Bull Volcanol (2017) 79: 30
DOI 10.1007/s00445-017-1109-9

RESEARCH ARTICLE

Geochemical evidences of seismo-volcanic unrests at the NW rift zone of Tenerife, Canary Islands, inferred from diffuse CO_2 emission

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Received: 7 May 2016 / Accepted: 26 February 2017

Abstract We report the results of 49 soil CO_2 efflux surveys by the accumulation chamber method at the North West Rift (NWR) Zone of Tenerife Island, Canary Islands. The surveys were carried out from 2000 to 2016 to evaluate the temporal and spatial variations of CO_2 efflux and their relationships with the volcanic and seismic activity at Tenerife. Soil CO_2 efflux values ranged from non-detectable (<0.5 g m^{-2} day^{-1}) up to 141 g m^{-2} day^{-1}, with the highest values measured in May 2005, whereas total CO_2 emission rates ranged between 52 and 867 t day^{-1} (metric tons per day). Isotopic analyses of soil gas in carbon dioxide ($\delta^{13}C$–CO_2) suggest a mixing between organic and atmospheric CO_2 with a small contribution of deep-seated CO_2. The main temporal variation in the total CO_2 output does not seem to be driven by external factors; it shows a clear temporal correlation with the onsets of seismic activity. Subsurface magma degassing affecting the central part of the island is proposed as a cause for the observed changes in the total output of diffuse CO_2 emission, as well as for the spatial distribution of soil CO_2 efflux.

Editorial responsibility: P. Allard

Electronic supplementary material The online version of this article (doi:10.1007/s00445-017-1109-9) contains supplementary material, which is available to authorized users.

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Keywords Tenerife · North west rift zone · CO_2 efflux · Volcanic unrest

Introduction

Surface manifestations of volcanic gases are usually controlled by the volcano tectonics and hydrology of the volcanic system, with the most permeable structures offering the main pathways for transport of gas to the surface. Among studied degassing phenomena, soil CO_2 efflux is important because of the characteristics of CO_2: it is the major gas species after water vapor in both volcanic fluids and magmas and it is an effective tracer of subsurface magma degassing due to its low solubility in silicate melts at low to moderate pressures (Gerlach and Graeber 1985). Studies of diffuse degassing become an even more important volcanic surveillance tool at those volcanic areas where visible manifestations of volcanic gases (i.e., crater plumes and fumaroles) are absent. Mapping soil CO_2 efflux along volcanic structures can provide a better understanding of the processes occurring at depth as well and allow monitoring the spatial distribution, magnitude, and temporal evolution of the surface anomalies (Chiodini et al. 2001; Frondini et al. 2004; Gerlach et al. 2001; Giammanco et al. 1998; Granieri et al. 2006; Hernández et al. 1998, 2001, 2003, 2012a, b; Lewicki et al. 2007; Melián et al. 2014; Notsu et al. 2005; Padrón et al. 2008a, b, 2015; Pérez et al. 2004b; Rogie et al. 2001; Salazar et al. 2001, 2004). The rate of diffuse CO_2 emissions can increase before a volcanic eruption (Hernández et al. 2001; Carapezza et al. 2004; Melián et al. 2014; Pérez et al. 2006, 2012), and it is also very important to estimate the total output of this gas over time in order to have a better understanding of which volcanic processes are occurring at depth.

The study area for this work is the North West volcanic Rift (NWR) of Tenerife (Fig. 1). Tenerife has remained in a state of volcanic and seismic calm since the Chinyero eruption in 1909. Before 2004, seismicity was mainly located in an offshore area southeast of Tenerife and was interpreted as occurring on regional tectonic structures (Mezcua et al. 1992). Prior to 2001, the National Seismic Network of the National Geographic Institute of Spain (IGN) registered several seismic events with magnitudes higher than 3.0. The largest one occurred on 9 May 1989, and had a magnitude of 5.2 (Mezcua et al. 1992). It was located between the Gran Canaria and Tenerife islands and was felt by inhabitants in both islands. Analysis of the focal mechanism of this earthquake suggests the existence of an inverse fault and shears trending NE-SW (N 37° E). Vicinguerra and Day 2013, reported that the spatial localization of seismic events and their time evolution appear to be related to magmatic rather than tectonic activity. From mid-2001, an increase in the number of earthquakes of low magnitude in and around Tenerife was detected by the IGN. In April 2004, IGN observed a significant increase in the seismicity in the northwest of Teide-Pico Viejo volcanic complex, with about 372 located events (Fig. 2). Some of these earthquakes ($M > 2.5$) were strong enough to be felt by the inhabitants of villages located close to the epicenters. This seismic crisis started to decline from the end of 2004 (Fig. 2a). A sharp increase in seismicity started again in 2010 with about 1159 seismic events registered by IGN in and around Tenerife Island, progressively decreasing to 683 in 2011 and to 60 in 2012 (Fig. 2a, c). According to the IGN-published national catalog (http://www.ign.es/ign/layoutIn/volcaFormularioCatalogo.do), however, the number of seismic events registered in and around Tenerife Island in 2010, was only approximately 60, implying the existence of two different accounts of seismic activity registered by the IGN (Pérez and Schmincke 2016; http://www.laopinion.es/opinion/2015/05/16/carta-abierta-responsables-ign-madrid/607012.html). Events with hypocenters at depths between 5 and 30 km, with shallower earthquakes recorded mostly underneath Tenerife Island (northwest and towards the southeast) and between Tenerife and Gran Canaria Islands, account for most of the activity recorded during the 15 years of study. Two separate sequences of shallow seismicity occurred between 2004 and 2005 (A vertical blue band in Fig. 2b), and between end of 2009 and the middle of 2011 (B vertical blue band in Fig. 2b).

Since Tenerife is a highly populated island with about 890,000 inhabitants (2014 census) and, according to the 2014 Canarian Statistics Centre's (ISTAC) Report on Tourism, Tenerife received 5,148,453 arrivals in 2014; any volcanic unrest may raise issues for the safety of this populated region. Volcano monitoring is thus an important issue and a priority for reduction of volcanic risk in Tenerife.

In this work, we present the results of 49 soil CO_2 efflux surveys carried out between 2000 and 2016 at the NWR zone of Tenerife to monitor the activity at this volcanic system. The main goals of this study are to study the spatial distribution and temporal evolution of CO_2 efflux anomalies, and to estimate the total CO_2 output to the atmosphere during the period of study and its relation to the level of seismic-volcanic activity of Tenerife Island.

