Authors' response letter – AMT-2017-355

The authors like to thank both referees for reviewing the discussion paper, and especially acknowledge the detailed comments and suggestions by Christoph Kern, which helped to significantly improve the manuscript.

Answer to comments from Referee 1 (Christoph Kern):

General Comment: The measurement results obtained during deployment at the authors' three study sites are also quite interesting, though they are somewhat difficult to interpret due to the limited amount of available UAS data and very limited supplemental information from other sources at each study site. For example, it remains unclear why C/S ratios measured by UAS at Stromboli are systematically higher than those measured by ground-based MultiGAS during the study period. Similarly, the three BrX/SO2 ratios measured at different distances from Stromboli's active vents do not follow a clear trend and are hard to interpret by themselves. Perhaps a bit more effort could be made to put these measurement results into context and/or offer possible explanations for the observations.

Reply: The referee is right, indicating that the part of measurement data interpretation in a volcanological context could be improved. Although the availability of data is concise and the focus of the manuscript is on the measurement techniques, we tried to improve the corresponding section, as much as we felt comfortable with and avoiding speculations. Detailed revision on the matter of MultiGAS and BrX/SO2 data interpretation can be found later in this response letter.

Comment: Title – Currently, the main focus of the manuscript appears to be the implementation of various sensors for characterizing volcanic degassing on a UAS platform. This is also in line with the scope of AMT. Unless the results section is significantly expanded, you might consider changing the title to something along the lines of "Implementation of electro-chemical, optical and denuder-based sensors and sampling techniques on UAS for volcanic gas measurements: examples from Masaya, Turrialba and Stromboli Volcanoes". This seems to capture the manuscript's focus a bit better than the current title.

Reply: We thank the referee for suggesting a new title and we followed that suggestion, changing the title to:

"Implementation of electrochemical, optical and denuder-based sensors and sampling techniques on UAV for volcanic gas measurements: examples from Masaya, Turrialba and Stromboli Volcanoes"

P1L32 – 'spatial and temporal proximity to explosions'? Is the spatial and temporal evolution of the C/S ratio actually discussed in the manuscript? It seems like this is a bit of a reach. Perhaps better to say that changes in the C/S ratio were observed that may have been associated with explosive activity at Stromboli?

Reply: The evolution of the C/S ratio associated with explosive activity is discussed rather briefly (P14L8), by stating that at Stromboli other studies found that C/S ratio changes with explosive activity (e.g. La Spina et al. 2013). We observed high C/S ratio values while flying directly above the crater and occasionally withdrawing the UAS just prior to explosions. Due to the lack of complete temporal records

of the explosive activity, we can only relate the C/S ratios to photograph recordings of the explosions. With that, we were able to observe elevated C/S ratios in proximity to the explosions.

"At Stromboli volcano, elevated CO_2/SO_2 ratios have been observed in spatial and temporal proximity to explosions by airborne in-situ measurements."

P1L31ff – Why are only the results from Stromboli mentioned explicitly in the abstract? Perhaps the most important results for each study site could be mentioned?

Reply: We added the most important results for each study site as the referee suggested.

"The new instrumental set-ups were compared with established instruments during ground-based measurements at Masaya volcano, which resulted in CO_2/SO_2 ratios of 3.6 ± 0.4. For total SO_2 flux estimations a small differential optical absorption spectroscopy (DOAS) system measured SO_2 column amounts on transversal flights below the plume at Turrialba Volcano, giving 1776 ± 1108 T/d and 1616 ± 1007 T/d of SO_2 during two traverses. At Stromboli volcano, elevated CO_2/SO_2 ratios have been observed in spatial and temporal proximity to explosions by airborne in-situ measurements. Reactive bromine to sulfur ratios of 0.19×10^{-4} to 9.8×10^{-4} were measured in-situ in the plume of Stromboli volcano downwind of the vent."

P2L13 – 'It has been shown. . .' This is much too general of a statement. There are accounts of increased C/S prior to eruptions. However, the opposite has also been observed (e.g. at Poas, see your reference de Moor et al 2016b). Please clarify.

Reply: We edited that sentence for clarification

"For instance, the CO2/SO2 emission ratio strongly varies with volcanic activity, which is associated to magma rising up a conduit. The solubility of magmatic gases is pressure dependent and different gases are released from the magma at different depths during the magma ascent, that is accompanied by pressure decrease. Gas ratio changes have been observed within the timescale of hours to weeks prior to eruptions (e.g. Giggenbach, 1975; Aiuppa et al., 2007; de Moor et al., 2016a, de Moor et al., 2016b) and their magnitude, direction, and pace are highly variable throughout different volcanic systems and state of activity."

P2L27 – 'It was observed. . .' Again, I feel like this statement is too general. I think that recent measurements at Cotopaxi seemed to show an increase in BrO/SO2 during a period of continuous activity? Is this true? Dr. Bobrowski would know more of the details. . . As you mention in the next sentence, BrO is a secondary compound formed in volcanic plumes from reaction of HBr with other species. Therefore, the link between measured BrO/SO2 ratios and volcanic activity will typically be quite complex and depend on a large number of environmental conditions.

Reply: We agree that this statement might be too general. We edited the paragraph on BrO/SO2 ratios to clarify that matter. Regarding BrO/SO2 emission at Cotopaxi, Dinger et al. (2017) observed higher values of BrO/SO2 only at a declining phase of activity, while prior and during the climax of activity the BrO/SO2 was lower.

"Although several studies observed decreases in the BrO/SO_2 ratio in advance to eruptive phases (Lübcke et al., 2014) and lower ratios during periods of continuous activity (Bobrowski and Giuffrida, 2012), it is not yet clear whether magma-gas partitioning of bromine occurs prior or after sulfur during

the pressure drop associated with magma ascents {Dinger 2017 #394}. Furthermore, BrO is not a directly emitted species rather than the product of complex heterogeneous chemistry in the volcanic plume involving reactions with magmatic gases with entrained air (e.g. Gerlach, 2004, Bobrowski et al., 2007). The variation of BrO by plume age and a transversal distribution in the plume for this species was observed by differential optical absorption spectroscopy (DOAS) measurements (Bobrowski et al., 2007). Additionally, other reactive halogen species with oxidation states ≠ -1 (e.g. Br_2, Cl_2, BrCl and others) have been measured in-situ in the plume of Mt. Etna, Italy (Rüdiger et al., 2017) and Mt Nyamuragira {Bobrowski 2017 #395}."

P5L5 – Clearly, Masaya is a large contributor to total arc emissions, but recently I believe that Turrialba has had similar emission rates. Dr. de Moor would know this better than I do, but characterizing Masaya as the 'single largest contributor' may no longer be quite accurate. See de Moor et al 2017:
de Moor, J. M., Kern, C., Avard, G., Muller, C., Aiuppa, A., Saballos, A., . . . Fischer, T. P. (2017). A new sulfur and carbon degassing inventory for the Southern Central American Volcanic Arc : The importance of accurate time-series datasets and possible tectonic processes responsible for temporal variations in arc-scale volatile emissions. Geochemistry Geophysics Geosystems, 18, 1–32. https://doi.org/doi: 10.1002/2017GC007141

Reply: The Referee is correct. Latest emission inventories show that Turrialba volcano emissions overtook those of Masaya volcano in 2015-2016. Furthermore, more recent but unpublished measurements showed similar emission strengths for both volcanoes. The paragraphs dealing with this case were edited.

"Masaya persistently emits voluminous quantities of SO_2, with fluxes typically ranging from 500 T/d to 2500 T/d (e.g. (Mather et al., 2006; de Moor et al., 2013; Carn et al., 2017), making this volcano currently to one of the largest contributor to volcanic gas emissions in the Central American Volcanic Arc (de Moor et al. 2017). […] In the 2000s, an almost 150 years long period of quiescence has ended and since 2010 several vent opening phreatic eruptions henceforth occurred marking an ongoing but erratic phase of unrest (Martini et al., 2010), characterized by variable ash and gas emission intensities (up to 5000 tons/day of SO_2 (de Moor et al., 2016a)), making Turrialba volcano to the second substantial emitter in the arc, besides Masaya volcano (de Moor et al. 2017)."

P5L23 – Does ash deposition really make maintenance risky or impossible? Please explain why. Obviously it makes frequent, tedious maintenance necessary. And if stations are very close to the summit, then ballistics pose a real threat that would make maintenance risky or impossible. But ash?

Reply: We added the aspect of ballistic impacts posing threats to maintenance personnel. While ash emissions itself might not pose an imminent threat, they make maintenance necessary at higher frequencies, which leads to longer exposition periods at the crater for the researcher.

"However, stations located near the active vent suffer from ash deposition and ballistic impacts during more frequent episodes, making maintenance demanding and risky or impossible."

P7L15 – Is the light source really a 'small light bulb'? I always thought it was a diode. The datasheet says 'IR lamp' which might really be a light bulb but I'm not sure. . . Thanks for clarifying.

Reply: Actually, we assumed the light source to be a light bulb due to the following observations: 1.) Every time the sensor performs a measurement, one can actually see the light flashing through the diffusion membrane with the typical warm yellowish color of a thermal emitter (unfortunately a spectral

analysis has not been performed). 2.) Switching the light source on and off occurs smoothly 3.) The whole sensor is very cost-effective (<100€). Even under mass-production this is unlikely to achieve with LEDs, emitting at appropriate wavelengths. Anyway, we will express it more carefully:

"[…], where it is exposed to the radiation of a small infra-red light source"

Table 1 – I have a few questions on information in this table: (1) the specifications on both instruments seem to require non-condensing plumes, yet the manuscript later describes problems with telemetry associated with condensed plumes. Could you comment further on the issue of condensation? How would it affect the measurements? Would you be able to determine and filter out poor quality data collected in condensed areas of the plume? Or how to deal with this? (2) I guess the 1/T temperature dependence of the CO2 sensor is simply from the ideal gas law? T would then be the air temperature, correct? (3) Later on in the manuscript, you explain that the pressure dependent diffusivity of the SO2 sensor membrane makes the readout insensitive to pressure, yet a (small) correction is listed here. This is probably a second-order effect, but it's probably worth pointing out for consistency. (4) I assume that 'resolution' is the precision of the sensor? If not, could you give the precision? Also, what is the assumed integration time for the values given? I assume you could improve precision by increasing the integration time, correct?

Reply: First of all, these specifications are from the manufacturers data sheets and not established by us. Also the typical applications for most of the parts are certainly not volcanic gas measurements and we like others probably expand the recommended boundaries of the parts specifications. We tried to answer the specific questions as follows:

(1) Condensed water inside the sensors would definitely affect the measurements. In the CO2 sensor, reflectivity of the optical cell would change and cause apparent absorption, for the SO2 sensor water on the electrode would change reactivity. To avoid this, we operated the instrument with a 0.45 µm pore filter at the gas inlet, retarding any particulate matter (including condensed water droplets) that might interfere with the measurement. Further, due heat dissipation of the electronics/electromechanics and the thermally isolating styrofoam housing of the Sunkist, the sensors are typically held at temperatures several degree above ambient conditions, such that condensation inside the instrument is unlikely when measuring in well diluted plumes (meaning that the sampled gases are close to ambient temperature). Therefore, the sensors inside the housing can be said to be operated at non-condensing conditions. If there is risk of condensation due to very extreme conditions (e. g. sampling hot plumes close to the vent), affected data can be identified by a) looking at the data of the humidity sensor inside the CO2 sensor housing or b) changes in the response behavior of the CO2 sensor (gas absorption signals rise and decline on sub second time scales, whereas condensation/drying of the sensor occurs much slower). Such slow responses can easily be recognized when comparing the CO2 VMR to the SO2 signal. In the case of SO2, we used the same sensor (CiTiceL) as other instrument manufacturer (e.g. INGV) and therefore applied a similar filter system in our sampling line.

(2) Correct. Also, this dependency was included in the calibration function used for the CO2 sensor.

(3) This pressure dependence again origins from the data sheet and is listed to give the complete specifications. With 0.0015% /kPa dependency a change of 1 bar would lead to 0.15% signal variation, which is negligible in applications at atmospheric pressure. Potentially important in industrial applications at unusual pressures.

(4) Indeed, "Resolution" is misleading. The given values are the 1-sigma instrument noise at a temporal resolution of 0.5 seconds, which is a measure for the short-term precision (neglecting drifting of the instrument). This precision can be improved on cost of temporal resolution by

averaging. Long-term drifts are considered in the "Accuracy", also given in the table. Further, we noticed a mistake in the table: the 0.5 ppm given by the supplier seem to apply for the low sensitivity version of the sensor. Our measured noise at the high sensitivity version (sensitivity increased by a factor of 10) is approximately 0.05 ppm. We corrected this in the table.

