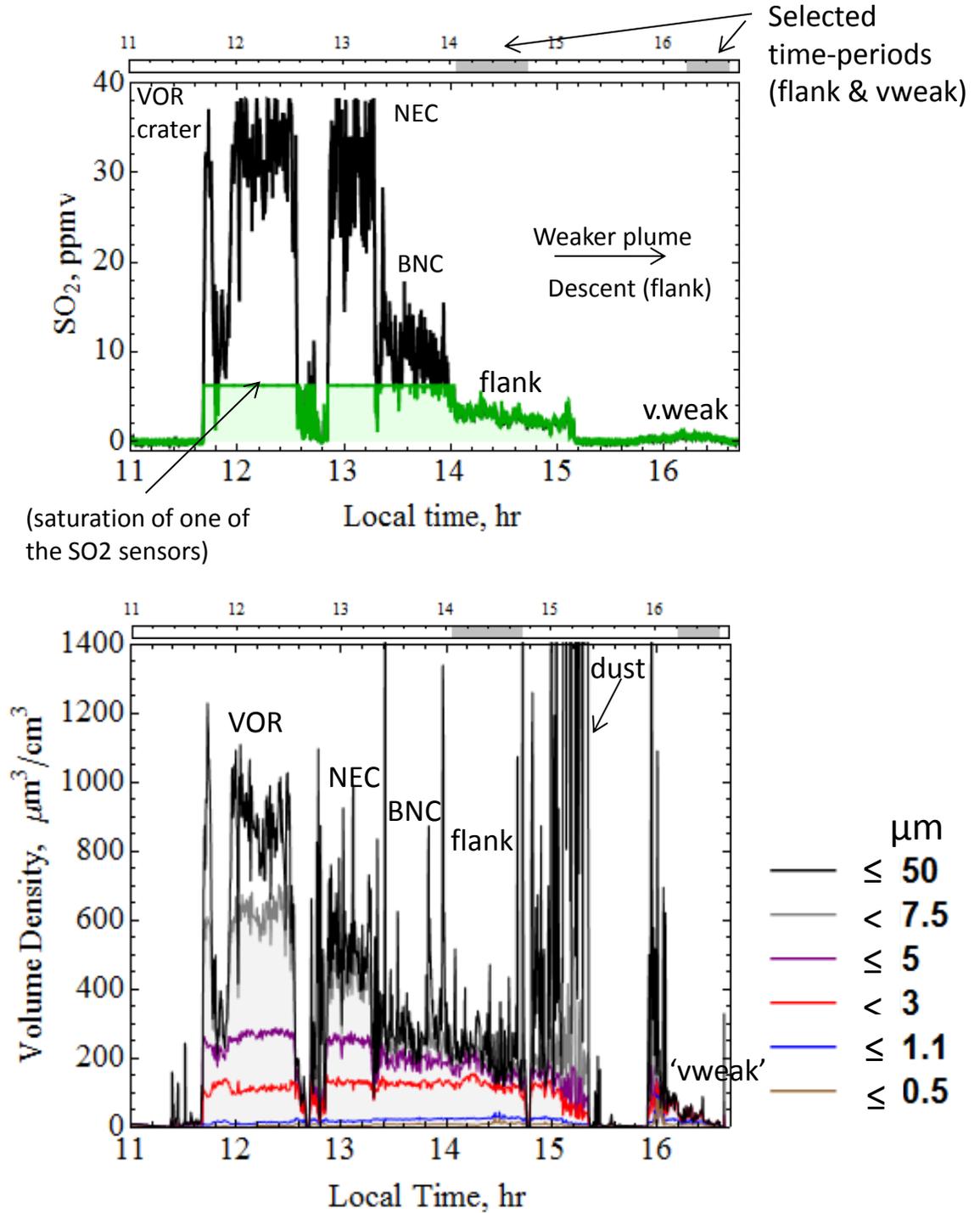


Figure 2  
 Number density in each size bin shown for summit craters and during descent on volcano flank. SO<sub>2</sub> time-series also shown for comparison.

