Authors response to review of EGU SE manuscript 2017-70

The authors would like to express their gratitude to the time invested by the two reviewers and the editor. Below you find a point to point response to the issues raised by the reviewers. Both reviewers pointed out that LARRS cannot replace in situ measurement but is a complementary technique. This has been amended accordingly in the manuscript. Changes are highlighted in yellow. As they are interrelated, we decided to put the responses to both reviewer comments in this one document.

Reviewer #1

General comments

The ms is very interesting and merits to be published in Solid Earth discussions. There is just one major point and few minor ones that should be answered by the authors. The main point regards the statement done in the ms that the proposed method is in some way alternative of the classical methods based on the accumulation chambers to monitor the CO2 emissions because, according to the authors, the measurement "... accounts for all possible CO2 vents and diffuse degassing ..... to obtain a quantitative picture of CO2 degassing" In my opinion the proposed method based on "....laser remote sensing spectrometer...." (LARSS) is a very useful additional method to have an almost complete picture of CO2 degassing from an hydrothermal site but the method, at least at this stage of development, can not substitute the accumulation chamber LARSS can in fact detect and measure the CO2 emitted by vents,
Reply:
We agree. The precision of LARRS at the moment does not allow this. In situ measurements are much more precise and accurate. However, as it measure path integrated, everything within the path contributes, meaning that LARRS may help to give representative measurements from large regions, the more its precision improves the more it will do so.
Changes: In abstract: Thanks to the integrated path soundings, LARSS <mark>may help to give</mark> representative measurements from large regions containing different CO_2 sources (…).

Added p3, l2:
<mark>On the other hand, point measurements are very precise and valuable in characterizing local degassing elements, such as</mark>

fractures. Path integrating, scanning gas measurement techniques, on the other hand, may add value by providing a spatially comprehensive measurement. To attempt a spatially inclusive measurement of all possible sources of CO_2, diffusive soil and vented degassing, we used a laser remote sensing spectrometer (LARSS), developed in the ERC proof-of-concept project CarbSens. Combined with point measurement techniques, such as accumulation chambers, LARRS may help to yield a more complete picture of degassing.

Added in conclusions:
Furthermore, point measurements should be added in the future to systematically test and verify the capability of LARRS to probe comprehensively all degassing elements in its path. For challenging degassing situations as at CF, integrating LARRS with point measurements may provide a powerful means to obtain a complete picture of degassing.

I am not sure that it can reliably measure a real diffuse emission. Diffuse degassing over large areas, such as at Solfatara and Pisciarelli, give rise in fact to some more complex structure than a single plume. So, low level anomalies, that can contribute significantly to the total CO2 release are probably not detectable and quantifiable by LARSS.
Reply: As said above, if the low level anomaly is in the measurement path and the precision is high enough (high SNR), it will be detected, why shouldn't it?

**In addition the method measure the CO2 concentration close to the ground (because the background can not be the sky but the ground) where, for example, the wind field is strongly affected by the interaction of the air with the terrain that implies a reduction
in the wind speed etc. This aspect should be a little discussed.**
Reply: Added at p5 l10: Given the complex terrain and the fact that the measurement was performed close to the ground the velocity field across the scanned plume was generally not constant, in addition to temperature variations causing different plume speeds across the plume. The corresponding variability has been accounted for by tracking different paths of propagating water vapor across the plume and using the variability in the error estimation. Plume speed is in fact one of the main sources of uncertainty, adding an uncertainty of the order of 30% to the flux.
In conclusions: To that end, the plume speed estimation will be further improved, especially with respect to resolving the plume speed variations (velocity field) across the scanned plume.

Furthermore another aspect of the accumulation chamber method is the possibility to draw detailed maps of the emission areas (and their variation during time), that can not be done with LARSS.

Reply: Not with one instrument, but with two you can do tomography. It is still unmature but it will improve. We have added this in the conclusions: Point measurements are able to draw detailed maps of the emission areas which LARRS is not capable of. However, using two instruments 2D tomography can be performed (Queisser et al., 2016b). Although much more improvement of this technique is needed to converge to degassing maps from point measurements.

Specific comments

- Page 1 line 25 and 28 Substitute d'Auria with D'Auria.
Done

- Page 2 line 4. "...feeding the overlying ~ 1.5 km deep hydrothermal reservoir.." There is any convincing prove of the depth of the hydrothermal reservoir, I suggest to write more generally "...feeding the overlying hydrothermal system(s)...."
Changed accordingly

- Page 2 line 19 "......Caliro et al., 2014....." Caliro et al., 2014 did not chose any specific depth for magma degassing but they presented a series of different scenarios including degassing fro the 8 km deep (200 Mpa) magma.
This section is not meant to split the world in two sides but it is just for the unoccupied reader to find some more information on the subject. Caliro et al. Is just an informative reference. We prefer to leave it.

- Page 2 line 24 I suggest to substitute alternative with additional.
changed.

**- Page 2 line 27-29 The cited works refer mainly to the emission of the vent of Pisciarelli. The diffuse degassing eventually included in these measurements is at least incomplete (see main point). I suggest to focus your considerations on the vent emis-
sion (that now at Pisciarelli is by far the main way of emission)**
Confronting point with spatial measurements is one of the main points of this paper, including Fig. 3. While we agree that LARRS

cannot replace point measurements and amended the MS accordingly (see above), LARRS is another way of probing degassing adding some value and we prefer to cite these works as they use a similar technique than LARRS and indeed measured at Pisciarelli (see Fig. 3). Accordingly, we changed

A spatially comprehensive measurement of CO_2 flux that accounts for all possible CO_2 vents and diffuse degassing is desirable to obtain a quantitative picture of CO_2 degassing, but has only been done a few times after 2012 at Pisciarelli (Pedone et al., 2014; Aiuppa et al., 2015; Queißer et al., 2016a).

to

A spatially <mark>integrated</mark> measurement of CO_2 flux has only been done a few times after 2012 at Pisciarelli (Pedone et al., 2014; Aiuppa et al., 2015; Queißer et al., 2016a).

- Page 3 line 27-28 " ... The plume speed is retrieved by digital video tracking of the
plume of condensed water vapor as described in Queißer et al. (2016).." Ok, the speed of the plume is measured and it is assumed constant in the plume. Is this assumption reasonable? In my opinion, the colder peripheral zones of the plume should move
at a speed lower than the central hot zone. Furthermore a further reduction of the
wind speed should be expected in the zones where the plume is just above the terrain
(at low height from the ground). In other words I think that this of the speed is still a
central parameter with many uncertainties... could you add some discussion about the
problem of assuming a constant wind speed?
Reply: Please see reply to one of your general comments above: In addition the method measure the CO2 concentration close to the ground …

- Page 4 line 8 Please define what is Delta/beta
It is defined on page 3 l 25.

