MULTI-INSTRUMENTAL INVESTIGATION OF VOLCANIC OUTGASSING AT PACAYA VOLCANO, GUATEMALA.

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MULTI-INSTRUMENTAL INVESTIGATION OF VOLCANIC OUTGASSING AT PACAYA VOLCANO, GUATEMALA.

By

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1) Abstract

Pacaya is one of the most active volcano in the world and it is only ≈30Km South of Guatemala City, the capital of Guatemala, that has a population of about 2 million of people and a surrounding metropolitan area where ≈4.5 million of people live. So mitigate the volcanic hazard improving the knowledge and the understanding of Pacaya is fundamental to decrease the risk factor at which the surrounding population is exposed. This study aims to furnish a new large database, the analysis, the comparison and the interpretations of data that come from different techniques of sampling, about the volcanic outgassing at Pacaya.

A total number of 440 samples were collected with the CO₂ accumulation chamber, principally from the northern side of the volcano; about 8000 images were obtained using an UV camera from the foot of Pacaya and about two weeks of seismological data were collected by a seismic station buried nearby the summit of the volcano. The processing of all these data produced the first CO₂ efflux map and the first comparison between SO₂ data and seismic data of this volcano; furthermore it gave back to us the emission rate values for both the volcanic gasses. Moreover we mapped a new possible system of faults, in this work called “secondary faults”, and, using Google Earth Pro, the opening of a new eruptive fissure on the South-Eastern side of the volcano. We also confirmed the NNW orientation of the magma ascension and that there is a direct relationship between low-frequencies seismic signal and the outgassing of the SO₂.

In the last chapter of this study we propose a list of much food for thought for future studies and also solutions and ideas to solve them.
2) Introduction

After 200 years of repose Pacaya resumed activity in 1961; since then it has been one of the most active volcanoes of Central America. The activity is primarily Strombolian and produces tephra falls, ballistic bombs, and lava flows which are relatively dangerous for the people that live in the area that surround the volcano. The biggest risk for the surrounding communities is represented by a possible failure of the new volcanic cone (Mackenney Cone) (Eggers, 1971; 1983; Vallance et al. 1995; Rose et al., 2013; Schaefer et al., 2013).

Despite this premise, the number of studies about this volcano remains small and the knowledge limited. In particular there are no published studies of the volcanic outgassing after the big eruption of the 2010, so we decided to address this with new information that comes the combination of three different instruments:

- A portable diffuse flux-meter made by West System S.r.l.
- A SO₂ camera Alta U6 made by Apogee Instruments Inc and equipped with a JENOPTIK's CoastalOpt 105mm UV-VIS SLR Lens and an Andover Optics Corp.
- Short-period seismic systems: Mark Products/Sercel 3-component L-22 sensors with a natural frequency of 2 Hz and a sensitivity of 88 V/m/s and RefTek 130 recorders.

From Pacaya’s outgassing studies we obtained information about the volcanic activity and about the geological features that are present underneath the surface. These structural information are particularly important for a better knowledge on how the magma’s ascent and the regional fields of stresses interact and a better idea on how these factors can result into a future collapse of the new volcanic cone.

In this work we present a geological description of the investigated area; a report of the fieldwork campaign; a chapter that contains the description of the principles and methodologies of the techniques used for this study; the results obtained with the associated discussion; some conclusions; and a chapter where we reported the recommendations for future works on this volcano.
3) Background

a) Regional geologic setting
Pacaya is an active compound stratovolcano located in the Central America Volcanic Arc, ~30km south of Guatemala City, that reaches a maximum elevation of ~2500 m above sea level (a.s.l.). Along with Fuego and Santiaguito, the other two open-vent volcanoes in Guatemala, Pacaya is part of the volcanic front associated with the subduction of the Cocos plate underneath the Caribbean plate. (Franco et al., 2010; Matías Gomez et al., 2012; Schafer et al., 2013; Rose et al., 2013).

The area is located south of the Motagua and Polochic faults system that is considered the left-lateral transform boundary between the Caribbean plate and North America plate (Guzman-Speziale, 2001; Schafer et al., 2013). This regional tectonic setting is characterized as an extensional regime, which forms a series of north-striking grabens in the region. The Guatemala City graben is presently the most active and absorbs most of the E–W extensional deformation. Moreover a right-lateral fault zone named Jalpatagua fault zone interacts with the Pacaya’s regional stress field (Carr 1976; Guzman-Speziale, 2001; Franco et al. 2010; Schafer et al., 2013). The location of this fault zone is not perfectly defined, but it can be approximated using the geological
maps of the area like those showed in the works of Eggers (1972) and Carr (1976); in particular Carr, 1976 has shown that this fault zone and others right-lateral fault zones are near and nearly parallel to active volcanoes, probably because the magma’s upwelling created zones of weakness in the crust (Eggers, 1972; Carr, 1976).

b) **Local geologic setting and evolution of the complex volcano**

An additional system of faults adds more local complexity to the tectonic framework of Pacaya, in fact the complex has grown on the southern rim of the Amatitlán caldera. This caldera is located 10km south of Guatemala City and it has a diameter of 16-14km (Fig. 2). The caldera’s most active period was between ~300,000 years to ~23,000 years before present with a total erupted volume of more than 70km³ of volcanic products. Amatitlán caldera is evidenced by gravity data, geological observations, circumferential faults, hot springs and well-logs of the area rocks. These data suggest that the caldera is active and probably will erupt in the future (Wunderman & Rose, 1984). The volcanism of the Amatitlán quadrangle is divided into four eruptive phases which characterize the evolution of Pacaya: (1) growth of a small andesitic stratovolcano, now much eroded, disrupted by faulting and landslides and covered by pyroclastic deposits; (2) A strong basaltic eruptive phase that formed the initial cone about 0.5Ma; (3) an extrusive andesitic-dacitic phase that emplaced domes as “Cerro Chiquito” and “Cerro Grande” ~0.16Ma, during this phase, between 600 and 1500 yr B.P., the south-western sector collapsed leaving a “horseshoe-shaped” caldera; (4) development of the modern complex composed of six cones including Cerro Grande, Cerro Chiquito, Cerro Chino, Pacaya Viejo, Pacaya, and Cerro Mackenney (Eggers, 1971; Bardintzeff and Deniel, 1992; Conway, 1992; Kitamura and Gómez, 1995; Vallance et al. 1995; Matías Gomez et al., 2012).