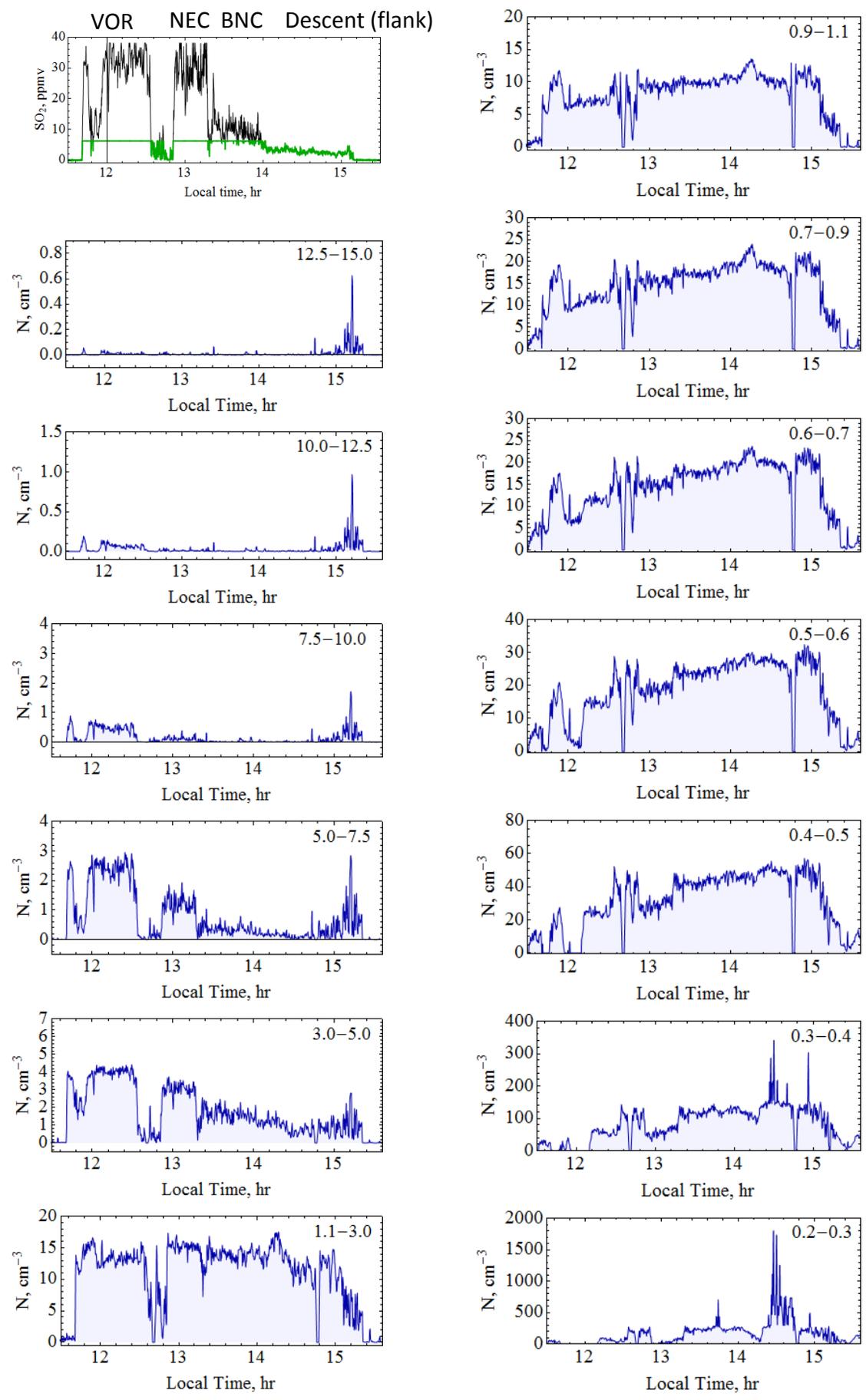


Figure 3

SO<sub>2</sub> mixing ratio and LOAC volume density time-series during Flank selected time-period

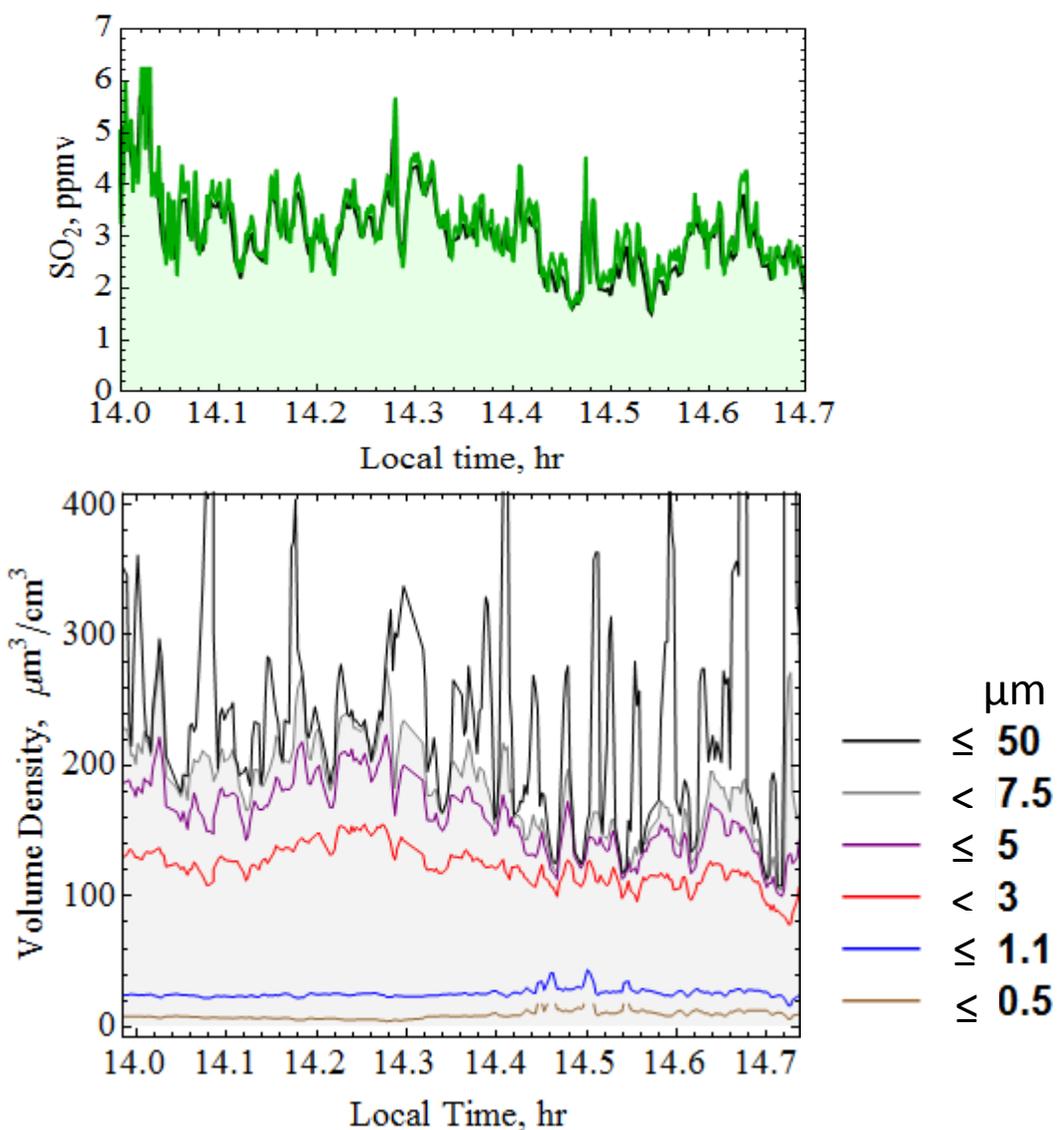


Figure 4 Number density in each size bin shown for flank period.