- Discussion and Conclusion I agree mostly with you, but I don't think that the Pisciarelli measurements alone could be very indicative without years of monitoring chemical and isotopic compositions of the fumaroles, seismicity and ground deformation. I suggest you to read (and in the case to cite) the most recent paper on Campi Flegrei unrest

where the different signals from geochemical and geophysical technique are compared
and discussed also in the frame of a physical model of the system (Chiodini et al., 2017). The paper shows further evidence on the pivotal role of the heating of the hydrothermal system in the present dynamic of the caldera. (Chiodini, G., Selva, J., Del Pezzo, E., Marsan, D., De Siena, L., D'Auria, L., Bianco, F., Caliro, S., De Martino, P., Ricciolino, P., and Petrillo, Z., 2017, Clues on the origin of post-2000 earthquakes
at Campi Flegrei caldera (Italy): Scientific Reports, doi:10.1038/s41598-017-04845-9)

Reply: In discussion we added: Recent findings indeed point towards an impulsive influx of hot magmatic fluids into the hydrothermal system as a possible source mechanism at CF that eventually cause the observed geophysical and geochemical time series, including the present one (Chiodini et al., 2017).

- References: check the citation of Cardellini et al., 2016, there is an error in the name
of one of the coauthors (Giovanni, G. instead of Chiodini, G.)

Reply. Corrected

Referee #2

General comments

The manuscript report on the use of a very interesting and valuable tool to monitor degassing at the active vents in volcanic area. A portable remote sensing spectrometer LARSS, which detects CO2 in a spatially integrated manner, was used to conduct CO2 flux surveys in Pisicairelli area, located within the Campi Flegrei caldera, Italy. Although measurements are associated with quite few uncertainties, the results indicate an increase in CO2 flux in the last 2 years – findings are well in agreement with other recent study in the area. Based on recent data indicating a deceleration of ground uplift at Campi Flegrei, the authors also suggest that the ongoing degassing it is related to a release of deep magmatic gases towards the hydrothermal system, possibly accompanied by an increased bulk permeability of the shallow crust. Finally, the authors highlight the importance of the technique in giving spatially comprehensive values of CO2 flux acquired which may help to estimate the degassing process as a whole and then provide clues about the strength of the CO2 source. The paper is very interesting and worthy of publication in Solid Earth discussions, and their results are very important for the understanding of degassing at Pisciarelli, which together with the nearby Solfatara crater, are attracting more and more the scientific attention nowadays.

However, the authors attempt a simplified explanation of the degassing behavior while they should consider the complex geology-fluids interaction in the shallow ground (tens of meter) and in the subsoil below the investigated area, which are controlling the surficial degassing.
Reply: Given the very limited data we obtained, any deeper insights in the source mechanism is utterly out of scope of this paper. The discussion is meant to relate our findings to other geomechanical, geophysical and geochemical observations. We cannot provide an explanation based on this paper and we say so in the introduction and the conclusions.

Though the proposed methodology is very valuable, it should also be considered (and discussed in the manuscript) that its integration with other punctual measurements techniques (e.g. accumulation chamber) is needed to better characterize the areal degassing and constrain the effect of local elements (e.g. fractures) on the degassing behavior.
Exactly this point has been raised already by reviewer 1 and treated accordingly. Please see our reply to his comments above.

Specific comments
Thus, I would suggest minor revisions on the following points in the manuscript:

- Page2, lines 3-6: here the recent work on the geology and the structure of the area should be mentioned (Isaia et al. 2015 and Vitale et al. 2014):
We added Vitale and Isaia, 2014.

- Page2, lines 9-10: here I would also discuss the effect of i) the subsoil in controlling the surficial degassing (Montanaro et al. 2016), and ii) passing of a seismic wave that can induce a strong increase in the total amount of gas (Gresse et al. 2016);
Reply: While we agree that these effects are important in modulating the degassing strength, the focus of this paper is more on the actual source of the CO_2 and the mechanisms which control it at the first place. But we deem it important to mention it in the discussion. Added both references: Finally, it should be mentioned that heterogeneity in the subsoil (Montanaro et al., 2016) and dynamic changes in subsoil rock matrix properties (Gresse et al., 2016) may modulate emission of stored gas.

- Page2, lines 20-21 (and in the discussion as well): the recent work of Mayer et al. (2016) and Piochi et al. (2015), concerning the effect solfataric alteration that increases porosity and permeability of altered rock, should be mentioned and discussed;
Reply: We already mention an increase in permeability. Adding this petrological results just leads to far away from the scope of this paper, which is not to explain why the permeability increased. For a review paper yes, but here we prefer to not discuss this. But we added a reference to Piochi on p2 l 20.

- In "Materials and methods": maybe here should be briefly discussed about other factors influencing the measurements, such as wind, change in humidity around the measured spots, etc., which are also mentioned in the results;
Wind, i.e. plume speed is treated in the response to reviewer #1. Humidity plays a role when you convert CO_2 number density to mixing ratio (which is relative to the total number of air molecules hence including water), but this is not done here to compute fluxes. Mixing ratios are only shown for display purposes. That said, the difference between dry and wet air mixing ratio is negligible

compared with the uncertainty we get from the plume speed estimation, for example.

- Page4, line 10: "gas plume" rather than volcanic;
changed to gas plume

- Page5, line 14: "td-1" rather than "kgs-1"(?);
No it is indeed kg s-1.

- Page6, line 8-9: here the works of Vanorio (2015) and Heap (2014) on the properties of the caldera-filling tuffs should also be cited and maybe briefly discuss about it.
We measure an increase in CO_2 output and think this result is robust because the method we use gives comprehensive CO_2 concentrations. That is all we say. Second order complication is relation this to other data and modeling results. Adding above work would cause third order detail branching that is out of scope of this short comm paper.

- Figure 2: can you reverse the Heading angle values in a way that is consistent with Figure 1B?
The headings are absolute values relative to north, that is why they are displayed in descending order. We prefer to leave it that way as this is was the direction of the scan.

No other changes were made.

Increasing CO$_2$ flux at Pisciarelli, Campi Flegrei, Italy

Manuel Queißer[1], Domenico Granieri[2], Mike Burton[1], Fabio Arzilli[1], Rosario Avino[3], Antonio Carandente[3]

[1]School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Oxford Road, Manchester M13 9PL, UK

[2]Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Pisa, 50126 Pisa, Italy

[3]Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Vesuviano, Napoli, 80124, Italy

Correspondence to: Manuel Queißer (manuel.queisser@manchester.ac.uk), Tel.: +44(0)161 2750778, Fax.: +44(0)161 306 9361

Abstract. Campi Flegrei caldera is located in the metropolitan nucleus of Naples (Italy), and has been undergoing different stages of unrest since 1950, evidenced by episodes of significant ground uplift followed by minor subsidence, increasing and fluctuating emission strengths of water vapor and CO$_2$ from fumaroles, and periodic seismic crises. We deployed a scanning laser remote sensing spectrometer (LARSS) that measures path integrated CO$_2$ concentrations at the Pisciarelli area in May 2017. The resulting mean CO$_2$ flux is 578 ± 246 t d^{-1}. Our data suggest a significant increase in CO$_2$ flux at this site since 2015. Together with recent geophysical observations, this suggests a greater contribution of the magmatic source to the degassing and/or an increase of permeability at shallow levels. Thanks to the integrated path soundings, LARSS may help to give representative measurements from large regions containing different CO$_2$ sources, including fumaroles, low-T vents, and degassing soils, helping to constrain the contribution of deep gases and their migration mechanisms towards the surface.