"

Accuracy	± 30 ppm ± 5 % signal (CO_2), ± 1 ppm ± 1 % signal (SO_2)	± 1ppm ± 1 % signal
Instrument noise (1σ)	5 ppm (CO_2), 0.05 ppm (SO_2)	0.05 ppm

"

P10L3 – Can you be a bit more specific with regards to which species can be detected with your denuder system? You mention reactive bromine (BrX). Am I correct in assuming that gaseous HBr cannot be detected? What about the other gaseous species involved in the 'bromine explosion' mechanism, i.e. Br2, Br, HOBr? They can all be detected? And what about bromine taken up onto aerosols? I guess it would be invisible to the instrument?

Reply: We applied two coatings, of which one is sensitive to HBr. TMB on the other hand is selectively sensitive towards gaseous molecular bromine species in which the bromine atom is in oxidation state +1 or 0 (e.g. Br_2 or BrCl). Particulate bromine would pass the denuder "undetected", since the diffusion coefficient of particles is rather high. However, since Br_2 and BrCl is rather insoluble in aqueous phase the assumption is that it's primarily found in the gas phase.

"Gas diffusion denuder sampling, which enriches gaseous compounds while being insensitive to the particle phase, was applied by using two types of coating materials as derivatization agent for the gas diffusion sampling. Total gaseous reactive molecular bromine species, BrX (Br_2, BrCl, (H)OBr), were determined by denuders coated with 15 µmol of 1,3,5-trimethoxybenzene (TMB) - which reacts to 1-bromo-2,4,6-trimethoxybenzene - and subsequent gas chromatography-mass spectrometry (GC-MS) analysis (Rüdiger et al., 2017)."

P11L2 and Author Comment from 15 Dec 2017 – There is significant literature on the issue of comparing data from sensors with different response times. For example, it would be good to cite one or both of these studies:

Roberts, T. J., Saffell, J. R., Oppenheimer, C., & Lurton, T. (2014). Electrochemical sensors applied to pollution monitoring: Measurement error and gas ratio bias at volcano plume case study. Journal of Volcanology and Geothermal Research, 281, 85–96. https://doi.org/10.1016/j.jvolgeores.2014.02.023

Roberts, T. J., Braban, C. F., Oppenheimer, C., Martin, R. S., Freshwater, R. A., Dawson, D. H., . . . Jones, R. L. (2012). Electrochemical sensing of volcanic gases. Chemical Geology, 332–333, 74–91. https://doi.org/10.1016/j.chemgeo.2012.08.027

In the author comment from 15 Dec 2017, an EGU presentation is cited in this context, but I was not able to find the presentation online. Only the abstract is available, and this makes no mention of a method

used to correct for different sensor response times. Also, please clarify how exactly the 'response time factor' is defined.

Reply: We replaced the former explanation by a more complete description, including the definition of the 'response time factor' and the first citation proposed by the referee (Roberts et al. 2014).

"In order to adjust the response times of the two sensors, a slow response signal for the CO2 sensor (CO2,sim) was simulated. This was achieved through convolution of the original signal with a typical sensor pulse response

$$f(t) = \begin{cases} 0, & t < 0 \\ \frac{1}{\tau} e^{-t/\tau}, & t \geq 0 \end{cases}$$

with t being time and τ being the 'response time factor', which in this context can be regarded as a measure for the degree of smoothing. The approach is mathematically equivalent to an approach shown by Roberts et al. (2014). The response time factor τ was tuned, such that the correlation of $CO_{2,sim}$ and SO_2 signal got maximized for discrete peaks (see Fig. 5 (a)). This was already done by Arellano et al. (2017), who also applied the Sunkist instrument in gas measurements in Papua New Guinea in 2016."

Figure 5: (a) Example of time series for mixing ratios of SO_2 and CO_2 (original data in red, resampled data in black), showing discrete gas masses at Stromboli volcano (1st flight on 05th April 2016), (b) Correlation plot for the determination of the relative time response factor for the CO_2 gas sensor with a maximum at a relative time response factor of 1.7, (c) CO_2 over SO_2 mixing ratios, showing the outcome of the resampling of the fast CO_2 with a relative time response factor of 1.7 (lower plot), linear regression results CO_2/SO_2 ratios of 64 ± 16 the first peak and 42 ± 4 for the second.

P11L22 – How long was the denuder sampling period? I.e. how long did the instrument need to hover in the plume to collect a good sample?

Reply: The sampling period is shown in table 4. We sampled between 1 and 5 minutes. Depending on the mixing ratio of reactive molecular bromine species and flow rates the sampling times were sufficient to trap about 1 to 3 ng of Br2 equivalents, which lead to detectable and quantifiable signals in with the used GC-MS method including a previous pre-concentration step during the sample preparation.

P13L14 – This is where condensed water is mentioned, despite the fact that the sensors are specified to require non-condensing conditions. Please explain the caveats with these measurements if possible.

Reply: As mentioned earlier, we used µm pore sized filters to filter out condensed/particle phase at the Sunkist instrument. At Masaya, we also compared the SO_2 sensors signals for both instruments (Sunkist and Black Box) and could not find significant differences. Most of the sensors used in volcanological applications are probably not specifically designed by the manufacturer for those environments and I would assume that the specifications from the data sheet are mostly for user, who do not calibrate or use the sensors in scientific applications.

P14L8 – At Stromboli, explosions may be associated with CO2-rich gas slugs rising through the conduit and venting into the atmosphere. However, in this model, all the CO2 and SO2 is emitted from the vent itself. Once in the atmosphere, the gas is diluted of course, but as far as I can tell, the ratio of volcano CO2 to SO2 should remain constant over time and space. It is not at all clear to me why the C/S ratio would be different once the plume becomes more dilute. Please explain the mechanism that you are suggesting may change that ratio as the plume moves in space and time.

Reply: The referee is correct here. Dilution does not change the C/S ratio. The statement might be phrased a bit unfortunate. It is stated that we measured high C/S values close to the vent in an undiluted plume region and not that it changes by dilution.

"[…] and therefore act as a possible explanation for the detected high CO_2/SO_2 ratios."

P14L14 – You state that the MultiGAS measurements broadly agree with the UAS measurements, but fail to mention that there appears to be quite a large systematic difference between the average values obtained by the two instruments. According to Figure 7, the MultiGAS seems to measure C/S of no more than 15, with an average of about 7, whereas the UAS instrument measured between about 10 and 65, with an average of around 30. This is a significant difference and should be addressed in the text. Simply stating that the measurements were not taken at the identical time and place is a little weak in terms of an explanation, especially given my previous comment.

Reply: We agreed with the referee that this issue could be addressed a bit more in detail. We state that our UAS measurement agree with only some of the MultiGAS measurements. The MultiGAS instrument only measures four times a day for 30 minutes and averages over this period, which already leads to attenuation of high C/S ratios associated with CO2 rich gas bubbles, e.g. when a gas cloud with high C/S ratios passes the instrument only for a period of seconds. Another point we made is that we observed the explosion, while the UAS was flying in direct proximity to the vent, while there is no record of the explosions for the MultiGAS data, because they were not measuring the plume at that time of the day due to the discontinuous monitoring (4 times a day) and the wind direction wasn't blowing to the MultiGAS station at this moment. Both instruments only present "snapshot" data, but of a different kind.

"The MG instrument only measures ~~twice~~ four times a day for 30 minutes and averages over this time, while with the SK instrument we identified discrete peaks of gas clouds with different CO_2/SO_2 ratios."

P14L17 – I don't understand why high C/S ratios should be left aside. You do have at least some observations of ongoing eruptive activity during the time that you were there for the UAS measurements, and clearly the datasets overlap in time so in first order approximation, you would think that the same activity was sampled by both instruments. Can you please clarify?

Reply: Hopefully the explanation above already clarified that matter. For a comparison of MG and SK, high values should be left aside since we do not know whether the MG measured any eruptive released gases. While those gas clouds probably only make up a minor period for the MultiGAS integration time.

Table 2 – I assume that the 'lower SO2 limit' refers to a limit below which the data was not used for deriving C/S ratios. Can you please explain how this limit was chosen and why it varied for different datasets?

Reply: For the calculation of the C/S ratios, we used a linear regression with error propagation (York et al. 2004). The size of the error obtained by this propagation is partly dependent from the number of data points. With a large number of data points (associated with a longer exposition to the same gas cloud) lower limits could be used for the scatter plot and linear regression, since the noisier signal at lower ppm values do not contribute significantly to the error propagation. On the other hand, for gas clouds which only briefly pass the sensors (or the sensors the clouds), we chose to only use the less noisy signals, meaning a higher SO2 limit to derive the ratio, since potential outliers would affect the C/S ratio and its error more. Lower limits are accompanied with larger errors and therefore lower confidence, which is a drawback related to short exposition times in UAS operations.

Figure 6 – Either I'm not understanding or something appears to be amiss with this figure and/or the caption. The bottom two plots are labeled the same. I assume that the bottom plot should actually be the MG SO2 mixing ratio, correct? And in the caption, I assume that you mean that the SK CO2 raw data is shown in grey and the resampled CO2 data is shown in black, correct?

Reply: We thank the referee for pointing out the flaws in the figure and caption.

"Figure 6: Comparison of SO_2 and CO_2 time series of a Multi-GAS (MG) instrument and the *Sunkist* (SK) unit at the Masaya volcano crater rim (for SK CO_2 raw data in grey, resampled data in black), both instruments inlets were place in proximity to each other (14th July 2016); SK CO_2/SO_2 = 3.63+/- 0.43 background CO_2 = 439 ppm); MG CO_2/SO_2 = 2.94 +/- 0.30 (background CO_2 = 413 ppm); (additional scatter plots in the supplementary material)"

P17L10 – Here you point out that BrX/SO2 appears to vary with CO2/SO2, though no trend can be derived from the three obtained data points. What does this observation really mean? If BrX/SO2 was in some way proportional or anti-proportional to CO2/SO2, then one might attribute the change to various gas compositions being emitted from the volcano at different times. However, a varying dependency seems to negate this explanation as being primarily responsible. So what could possible cause this? Or is this a sign that something is wrong with the derived CO2/SO2? (also see previous comments on comparison to MultiGAS).

Reply: As we stated in the text, an interpretation would be too ambitious with the few data we obtained. What we meant to show here is that we simply proofed the principle of our techniques and can use them to obtain that kind of data (BrX/SO2 vs. CO2/SO2 or time/distance). For the investigation of volcanological and atmospheric dependencies, a larger data set would be needed.

"CHANGES"

Figure 7 – What criteria were used to select valid MultiGAS data? You mention the different SO2 lower limits for the SK, but what about the MultiGAS? Also, as mentioned before, I think the systematic difference shown here is a bit alarming and needs some careful thought and discussion.

Reply: The MultiGAS data was derived by standard procedure (RatioCalc) and a lower limit of 4 ppm of SO2. The difference in this plot seems significant on the first view, for sure. But as discussed above the difference results from different measurement periods. The MultiGAS Data represents 5 days, while the UAS data only a few hours on different days and also shows C/S ratios obtained for discrete gas clouds.

"CHANGES"

P20L25 – What do you mean by 'previously unstudied plume regions'? Areas very close to the vent? What do you think are the limitations on this, e.g. with regards to heat exposure, ash concentration etc.?

Reply: With regards to spectroscopic methods, "unstudied" seems to miss the point we wanted to make. We rather meant 'previously physically inaccessible plume regions'. Heat exposure and ash concentration for sure limit UAS operations, but UAS could for sure fly to regions, which manned aircraft aren't able to access. In general, I would think that heat is a minor problem, since hot gas is diluted rather quickly and at Masaya drone flights have been made into Santiago crater into the gas above the lava lake, few hundred meters of distance though. After some flights at Turrialba we observed ash deposition on the UAS after flying into the plume for in-situ sampling, which did not affect the drone. After 50+ in-plume flights we now consider to change the motors of the drone.

"CHANGES"

P20L25 – I may be wrong, but I think that UAS operations with pre-programmed flight paths have already been done, see e.g.
Mori, T., Hashimoto, T., Terada, A., Yoshimoto, M., Kazahaya, R., Shinohara, H., & Tanaka, R. (2016). Volcanic plume measurements using a UAV for the 2014 Mt. Ontake eruption the Phreatic Eruption of Mt. Ontake Volcano in 2014 5. Volcanology. Earth, Planets and Space, 68(1). https://doi.org/10.1186/s40623-016-0418-0

Reply: You are correct. We already cited that reference. The emphasis of the statement at P20L25 was on the scheduled pre-preprogrammed flights. We were imagining hangars of UAVs at a volcano from which autonomous operations take place on a regular basis, rather than field campaigns. We rephrased that sentence.

"Technological advances promise to enable scheduled pre-programmed and autonomous UAV operations (e.g. from hangars close to volcanoes) with extended flight times for regular hazard assessments."

Minor corrections

The manuscript would benefit from careful proof-reading. A significant number of minor corrections would improve the legibility of the text. Listed below are some of the more important corrections needed for clarity, but there are likely several others.

Reply: We thank the referee for his help improving the manuscript and we corrected the specific items as follows.