![Figure 2](image_url)  
*Figure 2: Location of the Amatitlán caldera and the Guatemala City’s graben (map source: Google Earth. See the Appendix for documentation of permission to use this material). The orange lines indicate the borders of the Amatitlán caldera and the Guatemala City’s graben (Wunderman and Rose, 1984)*
The latest phase of volcanism, which continues today, is marked by several eruptive events that typically last for 100 to 300yr and repose periods which are generally 300-500yr long. The latest historical eruptions are dated 1585yr B.P., from ca. 1651 to 1678yr B.P. and 1775yr B.P., in this last event “Cerro Chino” was mainly formed (Eggers, 1971; Conway, 1992). In summary, Pacaya is a volcanic complex formed by the overlapping of several basaltic cones and it has and age of several thousand years (Rose et al. 2013).
Figure 3- Simplified map of recent Pacaya volcano eruptive features.
c) **Current activity**

The current eruptive period at Pacaya began in 1961. Matías Gomez et al. (2012) mapped 349 vents and 263 eruptive units (249 of these are lava flows and the remainder are: pyroclastic flows deposits, alluvial deposits, eolian sediments, spatter and air-fall units) deposited between 2012 and 2010. The eruptive style varies from purely effusive to Hawaiian and Strombolian (lava fountains and moderated explosions). The most energetic eruption culminated on 21 May 2010 and produced a 21km high ash column, which covered the down-wind areas with an estimated ash volume of $1.3 \times 10^7$ m$^3$. Furthermore, given the very strong wind of that day, some ballistics reached distances up to ~4 km to the north of Pacaya damaging several villages (Wardman et al., 2012). During this particular eruptive event some vents appeared outside the collapse amphitheater. The vents inside the collapse rim are distributed in clusters with the highest concentration at the summit of Mackenney cone. This distribution indicates two principal directions of vent alignments: SW-NE and SSE-NNW. The SSE-NNW alignment connects the 2010 vents with the summit vents and the Cerro Chino (Rose et al., 2013). In addition, Schaefer et al. (2013) have shown, by a morphometric analysis, how this vent orientation of clusters is correlated and justified by the orientation of fissures which follow the regional stress field. The regional ENE direction of the minimum principal stress axis is perpendicular to the volcanic rift, and plane of the ancestral SW collapse. This zone of weakness will likely drive future collapses due to the asymmetric growth of the new volcano.
4) Methods

a) Diffuse soil CO$_2$ flux

1. Principles

Multiple studies of volcanic areas have shown that the total flux of gas does not entirely come from the summit or active vents, but also diffuses from volcano-tectonic and tectonic features on and around the volcanic edifice. The quantity of diffuse degassing is very important to calculate the total output of gas for a certain area. The accumulation chamber technique has been widely used in order to measure this contribution and to map geological features in volcanic and geothermal areas (Giammanco et al., 1997, 1998; Chiodini et al. 1998, 2001; Frondini et al., 2004; Notsu et al., 2005; Padrón et al. 2008; Melian et al., 2014; Harvey 2015).

A portable diffuse flux-meter made by West System S.r.I. was utilized for this study (Fig. 4). The instrumental setup is composed of: 1) an accumulation chamber (Type B) with an electromechanical mixing device that causes a turbulence in the chamber, 2) a LICOR LI-820 infrared (IR) CO$_2$ gas analyzer, and 3) a Trimble handheld computer connected to the instrument by a Bluetooth connection that controls the acquisition of data in real time.

The internal volume of the Type B chamber is 6.186*10$^{-3}$ m$^3$, with a base area of 3.140*10$^{-2}$ m$^2$. The pump has a rated flow of 1000 SCCM (standard cubic centimeters per minute); this configuration results in a detection limit of 10 mmol/m$^2$/day (Personal communication from Davide Continanza – WestSystem S.r.I.).

Figure 4 - Illustration of the portable diffuse flux-meter components. 1) Handheld computer by Trimble. 2) Accumulation chamber (type B). 3) Rotor for the air mixing. 4) Hard case that contains a battery, a gas analyzer and a pump (modified from WestSystem S.r.I. Handbook).
2. Analytical procedure

Following the guidelines given by Chiodini et al. (1998) and by the WestSystem S.r.l. the chamber was set on the ground to ensure a tight seal for each measurement. During windy days some fine-grained material was piled around the chamber in order to reduce atmospheric contamination. The air coming from the soil is continuously pumped out from the chamber, sent to the IR spectrometer and then sent back to the chamber in order to avoid drops in the CO₂ concentration. Filters are placed between the chamber and the spectrometers to prevent dust from entering and damaging the IR cell.

The IR spectrometer measures the gas concentration once every second and transmits this measurement through an analog to digital converter for the handheld computer. On this device the user is able to see the increase in CO₂ concentration vs. time in real time. The typical measurement lasts for about two minutes, but when gas flux was low more than five minutes were necessary to reduce the error to acceptable values (regression >0.9). Note that, when the CO₂ flux is close to the limit of detection (low flux values), the ErrQ is always close to zero and it doesn’t increase with time.

An attempt was made to keep the spacing between measurements at roughly 55 meters, but the resultant grid is not regularly spaced because some areas are not accessible or too dangerous. In high flux areas the spacing was reduced to less than 10 meters in order to obtain more detailed
coverage. In areas where the flux variability was low, nearly zero, the spacing was increased to
greater than 60 meters to ensure measurements could be made over the largest possible surface.