1 Introduction

Of all the volcanic calderas in the world the ~12 km wide Campi Flegrei (CF) in southern Italy is arguably the one with the highest destructive potential, since it is in a state of unrest and located within an urban area of over 2 million residents, with Naples being the largest urban nucleus in the area (Fig. 1a). Its last eruption dates back to 1538 (Dvorak and Gasparini, 1991). Ever since, CF underwent various series of new, rather swift uplifts (bradyseisms), indicating unrest followed by a decrease in ground level usually at a much slower rate (Chiodini et al., 2010; Troiano et al., 2011; D'Auria, 2015; De Natale et al., 2017). Since the last energetic unrest of 1982-84 the caldera is subject to intense geophysical and geochemical monitoring, with greatest interest for the Solfatara crater, in the center of CF, and for the Pisciarelli area, on the eastern outer slope of Solfatara. Around 2005 a new net uplift, although at a relatively slow rate, has commenced. At Pisciarelli, where the more recent low-energetic seismic swarms are localized (D'Auria et al., 2011), the fumarole temperature increased from below 100°C in 2005 to ~ 115°C in 2015. The amount of water vapor has increased visibly and the strongly degassing area has been considerably enlarged in the past few years (Chiodini et al., 2015). Given these major signs as well as other signs,

1

mainly related to fluid geochemical variations at the fumaroles of Solfatara (Chiodini et al., 2015, 2016), national civil protection authorities have changed the state of CF from green (quite) to yellow (scientific attention).

As all calderas, CF represents a complicated makeup that includes a magmatic plumbing system up to a depth of ~ 8 km (Bodnar et al., 2007; Zollo et al., 2008; Vitale et al. 2014; Moretti et al., 2017), feeding the overlying hydrothermal
5 system (Chiodini et al., 2010; Troiano et al., 2011; De Siena et al., 2017a) through an intricate network of fractures (Zollo et al., 2008; De Siena et al., 2010; Byrdina et al., 2014). A clear picture of the feeding mechanisms and its dynamics is one of the central open questions of CF and subject to ongoing debate. There is a broad consensus among researchers that injections of deep, hot, and oxidized fluids into the hydrothermal system of CF causes increased CO_2 soil degassing (Cardellini et al., 2016), increased CO_2 content in the fumarole discharges (with consequent decreasing trends of H_2O/CO_2 or H_2S/CO_2 ratios)
10 and ground uplift (Caliro et al., 2007; Chiodini et al., 2012; Aiuppa et al., 2013). As a matter of fact, there is a fair correlation between soil/fumarole CO_2 degassing strength and episodes of ground uplift (D'Auria, 2011; Chiodini et al., 2012, 2016) following this order: uplift, and months later an increase in CO_2 relative to other gases. There appear to be two logical main causes for this:

i) An increase in supply of fluids and associated thermal energy into the hydrothermal system for
15 depressurization of the magmatic source (Allard et al., 1991; Chiodini et al., 2016). This increased supply is thought to stem from either the ~ 8 km deep main magma reservoir (Bodnar et al., 2007; Zollo et al., 2008; Moretti et al., 2017), or from a contribution of a magma batch that intruded the shallow subsurface (~ 3-4 km depth) concomitantly with the 1982–1984 unrest episode (Chiodini et al., 2010; Caliro et al., 2014) and periodically rejuvenated by arrivals of deep more primitive magma (Bagagli et al., 2017) and/or
20 ii) an increase in permeability at shallow levels, i.e., above the hydrothermal reservoir (Todesco et al., 2003; Acocella et al., 2015; Piochi et al., 2015).

Discriminating within those mechanisms is out of the scope of this study, but any insights towards a better understanding of these processes are important to improve early warning and civil protection measures at the CF area. Measuring emission rates (fluxes) of CO_2 provides an additional way to assess the hazard at CF. The fumarole area of
25 Piscarelli, approximately located in the center of the CF caldera (Fig. 1a) and recently scene of drastic changes in its activity, is a prime geochemical sampling spot to learn about the volcanic processes taking place beneath CF. A spatially integrated measurement of CO_2 flux that accounts for all possible CO_2 vents and diffuse degassing is desirable to obtain a quantitative picture of CO_2 degassing, but has only been done a few times after 2012 at Pisciarelli (Pedone et al., 2014; Aiuppa et al., 2015; Queißer et al., 2016a). To increase the number of observations it was decided to revisit CF 14 months after the last
30 such measurement (Queißer et al., 2016a) and re-measure CO_2 fluxes.

2 Materials and Methods

The CO_2 concentrations needed to estimate the CO_2 flux are commonly sampled at points, which may miss out sources, such as smaller fumarolic discharges (Chiodini et al., 2015). On the other hand, point measurements are very precise and valuable in characterizing local degassing elements, such as fractures. Path integrating, scanning gas measurement techniques, on the

5   other hand, may add value by providing a spatially comprehensive measurement. To attempt a spatially inclusive measurement of all possible sources of CO_2, diffusive soil and vented degassing, we used a laser remote sensing spectrometer (LARSS), developed in the ERC proof-of-concept project CarbSens. Combined with point measurement techniques, such as accumulation chambers, LARRS may help to yield a more complete picture of degassing. It represents a further miniaturization of a similar system developed in the ERC project CO_2Volc. The instrument and its working principle

10   are detailed elsewhere (Queißer et al., 2017). Only a brief overview is given therefore. LARSS consists of a main unit and a transmitter/receiver unit (TX/RX unit, Fig. 1b). The latter comprises of the telescope, transmitter and an integrating sphere for power reference measurement. It is portable (mass: 10 kg main unit + 6 kg TX/RX unit), which allows it to be transported easily and set up at any kind of surface, such as house roofs or airplanes.

The CO_2 absorption line at 1572.335 nm (*R*16 transition) is sampled at 40 wavelengths by sweeping the emission

15   wavelength of a diode laser. The laser light is amplified, transmitted, backscattered at a topographic target and received by the telescope. After the detected signal is digitized, the optical transmittance of the telescope's viewing path is deduced for each of the 40 wavelengths. A model absorption spectrum is fitted to the 40 measured transmittances, resulting in a best estimate of the path averaged CO_2 column density (in m^{-2}). The path length may be up to 2 km. Profiles of CO_2 concentrations, i.e., CO_2 concentrations versus angle, are attained by scanning the TX/RX unit across a degassing plume (see

20   Queißer et al. (2016a) for details on scanning geometry). Along with the plume transport speed these profiles are then used to obtain CO_2 fluxes, following

(1)

where refers to the component of the plume transport speed perpendicular the plane of the CO_2 concentration profile, i.e., the component perpendicular to the plane of the scan. is the molar mass of CO_2 (in kg mol^{-1}) and is Avogadro's constant (in

25   mol^{-1}). is the constant scan angle increment., the background corrected, or in-plume column density of CO_2, is retrieved by subtracting the total CO_2 column density by the ambient CO_2 column density measured outside the plume, i.e., , where is the total column density as measured, and depicts the ambient column density. The ranges are measured with a range finder LIDAR aligned with the telescope. For convenience and display purposes, if meteorological data are available, column densities may be converted to path averaged mixing ratios (in ppm) as detailed in Queißer et al. (2017). The plume speed is

30   retrieved by digital video tracking of the plume of condensed water vapor as described in Queißer et al. (2016a).