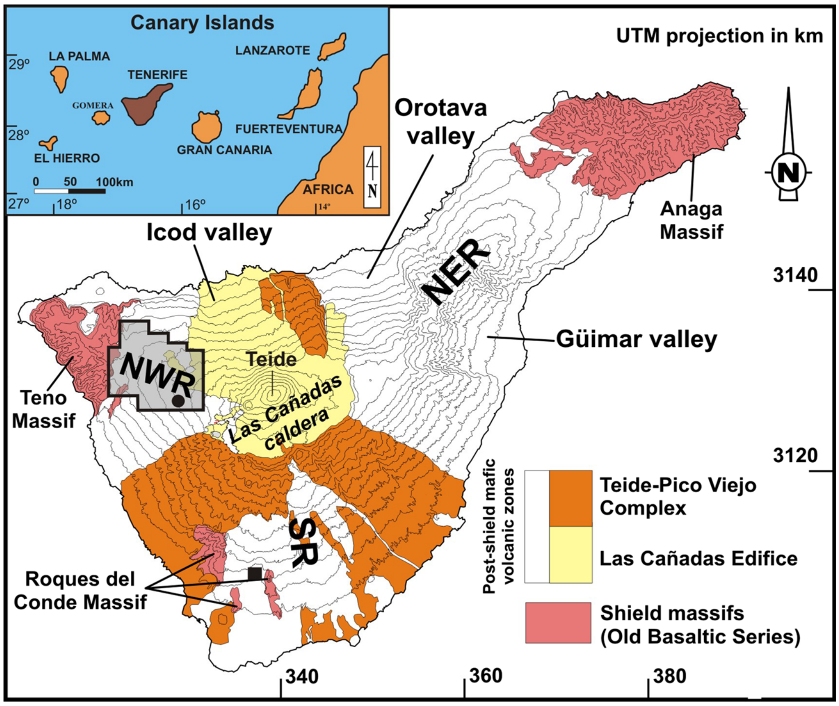


Fig. 1 Simplified geological map of Tenerife showing the main morphological features and the location of the NWR zone of Tenerife. *Filled circle and square* denote locations of Hoya de la Leña and Fuente del Valle galleries, respectively

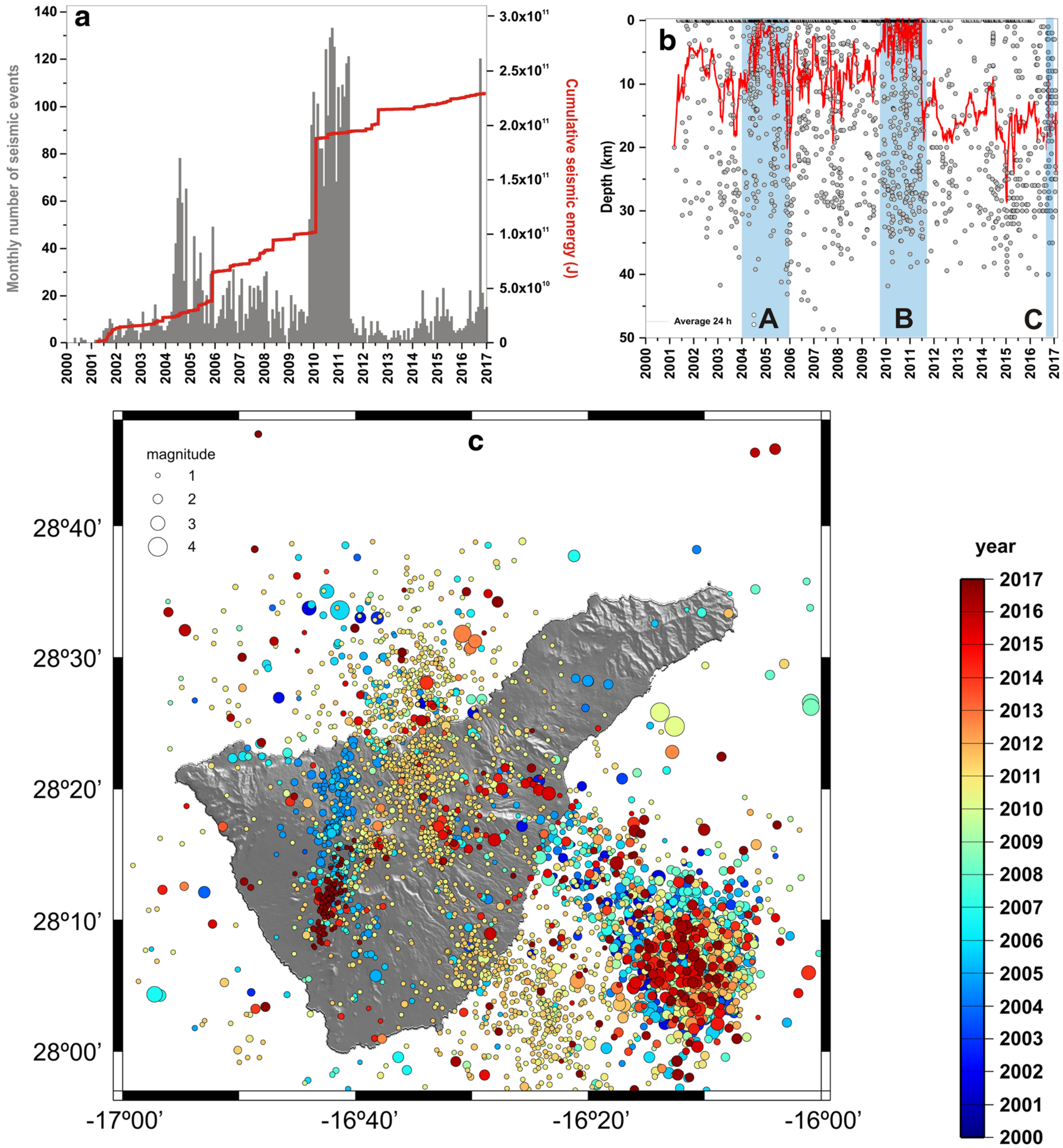


Fig. 2 **a** Monthly earthquake counts throughout the period of study 2000–2016. **b** Time-depth plot of seismicity between July 2001 and 2016. **c** Map of Tenerife Island showing the epicenters for the period 2000–2016 (source IGN). *Different colors and sizes of dots* are related to earthquake origin times and magnitudes, respectively

Geological setting

Tenerife is the largest of the Canary Islands and, together with Gran Canaria, is the only one that has developed a central volcanic complex characterized by the eruption of differentiated magmas. The oldest subaerial volcanic rocks (Old Basaltic Series) are found in the three ends of the island, namely in the Anaga (NE), Teno (NW), and Roque del Conde (S) Massifs (Ancoechea et al. 1990). Their ages range from 12 Ma for the lower part of the Roque del Conde up to 4.2 Ma for the Anaga Massif (Ancoechea et al. 1990). These massifs represent the subaerial remains of the main stages of shield volcanism (Thirlwall et al. 2000) and were built by Strombolian and/or Hawaiian-type basaltic eruptions mainly from fissure vents (Martínez-Pisón and Quirantes 1981). The Tenerife central volcanic complex, the Las Cañadas edifice, started to grow about 3.5 My ago, immediately after the construction of the basaltic shield, which forms the basement of the island. The construction of the Las Cañadas edifice has involved several constructive and destructive episodes, including caldera collapses and large-scale landslides (Ancoechea et al. 1990; Bravo 1962; Martí et al. 1997; Navarro and Coello 1989). One of the main morphological and structural features of Las Cañadas edifice is the Las Cañadas caldera, in which stands the active complex Teide-Pico Viejo. Coeval with the construction of the Cañadas edifice, shield basaltic volcanism continued until the present along rift zones oriented NW–SE and NE–SW (Fig. 1), and in a more scattered area on the south (Ancoechea et al. 1990; Galindo et al. 2005). This basaltic volcanism is responsible for the formation of hundreds of monogenetic volcanoes, grouped into three main volcanic rifts (Ablay and Marti 2000; Dóniz-Páez 2015).