3. Data Analysis
The data was processed using the software “FluxRevision” provided by WestSystem S.r.l. to obtain
flux value in ppm/s and ppm/m²/day with an associated ErrQ (Fig. 6).

![Figure 6- Example of the FluxRevision's interface. On the x-axis is shown the time in seconds, on the y-axis is shown
the relative concentration of the CO₂. The yellow line is the regression line that has the best fit with the points’ (green
and red x) trend. The two vertical lines define the interval with the highest ErrQ.]

The values in ppm/s were converted in g/m²/day using the following equations:

\[ F_g = F_{ppm} \times K \times mCO_2 \]

Where \( F_g \) is the flux value in g/m²/day, \( F_{ppm} \) is the flux value in ppm/s, \( mCO_2 \) is the molecular
weight of the carbon dioxide (44.01 g/mol) and \( K \) is:

\[ K = \frac{86400 \times P}{10^6 \times T_k + R} \times \frac{V}{A} \]

Where \( P \) is the atmospheric pressure in mBar (HPa), \( V \) is the volume of the chamber in m³, \( T_k \) is
the air temperature expressed in degrees Kelvin, \( R \) is the gas constant \( 8.314 \times 10^{-2} \text{bar}\text{L/K/mol} \) and
\( A \) is the chamber inlet net area in m². The final calculated flux is given in g/m²/day.
From these equations it is evident how the barometric pressure and air temperature influence the value of K. These two factors not only influence the K value, but Hinkle (1994) has proven how these factors influence the gas flux from the soil. Furthermore, Chiodini et al. (1998) demonstrated experimentally that the atmospheric pressure is inversely proportional to the flux of carbon dioxide from the soil. Both the barometric pressure and the air temperature are automatically recorded by the instrument (e.g. Fig. 6). Some unrealistic or zero value measurements of the barometric pressure were corrected using the data from the INSIVUMEH’s weather station that is ≈23km far from the volcano; this is the weather station of the La Aurora International Airport (GUA). These values have been corrected depending on the difference in elevation between the station and the sampling points using the equation:

\[ P_s = P_{gua} - (P_{icao} - P_{gua}) \]

Where:

\[ P_{icao} = A + B * P_{gua} \]

Where Ps is the atmospheric pressure at the sample points, Pgua is the atmospheric pressure at the La Aurora International Airport’s station, Picao is the correction value that is obtained multiplying Pgua by A and B that are 2 correction factors reported on the Manual of the ICAO Standard Atmosphere (ICAO Doc. 7488) and in the appendix (Table 3).

The values under the limit of detection (LOD) were retained and substituted with a value equal to LOD/√2 based on the methods of Croghan and Egeghy (2003) and Verbovsek (2011), which was shown to be preferable to any other replacement methods (e.g. LOD/2, LOD, zeros or no data).

In order to obtain the total flux output and create flux maps, the raw data were interpolated using a stochastic simulation technique. The sequential Gaussian simulation method (sGs) has been chosen because it can reproduce realistic maps of spatial variability of the flux. Furthermore, it gives an estimated uncertainty useful to calculate the range of the total flux over all the conducted simulations. (Cardellini et al., 2003; Frondini et al., 2004; Padrón et al., 2008; Harvey et al., 2015). The software used for these simulations is GSLIB; the guidelines and steps followed in this phase are meticulously reported in Deutsch and Journel (1998). Knowing the nearest neighbor measured points’ spatial position and flux value, the sGs method needs a semi-variogram model in order to correlate, estimate, and model each unknown point of the study area. The semi-variogram model is built on the empirical semi-variogram obtained from the data set. The best way to obtain the optimal input factors to create the semi-variograms is to use geostatistical analyst software. In this study we used the geostatistical analyst tool of ArcGis 10.2. The final output from GSLIB was imported in ArcGis 10.2 in order to obtain a better visualization of the resultant maps and calculate the final flux value for the carbon dioxide.
b) *UV camera and seismic data*

1. Principles

Since the 1970’s SO₂ spectrometers have been largely used to measure the sulfur dioxide emission from active volcanoes (Bluth et al., 2007; Burton et al., 2014), but technology advances have facilitated a new SO₂ monitoring instrument based on digital cameras. A key advantage of UV cameras is that they can quantify the rates of outgassing during the volcanic explosive activity and compare the outgassing data with the acoustic and seismic ones (Mori and Burton, 2006; Dalton et al., 2009; Nadeau et al., 2011; Tamburello et al., 2012; Tamburello et al., 2013; Burton et al., 2014).

In this study was utilized an Alta U6 made by Apogee Instruments Inc equipped with a JENOPTIK’s CoastalOpt 105mm UV-VIS SLR Lens and an Andover Optics Corp. bandpass optical filter centered at 307 nm. This camera was connected to a laptop and controlled using the software MaxIm DL. The set up time is in between 10 and 15 minutes. The most important specifics are summarized in the following table (Table 1): Table 1- specifics of the used UV-Cam

<table>
<thead>
<tr>
<th>Pixels</th>
<th>1024 x 1024, 16-bit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposure Time</td>
<td>20 milliseconds to 183 minutes (2.56 microsecond increments).</td>
</tr>
<tr>
<td>Image Sequencing</td>
<td>1-65535 image sequences under software control.</td>
</tr>
<tr>
<td>Cooling</td>
<td>Thermoelectric with forced air. Max 50°C below ambient temperature.</td>
</tr>
<tr>
<td>Temperature Stability</td>
<td>±0.1°C.</td>
</tr>
<tr>
<td>Color corrected</td>
<td>250nm - 650nm.</td>
</tr>
<tr>
<td>Manual focus</td>
<td>0.5 m – infinity.</td>
</tr>
<tr>
<td>Optical filter</td>
<td>Centered at 307nm.</td>
</tr>
</tbody>
</table>
For the acquisition of the seismic data a seismometer were positioned nearby the summit of Pacaya volcano at ≈180m E from the active vent Fig 8. The seismometer is a short-period Sercel 3-component L-22 with a natural frequency of 2 Hz.