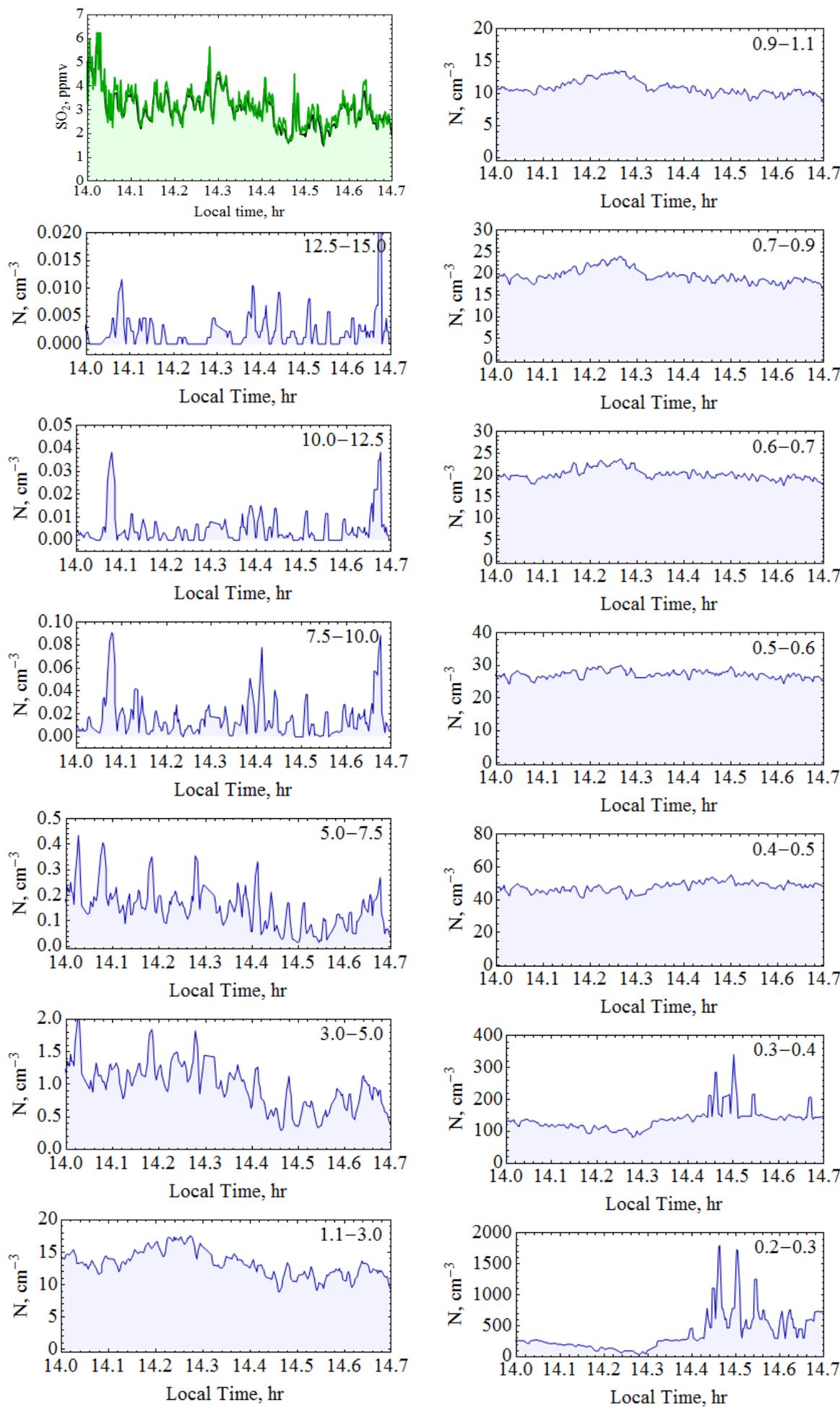


Figure 5

SO<sub>2</sub> mixing ratio and LOAC volume density time-series during vweak plume selected time-period

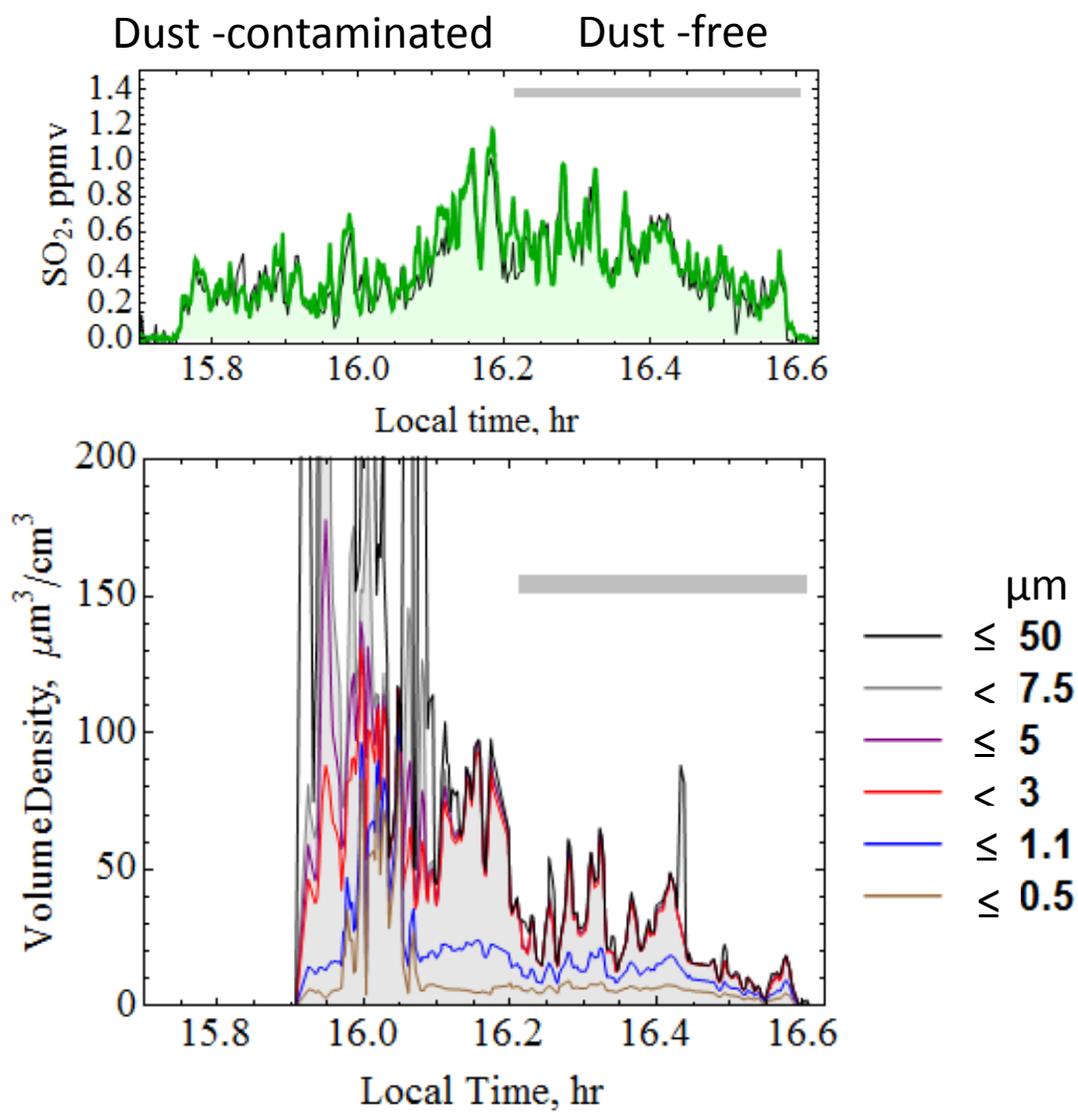


Figure 6

Number density in each size bin shown for weak plume period.