In the NWR zone of Tenerife, as well as in the Canarian historic eruptions, the eruptive style has been effusive. The eruptions usually take place along a fissure in which several vents are aligned. The eruptive fissures of the NWR trend WNW–ESE (Fig. 3a), with a mean value of N 115° E (Galindo et al. 2005). This strike of the NW rift zone eruptive fissures has been approximately constant throughout its eruptive history. Two historical eruptions have occurred in the NW rift zone: Arenas Negras in 1706 and Chinyero in 1909 (Romero 1992). These two eruptions, as well as the other historical eruptions in the archipelago, had pre-eruptive stages characterized by a felt earthquakes, gas emanations, thermal anomalies, underground noises, ground deformation, faulting, and changes in the volume and location of the natural water courses (Romero 1991). The periods of seismic activity have lasted from hours to a year before the eruptions (Romero 1991, 1992). The earthquakes related to these eruptions were usually of low intensity, with several notable exceptions, such as the 1706 and 1909 (intensity VII) (Galbis 1932).

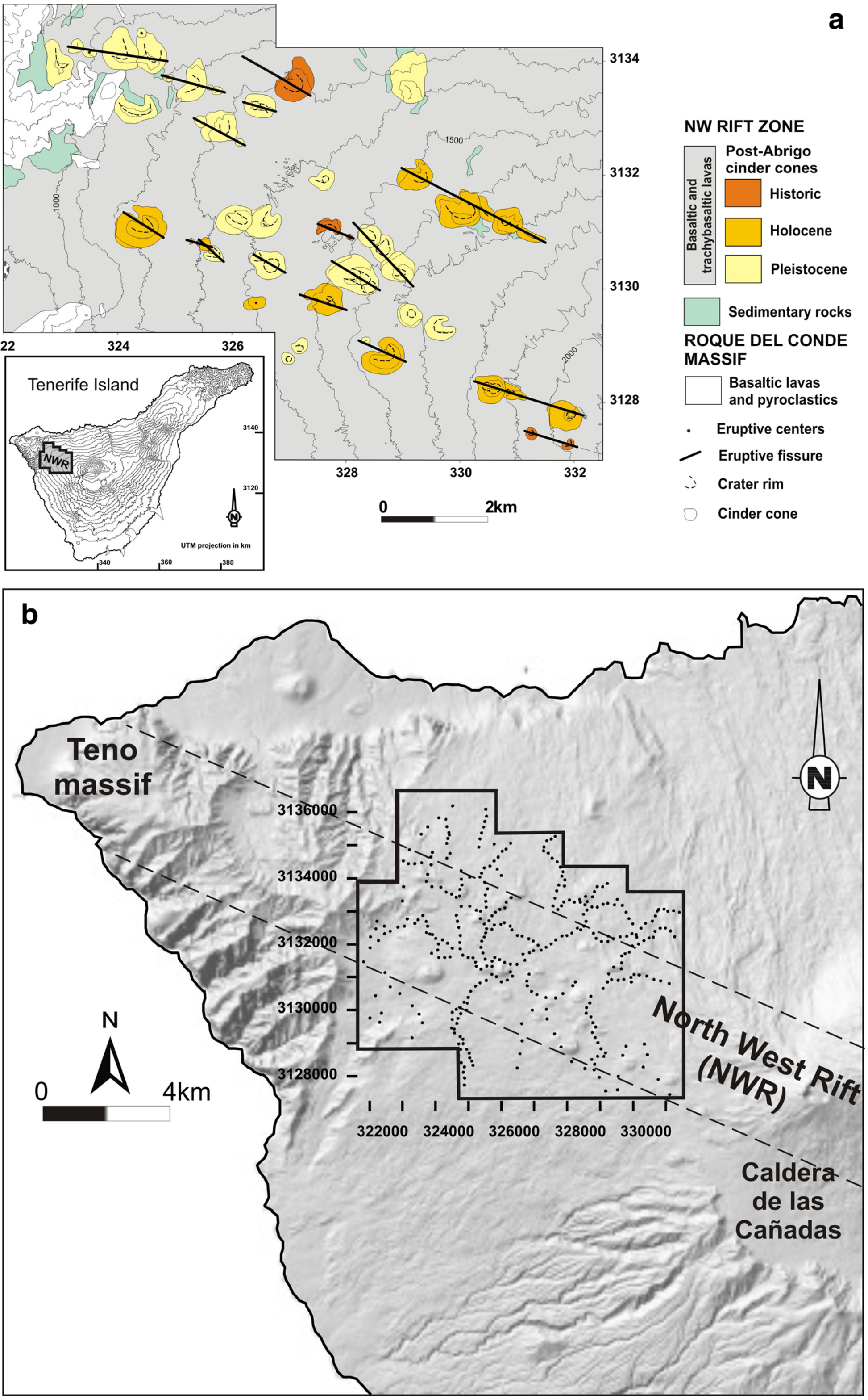
The 2004–2005 seismo-volcanic unrest

The average rate of seismic events located in and around Tenerife from 1997 to the first half of 2001 has been about 1 monthly event. However, and since the second half of 2001, IGN began to detect an increase in the seismic activity of Tenerife, registering an average of ~6 events per month during the 2001–2003 period (Domínguez et al. 2011). In 2004, the number of monthly seismic events increased, reaching up to 78 seismic events per month during August and 65 in November (Fig. 2a). Until the beginning of 2004, the seismic activity was concentrated in the zone where the 1989 earthquake occurred and along NW–SE direction extending from the fault detected in 1989 off the coast of the La Orotava valley (Fig. 2c). In April 2004, a change in the location of the epicenters of the earthquakes took place, and they concentrated in the northwestern sector of the island. Many of the epicenters in 2004 were located on the NWR zone, but in general, they formed an alignment of approximate N–S direction from the Icod valley to the southwestern flank of the Las Cañadas caldera (Fig. 2c). Between 22 and 29 April 2004, the IGN registered a seismic cluster not felt by the population. However, during a second seismic cluster that began on 7 May, an earthquake of magnitude 2.6 was recorded on 11 May. The epicenter of this earthquake was located in the Icod valley, where it was felt by the inhabitants creating an intense social alarm. Since 2005, seismicity has been characterized by (i) most of the more energetic earthquakes ($M > 1.5$) occurred between Tenerife and Gran Canaria islands as well as under North East volcanic rift of Tenerife Island, (ii) a sharp increase of located seismic events in 2010 (Fig. 2c), (iii) the occurrence of an earthquake of magnitude 4.2 on the Richter scale registered on 5 February 2010, and (iv) the occurrence of a seismic swarm in 2 October 2016, with more than 400 long-period events located SW of Teide. Epicenters of this seismic swarm were located south of the area affected by the 2004–2005 unrest episode.

The 2004–2005 seismic-volcanic unrest was preceded by geochemical and geophysical precursors. Pérez et al. (2012) reported a significant pulse in total CO_2 emission in 2001 at the summit of Teide volcano as well as a clear increase in the continuous record of diffuse CO_2 efflux at a geochemical station located at the summit of Teide, providing the first "volcanic unrest alert" to the local government (Pérez et al. 2004a, 2005). Melián et al. (2012), reported a significant pulse in total diffuse CO_2 emission at the crater of Teide in 2001 and changes in the chemical composition of the Teide fumaroles in December 2003 including the appearance of SO_2, an increase in the HCl and CO concentrations, and a decrease in the H_2S and in the gas/steam ratio. Other geochemical precursors of this seismic-volcanic unrest were observed in the local aquifer, such as an increase in ^{220}Rn and ^{222}Rn gas in the groundwater of "Fuente del Valle," a gallery located along the South-rift Zone of the island around the middle of 2003 (Pérez et al. 2007), and an increase in the SO_4/Cl ratio in the groundwater of the "Hoya de la leña" gallery in April of 2004 (Marrero et al. 2005).

