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REPLY

## Reply to comment from Liotta and Rizzo on “Evolution of CO<sub>2</sub>, SO<sub>2</sub>, HCl and HNO<sub>3</sub> in the volcanic plumes from Etna” by Voigt et al. [Geophys. Res. Lett.; 41, doi:10.1002/2013GL058974]

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### Editor’s Note:

The following comment and reply arise from an article published in Geophysical Research Letters by Voigt et al. (2014). The article addresses a volcanology topic, and the commenters take issue with some conclusions and offer an analysis of their own. Voigt and co-authors have responded.

Why is this comment-and-reply being published in the Bulletin? It is because Geophysical Research Letters is one of a number of journals that do not offer any published forum for discussion of the papers they

publish. This is a matter of editorial policy and a decision for each journal.

The Bulletin of Volcanology does provide a forum for discussion of articles published. When contacted by Marcello Liotta with the request that the Bulletin consider hosting a discussion of the Voigt et al. volcanology article in GRL, I agreed to do so if the GRL authors were willing to engage with the comment. Voigt and co-authors were willing to do so and have been allowed a small amount of additional space to summarize for Bulletin readers the key points of the GRL paper under discussion before responding directly to the comment from Liotta and Rizzo.

I hope that Bulletin readers find the discussion and reply of interest.

### Introduction

First, we summarize the paper “Evolution of CO<sub>2</sub>, SO<sub>2</sub>, HCl and HNO<sub>3</sub> in the volcanic plumes from Etna” by Voigt et al. (2014), and thereafter, we discuss the comment by Liotta and Rizzo (2014). In Voigt et al. (2014), we present novel in situ measurements of the composition of the volcanic plumes from the degassing Etna (Italy), performed with the DLR research aircraft Falcon during the CONCERT contrails, volcanos and cirrus experiment on 29 and 30 September 2011. Trace gas mixing ratios of SO<sub>2</sub>, HCl and HNO<sub>3</sub> were measured using mass spectrometry. Interestingly, HNO<sub>3</sub> was the dominant reactive nitrogen component of the plumes. In addition, H<sub>2</sub>O, CO<sub>2</sub> and reactive nitrogen species (NO<sub>y</sub>) were observed.

The age and dilution of the Etna plumes is calculated with the HYSPLIT model (Draxler and Hess 1998) initialized with the total volcanic SO<sub>2</sub> flux detected with the FLAME network (FLux Automatic Measurements; Salerno et al. 2009). Model and aircraft SO<sub>2</sub> mixing ratios at 0.5 to 5.4 h plume age agree,

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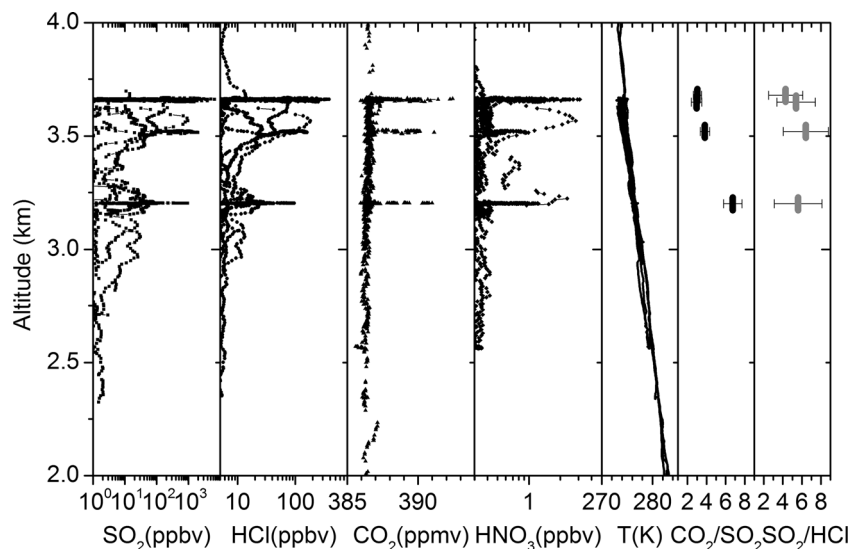
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**Fig. R1** Vertical profiles (in kilometer above sea level) of  $\text{SO}_2$ , HCl,  $\text{CO}_2$  and  $\text{HNO}_3$  mixing ratios and temperature detected with the instruments onboard the Falcon research aircraft in and near the Etna plume on 30 September 2011. In addition, the  $\text{CO}_2/\text{SO}_2$  and  $\text{SO}_2/\text{HCl}$  molar ratios integrated over individual plume encounters are shown



hence near and far-field observations can be linked by dispersion modelling.