3 Results

The data presented here are a subset of data acquired during a campaign probing CO_2 at the Pisciarelli-Solfatara area between 24th and 26th of May 2017. LARSS was placed on the roof of the *Tennis Hotel*, located ~ 320 m east of the Pisciarelli fumaroles, offering an unobstructed view on the complete fumarole degassing activity. Between 17:07 and 18:04 local time on the 24 May 2017, 9 lateral angular scans were performed, out of which 6 are displayed in Fig. 2. A step motor rotated the TX/RX unit between 257.4° and 243.4° (Fig. 1b) with a velocity of 2.5 mrad s^{-1}, corresponding to a lateral section of ~80 cm at the fumarole area per data point. was retrieved by multiplying the scanning angular speed with the time between subsequent measurements as recorded in the time stamps of the raw data files. Each scan took around 90 s. Meteorological data (temperature, pressure, humidity) were recorded using a Kestrel portable meteorological station placed next to LARSS. were measured by a scan upwind, outside of any <mark>gas</mark> plume, using a hill range between 700 and 900 m distance as target. The corresponding column averaged CO_2 mixing ratio was found to be 499 ppm. For comparison, two in-situ measurements with a LI-COR analyzer were performed at points near the optical paths of LARSS, yielding CO_2 mixing ratios of 550 ppm and 560 ppm, respectively. These are remarkably high CO_2 concentrations, given that the wind came from the sea (South). The proximity of the measurement points to the road and the dense network of roads in that area may well cause these values (Schmidt et al., 2014). Consequently, corresponding to an ambient CO_2 mixing ratio of 499 pm ± 61 ppm were considered.

Highest CO_2 concentrations were usually detected near the center of the probed area (near 250°, Figs. 2b to g). This main plume reveals a fine structure, suggesting three sub peaks, which could be related to three main vents in very close proximity to each other identified by Pedone et al. (2014). The highest column averaged CO_2 mixing ratio measured was 1777 ppm (Fig. 2e), which is, however, associated with a relatively large uncertainty of 236 ppm (1 STD). Note that Pedone et al. (2014) measured a peak value of 1444 ppm in early 2013 at approximately the same location. Elevated concentrations also occurred towards the southern edge of the probed area (~ 21 m south of the main plume), at the slope. The corresponding peak repeatedly arose near 246° (especially Figs. 2b, c, d and g).

Uncertainties of path averaged CO_2 mixing ratios were usually between 2% and 5% or 10 to 30 ppm (associated with a path averaged detection limit of ~10000 ppm.m). The main source of uncertainty was the contribution of the instrument itself (baseline drift) and the fitting error. The latter had been significantly improved (roughly halved) by increasing the number of sampled wavelengths from 20 to 40 recently. A detailed description of influences of various error sources is provided in Queißer et al. (2017). In-plume CO_2 concentrations found were mostly between 500 and 4000 ppm, with peaks around 6000 ppm, and agree well with those measured by the fixed in-situ station (Figs. 2b to g). In-plume concentrations had associated uncertainties naturally larger than those of the column averaged values, that is, typically between 4% and 15%, or around 150 ppm. Local wind eddies may lead to local maxima of CO_2 concentrations and may also explain the shift in the global concentration maximum after Fig. 2d, suggesting a generally "wobbly" character of the CO_2 plume.

The measured vertical plume speed component was 0.65 m s^{-1} (min 0.28 m s^{-1}, max 1.05 m s^{-1}) until 17:43:47 and 0.80 m s^{-1} (min 0.31 m s^{-1}, max 1.37 m s^{-1}) after that. The plume speed uncertainties were calculated from the student *t*-variance as detailed in Queißer et al. (2016a). Given the complex terrain and the fact that the measurement was performed close to the ground the velocity field across the scanned plume was generally not constant, in addition to temperature variations causing different plume speeds across the plume. The corresponding variability has been accounted for by tracking different paths of propagating water vapor across the plume and using the variability in the error estimation. Plume speed is in fact one of the main sources of uncertainty, adding an uncertainty of the order of 30% to the flux.

Table 1 shows the flux values computed using Eq. (1), with a mean value of 6.7 ± 2.9 kg s^{-1} (578 ± 246 t d^{-1}). As noted in previous measurements at Pisciarelli, the measured fluxes fluctuate by over 100% over the course of minutes (Aiuppa et al., 2015; Queißer et al., 2016a). However, an observational window of 1h length reflected the same variability as an 8h long window (Aiuppa et al., 2015). The rigorous error assessment, i.e., taking all relevant error sources into account, including conservative systematic errors estimates, led to a rather high uncertainty of the flux values. The conservatively chosen uncertainty of the ambient CO_2 concentration, an order of magnitude higher than usual, accounts for between 20% and 70% (depending on the profile) of the flux uncertainties presented in Table 1. The other chief source of flux uncertainty is the plume speed, which, depending on the scan, caused an increase in error by the same magnitude.

The mean flux of 6.7 kg s^{-1} corresponds to the complete extension of the scan, that is, the vegetation free zone of ~ 70 m in lateral diameter (Fig. 1c). When integrating over the central area only (between 252.5° and 247.0°), roughly including the aforementioned 3 major vents, the mean flux obtained is 284 ± 107 t d^{-1} and is compatible with the estimated area-integrated value from the in-situ automated flux measurement station FLXOV3 (Fig. 3). This may explain the offset between the fluxes of this work and FLXOV3. Focusing on the main vent area only, however, neglects persistent degassing features, such as at the southern edge of the fumarole area, as well as diffusive soil degassing taking place within the scanned sector (Caliro et al., 2007). This spatially comprehensive character of the measurement is one of the main merits of the remote sensing technique applied here.

4 Discussion

The soil CO_2 flux at CF is known to have increased in magnitude and spatial extension since 2005 (Cardellini et al., 2016) as well as the CO_2 content in CF high-T fumaroles (Chiodini et al., 2010; 2016). Figure 3 suggests a slight acceleration in CO_2 degassing from the soils of Pisciarelli since about 2009 (FLXOV3 series) confirmed by post-2012 CO_2 measurements integrated over the whole exhaling area, which fairly coincides with the observed acceleration in ground uplift. The similarity between the uplift and degassing trends suggests that both processes are intrinsically related. In fact, the preferential exsolution of CO_2 from the deep magmatic body due to its low solubility at high pressure implies an associated release of H_2O simultaneously to CO_2 output (Chiodini et al., 2001) or when CO_2 is completely exhausted in the magma (Chiodini et al., 2016). In any case, the participation of H_2O in the degassing process results in a very efficient mechanism to

convey heat from depth to the hydrothermal system and the overlying rocks, favoring thermally-induced dilation (ground deformation) and enhancing the permeability of fluids flowing through them (greater degassing at the surface). Recent findings indeed point towards an impulsive influx of hot magmatic fluids into the hydrothermal system as a possible source mechanism at CF that eventually cause the observed geophysical and geochemical time series, including the present one 5 (Chiodini et al., 2017).