2. Analytical procedure
Following the guidelines given by Bluth et al. (2007), Dalton et al. (2009), Kantzas et al. (2010) and Nadeau (2011) the camera was properly set, cooled and calibrated. The distance from where the UV images were taken during the 19th and the 21st is about 4.5km north of, and ≈900 m below, the summit; whereas during the 20th the distance was about 2.5km and the difference in elevation was ≈1000m (Fig. 8).
To calibrate the camera, and retrieve SO2 emission rates during the data processing, we used 2 calibration cells that contain a known concentration of SO2; the two concentrations are 395ppm*m and 1388ppm*m. The calibration process was done every 60 minutes in order to eliminate the differences due to the varying intensity of the light during the day. Both the camera’s and the laptop’s clocks were synchronized with the UTC time.

The seismometer was installed following the steps described in the PASSCAL installation guide (www.passcal.nmt.edu). The instrument was buried with a GPS timing system (that was synchronized with the UTC time) and its channel number two oriented toward the magnetic north pole using a Brunton compass. The built-in level permitted to orient the instrument in the three dimensions. With the seismometers was buried a RefTek 130 data acquisition system (DAS) with a 18V battery pack in order to supply the energy to the station.

3. Data analysis
The SO2 data have been processed using the UVCamSO2 suite of programs written by Nadeau (2011) and reported in Nadeau et al. (2014). The program was originally written for Matlab R2008b and it was modified to work with the latest version of Matlab R2014b. The different graphical user interfaces allow to process the digital images in different ways. In fact, the user can display imagery, create AVI files from sequences, derive the plume speed and the emission rate calibrating the program every different subset of images using a background image and an image of the
calibration cells. Instead of using background images (images obtained capturing the clear sky) to flatten the pictures, a “dummy image” was created in order to eliminate the effects of vignetting.

Matlab R2014b was also used to process the seismic data. The objective of this analysis was to evaluate any possible relationship between outgassing rate and seismicity. Because most of the seismic signals associated with outgassing are typically in the long-period band (0.5 – 5 Hz; e.g., McNutt, 2005), the data were filtered between 0.5Hz and 5Hz with a two-pole, two-pass Butterworth filter and then visualized them with two real-time seismic amplitude measurements (RSAM) of 10sec and 30sec (Endo and Murray, 1991).

The 10 seconds RSAM showed a better correlation with the UV-camera data so we decided to use those for our comparisons. In order to investigate this correlation between sets of data we interpolated the SO₂ data on the time vector of the RSAM and then we used the “xcorr” command of Matlab to extrapolate the lag (expressed in tens of seconds) that shows the best cross-correlation factor.

Finally the seismic and the SO₂ data have been plotted together in order to compare them following the Nadeau et al. (2011) example (Fig. 9).

Figure 9- Plots of the 10sec RSAM and the SO₂ data of the 20th Jan 2015. The time is in absolute seconds of the day.

c) Fieldwork Campaign in Guatemala
The campaign started on the 9th of January and ended on the 25th of January 2015 after 2 weeks of sampling on the volcano. Weather conditions in January are in general the best of the entire year;
November through April constitutes the dry season in the Guatemala City region. These months are generally also the coldest and the windiest of the year as shown in Table 2 in the appendix.

During the field work the weather was always sunny, but the summit of Pacaya Volcano was rarely free from clouds, especially during the morning. The wind was usually present and strong, and was a hazard that impeded access to the summit for most of the campaign.

A total number of 440 measurements were made with the CO₂ accumulation chamber, principally from the northern side of the volcano. The inaccessibility of the southern side was mainly due to the hazard related to rock-falls and also to the elevated gradient of this area. Therefore, only a small number of measurements were made on the southern slopes of the volcano.

About 8000 images were obtained using an UV camera from the foot of Pacaya; the maximum distance from where the images were collected has been of 4.5 km from the volcanic plume. The clouds that covered the summit most of the time, allowed the use of the camera for portions of the day on the 19th, 20th and 21st of January. The last day has been the noisiest, in fact were collected just 751 images versus the 5250 of the 19th and the 1917 of the 20th.

In addition to the diffuse degassing studies and UV camera images, seismological data were collected by a temporary network of seismic stations around the cone. We restrict our analysis to one station buried near the summit vent of the volcano, chosen because it is the closest point to the volcanic plume and also to the highest CO₂ fluxes.
5) Results

a) Diffuse soil CO₂ flux
The analysis of 440 flux measurements showed that the data can be divided into three different populations based on the cumulative frequency distribution. In fact, as shown in Fig. 10, two inflection points are observed in the cumulative frequency curve (red line). The first population, “background”, represents ~80% of the data, which range from 0.310 g/m²/day to 4 g/m²/day. The second population, “mixed”, represents 8.5% of the data, which range from 4 g/m²/day to 20 g/m²/day. The third population, “magmatic”, represents 11.5% of the data, which range from 20 g/m²/day to 15,489 g/m²/day.

Figure 10- Cumulative distribution plot of the data. The black vertical lines represent break points at 3 and 20 g/m²/day.

The area on the north-eastern flank of the Pacaya volcano, with an area of 1.0 km², is characterized by fluxes which vary from a minimum value of 0.31 g/m²/day (LOD/√2) to a maximum value of 15,489 g/m²/day. The mean value is equal to 17.04 g/m²/day with a standard deviation of 137.06 g/m²/day. A total CO₂ output of 13.6 t/day was calculated using the ArcGis calculator multiplying the cells, or pixels, of 5 m² that compose the map (expressed in g/m²/day). Furthermore, using the resultant values of the 100 sGs simulations - while retaining a 95% confidence interval - a minimum output of 9.6 t/day and a maximum output of 19.0 t/day, were simulated.
Figure 11- Flux map obtained from the sGs results. The population breaks has been kept as the first two colors. Warm colors correspond to high fluxes, vice versa the cold ones.