Combined aircraft and photo observations (new Fig. R1 and Fig. 1 in Voigt et al. (2014)) clearly show two plume layers spreading out above 3 km altitude in the free troposphere on both days, indicating plume origins from at least two craters. We derive mean bulk and layer-resolved  $\text{CO}_2/\text{SO}_2$  and  $\text{SO}_2/\text{HCl}$  molar ratios in the plumes. Higher  $\text{CO}_2/\text{SO}_2$  ratios were detected in the lower plume layer suggesting emissions mainly from Bocca Nuova (BN) crater. Lower  $\text{CO}_2/\text{SO}_2$  ratios in the upper plume layer measured on 30 September point to a plume origin from North East (NE) crater. A partial mixing of the two plumes during their injection to higher altitudes (see Fig. 1 in Voigt et al. (2014)) could explain a difference of aircraft far-field to near-field observations at the crater with a multi-gas sensor. We will expand on this hypothesis in the discussion.

The  $\text{CO}_2/\text{SO}_2$  ratios detected from aircraft are constant over 1 to 5 h plume age, suggesting that the OH-induced conversion of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  is small within time scales of few hours and below our detection limit, consistent with previous results (e.g. McGonigle et al. 2004; Jurkat et al. 2010). Within the experimental uncertainties, the mean bulk  $\text{SO}_2/\text{HCl}$  molar ratio is in agreement with a ground-based observation at BN from a Drechsler bottle on 30 September, implying that partitioning of HCl in acidic plume particles plays a minor role at dry tropospheric conditions in the quiescent degassing activity state of Etna.

Hence, the key points of Voigt et al. (2014) are as follows:

- Aircraft measurements were performed in the volcanic plumes from Etna.
- $\text{CO}_2/\text{SO}_2$  and  $\text{SO}_2/\text{HCl}$  molar ratios are stable during atmospheric plume evolution; chemical processing in the plumes could not be detected above the measurement

uncertainties and is small over time scales of 1 to 5 h at dry tropospheric conditions.

- Under these atmospheric conditions,  $\text{CO}_2/\text{SO}_2$  and  $\text{SO}_2/\text{HCl}$  molar ratios can be used to monitor volcanic activity up to 100 km distance to the crater.

## Discussion

In Voigt et al. (2014), we focus on new aircraft observations of the volcanic plumes from Etna. In fact, since pioneering work in the 1980s by Allard et al. (1991), to our knowledge, this is the only extensive study on the Etna plumes performed with a larger size research aircraft in recent years. The aircraft offers the unique opportunity to investigate the evolution of volcanic plumes in a quasi-Lagrangian approach. We investigate the temporal and spatial plume evolution in terms of dilution of  $\text{SO}_2$  and chemical processing of  $\text{CO}_2/\text{SO}_2$  and  $\text{SO}_2/\text{HCl}$  ratios in the upper and lower plume layers and draw our main conclusions based on a consistent set of novel aircraft measurements.

The comment by Liotta and Rizzo 2014 does not focus on the aircraft observations itself and the stability of the plume composition at 1 to 5 h plume age, which is the main topic of the paper. Liotta and Rizzo 2014 mainly address instrumental aspects, the evaluation of two plume layers on 29 September, the comparison of aircraft and ground-based observations and meteorological considerations.

The  $\text{SO}_2$  mixing ratio in the volcanic plumes was detected with the atmospheric chemical ionization mass spectrometer (AIMS); for details, see Jurkat et al. (2014). The inlet line of the mass spectrometer was continuously calibrated with isotopically labelled  $^{34}\text{SO}_2$  to monitor the instrument's performance. We subtracted the reference signal and used a  $\delta^{34}\text{SO}_2$

value of 2.7‰ derived from Allard (1986) for the volcanic plume contribution, which can be regarded as upper limit. Assuming instead  $\delta^{34}\text{SO}_2$  of 0‰ for magmatic  $\text{SO}_2$ , as recently reported by Liotta et al. (2012), would lead to an error <3 % in the measured  $\text{SO}_2$  mixing ratios, which is already included in the uncertainty analysis. The main contribution to the 17–36 % accuracy in  $\text{SO}_2$  results from the quantification of the dilution of the inlet flow.