Other authors have presented different hypotheses to explain the occurrence of the anomalous seismicity at Tenerife. Fernández et al. (2000) carried out a GPS survey and InSAR data analysis to detect volcanic deformation signals. They observed significant deformation signals near the NWR zone, but they were considered to be of a shallow origin and not related to a deep magma process. Gottsmann et al. (2006), observed a gravity increase between May 2004 and April 2005 at the NWR Zone. They considered three possible scenarios: (1) magma injection into a conjugated fault system beneath the NWR Zone triggering the reawakening of the volcanic complex, (2) fluid migration through the central volcanic complex of Tenerife, and (3) a hybrid of both. Almendros et al. (2007) explained the observed 2004 volcanic unrest and the appearance of fluid-related seismicity, including volcanic tremor, as a consequence of a deep magma injection beneath Teide volcano, which did not end in a volcanic eruption. Sagiya et al. (2007) reported that no significant crustal deformation has occurred at Tenerife Island even during the most active stage of the seismic crisis in the middle

Fig. 3 **a** Structural map of the NWR zone of Tenerife showing the location of the main faults and eruptive cones (from Galindo 2005). **b** Location of the study area and measurement sites. *Red dots* indicate sample sites for $\delta^{13}C(CO_2)$ analysis during 2011 survey



of 2004. However, they assume that since the seismic activity beneath the NWR Zone was already active at the beginning of the GPS monitoring, the results do not guarantee that there was no crustal deformation before the start of GPS monitoring. The analysis of these observations emphasizes that the observed changes of seismic activity had a clear disturbance of deep origin that affected the seismicity registered in the island, as well as to the gas discharge. These geochemical and geophysical observations seem to be premonitory signals of the intense and anomalous seismic activity detected in Tenerife from the end of April 2004 (Pérez et al. 2004a, 2007; Marrero et al. 2008).

Procedures and methods

Since 2000, we have monitored the diffuse CO_2 emission at the NWR Zone of Tenerife (75 km^2, Fig. 3a) because it is one of the youngest volcanic structures of the island with high probability of hosting a future eruption (Galindo et al. 2005; Pérez and Hernández 2008). As no visible emanations occur at the surface environment of the NWR zone, diffuse degassing studies are the most useful geochemical tool to monitor the volcanic activity in this area.

In all 49 surveys, measurements of soil CO_2 efflux were performed in situ following the accumulation chamber method (Parkinson 1981) by means of a portable non-dispersive infrared (NDIR) CO_2 analyzer LICOR-800 system, with a measurement range of 0–2000 ppm (14 cm optical bench). The LICOR analyzer was interfaced to a hand-sized computer running the data acquisition software. The measurements consisted of placing the chamber on the ground, obligating to recirculate the gas in a close loop between the chamber and the analyzer. In the hand-sized computer, the increase of CO_2 concentration as a function of time was recorded (Chiodini et al. 1996), allowing the operator to calculate the CO_2 efflux at each measuring site. To verify the performances and the reliability of this method, several calibration tests were made in the laboratory by injecting a known flow (using a mass flow controller) of gas into the accumulation chamber and the accuracy was estimated to be ±10%. The detection limit of the instrument was estimated in ~0.5 g m^{-2} day^{-1}. Soil CO_2 efflux measurements sites were selected to cover most of the NWR zone with site spacing about 200 m (Fig. 3b). From the end of 2004, a portable GPS receiver with an accuracy of ±10 m was used to locate the sampling sites. Most of the studied area comprises typical entisols and inceptisols and low organic matter content (Fernandez-Caldas et al. 1982) and is covered by a sparse pine forest. Since we carried out most of the surveys on a monthly basis, during the field work, rain and strong wind conditions were avoided. Soil CO_2 efflux data were used to construct spatial distribution maps using sequential Gaussian simulation (sGs), provided by the *sgsim* program (Deutsch and Journel 1998). Sequential Gaussian simulation has been widely applied in the study of soil diffuse degassing at volcanic and non-volcanic systems (Cardellini et al. 2003). The sGs procedure allows us to both interpolate the soil CO_2 efflux at non-sampled sites and assess the uncertainty of the total diffuse emission of carbon dioxide estimated for the entire studied area. The simulation is conditional and sequential, i.e., the variable is simulated at each unsampled location by random sampling of a Gaussian conditional cumulative distribution function (Cardellini et al. 2003). To quantify the diffuse CO_2 emission from the studied area at the NWR zone of Tenerife, 100 simulations for each survey were performed over an averaged grid of 30,000 squared cells (50 m × 50 m) following the variogram model. The search radii used for the GSLIB interpolation was selected taking great care not to oversize the CO_2 emission anomalies.

Soil gas was sampled where relatively high CO_2 effluxes occurred, during the 2011, 2013, 2014, 2015, and 2016 surveys. Samples were collected using a metallic probe inserted at a depth of 40–50 cm. The soil gas was sucked by a syringe and stored in glass vials to analyze soil CO_2 content and carbon isotopic composition. Analyses were performed at the laboratory by a micro-GC VARIAN CP-2002 and a Thermo Finnigan MAT 253 mass spectrometer. The $^{13}C/^{12}C$ ratio is shown as $\delta^{13}C$ values in per mille with respect to Vienna Pee Dee Belemnite (VPDB) standard and the uncertainty of each measurement is $\pm \leq 0.1‰$.