"CHANGES"

P1L18 – . . . (e.g. carbon dioxide) TO THE ATMOSPHERE.

"(e.g. carbon dioxide) to the atmosphere."

P1L19 – Consider rewording this sentence to something like: The relative abundance of carbon and sulfur in volcanic gas as well as the total sulfur dioxide emission rate from a volcanic vent are established parameters in current volcano monitoring strategies, and they oftentimes allow insights into subsurface processes. On the other hand, chemical reactions involving halogens are thought to have local to regional impact on the atmospheric chemistry around passively degassing volcanoes.

"*The relative abundance of carbon and sulfur in volcanic gas as well as the total sulfur dioxide emission rate from a volcanic vent are established parameters in current volcano monitoring strategies, and they oftentimes allow insights into subsurface processes. On the other hand, chemical reactions involving halogens are thought to have local to regional impact on the atmospheric chemistry around passively degassing volcanoes.*"

P1L21 – Recommend removing 'on board'

"[…] payloads for the compositional analysis […]"

P1L22 – Recommend removing 'with such new measurement strategy'

"[…] The various applications and their potential are presented and discussed on example studies at three […]"

P1L23 – Consider appending the altitudes to the individual volcanoes, e.g. Turrialba Volcano (3,300 m), Stromboli Volcano (930 m) . . .

Reply: For the abstract we think it's sufficient that the flight heights are mentioned and not the specific volcano elevation, which are given in the text already.

P1L27 – Remove ',' after including

"[…] including abundances […]"

P2L6 – Consider mentioning v. Glasow et al 2009 for a more complete treatise of plume chemistry? von Glasow, R., Bobrowski, N., & Kern, C. (2009). The effects of volcanic eruptions on atmospheric chemistry. Chemical Geology, 263(1–4), 131–142. https://doi.org/10.1016/j.chemgeo.2008.08.020
Reply: We thank the referee for this suggestion. We added the reference later in the text

"Furthermore, knowledge about in-plume chemical reactions can be drawn from compositional assessment of the gases, which also helps understanding their impact on atmospheric chemistry (e.g. Lee et al., 2005; von Glasow, 2009; Gliß et al., 2015)."

P2L11 – There are a few other recent articles that could be mentioned in this context: Mason, E., Edmonds, M., & Turchyn, A. V. (2017). Remobilization of Crustal Carbon May Dominate Volcanic Arc Emissions. Science, 357, 290–294. https://doi.org/10.1126/science.aan5049

de Moor, J. M., Kern, C., Avard, G., Muller, C., Aiuppa, A., Saballos, A., . . . Fischer, T. P. (2017). A new sulfur and carbon degassing inventory for the Southern Central American Volcanic Arc : The importance of accurate time-series datasets and possible tectonic processes responsible for temporal variations in arc-scale volatile emissions. Geochemistry Geophysics Geosystems, 18, 1–32. https://doi.org/doi:10.1002/2017GC007141

"Measuring the emitted gas composition can provide crucial information on understanding subsurface processes related to activity changes (e.g. Allard et al., 1991; Aiuppa et al., 2007; Bobrowski and Giuffrida, 2012; de Moor et al., 2016a; Liotta et al., 2017) and help to estimate fluxes of the geological carbon cycle (e.g. Burton et al., 2013; Mason et al., 2017) and tectonic processes controlling volcanic degassing (e.g. Aiuppa et al., 2017; de Moor et al. 2017)."

P2L12 – the observation of gas composition changes HAS BECOME an important tool

"[…] the observation of gas composition changes has become an important tool for detecting […]"

P2L18 - . . . characterization of volcanic ACTIVITY IS GAS EMISSION RATE. Particularly, the determination of SO2 FLUX has become. . .

"Another important parameter for the characterization of volcanic activity is gas emission rates. Particularly, the determination of SO_2 flux has become a standard procedure"

P2L21 - . . . manned AIRCRAFT, . . .

"or manned aircraft, but"

P2L22 - . . .poorly accessible TERRAIN.

"accessible terrain."

P3L13 – crater rim MAY BE ASSOCIATED WITH a considerable . . .

"crater rim may be associated with considerable risk."

P3L14 – Perhaps be more general and say that gas monitoring stations are deployed in close proximity to active volcanic vents (rather than 'at the crater rim')

"gas monitoring stations are deployed and maintained in close proximity to active volcanic vents by researchers, putting themselves at risks."

P3L25 – please specify that 'DRONE-BASED sampling' has not yet been reported.

Reply: This sentence was removed.

P3L27 – Change 'systems' to 'system'.

"[…] sensing (electrochemical/optical sensors) systems for the determination […]"

P4L7 – 'horseshoe-shaped area THAT IS NOT SAFELY ACCESSIBLE ON FOOT'

"horseshoe-shaped area (Sciara del Fuoco) that is not safely accessible on foot."

P4L8 – 'well accessible, and numerous monitoring stations have been installed here for continuous observation of the ongoing volcanic activity'

“The summit above the craters is well accessible, and numerous monitoring stations have been installed here for continuous observation of the ongoing volcanic activity”

P4:14 – The UAV was mostly launched at the northern shelter

“The UAV was mostly launched at the northern shelter (see Fig. 1).”

Figure 1 caption – Overview OF the sampling. . .

“Figure 1: Overview of the sampling […]”

P5L9 – the ‘DCO-DECADE’ and NOVAC acronyms should probably be explained and perhaps a reference can be added where more information can be found on DCO-DECADE?

“Continuous monitoring of the gas emissions is realized by a stationary Multi-GAS (MG) system (through the Deep Carbon Observatory – Deep Earth Carbon Degassing initiative (DCO-DECADE)) at the crater rim and two scanning DOAS instruments (Network for Observation of Volcanic and Atmospheric Change (NOVAC) (Galle et al., 2010)) in the downwind direction.”

P6L9 - . . .using PROPELLERS with a diameter. . .

“using propellers with”

P6L17 . . . areas of dense plume IN WHICH to hover the system. . .

“[…] dense plume in which to hover […]”

P7L1 – within a radius of a few meters AROUND THE INLET.

“[…] within a radius of a few meters around the inlet […]”

P7L2 – please clarify what you mean by ‘which represents homogeneous conditions for a widely spread out plume’. I did not understand this phrase. Figure 3 caption – (c) interior view OF the . . .

Reply: If the plume is widely spread we assume that the UAS samples air which represents the plume and is not attracting ambient air towards its inlet.

“[…] represents homogeneous plume gas for a widely spread out plume […]”
“[…] interior view of the Sunkist […].”

P9L6 . . . foam case AND HAS a total weight of 500 g.

“[…] foam case and has a total weight […]”

P9L8 – Gas was pumped through the sensors in series.

“[…] pumped through to the sensors in series […]”

P9L20 - . . . to ensure that weight requirements WERE MET.

“[…] ensure that weight requirements were met.”

P9L23 – change ‘mixing ration’ to ‘mixing ratio’.

“[…] SO2 mixing ratio […]”

P10L21 – Consider replacing ‘Evaluation’ with ‘Validation’

“Validation of the SO2 fluxes obtained […]”

P13L7 - . . .above ground level OF 1080 m was recorded

“[…] ground level of 1080 m was […]”

P14L4 – These flights covered distances OF between 11 and 419 m from the vent

“[…] distances of between […]”

P14L5 – Consider changing ‘gas masses’ to ‘gas clouds’ or similar to avoid confusion with a measure of weight.

“[…] gas clouds […]”

P14L8 – change ‘explosion’ to ‘explosions’

“[…] strombolian ash explosions occurred […]”

P14L13 – Recommend removing ‘has’

“[…] Multi-GAS station (placed on the SE rim of the crater terrace) discontinuously measured […]”

P14L15 – Remove ‘an’ before ordinary

“[…] exemplary for ordinary Strombolian activity […]”

P14L16 - . . . both instruments DID not MEASURE SIMULTANEOUSLY or. . .

“It has to be taken into account that both instruments did not measure simultaneously or in proximity to each other.”

P17L4 - . . . bromine SPECIATION in volcanic plumes has been THE subject of. . .

“Although the bromine speciation in volcanic […]”

P17L8 - . . . The DATA PRESENTED HERE for the first minute after emission HIGHLIGHT the potential. . .

“The DATA presented here for the first minute after emission highlight the potential […]”

P17L9 - . . . thus OBTAIN a better understanding. . .

“acquisition and thus obtain a better understanding […]”

Figure 7 caption – Perhaps include the volcano name (Stromboli) in the caption to clarify the measurement location.

[…] system at Stromboli volcano […]

P19L1 – . . . can significantly change THE PLUME’S travel direction. . .

“[…] can significantly change the plume’s travel direction […]”

P20L16 – Consider changing ‘high-class’ to ‘more sophisticated’

“[…] more sophisticated components […]”

P20L24 – . . . gain INSIGHTS into . . .

“[…] to gain insights into reactive […]”

P20L25 - . . . this method COULD yield data from. . .

“[…] this method could yield data […]”

Supplementary Material – is there a PDF document missing here? There is mention of a PDF containing the wiring diagram of the Black Box unit, but I don’t see that here. Please double check on this. Thank you!

Reply: We thank the referee for hinting at the missing document. It will be added to the supplementary material

Answer to comments from Referee 2 (J. A. Diaz):

“… . I do recommend the article for publication with the small corrections that the other referee is suggesting, which in most cases I concur.”

Reply: We thank the J.A. Diaz for reviewing the manuscript.

Answer to short comment by R. Campion:

“I would just like to point out that the first application of a UAV to the study of the chemistry of volcanic plumes dates back to the late 70s…”

Reply: We thank R. Campion for the reference suggestion and added it to the manuscript

“As in the last decade with the development of compact and cost effective unmanned aerial vehicles (UAV) several deployments of gas sensors and other in-situ methods (e.g. particle detection (Altstädter et al., 2015)) as well as applications of spectrometers were realized (e.g. McGonigle et al., 2008, Diaz et al., 2015, Mori et al., 2016, Villa et al., 2016 and references therein). Pioneering UAV deployments were conducted in the late 70’s (Faivre-Pierret et al, 1980).”

~~Multicopter measurements~~Implementation of electrochemical, optical and denuder-based sensors and sampling techniques on UAV for volcanic gas ~~emissions at~~measurements: examples from Masaya ~~(Nicaragua),~~, Turrialba ~~(Costa Rica)~~ and Stromboli ~~(Italy) volcanoes: Applications for volcano monitoring and insights into halogen speciation~~Volcanoes

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[7]Instituto Nicaragüense de Estudios Territoriales, Managua, Nicaragua

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Abstract. Volcanoes are a natural source of several reactive gases (e.g. sulfur and halogen containing species), as well as non-reactive gases (e.g. carbon dioxide~~). Besides that, halogen chemistry in volcanic plumes might have important impacts on atmospheric chemistry,~~) to the atmosphere. The relative abundance of carbon ~~to sulfur ratios~~ and sulfur in volcanic gas as well as the total sulfur dioxide ~~fluxes~~emission rate from a volcanic vent are ~~important~~ established parameters ~~to gain information on~~in current volcano monitoring strategies, and they oftentimes allow insights into subsurface processes. On the other hand, chemical reactions involving halogens are thought to have local to regional impact on the atmospheric chemistry around passively degassing volcanoes. In this study we demonstrate the successful deployment of a multirotor UAV (quadcopter) system with custom-made lightweight payloads ~~on board~~ for the compositional analysis and gas flux estimation of volcanic plumes. The various applications and their potential ~~with such new measurement strategy~~ are presented and discussed on example studies at three volcanoes encompassing flight heights of 450 m to 3300 m and various states of volcanic activity. Field applications were performed at Stromboli Volcano (Italy), Turrialba Volcano (Costa Rica) and Masaya Volcano (Nicaragua). Two in-situ gas-measuring systems adapted for autonomous airborne measurements, based on electrochemical and optical detection principles, as well as an airborne sampling unit, are introduced. We show volcanic gas composition results including~~,~~ abundances of CO_2, SO_2 and halogen species. The new instrumental set-ups were compared with established instruments during ground-based measurements~~.~~ at Masaya volcano, which resulted in CO_2/SO_2 ratios of

3.6 ± 0.4. For total SO_2 flux estimations a small differential optical absorption spectroscopy (DOAS) system measured SO_2 column amounts on transversal flights below the plume~~, showing the potential to replace ground based manned operations.~~ at Turrialba Volcano, giving 1776 ± 1108 T/d and 1616 ± 1007 T/d of SO_2 during two traverses. At Stromboli volcano, ~~short term fluctuation of the~~elevated CO_2/SO_2 ratios ~~could be determined and confirm an increased CO_2/SO_2 ratio~~have been observed in spatial and temporal proximity to explosions by airborne in-situ measurements. Reactive bromine to sulfur ratios of 0.19 x 10^{-4} to 9.8 x 10^{-4} were measured in-situ in the plume of Stromboli volcano downwind of the vent.