Dust -contaminated    Dust -free

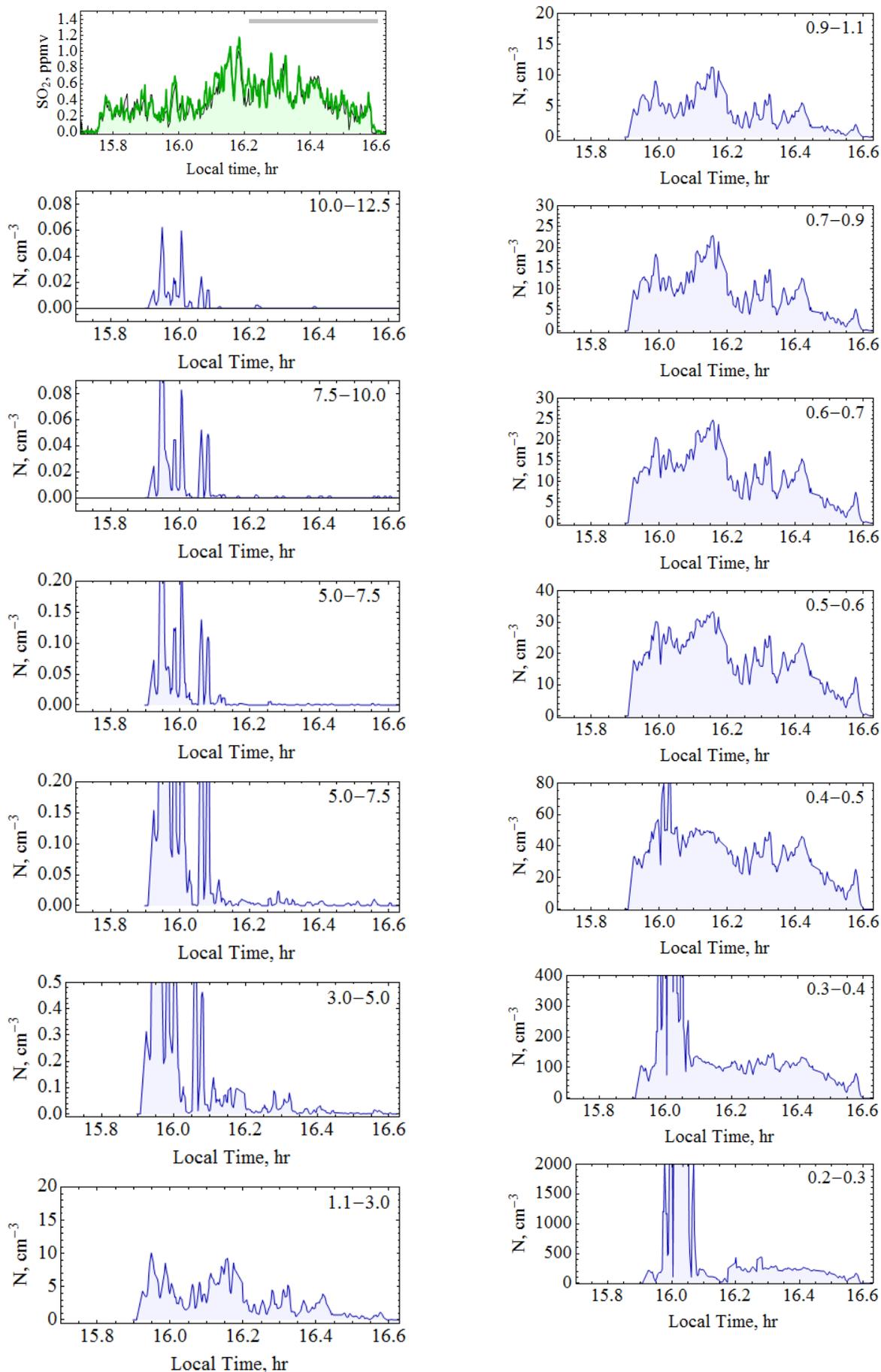


Figure 7

Scatter plots of particle number density versus SO<sub>2</sub> for Flank period, shown for individual size-bins.