Results and discussion

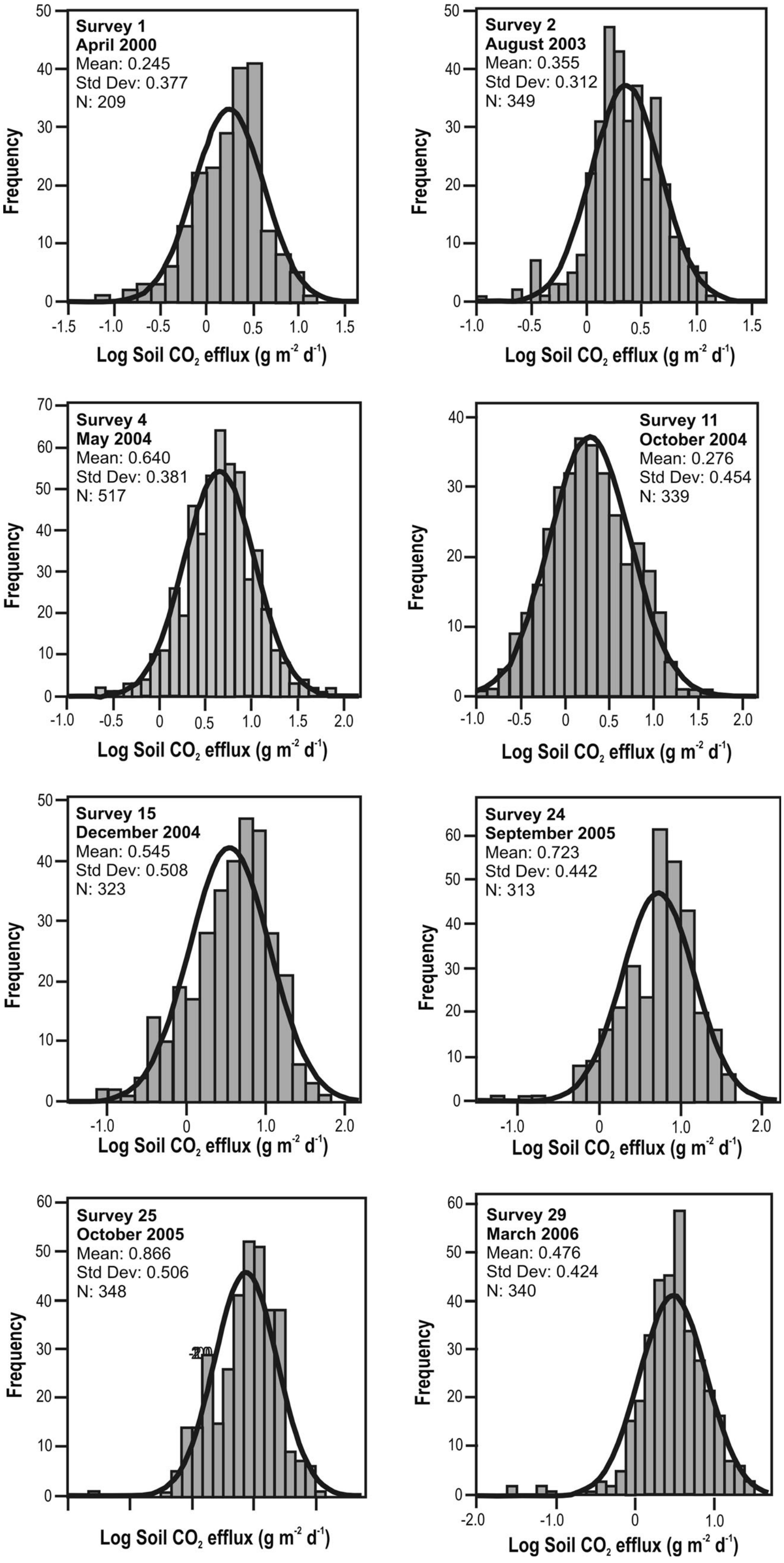
Table 1 shows a descriptive statistical summary of results from the 49 soil gas surveys at the NWR Zone of Tenerife. The number of measurements varied during this study, with most being close to 350. Measured CO_2 effluxes ranged from non-detectable up to 141.0 g m^{-2} day^{-1}. The measured $\delta^{13}C–CO_2$ values ranged from −28.7 to −6.5‰ vs. VPDB, suggesting different carbon sources for the CO_2 in the soil atmosphere. The annual average $\delta^{13}C–CO_2$ value during all the 4 years when soil gas samples were collected for isotopic analysis of $C–CO_2$ became heavier: −18.2 (2011 survey), −11.9 (2013 survey), −12.9‰ (2014 survey), −13.3‰ (2015 survey), −14.7‰ (July 2016 survey), and −15.4‰ (October 2016 survey) vs. VPDB.

Soil CO_2 efflux values in volcanic hydrothermal areas usually reflect the contribution of different CO_2 sources such as biogenic and endogenous (Cardellini et al. 2003, Hernández et al. 2012b). A probability-plot technique (Sinclair 1974) was applied to check whether the log of the data comes from unimodal or polymodal distributions (Fig. 4). Partitioning of different populations was done graphically. Two main maxima, and curves indicating distinct modes, were identified in most of the CO_2 efflux data sets: normal I and II (background and peak in Fig. 5). These two distinct populations are referred to as background and peak, respectively. The observed bimodal distributions reflect the existence of different sources for the CO_2. The mode normal I, or background, is representative of fluxes probably generated by biological activity and soil respiration and represents the bulk of most measured fluxes. However, recent studies of diffuse degassing in the course

Table 1 Summary of results of soil CO_2 efflux measured in the 49 soil gas surveys at the NWR zone of Tenerife Island

Date	Survey	No. samples	16 percentile	84 percentile	Mean *B* (g m^{-2} day^{-1})	Peak (×*B*)	Mean (t day^{-1})	Std dev (t day^{-1})
1 April 2000	1	437	0.61	2.64	1.40	7.81	52	2
1 August 2003	2	442	1.04	4.72	2.20	4.76	118	4
4 May 2004	3	443	2.08	6.89	3.90	5.68	399	14
26 May 2004	4	518	1.84	8.49	4.50	4.43	402	13
18 June 2004	5	511	0.61	4.04	1.60	13.35	164	7
7 July 2004	6	498	0.29	1.04	0.56	6.98	96	7
23 July 2004	7	416	0.48	3.74	0.72	4.75	137	6
20 August 2004	8	355	0.73	3.10	1.70	5.78	138	4
21 September 2004	9	351	0.26	1.64	0.70	5.44	74	3
10 October 2004	10	348	0.31	1.16	0.60	9.60	101	3
27 October 2004	11	345	0.59	2.54	1.60	6.19	225	13
03 November 2004	12	332	0.61	3.88	1.30	7.06	200	6
09 November 2004	13	358	1.97	8.65	4.10	4.53	355	15
24 November 2004	14	343	0.98	3.49	1.90	3.37	163	9
21 December 2004	15	354	0.91	0.69	2.00	5.29	329	10
12 December 2005	16	366	0.94	4.40	2.00	4.93	262	13
2 February 2005	17	355	0.63	6.42	2.20	8.31	275	18
22 March 2005	18	351	0.52	3.85	1.50	5.19	467	28
12 April 2005	19	355	1.35	8.49	3.50	4.74	437	24
24 May 2005	20	355	2.44	13.32	5.90	7.77	471	24
22 June 2005	21	356	0.57	3.94	1.50	4.19	217	6
13 July 2005	22	350	1.11	7.69	2.80	7.87	303	10
10 August 2005	23	356	0.77	3.57	1.80	9.09	209	3
21 September 2005	24	348	1.07	3.68	2.20	14.23	436	19
19 October 2005	25	354	3.46	13.64	6.70	7.80	867	21
5 November 2005	26	356	1.16	6.24	2.80	3.99	339	10
7 December 2005	27	349	1.02	4.25	2.20	3.80	324	11
1 March 2006	28	347	0.29	1.80	0.80	2.88	138	5
29 March 2006	29	352	3.41	6.46	2.50	0.98	292	9
26 April 2006	30	347	0.24	2.19	0.76	11.94	199	7
1 August 2006	31	359	1.08	4.01	2.30	1.35	168	6
3 December 2006	32	311	0.25	2.37	0.78	2.70	84	7
27 February 2007	33	354	0.72	4.26	1.76	1.82	287	8
21 June 2007	34	355		6.44	2.51	3.23	257	10
14 August 2007	35	331	0.91	3.59	1.80	4.72	157	3
11 November 2007	36	336	2.93	4.22	3.51	4.27	162	10
27 February 2008	37	341	0.12	0.76	0.31	6.22	476	23
13 June 2008	38	339	0.90	3.14	1.68	7.37	142	7
17 September 2008	39	339	0.51	0.65	0.72	8.51	243	10
3 December 2008	40	350	0.43	2.14	0.94	21.32	267	10
29 July 2009	41	357	0.88	2.93	1.58	5.66	177	4
7 July 2010	42	332	0.81	4.46	1.90	10.74	160	5
6 July 2011	43	345	0.29	0.92	0.52	20.27	192	7
7 July 2012	44	319	0.45	0.99	0.67	14.33	183	7
23 July 2013	45	330	0.36	1.32	0.68	27.73	221	7
6 August 2014	46	343	0.59	3.86	1.45	14.29	188	7
10 July 2015	47	341	1.83	10.41	4.50	8.05	403	17
14 July 2016	48	344	0.74	4.65	1.86	12.02	255	9
07 October 2016	49	345	0.35	1.96	0.84	35.05	338	18