1 Introduction

Gaseous volcanic emissions consist of a variety of different compounds and are dominated by water vapor (H_2O), carbon dioxide (CO_2), sulfur dioxide (SO_2), and hydrogen sulfide (H_2S) (Symonds et al., 1994). Minor abundant, but nonetheless important gas species are halogen-bearing compounds which are emitted as hydrogen halides (HF, HCl, HBr and HI) and later partly transformed by heterogeneous reactions into other halogen species, such as bromine monoxide (BrO) or chlorine dioxide (OClO) (Bobrowski et al., 2007). The relative gas composition varies with the types of volcanoes and magmas as well as with transport and degassing mechanisms. Changes in the magma degassing behavior and/or the hydrothermal systems beneath volcanoes generally influence the gas composition and gas fluxes. Measuring the emitted gas composition can provide crucial information on understanding subsurface processes related to activity changes (e.g. Allard et al., 1991; Aiuppa et al., 2007; Bobrowski and Giuffrida, 2012; de Moor et al., 2016a; Liotta et al., 2017) and help to estimate fluxes of the geological carbon cycle (e.g. Burton et al., 2013; Mason et al., 2017) and tectonic processes controlling volcanic degassing (e.g. Aiuppa et al., 2017; de Moor et al. 2017). In the field of volcanic monitoring, the observation of gas composition changes ~~became~~has become an important tool for detecting precursory processes for volcanic eruptions. ~~It has been shown that enhanced~~ For instance, the CO_2/SO_2 emission ~~ratios appear prior to eruptive~~ratio strongly varies with volcanic activity, which is associated to magma rising up a conduit. The solubility of magmatic gases is pressure dependent and different gases are released from the magma at different depths during the magma ascent, that is accompanied by pressure decrease. Gas ratio changes have been observed within the timescale of hours to weeks prior to eruptions (e.g. Giggenbach, 1975; Aiuppa et al., 2007; de Moor et al., 2016a, de Moor et al., 2016b~~).~~) and their magnitude, direction, and pace are highly variable throughout different volcanic systems and state of activity. In-situ measurements of this gas ratio has become a well-established method using electrochemical (SO_2) and infrared (CO_2) sensors, implemented in so-called Multi-GAS (MG) instruments, which may also contain other sensors and are field-deployable to work autonomously close to volcanic emission sources (Shinohara, 2005; Aiuppa et al., 2006).

Another important parameter for the characterization of volcanic ~~activities are~~activity is the gas emission ~~rates (fluxes).~~rate. Particularly, the determination of SO_2 ~~fluxes~~flux has become a standard procedure by traversing the plume and multiplying the integrated SO_2 cross-section with the estimated plume transport speed (e.g. McGonigle et al., 2002; Galle et al., 2003;

López et al., 2013). With the development of small DOAS instruments, traversing the plume is not only feasible by cars, boats, or manned ~~aircrafts~~aircraft, but also by walking in case of poorly accessible ~~terrains.~~ terrain. Furthermore, knowledge about in-plume chemical reactions can be drawn from compositional assessment of the gases, which also helps understanding their impact on atmospheric chemistry (e.g. Lee et al., 2005; Glasow et al., 2009, von Glasow, 2010; Gliß et al., 2015). Especially the halogen chemistry is of great interest as BrO/SO_2 ratios in volcanic plumes are readily measurable by remote sensing UV spectrometry (e.g. Bobrowski et al., 2003, Lübcke et al., 2014) and have been discussed in recent years as another potential precursory observable for volcanic activity changes. ~~It was~~Although several studies observed ~~that~~decreases in the BrO/SO_2 ratio ~~decreases~~ in advance to eruptive phases (e.g. Lübcke et al., 2014) and ~~is~~ lower ratios during periods of continuous activity (Bobrowski and Giuffrida, 2012~~). However~~), it is not yet clear whether magma-gas partitioning of bromine occurs prior or after sulfur during the pressure drop associated with magma ascents (Dinger et al., 2017). Furthermore, BrO is not a directly emitted species rather than the product of complex heterogeneous chemistry in the volcanic plume involving reactions with magmatic gases with entrained air (e.g. Gerlach, 2004, Bobrowski et al., 2007). The variation of BrO by plume age and a transversal distribution in the plume for this species was observed by differential optical absorption spectroscopy (DOAS) measurements (Bobrowski ~~and Platt,~~et al., 2007). ~~Furthermore~~Additionally, other reactive halogen species with oxidation states ≠ -1 (e.g. Br_2, Cl_2, BrCl and others) have been measured in-situ in the plume of Mt. Etna, Italy (Rüdiger et al., 2017) and Mt Nyamuragira (Bobrowski et al~~.~~., 2017~~, accepted~~). In the last decade, several model studies (e.g. Bobrowski et al., 2007, Roberts et al., 2009; von Glasow, 2010; Roberts et al., 2014; Jourdain et al., 2016) have engaged on the variation of halogen variability in volcanic plumes with respect to various atmospheric and magmatic parameters. In the case of bromine, it was modelled that the initial emitted hydrogen bromide is depleted shortly after emission under consumption of tropospheric ozone and is transformed to reactive species such as BrO, HOBr, Br_2, BrCl and $BrONO_2$. Due to the challenging task of accessing volcanic plumes on a timescale of minutes after emission, and the lack of spectroscopic methods for most of these reactive species, uncertainties about their relative abundances still exist. One approach towards the in-situ observation of reactive halogen species is the application of gas diffusion denuder sampling using a selectively reactive organic coating (1,3,5-trimethoxybenzen, TMB) to trap and enrich gaseous species containing a halogen atom with the oxidations state +1 or 0 (e.g. Br_2 or BrCl), while being insensitive to the particle phase (Rüdiger et al., 2017).

In the case of most volcanoes sampling on the crater rim ~~presents great~~may be associated with considerable logistical challenges and hazards for people and instruments. During phases of high activity crater rims are usually not accessible at all and even during quiescent degassing work at the crater rim represents a considerable risk. However, the knowledge of plume gas composition is an important component for activity assessments of volcanoes (e.g. Carroll and Holloway, 1994; Aiuppa et al., 2006) and therefore gas monitoring stations are deployed and maintained ~~at the crater rim~~in close proximity to active volcanic vents by researchers, putting themselves at risks. Advancements in the application of remote sensing techniques have helped to minimize personnel exposition to the volcanic danger zone (e.g. Galle et al., 2003; Tamburello et al., 2011). However, still today the detection of certain gas species and/or total amounts of all species of an element is not possible

remotely (neither ground based nor with satellites) and therefore in-situ measurements are an important tool, especially for resolving chemical reactions and speciation changes in aging volcanic plumes. With an in-situ sampling strategy, obtaining samples from the freshly emitted plume is feasible, while ground-based in-situ sampling of the aged plume further downwind is rarely possible and dependent on specific wind and geographical conditions. ~~In~~As in the last decade with the development of compact and cost effective unmanned aerial vehicles (UAV) several deployments of gas sensors and other in-situ methods (e.g. particle detection (Altstädter et al., 2015)) as well as applications of spectrometers were realized (e.g. McGonigle et al., 2008, Diaz et al., 2015, Mori et al., 2016, Villa et al., 2016 and references therein~~).~~). Pioneering UAV deployments were already conducted in the late 70's (Faivre-Pierret et al., 1980). While these drone-based applications focused mostly on the use of sensors and spectroscopy methods, ~~sampling (e.g. canister sampling (Chang et al., 2016)) of the plume has not been reported for volcanoes. Here~~ we present here a low-cost UAV-deployable sampling (gas diffusion denuder) and sensing (electrochemical/optical sensors) systems for the determination of CO_2, SO_2 and halogen species. Our system enabled us to access the plume close to an active vent as well as the aged plume several km downwind of the source and elevated from ground, without exposing operators to the risks in proximity to active vents or employing manned aircrafts to potential engine-damaging ash and gas plumes. In addition to that, the UAV-deployment of a lightweight DOAS instrument for SO_2 flux estimations is presented herein, which enables fast plume traversing in terrains that are usually not accessible by cars or even by foot.

2. Site description

2.1 Stromboli

Stromboli volcano, the northernmost island of the Aeolian volcanic arc (Italy), rises 924 m above sea level (a.s.l.). The island represents the top part of a large 2500-m-high stratovolcano emerging from the Tyrrhenian Sea floor. Stromboli is well known for its regular (~ every 10-20 min) explosive activity (Strombolian activity). Intermittently, continuous passive degassing occurs from the active vents, which are located in the so-called crater terrace at about 750 m a.s.l.. Ejected lava material is dominantly deposited in a northwestern direction, forming a ~~hardly safe-to non-accessible~~ horseshoe-shaped area (Sciara del Fuoco~~).~~) that is not safely accessible on foot. The summit above the craters is well accessible, and ~~characterized by a~~ numerous ~~amount of~~ monitoring stations ~~continuously observing~~ have been installed here for continuous observation of the ongoing volcanic activity. Thus, Stromboli has been a laboratory volcano for studying magma degassing processes (Allard et al. 2008) and field-testing new instrumentations for many years.

While most gas monitoring station positions benefit from a north westerly wind direction, a south easterly wind only allows gas plume detection by spectroscopic methods. In this study, due to the dominance of southeast winds in early April 2016 an approach from an eastern direction was chosen, using a multicopter as carrier for gas sampling and sensing instruments. The ~~take-off area~~UAV was ~~most of time~~mostly launched at the northern shelter (see Fig. 1).

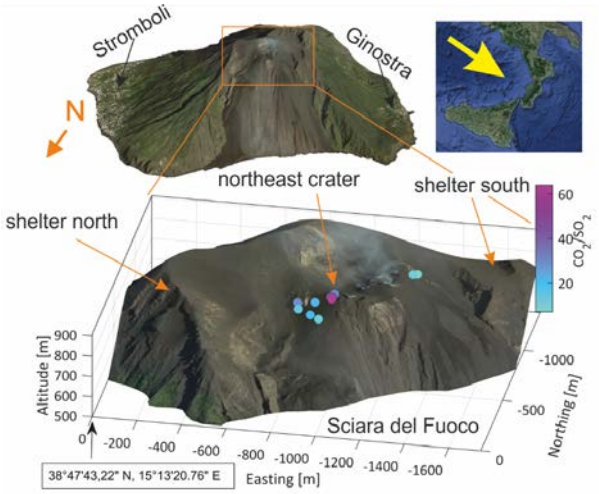

Figure 1: Overview ~~on~~of the sampling site at Stromboli Volcano with the locations of the retrieved CO_2/SO_2 mixing ratios given in Table 2

2. 2 Masaya

Masaya volcano (elevation ~ 600 m a.s.l.), Nicaragua, is a basaltic-andesite shield volcano caldera (6 x 11 km in size) hosting a set of vents. The currently active vent is situated in the Santiago pit crater, formed in 1858-1859 (McBirney, 1956). Masaya persistently emits voluminous quantities of SO_2, with fluxes typically ranging from 500 T/d to 2500 T/d (e.g. (Mather et al., 2006; de Moor et al., 2013; Carn et al., 2017), making this volcano currently to one of the ~~single~~ largest contributor to volcanic gas emissions in the Central American Volcanic Arc (~~Mather~~de Moor et al~~., 2006~~. 2017). In January 2016 the reoccurrence of a new superficial lava lake (~40 x 40 m) was observed together with an increase in activity. Due to high emission rates and the low-altitude plume, Masaya volcano has a detrimental environmental impact on the downwind areas, diminishing vegetation and potentially affecting human health (Delmelle et al., 2002). Continuous monitoring of the gas emissions is realized by a stationary Multi-GAS (MG) system (through the Deep Carbon Observatory – Deep Earth Carbon Degassing initiative (DCO-DECADE ~~program~~)) at the crater rim and two scanning DOAS instruments (Network for Observation of Volcanic and Atmospheric Change (NOVAC ~~network~~) (Galle et al., 2010)) in the downwind direction. Besides the presence of a strong plume, Masaya volcano provides perfect conditions for field-testing new methods and studying plume chemistry using UAVs: easy accessibility by car, low altitude, and relative stable dominant wind direction (northeast). In July 2016 flights were launched from the caldera bottom marked “flight area” in Fig. 2 (c).