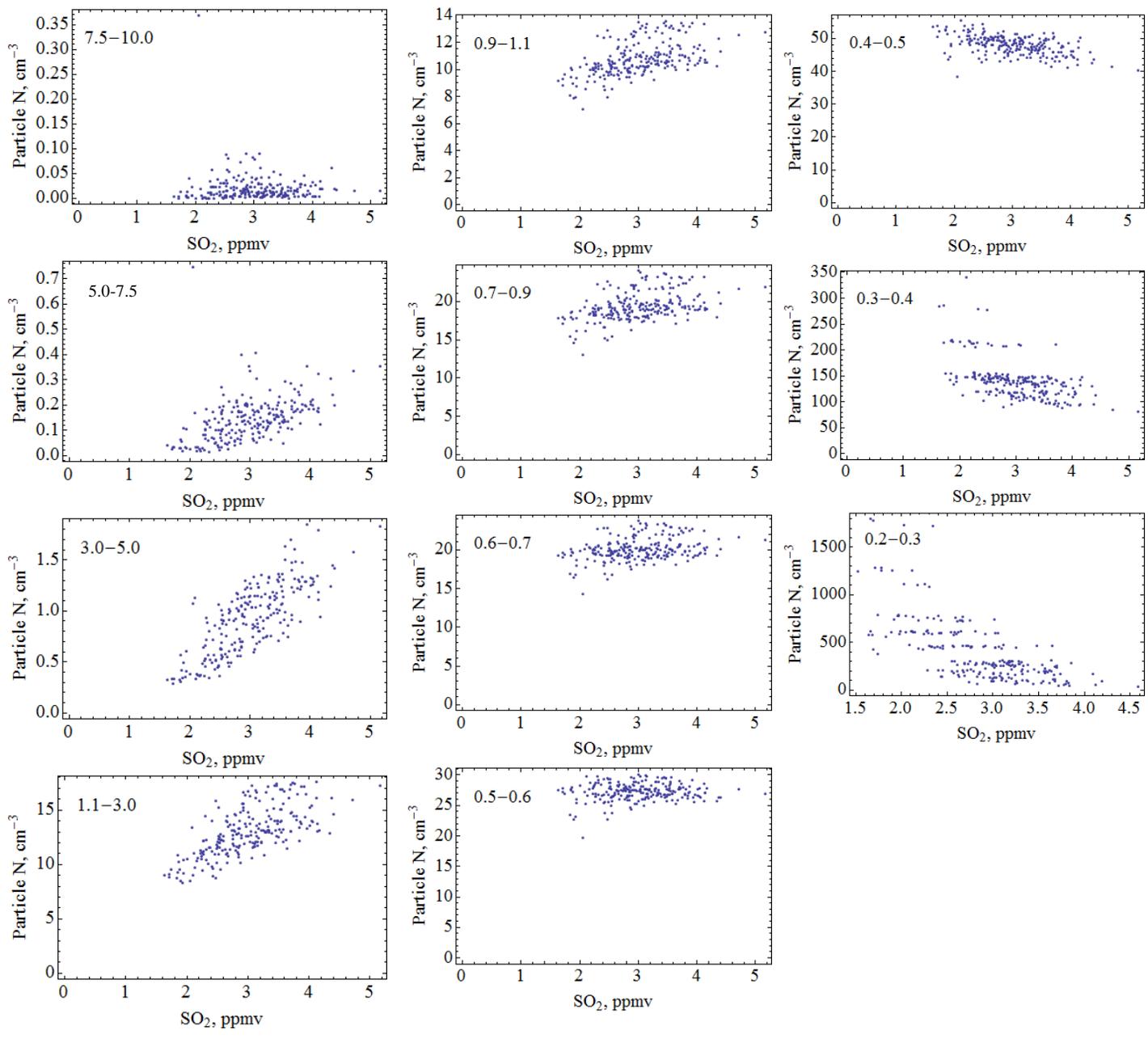


Figure 8

Scatter plots of particle number density versus SO<sub>2</sub> for vweak period (dust free part only), shown for individual size-bins.

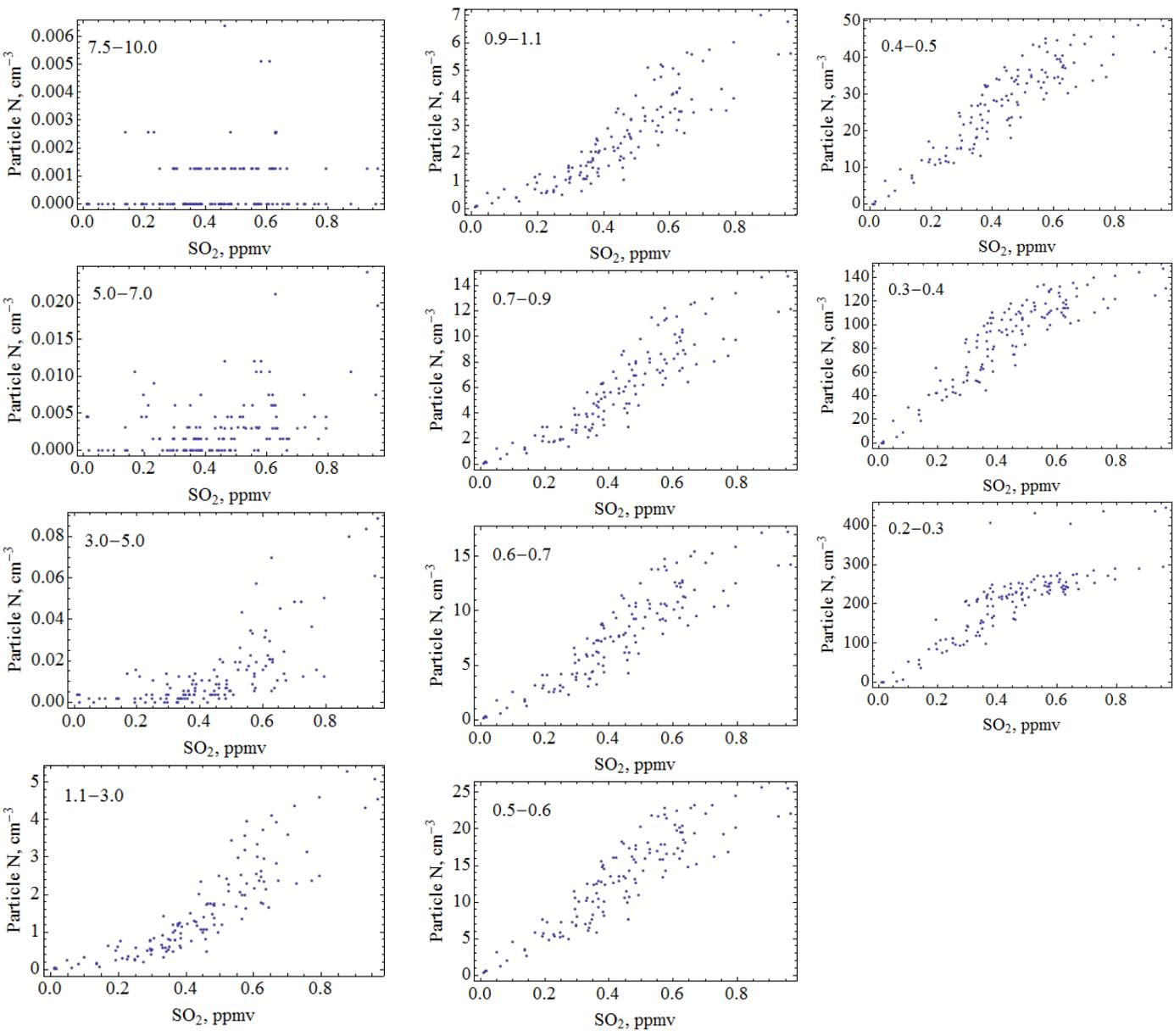


Figure 9

Scatter plots of particle number density versus SO<sub>2</sub> for both the flank and vweak (dust free ) period, shown for individual size-bins.