Fig. 4 Histogram plots of eight selected CO_2 efflux surveys at the NWR Zone of Tenerife. Curves represent ideal normal curve for each distribution



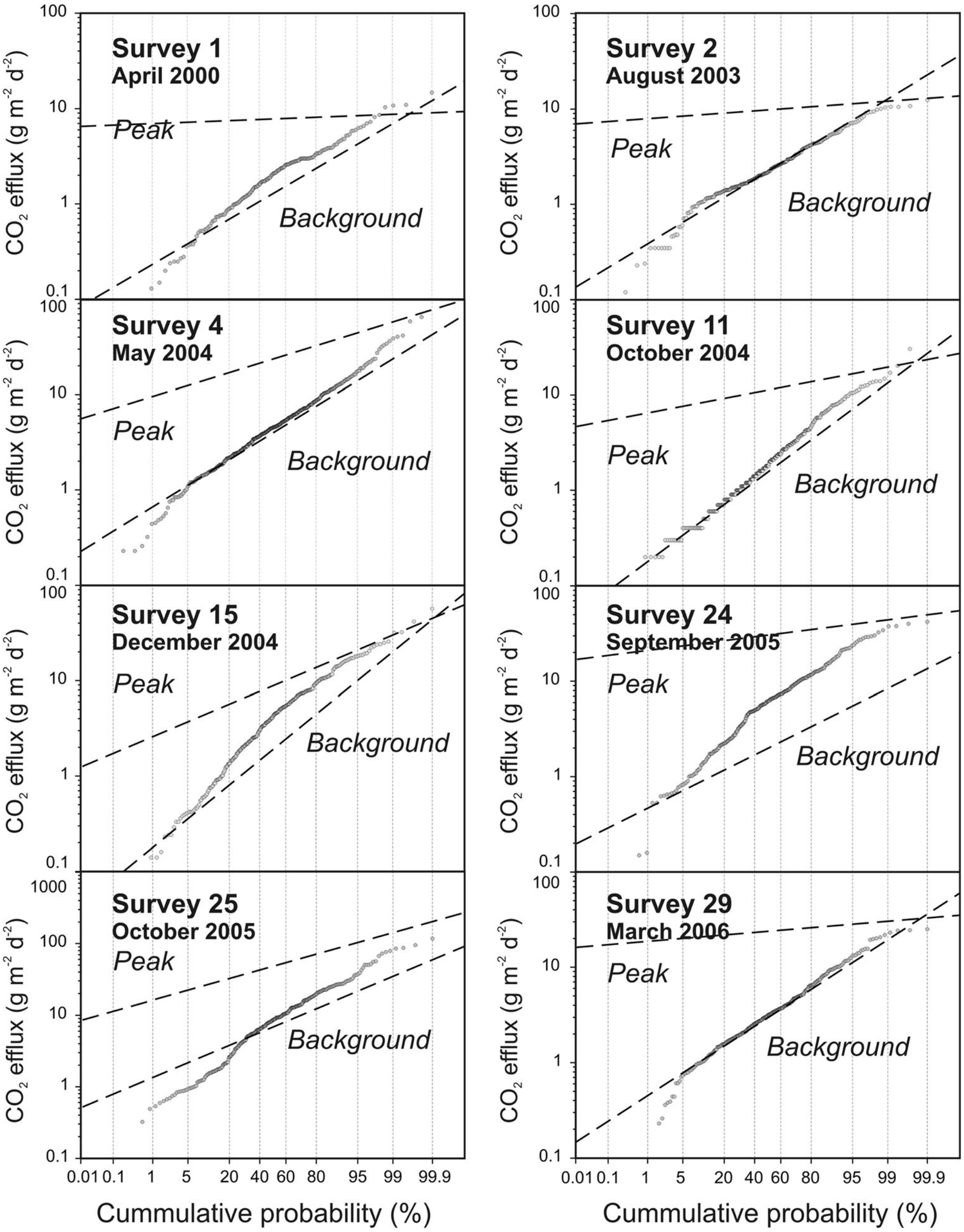


Fig. 5 Selected cumulative frequency plots of the diffuse CO_2 efflux data for the study period. The interception of *solid lines* is interpreted to indicate thresholds values that separate the different populations. *Dashed lines* indicate the background, intermediate, and peak log-normal populations

of volcano monitoring demonstrated that background values may also include endogenous inputs: Pérez et al. (2012) measured increases in the soil CO_2 efflux background emission values prior to an eruptive event at distances of 11 km from the eruptive vent. The authors conclude that measurements of even low-level CO_2 efflux (background values) are useful for volcanic surveillance programs. Background values for all the 49 surveys are summarized in Table 1. The second mode, or peak population, represents the CO_2 fluxes of mainly deep-sourced CO_2 linked to the volcanic hydrothermal system itself. The existence of this peak population may provide subtle surface evidence of endogenous degassing from the volcanic system at the NWR zone.

Origin of CO_2

To investigate the origin of the soil CO_2 at the NWR zone, a binary diagram of the $\delta^{13}C(CO_2)$ vs. $1/[CO_2]$ was constructed with two geochemical end members (Fig. 6a): air, characterized by $\delta^{13}C(CO_2) = -8.0‰$ and $[CO_2] = 400$ ppm and biogenic CO_2. To construct the range of the biogenic end-member, we considered the fact that biogenic soil CO_2 can be +4.4‰ heavier than the soil-respired CO_2 produced by roots, owing to the fractionation of diffusion within the soil (Cerling et al. 1991). Since the isotopic composition of soil organic matter is less than −20‰ (Craig 1953), the isotopic composition for the biogenic soil CO_2 was defined as ≤15.6‰. Most of the biogenic contribution may be due to the vegetation cover of