2. 3 Turrialba

Turrialba is a stratovolcano with a peak elevation of 3340 m a.s.l. and is located about 35 km east and directly upwind of San José, the capital of Costa Rica. It is the southernmost active volcano of the Central American Volcanic Arc. In the 2000s, an almost 150 years long period of quiescence has ended and since 2010 several vent opening phreatic eruptions henceforth occurred marking an ongoing but erratic phase of unrest (Martini et al., 2010), characterized by variable ash and gas emission intensities (up to 5000 tons/day of SO_2 (de Moor et al., 2016a~~)).~~)), making Turrialba volcano to the second substantial emitter in the arc, besides Masaya volcano (de Moor et al. 2017). The proximity of Turrialba volcano to the densely populated central valley with Costa Rica's major international airport and the dominant western wind direction is responsible for ash depositions, causing health and air traffic problems. Therefore, the activity of Turrialba is continuously monitored by various systems including permanent Multi-GAS stations to observe short-term precursory changes in the gas composition prior to eruptive events (de Moor et al., 2016a). However, stations located near the active vent suffer from ash deposition and ballistic impacts during more frequent episodes, making maintenance demanding and risky or impossible. Furthermore, the accessibility of the summit and surrounding areas is degrading due to intense erosion following vegetation destruction by acid rain, heavy rainfall, ash deposition and remobilization, and the lack of infrastructural maintenance following community evacuation. Thus, the use of UAV-based systems might represent the only viable approach for in-situ measurements of the open vent plume during periods of high activity. In 2016 flights were conducted starting at the "La Silva" site (Fig. 2 (d)) to investigate the feasibility of UAV-based gas sensing system at this challenging environment (high altitude and thick ash plumes).

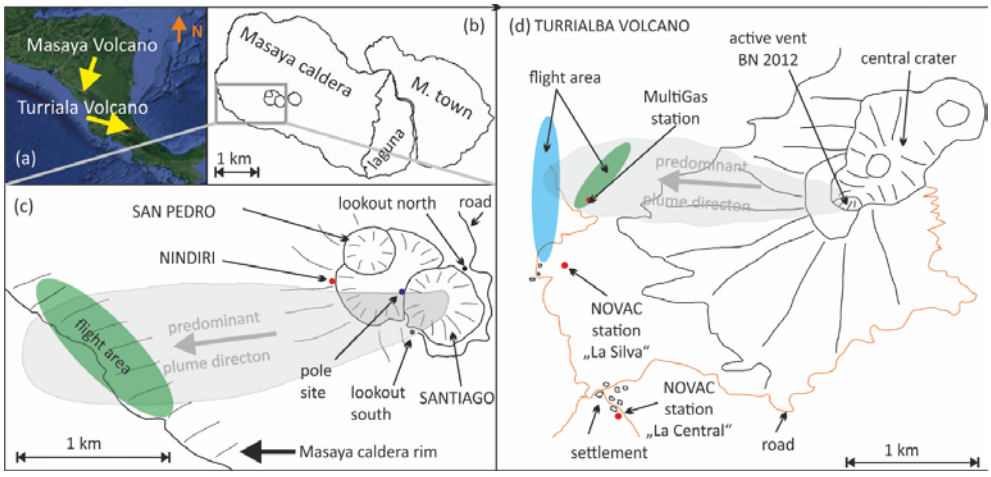

Figure 2: Overview on the field work sites at (a-c) Masaya volcano (Nicaragua) and (d) Turrialba volcano (Costa Rica). Sampling locations mentioned in Table 3 are marked in (c) as follows: Santiago rim, lookout south (black marker); Santiago rim, pole site (blue marker); Nindiri rim (red marker)

3. Instrumentation

3.1 Unmanned aerial vehicle

The UAV (called RAVEN, **r**emote-controlled **a**ircraft for **v**olcanic **e**mission a**n**alysis, see Fig. 3 (a) – (b)) used during the field campaigns was a four-rotor multicopter with foldable arms (Black Snapper, Globe Flight, Germany) with an E800 motor set using ~~propeller~~propellers with a diameter of 13 inch and a pitch of 4.5 inch (DJI Innovations, Shenzhen, China). It was flown manually in line-of-sight conditions. The multicopter had a weight of 2.3 kg including a 22.2 V (6S) 4.5 Ah battery. A maximum payload of 1.3 kg was achieved with various mounted instruments. The foldable frame of the UAV was beneficial in regards of the usual necessity to personally carry equipment into field, especially on volcanoes like Stromboli. Another advantage of this system was that the battery capacity is within the guidelines of air travel restrictions allowing the system to be transported on commercial airplanes. The main controller (NAZA M-2, DJI Innovations, Shenzhen, China) of the multicopter was connected with a combined denuder sampling and SO_2 sensing instrument (hereafter named Black Box (see Sec. 3.3)), to transmit the measured SO_2 data as an 0 V - 5 V signal to the remote control, where it is displayed. This allowed the operator to find areas with dense plume in which to hover the system for stationary sampling and to react to changes of the plume direction, which is challenging if relying only on visual observation of the plume. A data logger (Core 2, Flytrex Aviation, Tel Aviv, Israel) with micro SD card was used to log the flight data from the main controller consisting of GPS coordinates, pressure and temperature data at 2 Hz. The payloads were attached below the main body of the multicopter with an inlet for the in-situ CO_2 and SO_2 sensing instrument (hereafter called Sunkist (see Sec. 3.2)) close to the center of the copter. The sampled air volume can be assumed to originate from within a radius of a few meters around the inlet (see e.g. Roldan et al., 2015; Alvarado et al., 2017; Palomaki et al., 2017), which represents homogeneous ~~conditions~~plume gas for a widely spread out plume. This assumption is confirmed by a self-developed method for the estimation of the origin of sample air, which is described in the supplementary material (Chapter IV).

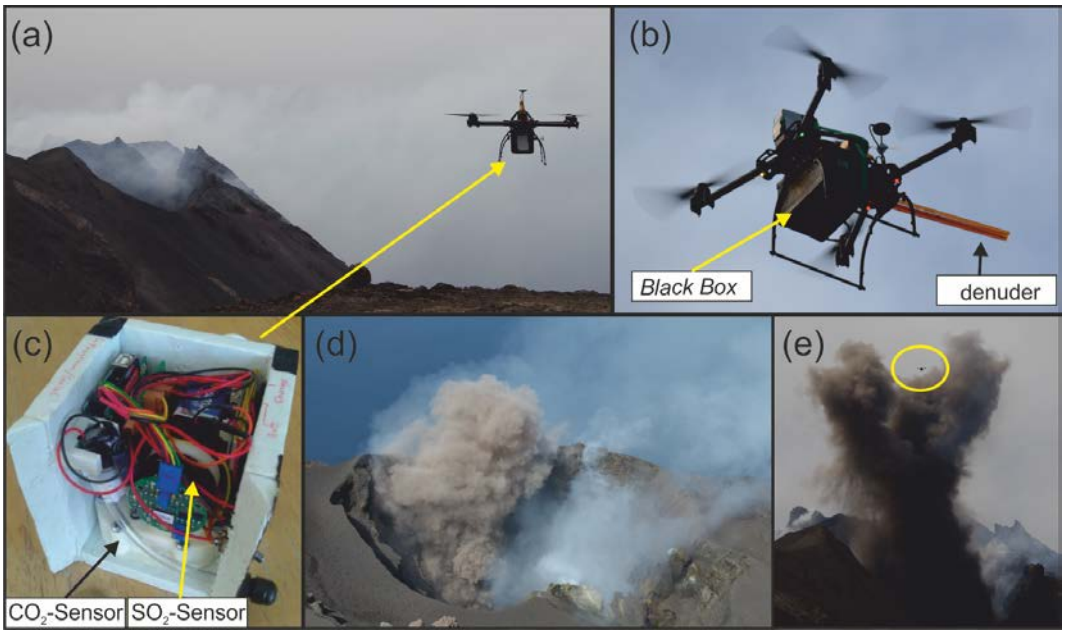

Figure 3: (a) Sampling site at Stromboli Volcano with Northeast crater in the background and the *RAVEN* UAV carrying the *Sunkist* gas monitor, (b) *RAVEN* UAV with the Black Box sampling unit and three gas diffusion denuders, (c) interior view ~~on~~of the *Sunkist* gas monitor, showing the CO_2 and SO_2 sensors, (d) passive degassing (white plume) and eruptive ash explosion (brown ash cloud) at the north east crater at Stromboli Volcano, (e) ash eruption at the Northeast crater producing an ascending ash plume with the RAVEN UAV in direct proximity (yellow circle), returning from sampling flight

3.2 CO_2/SO_2 gas sensors – Multi-GAS (Sunkist)

A gas sensor system was developed for use in volcanic environments with a focus on robustness and compact and lightweight design for application on UAVs. The system, called Sunkist (SK) contains two gas sensors: (1) A CO_2 sensor (K30 FR, SenseAir, Delsbo, Sweden), which uses the principle of non-dispersive infra-red absorption spectroscopy: The sample gas gets sucked into a multi reflection cell, where it is exposed to the radiation of a small infra-red light ~~bulb~~source. The CO_2 concentration is determined by measuring the light attenuation on distinct CO_2 absorption bands in the near infra-red. (2) An electrochemical SO_2 sensor (CiTiceL 3MST/F, City Technology, Portsmouth, United Kingdom), which basically consists of an electrochemical cell, where oxidation of SO_2 on one of the cell's electrodes creates charges and leads to a measureable compensating current between the two cell electrodes.

Table 1: Components and specifications of the sampling and sensing instruments

Component/ Parameter	Specifications Sunkist	Black Box

CO_2 sensor	NDIR, SenseAir CO_2 Engine K30 FR			
SO_2 sensor	Electrochemical, CiTiceL 3MST/F		Electrochemical, CiTiceL 3MST/F	
Operating temperature	0-50°C (CO_2), -20-50°C (SO_2)		-20-50°C	
Operating humidity	0-95% (CO_2), 15-90% (SO_2), non-condensing		15-90% (SO_2), non-condensing	
Operating pressure	Atmospheric ± 10% (SO_2)		Atmospheric ± 10%	
Temperature dependence	1/T (assumed for CO_2), 0.25 %/°C (SO_2)		0.25 %/°C	
Pressure dependence	1.6 %/kPa (CO_2), 0.0015 %/kPa (SO_2) #		0.0015 %/kPa #	
Response time	2 s (CO_2), <20 s (SO_2)		<20 s	
Accuracy	~~+~~± 30 ppm ± 5 % signal (CO_2), ± 1 ppm ± 1 % signal (SO_2)		± 1ppm ± 1 % signal	
~~Resolution~~ Instrument noise (1σ)	5 ppm (CO_2), 0.~~5~~05 ppm (SO_2~~), 5 ppm (CO_2)~~		0.~~5~~05 ppm	
Range	0-5000 ppm (CO_2), 0-200 ppm (SO_2)		0-100 ppm	
Sampling rate	2 Hz		2 Hz	
Computer	Arduino, with microSD card logger		Arduino, with SD card data logger and motor-shield to power the pump	
Voltage	9 V for SO_2 sensor (alkaline battery), 3.7 V LiPo battery for Arduino		9 V for SO_2 sensor (alkaline battery), 11.1 V LiPo battery for Arduino and pump	
Inlet	particle filter		3 denuders (50 cm) or 3 x 2 denuders (15 cm)	
Others	Warm up time	1 min (CO_2)	Micro solenoid valves	First Sensor, Germany TN2P006LM05LB
	Additional Sensors	Temperature, pressure, relative humidity	Mass flow meter	First Sensor, Germany, WBAL001DUH0
			Micro pump	TCS micropumps, UK, DS250BL
Weight	500 g		500 g	
Dimensions	14x13x14 cm (LxWxH)		20x13x14 cm (LxWxH)	

The pressure dependence of 0.0015 %/kPa is a second order effect and is negligible for our application

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The CO_2 sensor is placed inside a hermetic box, which is part of the air path (Fig. 4 (a)). It is equipped with further on-chip sensors for humidity (SHT21 from Sensirion, Staefa, Switzerland), temperature and pressure (BMP180 by Bosch Sensortec, Reutlingen, Germany), which allow to correct the gas data for dependencies on named environmental parameters.

The sensors are read out by a custom-built Arduino Uno Rev 3 computer with a micro SD card logger at a sampling rate of 2 Hz and powered by a rechargeable 3.7 V lithium polymer (LiPo) battery (Fig. 4 (b)). The SO_2 sensor was powered by a separate 9 V alkaline battery. The whole system is sheltered in a polystyrene foam case ~~with~~and has a total weight of 500 g (Fig. 3 (c)). A 45-µm pore size PTFE filter was attached to the inlet to prevent particles from entering the sensors. Gas was pumped through to the sensors in~~-~~ series ~~connected sensors~~ (1. SO_2, 2. CO_2) by a small pump using a flow rate of 500 ml/min. The system was calibrated before and after field deployments with CO_2 (0-1500 ppm) and SO_2 (0-30 ppm) test gases. Detailed information on the specifications of the sensors is shown in Table 1 and in the supplementary material (Fig. S1).