The inspection of Fig. 3 confirms this general scheme although the CO_2 fluxes measured at Pisciarelli in May 2017 (this study) and in March 2016 (Queißer et al., 2016a) seem to suggest an increase at a larger rate than the observed uplift would imply. In particular, the latest available data, up to April 2017, suggests a deceleration of ground uplift at CF as of 2016 (Fig. 3 and in more detail INGV, 2017), which, as far as the resolution of our data permits to say, is not accompanied by 10 a leveling out of degassing strength.

Our results related to the CO_2 degassing are compatible with findings, which state that the elastic rock matrix of CF is transitioning to inelastic behavior under long-term stress accumulation, accompanied by a permeability increase of the shallow crust, disguising any direct indicator of unrest, such as rapid ground uplift or enhanced seismicity (Bodnar et al., 2007; Di Luccio et al., 2015; Kilburn et al., 2017). In line with this prospect is a clear seismic velocity decrease since 2012 15 (Zaccarelli and Bianco, 2017), which could be due to, for instance, a softening bulk or increase in CO_2 saturation in the CF aquifer (Queißer and Singh, 2012) that may also explain the strong seismic attenuation observed (De Siena et al., 2017b).

The aforesaid could justify the discrepancy recently highlighted by Moretti et al. (2017) between weak geophysical signals (moderate uplift and low seismicity) and drastic changes in geochemical indicators characterizing the present stage of the CF history.

20 Finally, it should be mentioned that heterogeneity in the subsoil (Montanaro et al., 2016) and dynamic alterations in subsoil rock matrix properties such as due to seismic energy (Gresse et al., 2016) may modulate emission of stored gas and therefore cause changes in degassing strength.

5 Conclusions and Perspectives

About 14 months after the last survey we have revisited the Pisciarelli area. The current CO_2 flux was quantified using the 25 portable remote sensing spectrometer LARSS, which detects CO_2 in a spatially integrated manner. Although associated with a fairly conservative uncertainty, the result along with fluxes measured in 2016, imply an increase in CO_2 flux in the last 2 years. Drawing solid conclusions based on our data is not possible. Nonetheless, given the slow, almost halted ground uplift since 2016, our result could indicate a release of deep magmatic gases towards the hydrothermal system, possibly accompanied by an increased bulk permeability of the shallow crust.

30 Our measurements, although reasonable, do not permit an unequivocal conclusion whether the origin of the gas emitted at surface is purely hydrothermal or magmatic nor regarding the migration mechanisms from the bottom to the top of the CF plumbing system. Nevertheless, the spatially comprehensive values of CO_2 flux acquired through LARSS may help

constraining the degassing process as a whole and then provide clues about the strength of the CO_2 source, for example via mass balance considerations (Allard et al., 1991) possibly adding to geochemical appraisals (Moretti et al., 2013). However, more measurements of this kind are needed (higher temporal resolution). Furthermore, point measurements should be added in the future to systematically test and verify the capability of LARRS to probe comprehensively all degassing elements in its path. For challenging degassing situations as at CF, integrating LARRS with point measurements may provide a powerful means to obtain a complete picture of degassing. Point measurements are able to draw detailed maps of the emission areas which LARRS is not capable of. However, using two instruments 2D tomography can be performed (Queisser et al., 2016b). Although much more improvement of this technique is needed to converge to degassing maps from point measurements. Moreover, there is potential to further reduce uncertainty of the measured fluxes. To that end, the plume speed estimation will be further improved, especially with respect to resolving the plume speed variations (velocity field) across the scanned plume.

Author contributions. M. Queiβer developed LARSS, conducted the measurements and drafted the manuscript, D. Granieri conducted the measurement and drafted the manuscript, M. Burton developed LARSS and drafted the manuscript, F. Arzilli drafted the manuscript, R. Avino and A. Carandente conducted the measurements.

References

Acocella, V., Di Lorenzo, R., Newhall, C., and Scandone, R.: An overview of recent (1988 to 2014) caldera unrest: Knowledge and perspectives, Rev. Geophys., 53, 896–955, doi:10.1002/2015RG000492, 2015.

Aiuppa, A, Fiorani, L., Santoro, S., Parracino, S., Nuvoli, M., Chiodini, G., Minopoli, C., and Tamburello, G.: New ground-based lidar enables volcanic CO_2 flux measurements, Sci. Rep., 5, 13614, doi: 10.1038/srep13614, 2015.

Aiuppa, A., Moretti, R., Federico, C., Giudice, G., Gurrieri, S., Liuzzo, M., Papale, P., Shinohara, H., and Valenza, M.: Forecasting Etna eruptions by real-time observation of volcanic gas composition, Geology, 35, 1115-1118, doi:10.1130/G24149A.1, http://geology.gsapubs.org/content/35/12/1115.abstract, 2007.

5   Aiuppa, A., Tamburello, G., Di Napoli, R., Cardellini, C., Chiodini, G., Giudice, G., Grassa, F., and Pedone, M.: First observations of the fumarolic gas output from a restless caldera: Implications for the current period of unrest (2005–2013) at Campi Flegrei, Geochem. Geophys. Geosyst., 14, 4153–4169, doi:10.1002/ggge.20261, 2013.

Allard, P., Maiorani, A., Tedesco, D., Cortecci, G., and Turi, B.: Isotopic study of the origin of sulfur and carbon in Solfatara
10   fumaroles, Campi Flegrei Caldera, J. Volcanol. Geotherm. Res., 48(1-2), 139-159, doi :10.1016/0377- 0273(91)90039-3, 1991.

Bagagli, M., Montagna, C. P., Papale, P., and Longo, A.: Signature of magmatic processes in strainmeter records at Campi Flegrei (Italy), Geophys. Res. Lett., 44, 718-725, doi:10.1002/2016GL071875, 2017.

15

Bodnar, R. J., Cannatelli, C., De Vivo, B., Lima, A., Belkin, H. E., and Milia, A.: Quantitative model for magma degassing and ground deformation (bradyseism) at Campi Flegrei, Italy: Implications for future eruptions, Geology, 35, 791-794, 2007.

Byrdina, S., Vandemeulebrouck, J., Cardellini, C., Legaz, A., Camerlynck, C., Chiodini, G., Lebourg, T., Gresse, M., Bascou,
20   P., Motos, G., Carrier, A., and Caliro, S.: Relations between electrical resistivity, carbon dioxide flux, and self-potential in the shallow hydrothermal system of Solfatara (Phlegrean Fields, Italy), Journal of Volcanology and Geothermal Research 283 (2014) 172-182, http://dx.doi.org/10.1016/j.jvolgeores.2014.07.010, 2014.