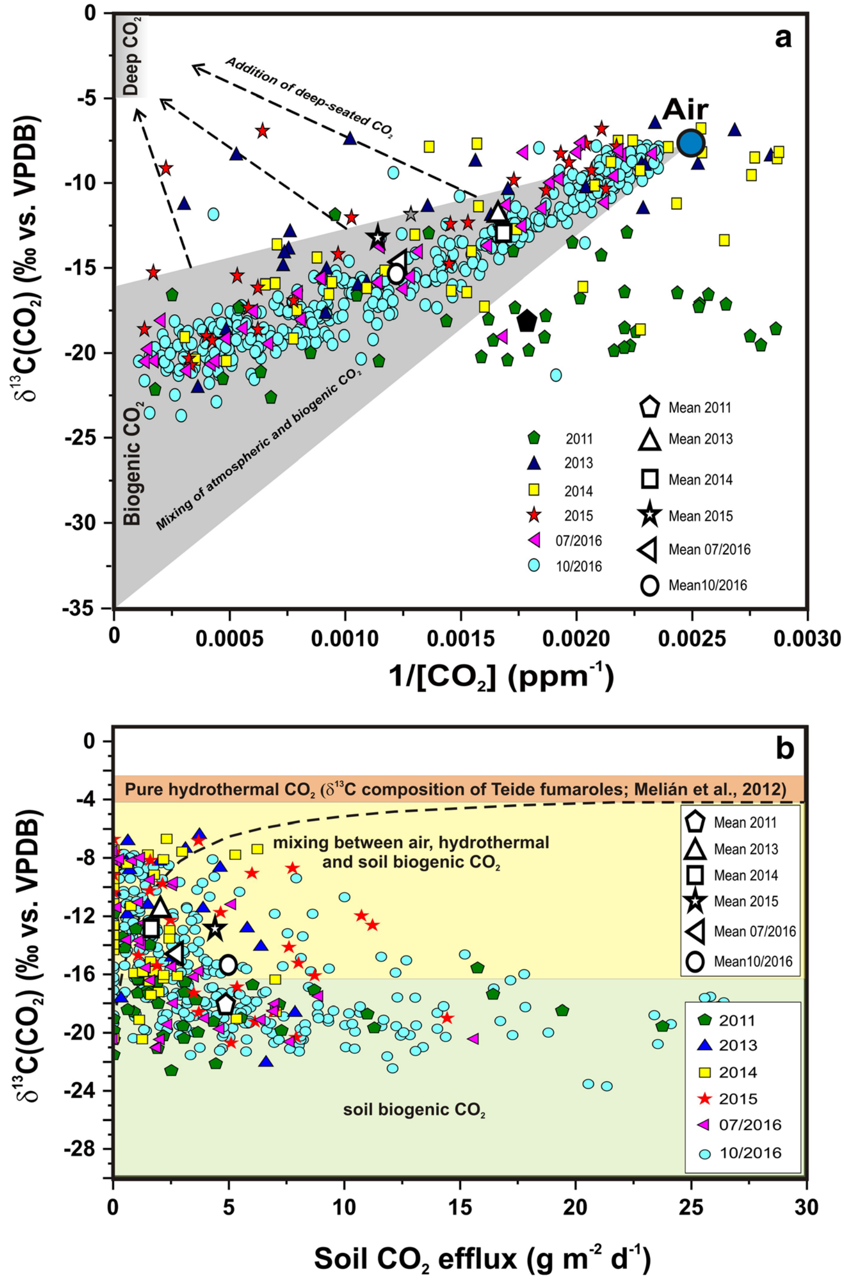


Fig. 6 **a** Correlation diagram of δ^{13}C(CO$_2$) against 1/[CO$_2$] (ppm^{-1}) based on 2011, 2013, 2014, 2015, and 2016 surveys. The *shaded area* extending from the atmospheric to biogenic end members represent samples affected by mixing of atmospheric and biogenic CO$_2$. **b** Diagram plotting soil CO$_2$ efflux vs. carbon isotopic composition of soil CO$_2$ efflux. Also plotted is the theoretical mixing line (*dashed line*) between biogenic and hydrothermal CO$_2$ fluxes

sparse pine forest. The addition of deep-seated CO$_2$ (which includes mantle-derived CO$_2$ and CO$_2$ from metamorphism of marine carbonate rocks) causes a graphical trend of samples along the arrows shown in Fig. 6a, towards δ^{13}C (CO$_2$) ≥8‰ (Javoy et al. 1978; Barnes et al. 1988) and [CO$_2$] ~100%.

Figure 6a indicates that most of analyzed samples showed CO$_2$ compositions reflecting different degrees of mixing between atmospheric and biogenic CO$_2$. The vertical mixing trend between the biogenic atmospheric CO$_2$ indicates also a small addition of deep-seated CO$_2$. Soil gases collected for δ^{13}C(CO$_2$) analysis show the typical chemical and isotopic composition of gases with a strong biogenic and air contribution. Therefore, it is to be expected that the data have a large dispersion. Standard deviation values for all the six data sets are quite similar, 3.00, 3.94, 4.30, 4.32, 4.59, and 4.04 for 2011, 2013, 2014, 2015, and July and October 2016 surveys, respectively, considering the large range of values for each survey, whereas average values show a range between −11.90 and −15.40‰. The mean value gives us different information, indicating the value around which most of the values are distributed. As pointed out before, the annual average δ^{13}C-CO$_2$ value between 2011 and 2013 becomes heavier, with a tendency towards lighter values from 2013 to 2016. This observation might suggest a small contribution of an endogenous CO$_2$ component, coinciding with an increasing diffuse CO$_2$ emission rate in 2015 and the continuous increase in peak values (xBackground) between 2011 and 2014. A value expressing the magnitude of anomalous degassing is calculated by dividing the peak value by the mean of the background population for each survey. The latest value, observed during the survey carried out on October 2016, may herald oncoming volcanic unrest episodes. The diffuse CO_2 emission and isotopic composition of the soil CO_2 values reported here suggest the presence of different contributions to the measured gas from the NWR zone. Most of the area lies beneath a pine forest, and we infer that biological processes such as degradation of organic matter are the main source for background CO_2 emission values in the observed surficial effluxes during the study period. In addition, we infer a small contribution of deep-seated CO_2 that should not be neglected.

Figure 6b shows the $\delta C^{13}C$ compositions of the CO_2 soil gas at the NWR zone of Tenerife plotted vs. their respective soil CO_2 efflux values, as well as with the $\delta C^{13}C$ range of values expected for soil CO_2 degassing from a deep source. The carbon isotope composition of the fumarolic discharges from summit crater of Teide volcano is well determined, and ranges from −2.3 to −4.2‰ (Melián et al. 2012). This composition is assumed representative of the volcanic-hydrothermal source and represented as a horizontal orange band labeled "hydrothermal CO_2" in Fig. 6b. Distribution of selected samples from 2011, 2013, 2014, and 2015 surveys shows a wide range of $\delta^{13}C$ CO_2 values (from ~−20 to ~−6‰, close to hydrothermal CO_2 isotopic composition). The observed dispersion of the CO_2 efflux isotope compositions can be mainly ascribed to the simultaneous contribution of different sources for the CO_2 as well as different processes. The dispersion results from the natural isotopic variability of biogenic CO_2 produced in the soils, mixing of the biogenic CO_2 with variable amounts of hydrothermal gas and uncertainties of the method which are higher at low CO_2 flux values (Chiodini et al. 2008; Dionis et al. 2015).