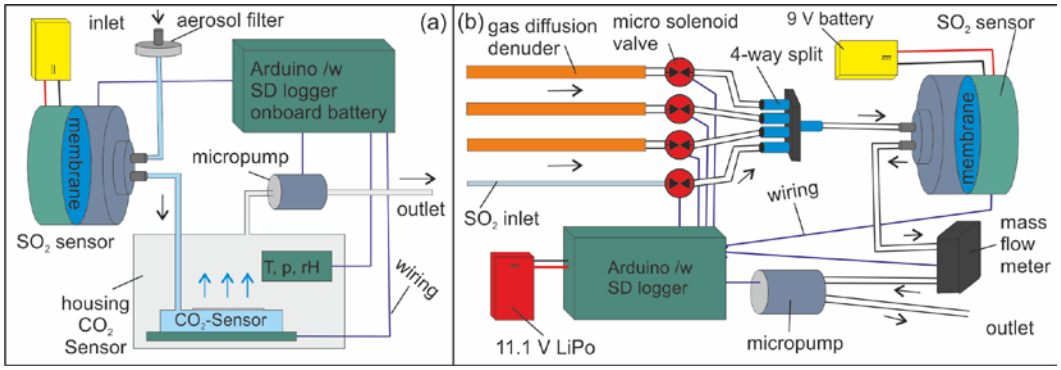

Figure 4: Schematics of the (a) *Sunkist* monitoring unit and the (b) *Black Box* gas sampling system

3.3 Gas diffusion denuder sampler (Black Box)

An in-situ gas sampling system was constructed to enable gas diffusion denuder sampling in the plume at various distances from the vent using the UAV. To compensate for dilution, a CiTiceL 3MST/F SO_2 sensor (City Technology, Portsmouth, United Kingdom) was implemented to obtain halogen/sulfur ratios combining denuder samples and sensor data. The sampler (called Black Box (BB)) consisted of the following components, which are introduced in the order the gas passes through: I) inlet system for three denuders; II) electrochemical SO_2 sensor; III) mass flow sensor; IV) micro gas pump (see Figure 4 (b) and Table 1). The housing was made of polystyrene foam to ensure that weight requirements were met. An Arduino microcontroller (Uno Rev 3) for signal processing and data logging on a SD card was built in. Various 11.1 V LiPo batteries (500 and 1000 mAh) supplied the power, with different capacities depending on the desired payload and operation time. The Arduino computer transmitted a pulse width modulated signal between 0 V and 5 V, proportional to the detected SO_2 mixing

~~ration~~ratio, to the main controller of the multicopter via cable connection, which then was sent by telemetry to the remote control to allow the operator to assess plume strength in real time to optimize denuder exposure time. The SO_2 gas sensor was calibrated in the laboratory and close to field conditions with SO_2 gas standards in N_2 (0 – 54.1 ppm).

~~Two~~Gas diffusion denuder sampling, which enriches gaseous compounds while being insensitive to the particle phase, was applied by using two types of coating materials ~~were used~~ as derivatization agent for the gas diffusion sampling. Total gaseous reactive molecular bromine species~~ (~~, BrX~~)~~ (Br_2, BrCl, (H)OBr), were determined by denuders coated with 15 µmol of 1,3,5-trimethoxybenzene (TMB) - which reacts to 1-bromo-2,4,6-trimethoxybenzene - and subsequent gas chromatography-mass spectrometry (GC-MS) analysis (Rüdiger et al., 2017). Hydrogen bromide (HBr) was sampled with denuders coated with 7.2 µmol of 5,6-epoxy-5,6-dihydro-1,10-phenanthroline (EP) - which is selectively reactive towards halogen acids through its epoxy function forming 5-halogeno-6-hyrdroxy-5,6-dihydro-1,10-phenanthroline - and analyzed by liquid chromatography-mass spectrometry (LC-MS). For the UAV-based application 15 cm long denuders were used at a sampling flow rate of 208 ml/min to ensure quantitative sampling. Denuders with both coating types were sampled at the same flow rate simultaneously to the recording of Multi-GAS (Sunkist) data.

3.4 Drone-operated miniature differential optical absorption spectroscopy (DROAS)

A miniature UV spectrometer system (Galle et al., 2003) was employed for flying mobile DOAS traverse measurements to conduct estimations of the SO_2 flux at Turrialba volcano. This system consisted (Fig. 8 (a)) of an UV spectrometer (USB2000+, Ocean Optics, USA), a miniature telescope (Ocean Optics 74-DA collimating lens, diameter: 5 mm, focal length 10 mm), a GPS Antenna (BU-353-S4, GlobalSat, Taipei, Taiwan) and a miniature on-board computer (VivoStick TS10, ASUS, Taipei, Taiwan). The system was powered by a 11.1 V LiPo battery (1000 mAh), which was connected via a switching regulator (CC BEC 10 A, Castle Creations, USA) to give 9 V at 2 A. The spectrometer and the GPS antenna were connected (and powered) at the computer via USB ports. The NOVAC software "mobile DOAS" developed at the Chalmers University (Sweden) was run on the computer for data acquisition and later evaluation. The miniature PC in the spectrometer system was accessed via a remote desktop connection by a different computer to initialize the data acquisition by the "mobile DOAS" software. ~~Evaluation~~Validation of the SO_2 fluxes obtained by DROAS traverses was achieved by a comparison with the SO_2 fluxes derived by two NOVAC stationary DOAS instruments (*La Silva* and *La Central*, see Fig. 2 (d)) located in proximity to the flight area.

3.5. Data Processing

3.5.1 Sensor calibration

All three in-situ gas sensors (two identical SO_2, one CO_2) were calibrated using test gas standards mixed with nitrogen, using either tedlar bags, dynamic dilution or readily mixed test gases. The sensors were exposed to different mixing ratios by pumping the gas mixes through the system. Calibration functions were fitted, including errors in mixing ratio and signal

(York et al., 2004) to give sensitivities (slope) and offset levels (intercept) (Supplementary Material Fig. S2 – S4). As the CO_2 sensor responds to the gas concentration (molecules per volume), CO_2 mixing ratios (molecules per molecules of air) were obtained by compensating the concentration signals with pressure and temperature data recorded by the built in sensors, assuming ideal gas behavior. The SO_2 sensor output however, relates directly to the mixing ratio, due to the diffusivity of the transport membrane being inversely proportional to the pressure and therefore cancelling out the pressure dependency of the concentration. The two gas sensors operate with significantly different response times (T_{90} for CO_2 ~ 2 s, for SO_2 ~ <20 s), since sample gas enters the SO_2 sensor only by molecular diffusion, whereas in the CO_2 sensor it is directly driven through the optical cell. ~~To adapt~~In order to adjust the response times of the two sensors, a slow response signal for the CO_2 ~~signal~~ sensor ($CO_{2,sim}$) was ~~smoothed~~simulated. This was achieved through convolution ~~with a first-order transfer function. The transfer function's response time factor was chosen, such that~~ of the ~~correlation of CO_2 and SO_2~~original signal ~~got maximized for discrete peaks (see Fig. 5 (a)).~~with a typical sensor pulse response

$$f(t) = \begin{cases} 0, & t < 0 \\ \frac{1}{\tau} e^{-t/\tau}, & t \geq 0 \end{cases}$$

with t being time and τ being the 'response time factor', which in this context can be regarded as a measure for the degree of smoothing. The approach is mathematically equivalent to an approach shown by Roberts et al. (2014). The response time factor τ was tuned, such that the correlation of $CO_{2,sim}$ and SO_2 signal got maximized for discrete peaks (see Fig. 5 (a)). This was already done by Arellano et al. (2017), who also applied the Sunkist instrument in gas measurements in Papua New Guinea in 2016.

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3.5.2 Gas diffusion denuder analysis

The sampled gas diffusion denuders were sealed air tight and stored in darkness for subsequent analysis. The coating, which contained the derivate and derivatization agent in excess (TMB or EP), was eluted off the denuders using 5 times 2 mL of 1:1 of ethyl acetate and ethanol (in case of TMB) or 5 times 2 mL methanol (EP). After the elution, the solvent was evaporated (at 35 °C under gentle N_2 gas stream) to a volume of approximately 100 µL. Internal standards (with TMB: 2,4,6-tribromoaniline; with EP: neocuproine) were added to each sample solution to account for evaporation losses. The condensed samples were analyzed by GC-MS (TMB) and LC-MS (EP) and quantified using external calibration. Due to the lack of a pure calibration standard hydrogen bromide was only measured qualitatively. Halogen mixing ratios in air were derived from the measured halogen amounts on the denuders and the respective sampling volume obtained by the sampling pump data. In addition to the actual sample denuders open field blank denuders were prepared to account for potential diffusive gas precipitation during the flights.

3.5.3 Gas ratios

For a feasible data interpretation, gas ratios were calculated from the sensor data and the denuder analysis results. Halogen mixing ratios were interpreted concerning dilution with ambient air by relating to SO_2, which is rather slow in its oxidation,

and therefore can be treated as a stable dilution proxy for a short term plume observation (Porter et al., 2002). Thus, the derived halogen mixing ratio was divided by the time-integrated SO_2 mixing ratios obtained during the denuder sampling period to obtain BrX/SO_2 ratios. Due to a baseline drift in the CO_2 sensor data, which was only observable during long-term measurements (> 45 minutes), the pressure and time-response corrected CO_2 data was additionally drift corrected for long-term measurements. To do so, a linear fit was made to the sloped background signal and subtracted from the CO_2 signal (see supplementary material Fig. S5). CO_2/SO_2 ratios were calculated with a linear fit to CO_2 vs. SO_2 scatter plots, considering the deviations (York et al., 2004) of the two sensor signals.

3.5.4 DROAS evaluation and gas fluxes

SO_2 emission rates during the flights at Turrialba were derived by traversing the plume with the DROAS instrument pointing vertically upwards in the direction of the plume. The "mobile DOAS" software developed at Chalmers University was used to control the spectrometer and to retrieve SO_2 column amounts from the spectra. The SO_2 columns were achieved using a wavelength evaluation window of 310-330 nm and including O_3 and SO_2 absorption cross sections convoluted with a slit function as well as a Ring Spectrum and a 3rd order polynomial in the DOAS fitting routine. The calculation of the SO_2 emission rate involves the integration of the SO_2 column amounts measured along the flight path resulting in a cross-sectional SO_2 area, which was geometrically corrected to obtain a surface that is orthogonal to the plume direction, and then multiplied by the wind speed (obtained from the NOAA National Center for Environmental Predictions (NCEP) Global Forecast System) to calculate SO_2 fluxes. Further details on the spectral evaluation routines and flux calculations can be found elsewhere (de Moor et al., 2017).

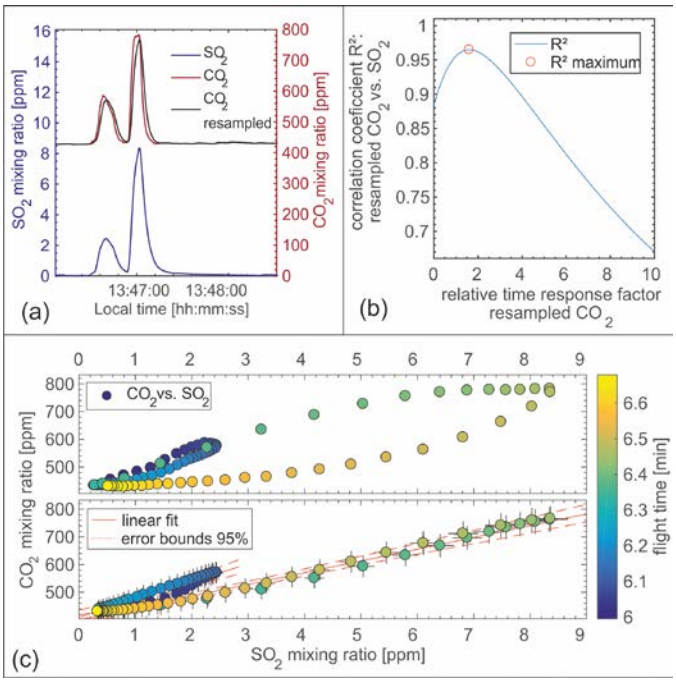

Figure 5: (a) Example of time series for mixing ratios of SO_2 and CO_2 (original data in red, resampled data in black), showing discrete gas masses at Stromboli volcano (1st flight on 05th April 2016), (b) Correlation plot for the determination of the relative time response factor for the CO_2 gas sensor with a maximum at a relative time response factor of 1.7, (c) CO_2 over SO_2 mixing ratios, showing the outcome of the resampling of the fast CO_2 with a relative time response factor of 1.7 (lower plot), linear regression results CO_2/SO_2 ratios of 64 ± 16 the first peak and 42 ± 4 for the second.