Cardellini, C., Chiodini, G., Rosiello, A., Bagnato, E., Avino, R., Frondini, F., Caliro, S., Beddini, G., Donnini, M., and Lelli,
25   M.: Long time series of soil CO2 degassing measurements at Solfatara of Pozzuoli (Campi Flegrei, Italy), 18th EGU General Assembly, EGU2016, proceedings from the conference held 17-22 April, 2016 in Vienna, Austria, p. 3540, 2016.

Chiodini, G., Frondini, F., Cardellini, C., Granieri, D., Marini, L., and Ventura, G.: CO_2 degassing and energy release at Solfatara Volcano, Campi Flegrei, Italy, J. Geophys. Res., 106, 16,213–16, 223, 2001.

30

Chiodini, G., Caliro, S., Cardellini, C., Granieri, D., Avino, R., Baldini, A., Donnini, M., and Minopoli, C.: Long-term variations of the Campi Flegrei, Italy, volcanic system as revealed by the monitoring of hydrothermal activity, J. Geophys. Res., 115, B03205, doi:10.1029/2008JB006258, 2010.

Chiodini, G., Caliro, S., De Martino, P., Avino, R., and Gherardi, F.: Early signals of new volcanic unrest at Campi Flegrei caldera? Insights from geochemical data and physical simulations, Geology, 40, 943-946, 2012.

Chiodini, G., Paonita, A., Aiuppa, A., Costa, A., Caliro, S., De Martino, P., Acocella, V., and Vandemeulebrouck, J.: Magmas
5 near the critical degassing pressure drive volcanic unrest towards a critical state, Nat. Commun., 7, 13712, doi:10.1038/ncomms13712, 2016.

Chiodini, G., Selva, J., Del Pezzo, E., Marsan, D., De Siena, L., D'Auria, L., Bianco, F., Caliro, S., De Martino, P., Ricciolino, P., and Petrillo, Z.: Clues on the origin of post-2000 earthquakes at Campi Flegrei caldera (Italy): Sci. Rep.,
10 doi:10.1038/s41598-017-04845-9, 2017.

Chiodini, G., Vandemeulebrouck, J., Caliro, S., D'Auria, L., De Martino, P., Mangiacapra, A., and Petrillo, Z.: Evidence of thermal-driven processes triggering the 2005-2014 unrest at Campi Flegrei caldera, Earth Planet. Sci. Lett., 414, 58-67, 2015.
15

Dvorak, J. J., and Gasparini, P.: History of earthquakes and vertical ground movements in Campi Flegrei caldera, Southern Italy: a comparison of precursor events to the A.D. eruption of Monte Nuovo and of activity since 1968, J. Volcanol. Geotherm. Res., 48, 77-92, 1991.

20 D'Auria, L.: Update sullo stato dei Campi Flegrei, INGV, Sezione di Napoli, Report, last accessed: June 2017, ftp://ftp.ingv.it/pro/web_ingv/Convegno_Struttura %20_Vulcani/presentazioni/15_D'auria_CampiFlegrei/dauria_cf.pdf, 2015.

25 D'Auria, L., Giudicepietro, F., Aquino, I., Borriello, G., Del Gaudio, C., Lo Bascio, D., Martini, M., Ricciardi, G. P., Ricciolino, P., and Ricco, C.: Repeated fluid transfer episodes as a mechanism for the recent dynamics of Campi Flegrei caldera (1989-2010), J. Geophys. Res. 116, B04313, doi:10.1029/2010JB007837, 2011.

De Natale, G., Troise, C., Kilburn, C. R. J., Somma, R., and Moretti, R.: Understanding volcanic hazard at the most
30 populated caldera in the world: Campi Flegrei, Southern Italy, Geochem. Geophys. Geosyst., 18, doi:10.1002/2017GC006972, 2017.

Di Luccio, F., Pino, N. A., Piscini, A., and Ventura, G.: Significance of the 1982-2014 Campi Flegrei seismicity: Preexisting structures, hydrothermal processes, and hazard assessment, Geophys. Res. Lett., 42, 7498-7506, doi:10.1002/2015GL064962, 2015.

5 De Siena, L., Amoruso, A., Del Pezzo, E., Wakeford, Z., Castellano, M., and Crescentini, L.: Space-weighted seismic attenuation mapping of the aseismic source of Campi Flegrei 1983-1984 unrest, Geophys. Res. Lett., 44, 1740-1748, doi:10.1002/2017GL072507, 2017a.

De Siena, L., Chiodini, G., Vilardo, G., Del Pezzo, E., Castellano, M., Colombelli, S., Tisato, N., and Ventura, G.: Seismic
10 imaging of the hot source of Campi Flegrei unrest, 19th EGU General Assembly, EGU2017, proceedings from the conference held 23-28 April, 2017 in Vienna, Austria, p. 1882, 2017b.

De Siena, L., Del Pezzo, E., and Bianco, F.: Seismic attenuation imaging of Campi Flegrei: Evidence of gas reservoirs, hydrothermal basins, and feeding systems, J. Geophys. Res., 115, B09312, doi:10.1029/2009JB006938, 2010.
15

Gresse, M., Vandemeulebrouck, J., Byrdina, S., Chiodini, G., Bruno, P. P.: Changes in CO_2 diffuse degassing induced by the passing of seismic waves, J. Volcanol Geotherm. Res., 320, 12-18. doi:10.1016/j.jvolgeores.2016.04.019, 2016.

INGV: Bollettino di Sorgevlianza Campi Flegrei Aprile 2017, INGV, Osservatorio Vesuviano, Report, last accessed: June,
20 2017,   http://www.ov.ingv.it/ov/bollettini-mensili-campania/Bollettino%20Mensile%20Campi%20Flegrei%202017_04.pdf, 2017.

Kilburn, C. R. J., De Natale, G., and Carlino, S.: Progressive approach to eruption at Campi Flegrei caldera in southern Italy, Nat. Commun., 8, 15312, doi:10.1038/ncomms15312, 2017.
25

Montanaro, C., Mayer, K., Scheu, B., Isaia, R., Mangiacapra, A., Gresse, M., Vandemeulebrouck, J., Moretti, R., Dingwell, D. B.: Hydrothermal activity and subsurface soil complexity: implication for outgassing processes at Solfatara crater, Campi Flegrei caldera. In EGU General Assembly Conference Abstracts, 18, 12509, 2016.

30 Moretti, R., Orsi, G., Civetta, L., Arienzo, I., and Papale, P.: Multiple magma degassing sources at an explosive volcano, Earth Planet. Sci. Lett., 367, 95-104, 2013.

Piochi M., Mormone, A., Balassone, G., Strauss, H., Troise, C., De Natale, G.: Native sulfur, sulfates and sulfides from the active Campi Flegrei volcano (southern Italy): Genetic environments and degassing dynamics revealed by mineralogy and isotope geochemistry, J. Volc. Geotherm. Res., 304, 180-193, http://dx.doi.org/10.1016/j.jvolgeores.2015.08.017, 2015.

5 Pedone, M., Aiuppa, A., Giudice, G., Grassa, F., Cardellini, C., Chiodini, G., and Valenza, M.: Volcanic CO_2 flux measurement at Campi Flegrei by Tunable Diode Laser absorption Spectroscopy, Bull. Volc., 76, 812, doi: 10.1007/s00445-014-0812-z, 2014.