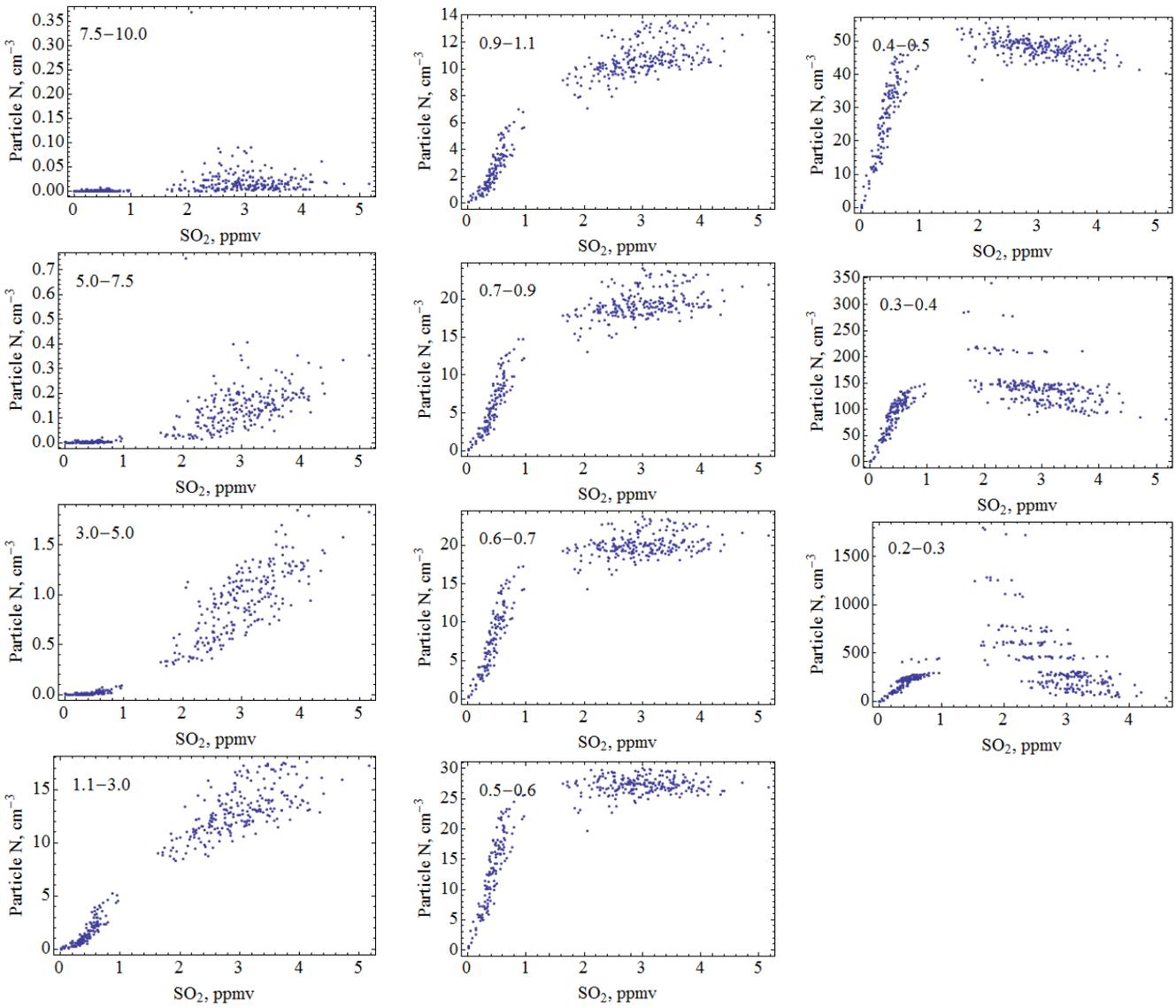


Figure 10

Aerosol size distributions in the Flank time-period

- ppmv
- $\text{SO}_2 < 2.5$  ppmv
- $2.5 < \text{SO}_2 < 3.0$  ppmv
- $3.0 < \text{SO}_2 < 3.5$  ppmv
- $3.5 < \text{SO}_2$