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4. Results and discussion

4.1. Multicopter performance assessment

During the deployment at three volcanoes, the RAVEN multicopter conducted more than 50 flights under moderate wind conditions, in most cases below 10 m/s. The multicopter achieved a maximum operation altitude of 3320 m at Turrialba volcano and records showed a maximum speed of 85 km/h. With a takeoff weight of 2.45 kg and a payload of maximum 1.3 kg flights at Turrialba volcano were still possible, although the flight time was reduced to about 5 to 8 minutes. At the Masaya volcano sites (takeoff altitude ~ 500 m), a maximum ascent above ground level of 1080 m was recorded. A typical flight time at this site was between 10 and 15 minutes. The telemetrically transmitted SO_2 mixing ratios from the Black Box

apparatus allowed the localization of high plume densities and therefore adjustments on the optimal hover location. While flying in the line of sight the system could be reliably controlled within a distance of 1-2 km to the operator. However, entering the dense plume proved to challenge the connection between remote control and receiver, resulting in multiple connection losses during flights, in which the UAV also left the line-of-sight of the operator. Nevertheless, GPS connection was still present and an automated return mechanism allowed regaining control after the UAV left areas of high plume densities. At Masaya this phenomenon was observed mostly in a plume with condensed water and SO_2 mixing ratios in low one-digit ppmv numbers, while in a plume without condensation close to the crater control was maintained even with SO_2 levels up to 40 ppmv. This is probably due to the attenuation effect of fog and cloud droplets on millimeter-waves, as they are used with the 2.4 Ghz transmitter of the remote control (Zhao and Wu, 2000).

4.2 CO_2/SO_2 gas sensors

During two field deployments at Stromboli (Table 2) and Masaya (Table 3) volcanoes, the lightweight gas monitoring system Sunkist (SK) determined CO_2/SO_2 gas ratios at various airborne and ground-based locations. A comparison with a stationary Multi-GAS (MG) instrument at Masaya volcano for the same site and time (lookout point south, 14th July2016, 11:19) and with inlets of both systems in proximity to each other gave results on CO_2/SO_2 ratios that were within each other's 2-sigma intervals (CO_2/SO_2 of 2.9 ± 0.3 for MG and 3.6 ± 0.4 for SK). The time series of the SO_2 mixing ratios of SK and MG also showed a good agreement (R^2 = 0.89) (Fig. 6). An application of SK further downwind (0.5 km from the rim) gave a CO_2/SO_2 ratio of 3.3 ± 1.2, while the MG measured a CO_2/SO_2 ratio of 3.1 ± 0.1 during the same time at the rim. This is showing SK's ability for deployment in a more diluted plume, although with the disadvantage of higher errors, due to the higher relative background in CO_2 at more distant locations. Furthermore, UAV-based application (9 flights, 17th – 20th July 2017) between 1.5 km and 2 km downwind of the Masaya plume resulted in average 42 % higher CO_2/SO_2 ratios with a larger standard deviation compared to the crater rim (14th – 16th July 2017), but still within each other's errors (CO_2/SO_2: 5.4 ± 2.3 at 1.5 - 2 km; 3.8 ± 0.3 at the rim). Due to the limitations of the CO_2 sensing, acquirement of useful CO_2/SO_2 data with SK is more feasible in dense plumes close to, but not limited to the crater rim, as the airborne application has shown. Additionally, SO_2 mixing ratios were measured as a plume dilution proxy by the Black Box (BB) system. Both the BB and SK systems use an identical SO_2 sensor and showed a good agreement of their SO_2 time series and time integrated SO_2 mixing ratio (SK: 1.75 ± 0.08 ppmv, BB: 1,84 ± 0.08 ppmv) (supplement material S6).

At Stromboli volcano, the Sunkist and Black Box systems were deployed on two days (05th & 06th April 2016), resulting in seven flights into the plume. These flights covered distances~~,~~ of between 11 m and 419 m from the vent in a downwind direction (northeast), above the Sciara del Fuoco. As shown in Figure 1, discrete gas ~~masses~~clouds with different CO_2/SO_2 compositions were measured. The retrieved CO_2/SO_2 ratios ranged between 7 and 64, with the higher values typically detected directly above the vent (11 m to 26 m) (see Tab. 3 and Fig. 1). During the multicopter operations close to the vent regular strombolian ash ~~explosion~~explosions occurred (see Fig. 3 (d) and (e)), which are likely accompanied by CO_2-rich gas

~~masses~~clouds (La Spina et al., 2013) and therefore act as a possible explanation for the detected high CO_2/SO_2 ~~in a rather undiluted plume region.~~

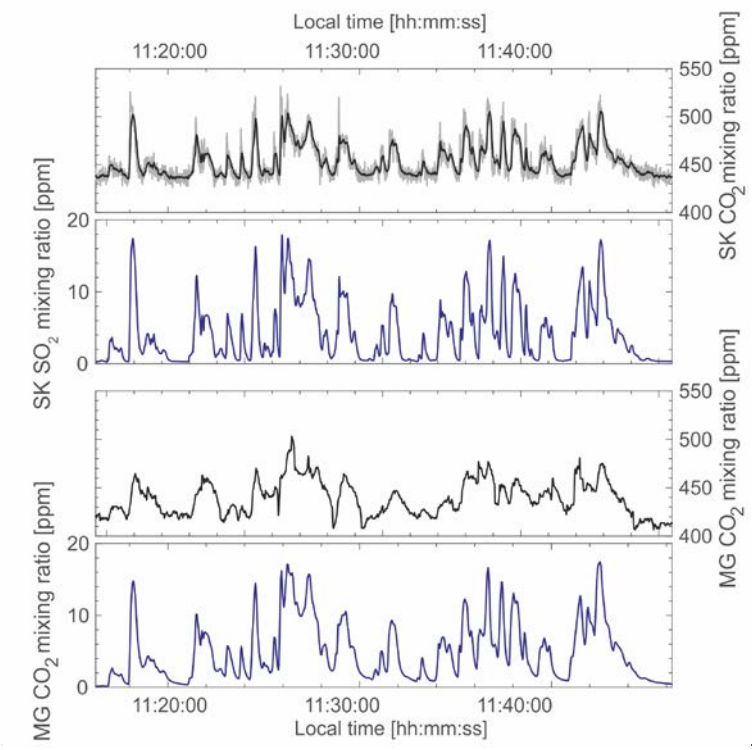
ratios. On both flight days the predominant wind direction was southwest (207° ± 15° and 210° ± 18°, data from weather station at 77 m a.s.l., commercially available from windfinder.com, Kiel, Germany), which resulted in the plume mostly being present across the Sciara del Fuoco and therefore only accessible by UAV. Nevertheless, a local Multi-GAS station (placed on the SE rim of the crater terrace) ~~has~~ discontinuously measured the plume during the period of the UAV survey, showing CO_2/SO_2 ratios between 2.2 and 13.6, which is in agreement with some of the multicopter-based measurements. Similar CO_2/SO_2 ratios have been observed in the past and are exemplary for ~~an~~ ordinary Strombolian activity (Aiuppa et al., 2009). It has to be taken into account that both instruments ~~have not measured simultaneous or in proximity to each other.~~did not measure simultaneously or in proximity to each other. The MG instrument only measures four times a day for 30 minutes and averages over this time, while with the SK instrument we identified discrete peaks of gas clouds with different CO_2/SO_2 ratios. Furthermore, a comparison of SK and MG CO_2/SO_2 data might be more accurate with the high SK CO_2/SO_2 values (associated with eruptive degassing) left aside, as we lack the observations on passive, respectively eruptive degassing behavior for the MG data records.

Table 2: Overview on the retrieved CO2/SO2 ratios with parameters for the linear fit at Stromboli volcano

Date	Time	Flight / Peak	CO_2/SO_2	lower SO_2 limit /ppmv	Data Points	max. SO_2 /ppmv	estimated distance /m
05.04	13:46	1 / 1	64 ± 16	1	39	2.6	26
05.04	13:46	1 / 2	42 ± 4	1	48	8.5	11
05.04	14:31	2 / 1	43 ± 8	1	31	4.5	18
05.04	14:32	2 / 2	31 ± 12	1	29	4.7	25
05.04	16:18	3 / 1	7 ± 5	0.1	101	5.8	419
05.04	16:23	3 / 2	11 ± 11	0.1	133	1.9	399
06.04	13:03	4 / 1	27 ± 25	0.2	326	0.9	155
06.04	13:44	5 / 1	22 ± 5	0.5	324	5.2	80
06.04	14:44	6 / 1	10 ± 13	0.2	111	1.6	170
06.04	14:45	6 / 2	21 ± 7	0.5	415	2.3	177
06.04	15:10	7 / 1	9 ± 5	0.2	516	1.6	167
06.04	15:16	7 / 2	21 ± 5	0.5	35	2.3	107

Table 3: CO_2/SO_2mixing ratios and calculation parameters obtained from the Sunkist (SK) and Multi-GAS (MG) instrument at Masaya Volcano. The exact locations are given in Fig 2, errors indicate 2 sigma interval (95.5 %) retrieved by a linear regression (York et al., 2004) including the measurement errors of both the SO_2 (error: 5-10 %) and CO_2 (error: 5.5 %) sensor

Date	Time	Instru-ment	Location / Flight	CO_2/SO_2	lower SO_2 limit /ppmv	Data Points	max. SO_2	distance to rim /km
14.07.2016	09:43 - 15:10	MG	Santiago rim; lookout south	2.9 ± 0.1	4	3200	31.1	0
14.07.2016	11:18 - 11:44	MG	Santiago rim; lookout south	2.9 ± 0.3	4	440	17.5	0
14.07.2016	11:19 - 11:45	SK	Santiago rim; lookout south	3.8 ± 0.5	4	1460	17.9	0
14.07.2016	10:42 - 12:09	SK	Santiago rim; lookout south	3.6 ± 0.4	4	2600	18.5	0
15.07.2016	09:43 - 16:23	MG	Santiago rim; pole site	3.1 ± 0.1	4	2950	29.6	0
15.07.2016	15:28 - 16:19	SK	Nindiri rim	3.3 ± 1.2	1	3100	5.8	0.5
16.07.2016	11:18 - 12:19	SK	Santiago rim; pole site	4.7 ± 0.3	4	3000	28	0
17.07.2016	08:56 - 08:59	SK	caldera valley; flight #A2	2.9 ± 13	1	150	2.8	1.8
17.07.2016	11:21 - 11:28	SK	caldera valley; flight #A5	4.8 ± 3.2	1	630	4.8	1.8
17.07.2016	11:53 - 12:01	SK	caldera valley; flight #A6	6.5 ± 3.4	0.2	620	3.4	1.9
17.07.2016	12:10 - 12:20	SK	caldera valley; flight #A7	6.2 ± 5.6	0.4	1150	2.2	1.5
18.07.2016	07:55 - 09:36	SK	Santiago rim; pole site	4.1 ± 0.3	4	4350	36.7	0
18.07.2016	13:19 - 13:27	SK	caldera valley; flight #B4	5.1 ± 4	1	560	4.4	1.7
20.07.2016	12:55 - 13:04	SK	caldera valley; flight #C1	7.5 ± 5.8	0.5	310	2.8	1.9
20.07.2016	13:29 - 13:35	SK	caldera valley; flight #C2	7.7 ± 5.1	0.75	470	2.9	1.9
20.07.2016	13:58 - 14:07	SK	caldera valley; flight #C3	2.2 ± 11	0.5	380	1.9	1.9
20.07.2016	16:22 - 16:29	SK	caldera valley; flight #C7	5.3 ± 4.4	0.5	550	3.4	2


Local time [hh:mm:ss]
11:20:00
11:30:00
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SK CO2 mixing ratio [ppm]
SK SO2 mixing ratio [ppm]
MG CO2 mixing ratio [ppm]
MG CO2 mixing ratio [ppm]
550
500
450
400
20
10
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11:20:00
11:30:00
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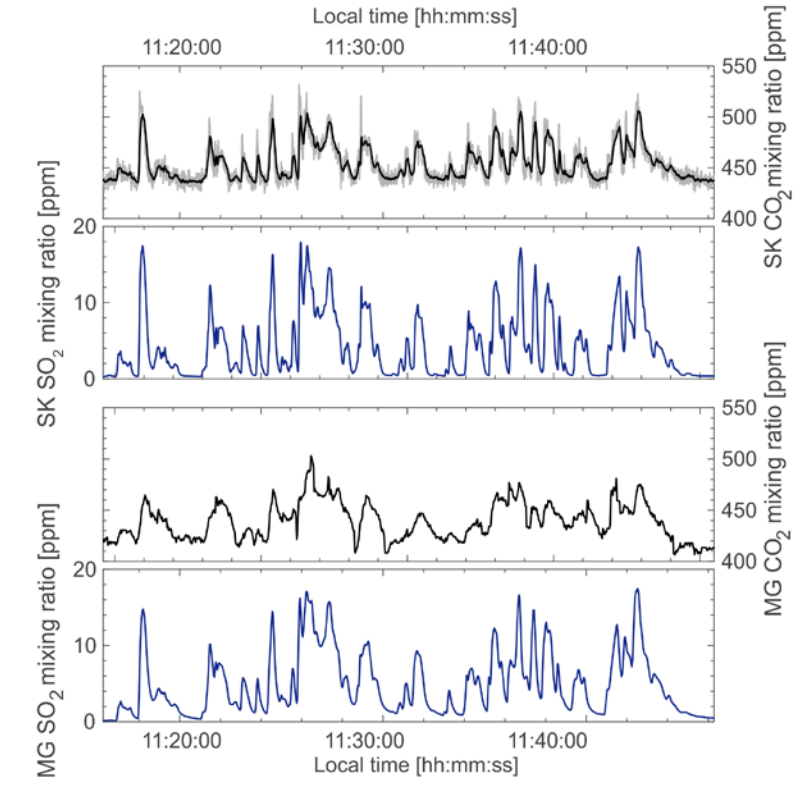

Figure 6: Comparison of SO_2 and CO_2 time series of a Multi-GAS (MG) instrument and the *Sunkist* (SK) unit at the Masaya volcano crater rim (for SK ~~SO_2~~CO_2 raw data in grey, resampled data in black), both instruments inlets were place in proximity to each other (14th July 2016); SK CO_2/SO_2 = 3.63+/- 0.43 background CO_2 = 439 ppm); MG CO_2/SO_2 = 2.94 +/- 0.30 (background CO_2 = 413 ppm); (additional scatter plots in the supplementary material)

4.3 Halogen measurements

Bromine species were detected by gas diffusion denuder sampling on three of the seven flights at Stromboli volcano. Reactive bromine species were measured between 0.14 and 0.65 ppb (see Table 4), while HBr was determined qualitatively in all three samples.