The pressure in the flow reactor was controlled to 40 hPa using a pressure control valve to eliminate pressure dependence. The in-flight calibration for  $\text{SO}_2$  allowed correcting for the humidity dependence of the  $\text{SO}_2$  signal. The other species ( $\text{HCl}$  and  $\text{HNO}_3$ ) were calibrated in the laboratory for the lower tropospheric humidity range of 800 to 1,600 ppmv  $\text{H}_2\text{O}$ , and the humidity dependence of the signal and its background were corrected.

On 29 and 30 September 2011, we measured a bulk mean  $\text{CO}_2/\text{SO}_2$  ratio of 5.2 in the quiescent degassing Etna plumes. We thank Liotta and Rizzo for pointing to Patanè et al. (2013), who interpret an impressive time series of Etna measurements. Their 2011 annual mean  $\text{CO}_2/\text{SO}_2$  ratio of 5.9 is similar to our and to earlier values of 5.7 (Aiuppa et al. 2008) which were cited in our article. A direct comparison on 29 and 30 September is difficult, due to the coarse data resolution of their 3-year time series. Further, the relative contributions of the emissions of the individual central craters (BN and Voragine) are not specified for those days.

Two plume layers were clearly visible on 29 and 30 September 2011 (Voigt et al. 2014). Since we mainly probed the lower plume on 29 September, the plume layering on 30 September is thoroughly investigated below. Fig. R1 shows vertical profiles of  $\text{SO}_2$ ,  $\text{HCl}$  and  $\text{HNO}_3$  mixing ratios at a time resolution of 0.5 Hz and of  $\text{CO}_2$  at 0.2 Hz. A lower plume layer at 3 to 3.3 km altitude and an upper plume layer at 3.4 to 3.7 km altitudes were detected. Elongated measurement periods near 3.2, 3.5 to 3.7 km altitudes result in enhanced numbers of observations at these flight levels.  $\text{CO}_2$  peaks confined to these levels can be explained by the linear scaling in  $\text{CO}_2$ , while the other trace gases are shown on a logarithmic scale. In particular, the upper plume exhibits a characteristic structuring, which is caused by several plume crossings at 1.5 to 2.3 h plume age.

Based on these measurements and the visible observations, the assumption that the probed gas is emitted by at least two different craters is straightforward. The formation of more than one plume depends on the strength of the individual crater emissions and on meteorological conditions and may be subject to temporal changes. On 30 September,  $\text{CO}_2/\text{SO}_2$  ratios of 6.7 in the lower plume near the 3.2-km altitude suggest the lower Bocca Nuova crater as primary emission site, while the upper plume exhibits a  $\text{CO}_2/\text{SO}_2$  ratio of 3.3, indicative for emissions from North East crater. Similarly, higher  $\text{CO}_2/\text{SO}_2$  ratios of 12.4 (+/−0.8) were detected with a

multi-gas instrument (Aiuppa et al. 2008) near BN and lower  $\text{CO}_2/\text{SO}_2$  ratios of 0.9 (+/−0.3) near NE crater. While the trends are similar, instrumental uncertainties alone cannot explain the differences between the two methods. We suggest that the two plumes could have partially mixed during their injection to the free troposphere within the first minutes of plume transport (see also Fig. 1 in Voigt et al. (2014)). Complete mixing of the crater emissions would lead to a single well-mixed plume. However, the entrainment of a fraction of the BN plume into the NE crater plume and vice versa could explain  $\text{CO}_2/\text{SO}_2$  observations in the near field from the ground and the far field from aircraft. In the quiescent degassing activity state, temporal changes in the  $\text{CO}_2/\text{SO}_2$  emission ratios at the crater rim are small (La Spina et al. 2010; Patanè et al. 2013); however, they could be at the same size as the variability observed by the aircraft measurements. Significantly higher ratios up to 25 were observed before and during eruptive events (Aiuppa et al. 2008; Patanè et al. 2013).

Within the experimental uncertainties, the mean bulk aircraft  $\text{SO}_2/\text{HCl}$  molar ratio of 4.8 (+/−1.8) on 30 September is consistent with an alkaline trap observation of the BN plume (Wittmer et al. 2014) and with the range of previous ground-based observations (e.g. La Spina et al. 2010; Rizzo et al. 2013). Generally higher  $\text{SO}_2/\text{HCl}$  ratios have been detected in the BN and lower ratios in the NE crater plumes (Rizzo et al. 2013; Wittmer et al. 2014). Related to the comment by Liotta and Rizzo 2014, we now modified the interpretation of the  $\text{HCl}$  data. We observed a higher variability of the  $\text{SO}_2/\text{HCl}$  compared to  $\text{CO}_2/\text{SO}_2$  ratios. In addition, large instrumental uncertainties particularly in the lower plume observation on 30 September caused by a high dilution of the inlet flow prevent a trend analysis of the  $\text{SO}_2/\text{HCl}$  ratio in the two plume layers.