To construct this map, the GSLIB software requests the input of a semi-variogram model (blue line in Fig. 12). This model is built on the empirical semi-variogram (red dots in Fig. 12), that is obtained using the factors’ values given by the geostatistical analyst tool of ArcGis 10.2 (e.g., lag size,
number of lags, lag tolerance). The parameters input to obtain the model are: a nugget effect of 0.35, 400 lags, an a_hmax of 150 m, an a_hmin 60 m and no preferred directions for the diffuse degassing. The semi-variogram model shown in Fig. 12, which determines the spatial relationship between measurement locations and pixels of the map, is exponential and shows a spatial auto-correlation in the data (red dots) until a distance of about 400m. The data doesn’t fit the semi-variogram well after a distance of 160m; in fact the model’s variance reaches a value of 1 at about 200m, indicating that the modeled absence of spatial correlation between different measurement points has been set at distances bigger than 200m.

Figure 12- Semi-Variogram used for sGs of the CO2 flux. The Y-axis shows the variance value. The X-axis shows the distance in meters related to a certain value of variance. Red dots represent the data empirical semi-variogram. The blue line is the semi-variogram model fitted on the data.

The map shows a marked clustering of degassing structures. In fact, very high-fluxes are localized in the southern sector; whereas in the north-western sector some centers of diffuse degassing are noticeable and characterized by medium-high-fluxes of CO₂. Finally, the central area and the eastern corner present predominantly low fluxes related to the “background” and the “mixed” populations.

\[ b) \quad UV \text{ camera and seismic data} \]

In order to reduce the error and the noise due to poor weather conditions (e.g. high wind speed and clouds), some UV images have been discarded; the resultant number of images is 2985 for the 19th
January, 1600 for the 20th January and 400 for the 21st. Recording times were ≈3.6, ≈1.25 and ≈0.9 hours, respectively. Only one ash-rich explosion was observed during the 3 days of sampling, it happened on the 20th at 20:05 UTC time and images that included that event were not used for emission calculations. So the passive degassing was almost always continuous but variable in magnitude. In Fig. 13 is shown the best day of acquisition with the UV camera. In fact during the 20th of January there were the best weather conditions and we needed to calibrate the camera only one time. The maximum obtained values for the emission rate are: 3.706 kg/s for the 19th, 1.148 kg/s for the 20th and 3.657 kg/s for the 21st.

![Figure 13- SO2 Emission rate plot of the 20th of January. The grey box in the picture represents the no data interval due to both a period of poor weather conditions and a calibration break.](image)

The RSAM of all the three days were computed with a selected interval of time of 10 seconds (Fig. 14b) using the previously filtered seismic signals (Fig. 14a). Then from the interpolation of the SO2 datasets we obtained vectors which have the same time spacing of the 10 seconds RSAM vectors, so they can be compared using the cross-correlation command.
Figure 14- A) Selected interval of time (absolute seconds) of the seismic signal recorded on the 20th of January, the signal was filtered before plotting it. B) 10 seconds RSAM of the filtered seismic signal.

From the cross-correlation process we obtained three plots, one per day, that show the lag in time between the two vectors at a certain value of time shifting (Fig. 15). The best cross-correlation value was obtained from the datasets of the 20th January; it has a value of 0.13 when the SO$_2$ is lagging 20 seconds behind the RSAM. The other days had different values of correlation and lags; in particular for the 19th we had the best correlation at 70 seconds of lag with a value of 0.08, whereas the data of the 21st shown a factor of 0.06 at 40 seconds of lag.
Finally the 10 seconds RSAM have been plotted with the SO₂ emission rate plots to have a visual comparison of the datasets. In Fig. 16 is shown the plot of the day 20th of January 2015.

Figure 15- Cross correlation plot between the seismic data and the interpolated SO₂ data.

Figure 16- Example of similarity between SO₂ emission rate (orange line) and low-frequencies 10 seconds RSAM (20th Jan).
6) Discussion

a) Diffuse soil CO₂ flux

The data collected in the investigated area of 1.0 km² on the north-eastern flank of Pacaya volcano permitted the calculation of total CO₂ output, which was 13.6 t/day. The first consideration to make about this result is that we have not discerned the “background” and the “mixed” flux populations from the “magmatic” one in our calculation process. In the entire sampled area the vegetation was poorly developed or lacking, the organic soil was absent and the ground was covered by tephra and new lava-flows. Furthermore, the absence of chemical data useful to distinguish between isotopes of carbon dioxide, which are fundamental to understand the origin of the flowing CO₂, didn’t allow us to separate the populations (Chiodini et al., 2008; Rissmann et al., 2012; Harvey et al., 2015). Moreover the samples taken in proximity of the 2010 vents and outside the collapse rim don’t show any peculiarity in terms of flux value; the 2010 vents’ area is also characterized by developed vegetation but it doesn’t induce any difference. This is probably because the dry season that causes a kind of dormancy in the vegetal apparatuses. Therefore, all of the measured CO₂ flux is considered magmatic in origin.

Our total CO₂ flux value is comparable with other studies conducted on active volcanoes. The typical flux is about 35-40 t/km²/day as demonstrated by Chiodini et al. (1998), Frondini et al. (2004), Notsu et al. (2004), on Vulcano, Vesuvio and Iwojima volcanoes, respectively; although this is highly temporally variable and specific to each volcano. For example, Padrón et al. (2008) on Pululahua volcano found an output of only 9.8 t/km²/day, whereas Salazar et al. (2001) obtained a final value of 2,800 t/day from an area of only 0.58 km² on Cerro Negro Volcano. Furthermore, Hernández et al. (2012) have demonstrated how the output of carbon dioxide of the same study area can be largely variable depending on the season and changes in weather conditions. Giannanco et al. (1998) and Melián et al. (2014) have also shown how the CO₂ output is variable through time also because the different level of activity of a volcanic system.