The obtained ratios of reactive bromine (BrX) to SO_2 ($1.9*10^{-4}$ – $9.8*10^{-4}$) are within the range of bromine to sulfur ratios produced by other methods at Stromboli volcano, e.g. alkaline trap sampling by Wittmer et al. (Wittmer et al., 2014) ($4.3*10^{-4}$ – $2.36*10^{-2}$). Figure 7 (b) shows the BrX/SO_2 ratios for different plume ages, which was calculated by taking wind speeds into account. Although the general feasibility of the used methods for the investigation of reactive halogen species in an

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aging plume is demonstrated in this proof-of-principle approach, a trend in the BrX/SO_2 ratio over age is not recognizable for this limited data set. Without information on abundances of other halogen species such as $BrO_{(g)}$, $HBr_{(g)}$ and aqueous particulate bromine ($HBr_{(aq)}$), interpretation of the BrX/SO_2 ratio is difficult as the emitted gas composition may also change on shorter time scales (La Spina et al., 2013) compared to the campaign duration. However, an increase of the reactive bromine species BrO with distance from the crater rim has been observed previously by DOAS measurements at various volcanoes and is well described in the literature (Oppenheimer et al., 2006; Bobrowski et al., 2007). Although the bromine ~~species~~speciation in volcanic plumes has been subject of several ground-based (e.g. Gliß et al., 2015) airplane (e.g. General et al., 2015), satellite (e.g. Theys et al., 2009; Hörmann et al., 2013) and model studies (e.g. Bobrowski et al., 2007; Roberts et al., 2009; von Glasow, 2010; Roberts et al., 2014; Jourdain et al., 2016) in recent years, in-situ measurements are scarce. The ~~here~~data presented ~~data~~here for the first minute after emission ~~highlights~~highlight the potential of UAV-based measurements to improve sample acquisition and thus obtain a better understanding of plume aging.

As shown in Figure 7 (c), the BrX to SO_2 ratio seems to change not only with the plume age but also with CO_2/SO_2 mixing ratios, which were simultaneously measured. However, with only three data points a further interpretation is inadequate due to lack of a statistical basis. Nevertheless, these first results show the principal practicality of the used denuder sampling and gas sensing methods for simultaneous investigation of halogen, carbon and sulfur emissions.

Table 4: Sample parameter and bromine measurement results for three denuder samples at Stromboli volcano.

Sample number	1	2	3
Date	05.04.2016	06.04.2016	06.04.2016
Time	14:31	13:46	14:45
Duration /s	53	364	320
Sample volume /L	0.18	1.26	1.11
pressure /mbar	906	914	914
integrated SO_2 /ppmv	1.85 ± 0.09	0.34 ± 0.04	0.74 ± 0.05
BrX /ppb	0.65 ± 0.06	0.34 ± 0.01	0.14 ± 0.1
BrX/SO_2 *10^{-4}	3.5 ± 0.4	9.8 ± 1.3	1.9 ± 0.2
CO_2/SO_2	43 ± 9	27 ± 4	17 ± 8
distance /m	21 ± 2	80 ± 2	177 ± 2
wind speed /m s^{-1}	3.4 ± 0.5	4.8 ± 0.5	4.8 ± 0.5
plume age /s	6 ± 1	17 ± 2	37 ± 4

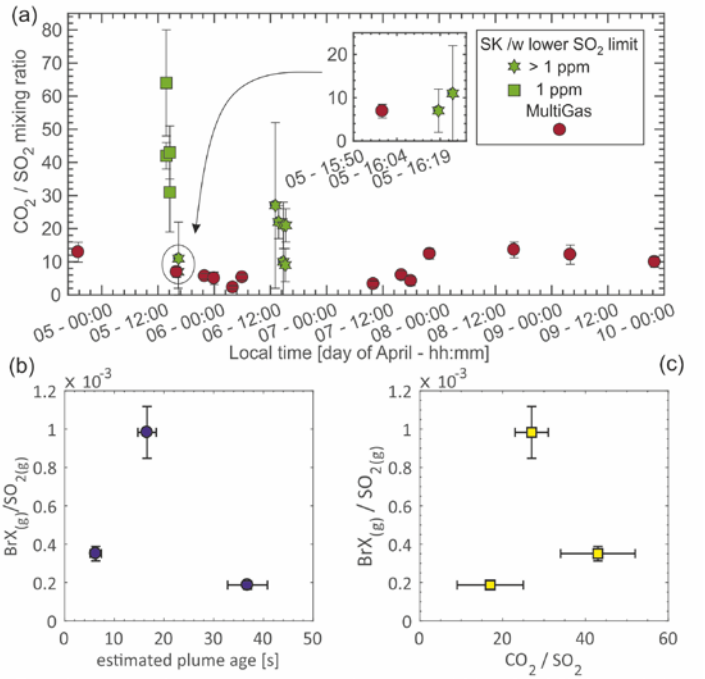

Figure 7: (a) Measured CO_2/SO_2 gas ratios over a 5-day period by a Multi-GAS station (located east of the crater terrace) and airborne measurements with the *Sunkist* system at Stromboli volcano, data point shapes indicate the lower SO_2 mixing ratio limits for the linear fit over the CO_2 vs SO_2 data, (b) development of the gaseous reactive bromine species over SO_2 over the estimated plume age (derived from distance to crater and estimated wind speed), (c) gaseous reactive bromine/SO_2 ratios vs. CO_2/SO_2 ratio

4.4. DROAS measurements

On September 27th, two DROAS plume transects were performed at Turrialba volcano during mild ash emission at around 2800 m a.s.l. with a total flight time of approximately 10 minutes. The flight was conducted in the downwind direction west of the active vent and crossed underneath the plume on a south-north axis (Fig. 8 (b)), exiting the plume on both ends of the flight path, which is indicated by the low SO_2 column amounts close to the baseline in the northern- and southern-most section of the flightpath (Fig. 8 (c)). SO_2 fluxes were calculated for that flight and resulted in 1776 ± 1108 T/d SO_2 for traverse A and 1616 ± 1007 T/d SO_2 for traverse B (see Table 5). Calculation of the SO_2 fluxes obtained by the two scanning DOAS instrument from the NOVAC network, located on the southern edge of the plume, gave average results of 1533 ± 986 T/d SO_2 for *La Silva* and 1094 ± 704 T/d SO_2 from *La Cetral* for a 2-hour period, in which the flight took place. Therefore, the results of the DROAS traverses are in a good agreement with the scanning DOAS stations. De Moor et al. (de Moor et al., 2016a) conducted car based mobile DOAS transects, which typically take ~45 minutes for a round trip due to rough

terrain. Dynamic gas plumes can significantly change the plume's travel direction on scales of minutes, introducing a significant source of error to car traverses. A major advantage of the UAV method is that it is much quicker, about 10 minutes for a round trip, thus providing a more accurate snapshot of the plume.

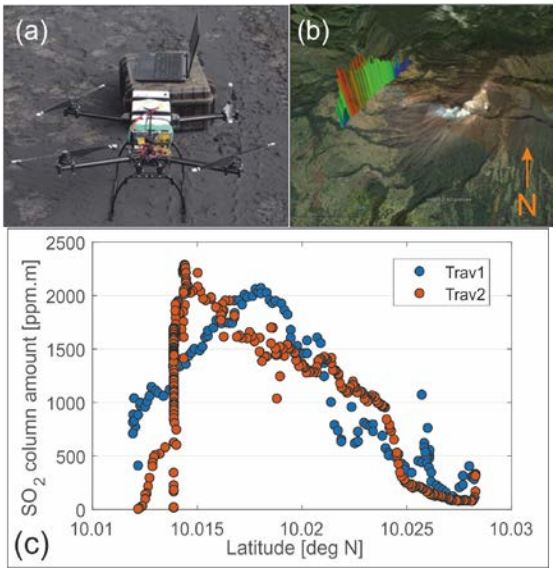

Figure 8: (a) Drone-operated miniature DOAS setup, (b) Illustration of SO_2 column amounts measured by DROAS at Turrialba volcano, (c) SO_2 column amounts during the transversal flight underneath the plume

Table 5: SO_2 fluxes obtained by DROAS traverses and two stationary scanning DOAS instruments at Turrilaba volcano. The average fluxes from La Silva and La Central were derived for a 2-hour period in which the DROAS flights were conducted, maximum fluxes for this period as presented as well

Instrument/Traverse	SO_2 flux at 1 m/s	error	windspeed	SO_2 flux
[unit]	[T/d]	[%]	[m/s]	[T/d]
DROAS Traverse A	419.9 ± 38.6	9.2	3.78 ± 2.62	**1776 ± 1108**
DROAS Traverse B	381.6 ± 35.5	9.3	3.78 ± 2.62	**1614 ± 1007**
La Silvia NOVAC station AVERAGE	362.3 ± 72.5	20	3.78 ± 2.62	**1533 ± 986**
La Silvia NOVAC station MAX	481.72 ± 96.3	20	3.78 ± 2.62	**2038 ± 1312**
La Central NOVAC station AVERAGE	258.6 ± 51.7	20	3.78 ± 2.62	**1094 ± 704**
La Central NOVAC station MAX	448.1 ± 89.6	20	3.78 ± 2.62	**1896 ± 1220**

5. Conclusion and outlook

In this study we have demonstrated the feasibility of a multicopter-based approach for volcanic in-situ plume measurements to achieve investigations on the compositional variability of an aging plume. The use of a multicopter UAV proved to be a suitable alternative to ground-based operations, especially in hard to access or not at all accessible areas, like active volcanic vents or elevated downwind plumes. The aerial sampling systems demonstrated robustness and effectiveness during the field missions with harsh environmental and meteorological conditions, including ash-laden plumes. With the newly developed sampling system, reactive halogen species were observable in previously inaccessible downwind plume areas. Halogen speciation information enhances our understanding of plume chemistry in the aging plume, which represents important knowledge for new volcano monitoring approaches. Therefore, in-situ speciation methods for halogens should be extended and optimized for other gaseous and aqueous compounds including chlorine and iodine species. Additionally, at Stromboli volcano changes in the BrX/SO_2 ratios were observed with different CO_2/SO_2 ratios, which represents an interesting matter and should be further explored in future studies.

Furthermore, multicopter-based CO_2/SO_2 ratio measurements showed its reliability, opening a promising approach for monitoring inaccessible volcanoes or during dangerous eruptions minimizing personnel risk at highly active volcanoes. Although we demonstrated the applicability of the Sunkist lightweight gas sensing system for potential UAV based monitoring, challenges in the acquisition of high-quality data for diluted plumes still exist. Thus, ~~high class~~more sophisticated components (e.g. sensors, microcontroller or data logger) promise to achieve better sensitivities, but with the disadvantage of higher losses in the case of a crash.

Moreover, the herein presented UAV application of a miniature DOAS instrument (DROAS) for SO_2 gas flux measurements has shown its quality in the harsh environment of Turrialba volcano. The potential to be an excellent alternative to walking or car-based traverses for SO_2 flux acquisition has been proven with a significant reduction of risks and operation time.

The case studies presented here explored the general feasibility of multirotor UAVs in volcanic plume studies and are an initial step in the direction of remotely operated gas measurements at active volcanoes. We have shown the potential of UAV-based sampling to gain ~~insight~~insights into reactive halogen chemistry and processes of plume aging, and further application of this method ~~will~~could yield data from previously unstudied plume regions. Technological advances promise to enable scheduled pre-programmed and autonomous UAV operations~~,~~ (e.g. from hangars close to volcanoes) with extended flight times~~, such as scheduled pre-programmed flight paths through volcanic gas plumes~~ for regular hazard ~~assessment.~~assessments.

Competing interests

The authors declare that they have no conflict of interest.

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