Queißer, M., Granieri, D., and Burton, M.: A new frontier in CO_2 flux measurements using a highly portable DIAL
10 laser system, Sci. Rep., 6, 33834, doi:10.1038/srep33834, 2016a.

Queißer, M., Granieri, D., and Burton, M.: 2-D tomography of volcanic CO_2 from scanning hard-target differential absorption lidar: the case of Solfatara, Campi Flegrei (Italy), Atmos. Meas. Tech., 9, 5721-5734, https://doi.org/10.5194/amt-9-5721-2016, 2016b.

15

Queißer, M., Burton, M. R., Arzilli, F., Chiarugi, A., Marliyani, G. I., Anggara, F., and Harijoko, A.: CO_2 flux from Javanese mud volcanism, J. Geophys. Res. Solid Earth, 122, doi:10.1002/ 2017JB013968, 2017.

Queißer, M., and Singh, S. C.: Full waveform inversion in the time lapse mode applied to CO_2 storage at Sleipner, Geophys.
20 Prospect., 61, 537-555, doi: 10.1111/j.1365-2478.2012.01072.x, 2012.

Schmidt, A., Rella, C. W., Göckede, M., Hanson, C., Yang, Z., and Law, B. E.: Removing traffic emissions from CO_2 time series measured at a tall tower using mobile measurements and transport modeling, Atmos. Environ., 97, 94-108, 2014.

25 Todesco, M., Chiodini, G., and Macedonio. G.: Monitoring and modelling hydrothermal fluid emission at La Solfatara (Phlegrean Fields, Italy). An interdisciplinary approach to the study of diffuse degassing, J. Volcanol. Geotherm. Res., 125, 57-79, doi:10.1016/S0377-0273(03)00089-1, 2003.

Troiano, A., Di Giuseppe, M. G., Petrillo, Z., Troise, C., and De Natale, G.: Ground deformation at calderas driven by fluid
30 injection: modelling unrest episodes at Campi Flegrei (Italy), Geophys. J. Int., 187, 833-847, doi: 10.1111/j.1365-246X.2011.05149.x, 2011.

Vitale S, and Isaia R.: Fractures and faults in volcanic rocks (Campi Flegrei, southern Italy): Insight into volcano-tectonic processes, Int. J. Earth Sci., 103, 801-819, 2014.

Zaccarelli, L., and Bianco, F.: Noise-based seismic monitoring of the Campi Flegrei caldera, Geophys. Res. Lett., 44, 2237-2244, doi:10.1002/2016GL072477, 2017.