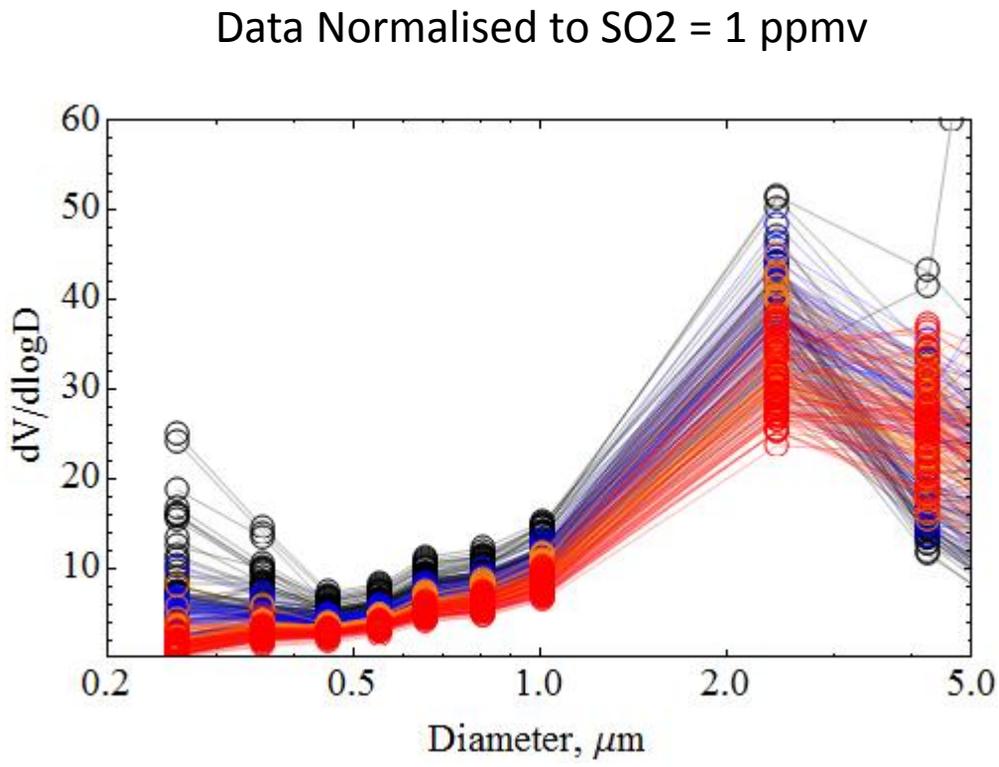
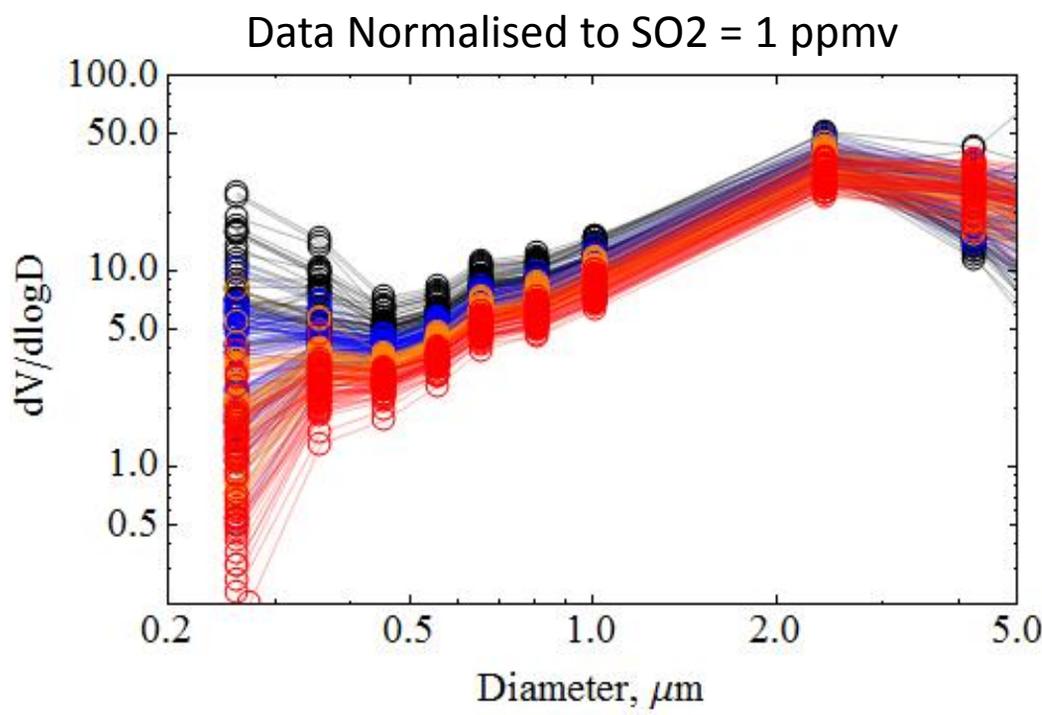


Figure 11

Aerosol size distributions in the weak time-period

- ppmv
- $\text{SO}_2 < 0.3$  ppmv
- $0.3 < \text{SO}_2 < 0.4$  ppmv
- $0.4 < \text{SO}_2 < 0.6$  ppmv
- $0.6 < \text{SO}_2$

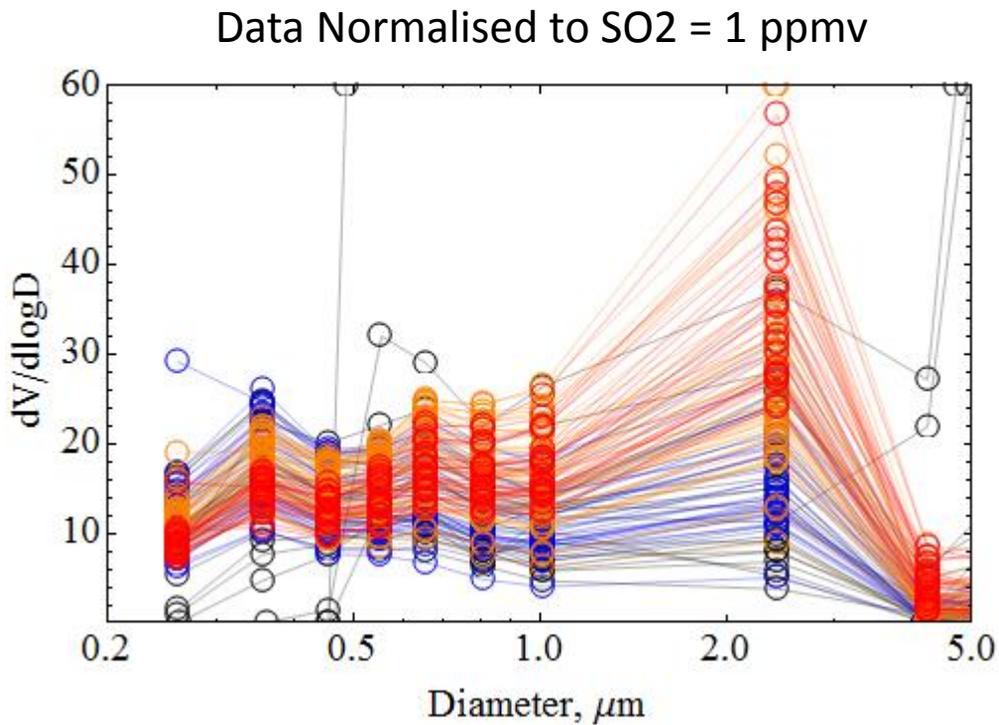
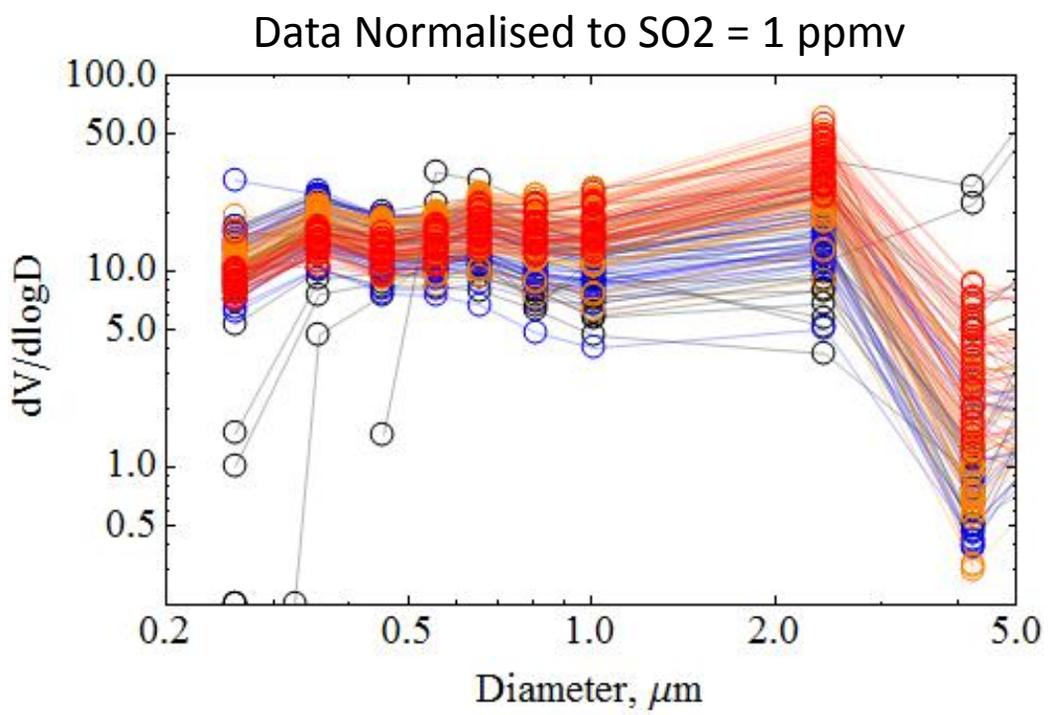