Generally, lower  $\text{CO}_2/\text{SO}_2$  and  $\text{SO}_2/\text{HCl}$  molar ratios are characteristic for quiescent degassing and higher ratios (e.g. up to 25 for  $\text{CO}_2/\text{SO}_2$  (Aiuppa et al. 2008) and up to 15 for  $\text{SO}_2/\text{HCl}$  (Allard et al. 2005) indicate new magma ascents weeks to days before the eruptive events. The reason is a pressure and therefore depth-dependent solubility of volatiles in the magma causing significantly higher atmospheric  $\text{CO}_2/\text{SO}_2$  and  $\text{SO}_2/\text{HCl}$  molar ratios before and during eruptions (Aiuppa et al. 2008; Patanè et al. 2013). Our observations were made in a quiescent degassing state shortly after a paroxysm episode on 28 September. We investigate the plume composition at 1 to 5 h plume age and find stable  $\text{CO}_2/\text{SO}_2$  and  $\text{SO}_2/\text{HCl}$  molar ratios within the experimental uncertainties, significantly lower compared to previous observation during eruptive episodes. Hence, in the degassing state, chemical processing of  $\text{SO}_2$  and heterogeneous  $\text{HCl}$  uptake in plume particles is small at these time scales under dry tropospheric conditions. Therefore, these trace gas ratios can be used to monitor volcanic activity far from the crater.

Finally, the general meteorological situation was influenced by the passing of a cyclonic system on 29 September. However, on both days, the plumes were observed above the boundary layer in clear air (Fig. 1 in Voigt et al. 2014) at temperatures of 273–277 K and at dry conditions (RH<sub>i</sub> between 10 and 20 %). Near the injection site, the warm and humid Etna crater gas emissions formed a cloudy white plume on both days. During further plume evolution above the boundary layer in the far field, the brownish plumes spread out and were not further influenced by cloud processing.

## Conclusion

In this response, we could add a thorough data analysis of the Etna plume observations to Voigt et al. (2014). The additional Fig. R1 explicitly illustrates vertical profiles of the trace gas observations presented in Voigt et al. (2014). Hence the conclusions regarding the two plume layers do not arise from a single measurement, but from a statistically significant large data set. Summarized, we are convinced that the interpretation of two separated, although not completely independent plume layers, is reasonable. As stated in Voigt et al. (2014), the two plumes probably were partly, but not completely, mixed and therefore retained a different chemical signature in terms of CO<sub>2</sub>/SO<sub>2</sub> ratios compared to the individual crater emissions. Our exploratory study provides a first attempt to link crater to distant plume observations. Future work bridging ground-based and airborne data sets is needed.

We agree with Liotta and Rizzo regarding the interpretation of the SO<sub>2</sub>/HCl ratios, which was disproportionate considering the measurement error. Still, SO<sub>2</sub>/HCl ratios often vary by a factor 5 or more during magma ascent (e.g. Noguchi and Kamiya 1963; Allard et al. 2005). Hence, the uncertainty of slight variations in the SO<sub>2</sub>/HCl ratio, which might be hidden by our instrumental error, is significantly smaller than the SO<sub>2</sub>/HCl change caused by magma ascent. Therefore, in contrast to the view of Liotta and Rizzo, our main conclusions remain unchanged, namely CO<sub>2</sub>/SO<sub>2</sub> and SO<sub>2</sub>/HCl ratios are sufficiently stable in the ageing plume to allow their use as monitoring parameters even when measurements take place in 100 km distance to the crater.

We further show that the error caused by using the δ<sup>34</sup>S<sub>O<sub>2</sub> value of Liotta et al. (2012), instead of Allard (1986), leads to <3 % uncertainties in SO<sub>2</sub>, hence is of minor relevance at all and was already taken into account in the uncertainty given by Voigt et al. (2014).</sub>

Finally, we agree with Liotta and Rizzo (2014) that the meteorological situations over Sicily were not identical on 29 and 30 September. This difference is of minor relevance for our data sets with plume encounters above the boundary layer in local dry clear sky conditions measured during the flights.

In general, however, meteorological conditions can have an impact on plume dilution and chemistry.

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