Obviously the location and the dimension of the surveys’ area play a prime role in the quantification of the carbon dioxide efflux. We separated our investigated area into several discrete regions in order to remove the central “no flux” area (Fig. 11) and reduce the error related to the larger spacing between samples adopted in this portion of the map.

Figure 17 shows the maps of the two areas with “high-flux”. The “Cerro Chino and Collapse Rim” (Fig. 17 section C) map covers an area of 0.180 km², whereas the “Summit Area” (Fig. 17 section B) covers 0.015km²; these maps were created by 120 and 250 sGs simulations, respectively. The semi-variogram models are shown in Fig. 18 and show a spatial correlation up to 80 meters. The “Cerro Chino and Collapse Rim” (Fig. 17 section A) semi-variogram model is spherical; it has a nugget effect of 0.45, 150 lags, an a_hmax of 70 m, an a_hmin 25 m and no preferred orientation angles. The “Summit-area” (Fig. 17 section B) semi-variogram model is exponential; it has a nugget effect of 0.1, 120 lags, an a_hmax of 55 m, an a_hmin 15 m and no preferred orientation angles. Summing these two areas’ outputs produced a total CO₂ output of 8 t/day with a 5th percentile of 4.7 t/day and a 95th percentile of 12.9 t/day from an area that is only 0.195 km². This
value of 41 t/km²/day is consistent with those that were found by Chiodini et al., Frondini et al. and Notsu et al.

Figure 17- CO2 flux map of the "high-flux" areas. A) Overview of the areas. B) Zoom in of the summit area. C) Zoom in of the Cerro Chino-and-Collapse Rim area.
Besides the estimation of the total CO₂ output, the carbon dioxide diffuse degassing investigations can also be used for geo-structural characterization of the studied areas. A large number of studies in the last two decades have demonstrated how the distribution of the highest flux in a map is localized along faults, a system of faults, eruptive fissures, fumaroles, or crater and collapse rims (Giammanco et al., 1998; Lewicki and Brantley, 2000; Chiodini et al. 2001; Cardellini et al., 2003; Frondini et al., 2004; Giammanco et al., 2006; Padrón et al., 2008; Ranaldi, 2008; Melián et al., 2014; Harvey and Harvey, 2015).

In our studied area, as is noticeable in Fig. 11 and in Fig. 17, we observed three different alignments of degassing spots and fissures. Overlaying the flux map with the most recent DEM on ArcGis we can highlight how the diffuse degassing follows the regional and local orientation of principal stresses and the geological structures (Fig 19). In this image it is evident that along the horse-shaped collapse rim and crater rim border of the Cerro Chino (Fig. 19), areas of the highest efflux of CO₂ are observed, reaching values greater than 500 g/m²/day. We interpret these aligned degassing areas as being driven by the higher permeability due to the historic evolution of the volcanic complex; the horse-shaped rim is the continuation of the surface of contact between the materials of the “pre-phase three materials” and the “post-collapse materials”. This surface of contact has been analyzed and described in detail by Schaefer et al. (2013).
In contrast, the degassing along the collapse-rim area of the Cerro Chino border is not interpreted to be related to the contact’s surface, but is instead associated with a more complex interaction of structural features. First, the dip slope strata of the Cerro-Chino cone could concentrate the CO$_2$ diffuse degassing along the crater rim playing the role of a kind of upside down funnel. Second, they could be driven by the NNW magma ascent also described in Schaefer et al. (2013). The
intrusion of the magma along the Jalpatagua fault zone (JFZ) creates a weakness zone that is more permeable and where the magma is closer to the surface; so this zone could be a preferable pathway for the degassing. This zone of weakness has been highlighted in Fig. 19 with a pink box showing the 2010 collapses (orange lines); important features that provide evidence of the enormous NNW collapse feature and orientation of the magma ascent. Aligned with the Cerro Chino’s efflux points and the collapse is the summit area, where we recorded the highest fluxes. Furthermore, the field observations of this area highlight a highly fractured soil with numerous cracks and alignment of fumaroles with directions in between 300° N and 340° N. All these features can be linked with the 2010 vent locations as indicated by Rose et al. (2013) and Schaefer et al. (2013), which are well aligned with the NNW trend on the south-eastern flank of the volcano too.

Analyzing the Google Earth® imagery since the 2010 event we noticed that the opening of cracks, that probably caused the collapse through the NW flank, is not exclusive of the northern sector of the volcano. In fact, we mapped for the first time the opening of an eruptive fissure on the South-Eastern flank of the new cone; the opening has started after the 2010 eruption and continued during the 2014 eruption between February and March. Figure 20 shows the sequence of images captured on Google Earth, the orange ovals have been drawn to help visualize the features of interest during the three main steps: before the 2010 eruption, after the 2010 eruption and after the 2014 eruption. Figure 21 shows a comparison between the “after 2010 eruption” and the “after the 2014 eruption” digitized features.

In Fig. 19 a system of possible secondary faults has been highlighted (green lines); these hypothetical faults have no surface expressions, but are inferred based on the higher CO₂ flux values in coincident with the interceptions between these secondary faults and the principal geologic features of the volcanic complex (e.g. the NNW weakness zone and the collapse rim). In Fig. 17 it is evident how the degassing is “spotted” along the collapse rim; in order to highlight this in Fig. 22 we show the simple kriging map obtained with the GSLIB software using the same semi-variogram model used for the general map in Fig. 12 with a radius of 20 meters. Jolie et al. (2015) has also shown how the interceptions between faults are related to elevated values in the CO₂ diffuse degassing. Furthermore, it is clear in Fig. 17 section B that in the summit area there is an alignment of very-high flux values in the NNE direction. Rose et al. (2013) have also shown that on Pacaya there exists two different directions along which the vents are clustered; besides the NNW alignment of vents they have also recognized a NNE alignment that is the same direction found in this study for the secondary faults. Based on the preceding evidence we interpret the distribution of high gas emissions to be related to magma intruding in a direction NNW, which causes a field of stress that has a local maximum compression axis in the direction NNE; in preexisting weakness zones with direction parallel to the local σ₁, the compression could cause the opening of the cracks – a major permeable network that increases the CO₂ efflux in these zones.
Figure 20- Sequence of images of Pacaya volcano captured using Google Earth. The orange ovals represent the "interest area" (map source: Google Earth. See the Appendix for documentation of permission to use this material)
Figure 21 - Comparison between features originated in the 2010 eruption and features originated by the 2014 event.