Figure 12

Aerosol size distributions in the vweak time-period for SO2 between 0.3 and 0.4 ppmv only. Observed data (not normalized)

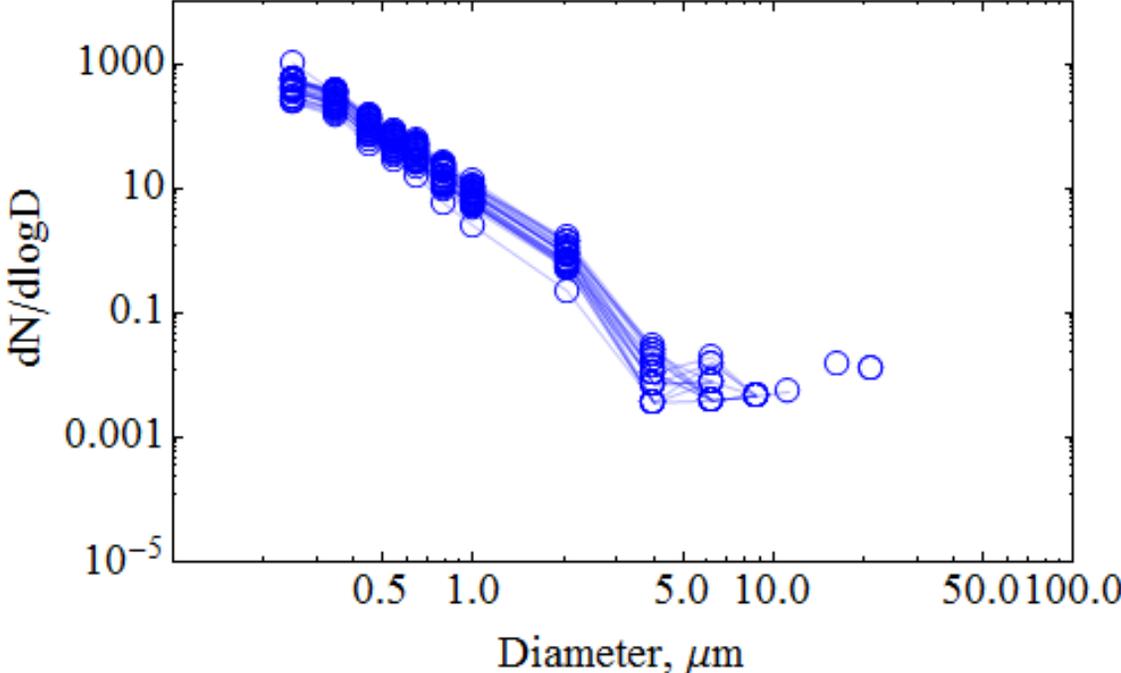
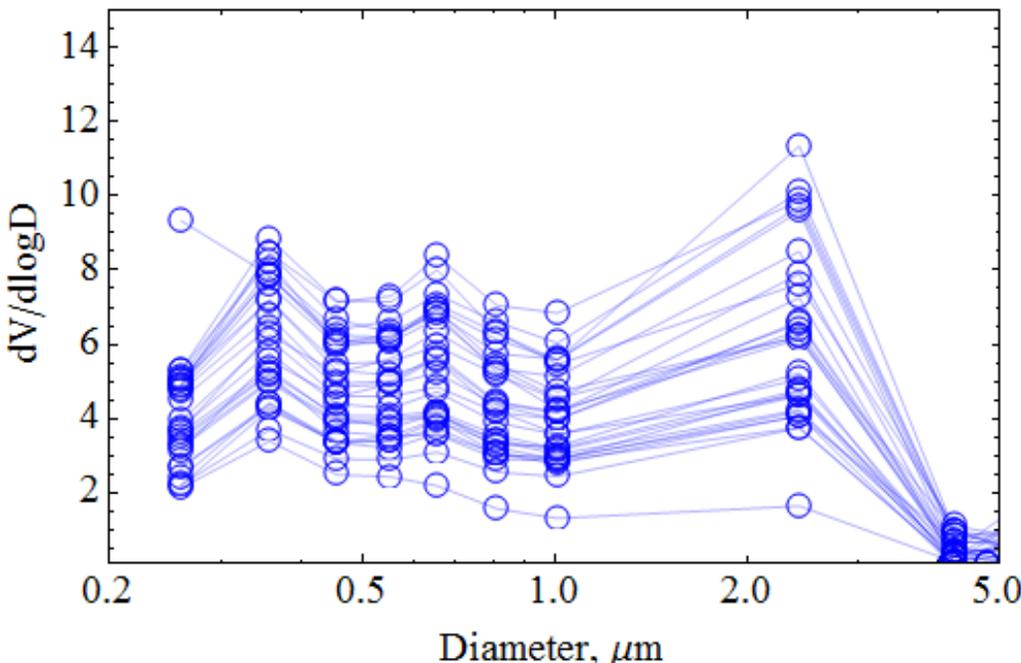


Figure 13

Model prediction of LOAC volcanic aerosol measurement, with input size distribution in red and modelled measured size distribution in blue.