5   Zollo, A., Maercklin, N., Vassallo, M., Dello Iacono, D., Virieux, J., and Gasparini, P.: Seismic reflections reveal a massive melt layer feeding Campi Flegrei caldera, Geophys. Res. Lett., 35, L12306, doi:10.1029/2008GL034242, 2008.
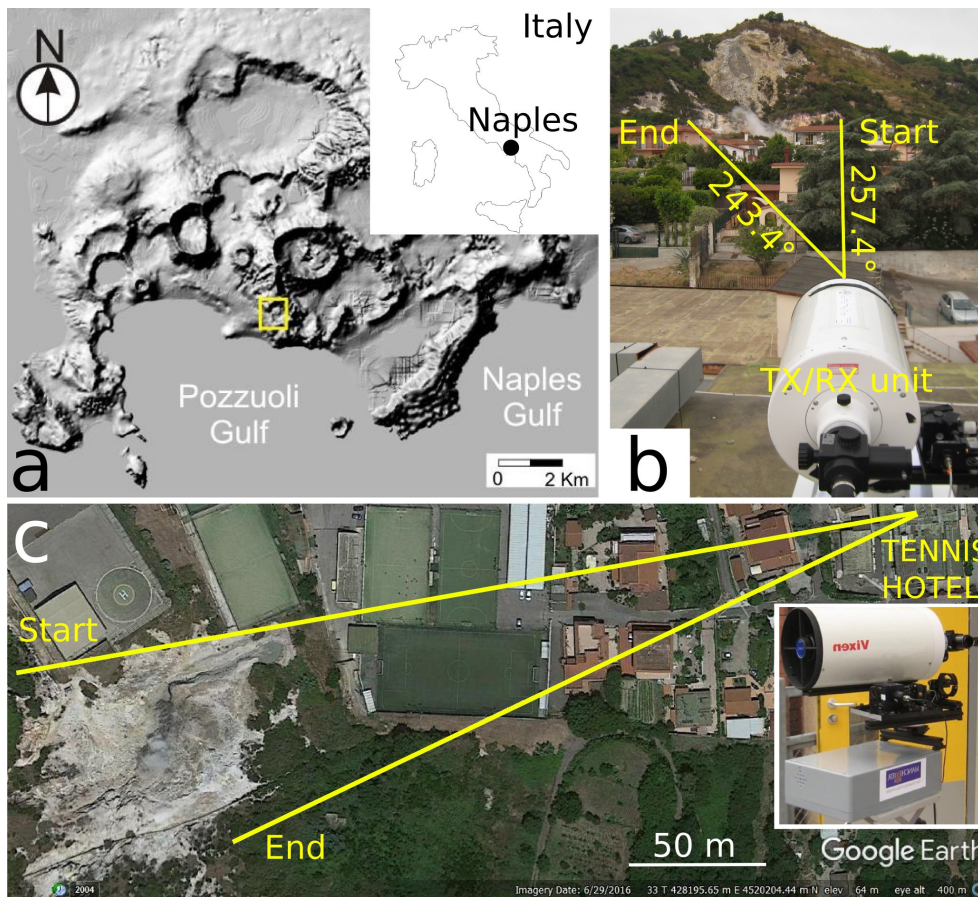
Figure 1: The location of Campi Flegrei (CF) and the measurement geometry. (a) Map of Italy and relief of the region of CF. The yellow square depicts the zone of Solfatara-Pisciarelli. (b) View from the roof of the Tennis Hotel and the telescope looking towards the Pisciarelli fumarole area concentrated within a zone of ~ 60 m diameter visible in the background. Indicated are the start and the end position of the TX/RX unit's line of sight and the corresponding angles. A total of ~14° was covered during each scan. (c) Nadir view of the situation depicted in (b). The inset shows a complete view of LARSS.
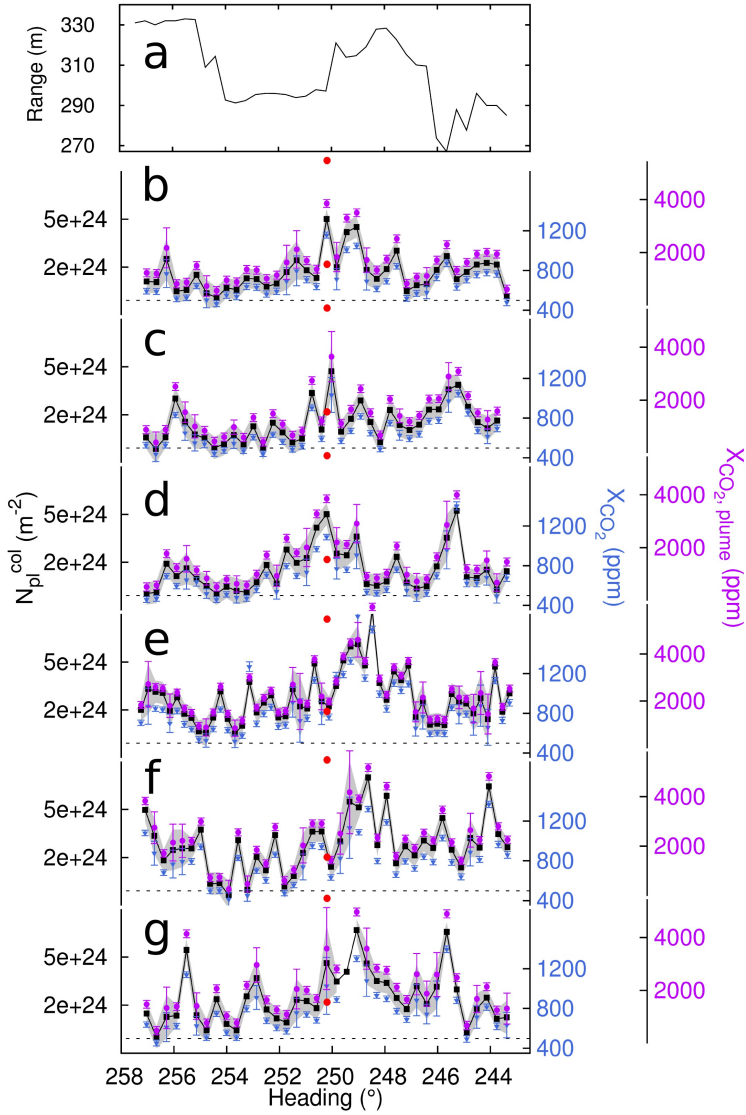
Figure 2. CO₂ concentration profiles of horizontal scans of the Pisciarelli fumaroles. (a) Ranges to hard target per heading angle. The target was the slope behind the fumaroles (Figs. 1b and c). (b) to (g) Background corrected CO₂ column densities versus angle as used for flux computation [Eq. (1)]. The grey envelope depicts the confidence (1 STD, for details see Queißer et al., 2017). On the right are the corresponding path averaged mixing ratios (blue) with confidence interval (1 STD). The dotted line depicts the ambient CO₂ mixing ratio of 499 ppm. Also shown are the in-plume mixing ratios (magenta), estimated from the path averaged mixing ratios, assuming 62 m plume extension (Queißer et al., 2016a). The red circles mark the minimum and maximum mixing ratio of the same day the measurement took place, registered between 0:00 until midnight in 2h intervals by an in-situ station operated by INGV Naples, located near the center of the scanned area. The scans shown were performed in the order they appear. Their respective acquisition start times were (b to g): 17:15:17, 17:19:43, 17:22:48, 17:39:00, 17:43:47 and 17:52:05.
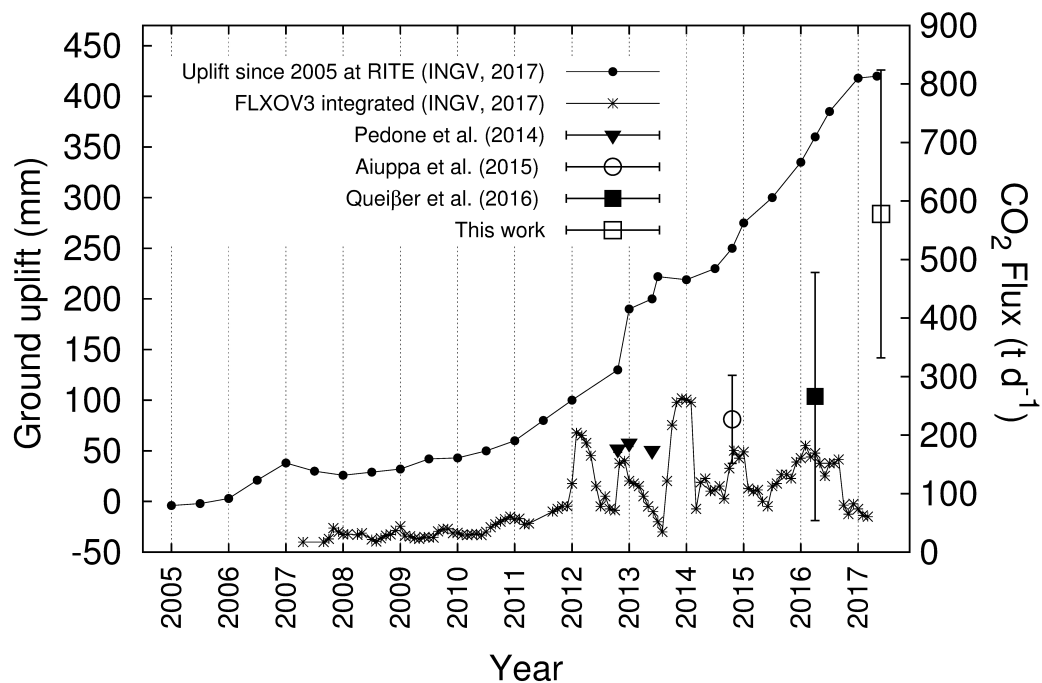
Figure 3. Ground elevation GPS data from RITE GPS station near the center of CF and CO₂ fluxes measured at the Pisciarelli fumarole field. All flux values except FLXOV3 data are spatially integrated. FLXOV3 data is being acquired by an automatic in-situ station in units of g m^{-2} d^{-1}. To be comparable to the area-integrated flux values, the data were multiplied with the surface area of the Pisciarelli fumarole area. Two methods of calculating the area yielded very similar results. Approximating the vegetation free area with a polygon yielded 4200 m^2, while approximating the surface with a rectangle of dimensions 70 m by 62 m yielded 4340 m^2, which was used as it provides a lower limit estimate of the flux.

14

Time of scan	Plume speed (ms^{-1})	Flux ($kg\ s^{-1}$)
17:07:29	0.65 ± 0.20	6.75 ± 2.63
17:12:29	0.65 ± 0.20	5.34 ± 2.72
17:15:17 (b)	0.65 ± 0.20	4.06 ± 1.98
17:19:43 (c)	0.65 ± 0.20	3.67 ± 2.18
17:22:48 (d)	0.65 ± 0.20	3.89 ± 2.06
17:39:00 (e)	0.65 ± 0.20	8.88 ± 3.24
17:43:47 (f)	0.65 ± 0.20	8.82 ± 3.29
17:52:05 (g)	0.80 ± 0.28	8.45 ± 3.56
17:58:36	0.80 ± 0.28	10.33 ± 4.00
Mean flux	**6.7 ± 2.9 (578 ± 246 t d^{-1})**	

Table 1. Start of the scans performed (local time), the vertical plume speed components with uncertainties (student *t*-deviation) and the corresponding CO_2 fluxes with uncertainties (1 STD). Those profiles shown in Fig. 2 have their subfigure identifier written after the time.