Figure 22 - GSLIB Simple-Kriging map.
b) **UV camera and seismic data**

The fact that UV cameras can collect nearly an image every second makes of this instrument one of the most promising tools in the study of volcano degassing (Mori and Burton, 2006; Bluth et al., 2007; Dalton et al., 2009; Nadeau et al., 2011). In particular, the high sample rate of 1 sample every 1-3 seconds permitted to us to relate the UV camera data with the seismic dataset. For this comparison we used just the seismic signal that is in the long-period (LP) band between 0.5 and 5 Hz; this is because tremors and LP earthquakes are triggered by different processes that involve volcanic fluids. Numerous authors modeled these processes: Julian (1994 and 2000) affirmed that the fluid flow could be the responsible for very low-frequency events; Chouet proposed a model where he linked the seismic signal to conduit resonance (Chouet, 1992) and one in which he showed how the bubbles oscillation can effect the generation of low-frequency events (Chouet, 1996). Furthermore, working with Kumagai in 2000 (Kumagai and Chouet, 2000), he demonstrated how a crack filled by bubbly fluid can have enough impedance in respect the surrounding materials such that the crack can sustain resonance at certain frequencies for relatively long time. Ripepe and Gordeev (1999) linked the tremors and LP to bubble coalescence. Finally Métaxian et al. (1997) and Palma et al. (2008) show how the low-frequencies events can be related to the outgassing activity. The basic idea for linking outgassing with shallow LP seismicity is as follows: the larger is the quantity of gasses involved, the stronger the low-frequency seismic signal related to the same system (Fig. 23).
Following this principle we compared the two dataset without giving too much importance to the value of mass of gasses emitted during the day, but caring much more about the trend of the degassing. We chose to use a RSAM of 10 seconds because it is the interval that produced the best cross correlation values. The cross correlation values are not very high compared with those in the studies of Kazahaya et al. (2011) and Nadeau et al. (2011), most likely because of suboptimal weather conditions for much of the field campaign. Nonetheless, the datasets show a correlation that permits to us to suggest that the trend of the SO$_2$ degassing is linked to the seismic signal (Fig. 23). This is evident if you in the clear correspondence of the troughs of the two datasets. With a bigger database, the correlation factor would likely be greater, but having a clear view of the Pacaya’s plume and at the same time a clear sky for the background is really difficult.

The different lag values that we have found during the three days could be related to changes in the conduit, for example a different depth of the magma’s surface, but also in this case the uncertainty, especially for the 19th and the 21st is too big to permit any comparison between different days.

Interestingly, although the outgassing characteristics were apparently different in January 2015 than they were in 2008 when Dalton et al. (2010) got their data, we calculate a comparable output of SO$_2$ So while it was easier to distinguish individual explosions in 2008 due, presumeabley to a
much shallower magma free surface, it seems that the SO₂ degassing from Pacaya continues to driven by small bubble-burst events.
7) Conclusions

This study was based on field data collected on Pacaya volcano (Guatemala) in January 2015. The use of advanced techniques and software for the investigation of the volcanic degassing permitted the collection of a large amount of new data, which are important, not only for this work, but also for future studies that will be carried out on this volcano.

The portable diffuse flux-meter made by West System S.r.l. proved to be a reliable instrument that permits a detailed characterization of a large area. Diffuse efflux measurements of volcanic CO$_2$ were used to calculate total outputs of: 13.6 t/km$^2$/day from the northern side and 41 t/km$^2$/day from the only other area where there are degassing features. These estimates are slightly lower than, but consistent with, those previously reported in the literature for other volcanoes.

Besides the estimation of the total CO$_2$ output, this study has demonstrated that the accumulation chamber method is complementary to structural studies. In fact, we show how the diffuse efflux measurements on Pacaya highlighted not only the NNW oriented faults and fractures, but also the structural features such as the collapse rim. Furthermore, this technique has revealed a NNE orientation of structural features, which are not evident on the surface. This orientation is similar to the trend of alignment of vent clusters recently summarized by Rose et al. (2013), and could be related to the interaction between local and regional stresses with preexisting structures, or to the intersection of faults. However the combination of all these factors is, most likely the cause of the NNE alignment of fluxes.

By combining the high-resolution SO$_2$ emission rates obtained with the UV-camera and the 10 seconds RSAM we identified similar time scales for plume degassing and low-frequencies seismic events. In particular we observed a SO$_2$ signal that lags 20-40 seconds behind the seismic one with a peak of emission rate of 3.706 kg/s registered on the 19th January 2015.

Even if during our field campaign we didn’t recorded any noticeable explosive event, our field observations and results support the thesis of a Strombolian bubble-burst activity proposed by Dalton et al. in the 2010; this activity is less noticeable in our data because a deeper source of the events (the lava free surface must be deep in the conduit).

In light of what we showed and what we observed in the field, we suggest that Pacaya has an open conduit with a small lava lake (Fig. 24) that is fed by a very shallow intruding magma body elongated in the NNW direction. Magma ascent and intrusions are opening new cracks all over the volcano, which will probably create instabilities - especially in the new dome.
Figure 24 - Landsat 8 band #7 image of the Pacaya's summit of the 18 February 2015. In the center of the image (active crater’s position) is evident an incandescence (white and yellow pixels) that proves the presence of a really high temperature source nearby the surface (R. Escobar-Wolf, personal communication, July 2015. See the Appendix for documentation of permission to use this material).
8) Recommendations for future research

Below we summarize some ideas for further investigations about the outgassing of Pacaya. In fact, our observations – in addition to improving our immediate knowledge of the structural magmatic, and gas emissions - reveal future avenues for studies that will expand the utility of this work. In this chapter we made a list of questions that need a solution and make some suggestions for how to answer them.

Variable fluxes

During our field work and data processing we observed ten flux curves that are not linear as the “perfect” curve described in the West System’s handbook. They show a trend that is similar to the curves that present air contamination during the sampling procedure (Fig. 25). All these samples were taken near the summit, where the immature soil and rock are highly fractured and covered by fresh tephra, directly on fumaroles. The outgassing of these vents was following the outgassing through the volcano summit with only a short lag of time. Also the CO2 curves followed the trend of the fumaroles and they were going up and down just after respectively growths and the drops of the principal summit plume. We interpret the non-linear trends in our curves as not being due to air contamination, but rather the gas pulses observed at the summit. We attempted to test this hypothesis by plotting the CO2 “variable” fluxes with the 5 second RSAM of the seismic signal using a code written for Matlab. In order to have a better visualization of the data we normalized and de-trended the CO2 curves (Fig. 26). The biggest problem that we noticed in this process was the uncertainty linked to the time that is necessary to save the data using the West Systems hand-held Trimble computer after the measurement has been stopped. In fact, the hand-held computer records the samples imprinting the saving time instead of the time related to the end of the measurements. The time between the end of a measurement and that for saving is artificially shifted for the CO2 curve, so it’s possible to have the CO2 signal precede the seismic signal. Although this method of ‘correcting’ for the time lag between measurement and recording induces some uncertainty in our interpretations, there appears to be a correlation between seismic and diffuse CO2 degassing signals. Further research on these observations could open a new field of studies in the possible uses of the accumulation chamber and also it will be out of this a new tool for the Early warning system.

Solutions: Install a permanent CO2 accumulation chamber station upon the cracks nearby the summit or collect more samples with a standard procedure, in order to eliminate the lag of time between the end of the sampling and the saving, from the same area.

UV-camera data vs. accumulation chamber data

The comparison between these two instruments’ datasets could be interesting to see if there is a relationship between the CO2 efflux from the soil and the SO2 outgassing from the volcanic plume. Furthermore the lag of time between the UV-camera and the accumulation chamber data could give back information about the permeability of the soil and so its grade of fracturing.

Solutions: Install a permanent CO2 accumulation chamber station upon the cracks nearby the summit or work simultaneously in two separate teams one with the UV-cam and the other with the accumulation chamber on the summit area and a standard procedure.
Figure 25- Example of variable flux (sample #300). In the white box is reported an example of a curve with air contamination.
Figure 26- Comparison between seismic and CO2 samples of the 19th January 2015. The bottom part of the picture shows the zoom on the sample #300 showed in the previous figure.

Better CO2 efflux map
Making additional measurements of diffuse CO2 flux with the smaller accumulation chamber could provide a more detailed map with less points where the flux is smaller than the LOD. Furthermore, more samples on the south-eastern side could also provide some interesting information about the opening crack and the location of future vents. However, we are aware that measurements will be limited to the areas that are away from the rockfalls and if work is to be done near the summit fireproof and protective equipment will need to be worn.
Solutions: make a grid with a smaller spacing between sample points. Use a chamber type A that has a smaller LOD. Try to expand the examined area.

Structural map
A detailed geo-structural map can confirm our thesis about the secondary faults that we have found with the accumulation chamber, and provides more details that will improve the knowledge of the volcano.

Solution: **field campaign or campaigns of structural survey.**

**More UV-cam data associated with both infrasound and seismic data**
Collecting more data from the same period of time with more samples per day and relate them with both the infrasound and seismic data will be important to confirm and support this study’s results.

Solutions: a dedicated team for the UV-camera sampling and a longer period of time on Pacaya.

**Accurate SO2 fraction in the plume**
Having an accurate estimation of the SO2 fraction in the plume is important to reduce the error linked to the measurements with the UV-camera that is caused by other gasses in the plume.

Solution: analysis with the **Fourier Transform Infrared Spectroscopy (FTIR).**

**Origin of the CO2 and SO2**
Knowing the original composition of the magmatic fluid could reveal how much CO2 and SO2 are dissolved in the magma underneath the volcano and at what deep they start to escape from the magma. Regarding the CO2 it’s important to distinguish between the biogenic and the magmatic source using the carbon isotopes.

Solution: **Measurement of molten inclusions** and **Chemical analysis of carbon isotopes.**

**Seasonal variation**
Understand how the CO2 total flux varies seasonally could be interesting to have an idea on how the weather, especially the rainfalls, influences the efflux.

Solution: **a field campaign every 4-6 months** (at least one for the dry season and one for the wet season).

**CO2 captured by the groundwater**
A large fraction of the CO2 degassed from the magma could be trapped and washed away by the groundwater, knowing this fraction is fundamental to understand the total output of Pacaya.

Solution: **groundwater analysis.**
9) Acknowledgements

First of all I would like to thank my advisers Gregory P. Waite and Chad Deering for the amazing opportunity to go in Guatemala on Pacaya Volcano. Their fundamental guidance, suggestions and ideas made me work hard but now I’m very proud of this work. Finally I would like to thank them for their personal kindness and for their time spent with me.

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10) References


Manual of the ICAO Standard Atmosphere (ICAO Doc. 7488)


### Appendix

Table 2- Meteorological data from 1990 to 2012 from the station "Insivumeh" (data source: INSIVUMEHs website)

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