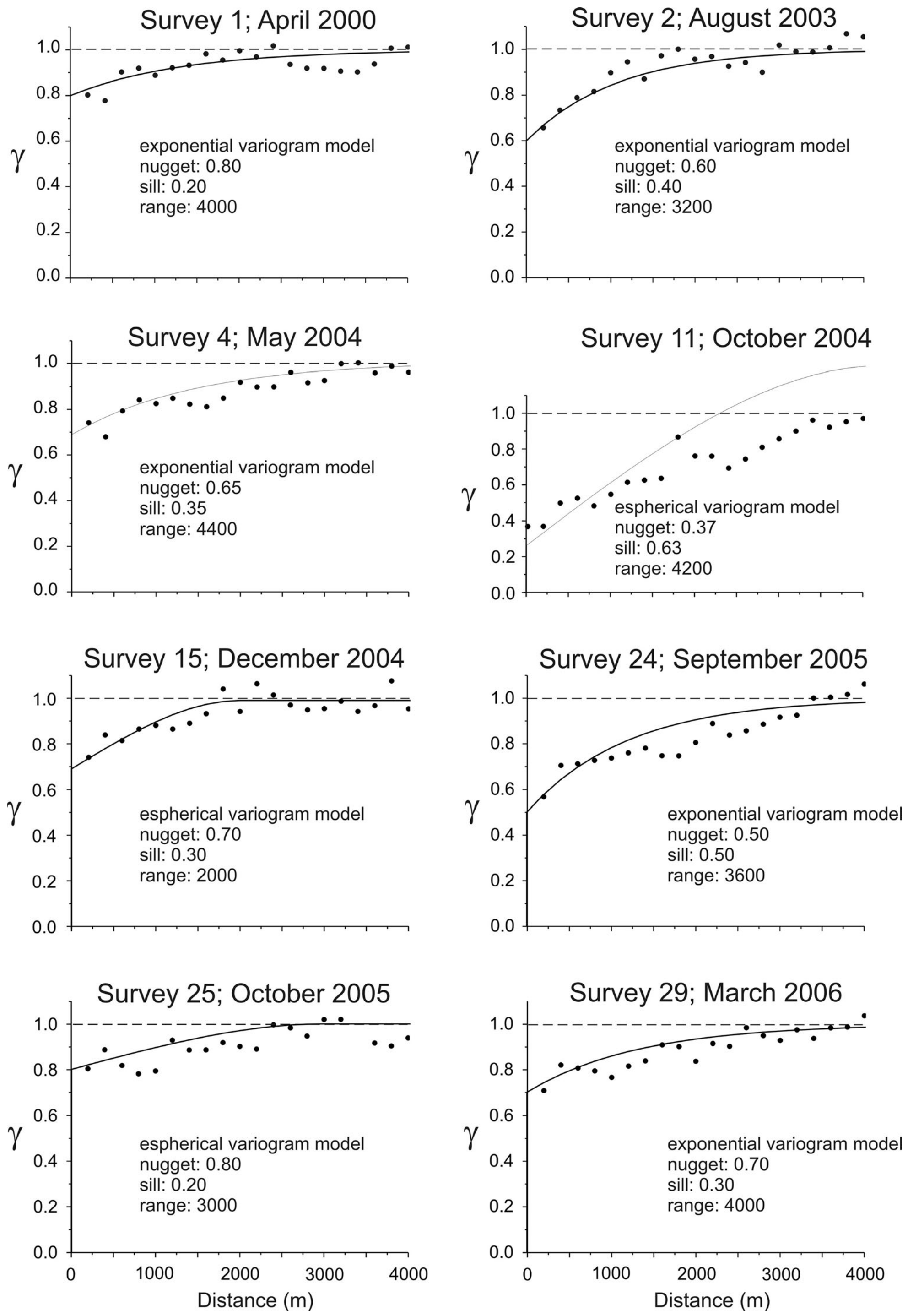
Temporal evolution of diffuse CO_2 output

With the aim of evaluating the temporal evolution of the diffuse soil CO_2 emission at the NWR zone of Tenerife and its possible relationship with seismic-volcanic unrest episodes, we have considered the value of diffuse CO_2 emission for each of the 49 surveys. The experimental variograms for the 49 surveys were fitted with spherical and exponential models. The high-range values estimated for the variograms might be due to the spacing between measuring sites and also the areas without measurements. As examples, Fig. 7 shows eight of them with the "nugget" effect, sill, and range parameters of the variogram model used. The nugget effect represents variability at distances smaller than the sample spacing and includes the measurement error. The relatively high values of this parameter are likely the result of the low diffuse CO_2 emission values used to construct the spatial distribution maps presented in Figs. 8, 9, and 10; most values are close to the detection limit of the instrument (~0.5 g m^{-2} day^{-1}) (large blue areas in Figs. 8, 9, and 10). Similar nugget effect values were found in Cumbre Vieja volcano (Padrón et al. 2015) also in the Canaries, Spain.

A map of average values was then constructed for each survey using the average of the different values simulated at each cell. Since quantification of the uncertainty of the diffuse CO_2 is important for correctly interpreting the temporal variations, the mean and the standard deviation of the 100 simulated values of diffuse CO_2 output were assumed to be the characteristic values of the CO_2 released and of its uncertainty (Cardellini et al. 2003). Figures 8, 9, and 10 show maps presenting the mean of simulated CO_2 efflux values of the 49 surveys. Observed differences in spatial distribution of CO_2 efflux anomalies and of their intensities during campaigns performed very close together in time may be due to the occurrence of pulses of CO_2 during the unrest period. Table 1 shows the calculated mean value for diffuse CO_2 output for each survey and the uncertainties (standard deviation). The soil CO_2 efflux anomalies do not exactly agree, in either location or in intensity, from one survey to another, but they are concentrated mainly throughout the axis of the NWR zone. In the southwestern sector of the study area, which corresponds to one of the NWR zone flanks, the background values clearly dominate. The observed surface geochemical anomalies seem to show a spatial correlation with major structural features of the study area, at least during the campaigns when higher CO_2 emission rates were measured (13, 18, 20, 24, and 25).

In order to establish a cutoff for separating background soil efflux from the anomalous CO_2 efflux of the NWR zone, we assumed that the mean value of background emission from the studied area of NWR zone was the more representative cutoff value with a confidence level of two times the standard deviation (±2σ). We calculated the mean value of all the background populations (2.0 g m^{-2} day^{-1}), which was found to be similar to the background values calculated for other volcanic systems in the Canary Islands with similar soils, vegetation and climate: Cumbre Vieja in La Palma Island (1.4 g^{-2} day^{-1}) (Padrón et al. 2015), Timanfaya in Lanzarote Island (0.4 g^{-2} day^{-1}) (Hernández et al. 2012a), and El Hierro Island (1.5 g^{-2} day^{-1}) (Melián et al. 2014). Assuming an average surface for the studied area of 75 km^2, a diffuse CO_2 output of 143 t day^{-1} is considered as cutoff background emission. The standard deviation of the background emission was computed by considering the mean of the 16th (−1σ, 21 t day^{-1}) and 84th (+1σ, 159 t day^{-1}) percentiles of all the surveys as well as 2σ (180 t day^{-1}). Figure 11a shows the temporal evolution of the mean simulated values of diffuse CO_2 output for the 49 surveys with the box limits representing the one and two standard deviations of the cutoff mean value. Anomalous values of diffuse CO_2 output are observed between the years 2004–2005, 2009, and from 2015.

Fig. 7 Omnidirectional experimental variograms of CO_2 efflux normal scores from eight selected surveys at the NWR zone of Tenerife. *Solid lines* represent the isotropic variogram models used in the simulation procedure. The parameters nugget, sill, and range refer to the variogram models



The first period (A in Fig. 2b) coincides with the start of the 2004–2005 seismic-volcanic unrest at Tenerife and the onset of volcanic tremor. Almendros et al. 2007, observed at this time the maximum level of volcanic tremor suggesting the arrival of a gas pressure front to the surface. Between April–May 2004, an earthquake of magnitude 2.7 was felt by the inhabitants of nearby villages. Later, in July 2004, a significant reduction in diffuse CO_2 output, to 96 t day^{-1}, was observed. This value is the same order of magnitude as those estimated for the 2000 and 2003 surveys. In 2005, two new significant pulses in diffuse CO_2 output occurred, between March–May and in October, when the maximum CO_2 output value of this study was recorded (867 ± 21 t day^{-1}). In February 2008, a pulse in diffuse CO_2 output was observed

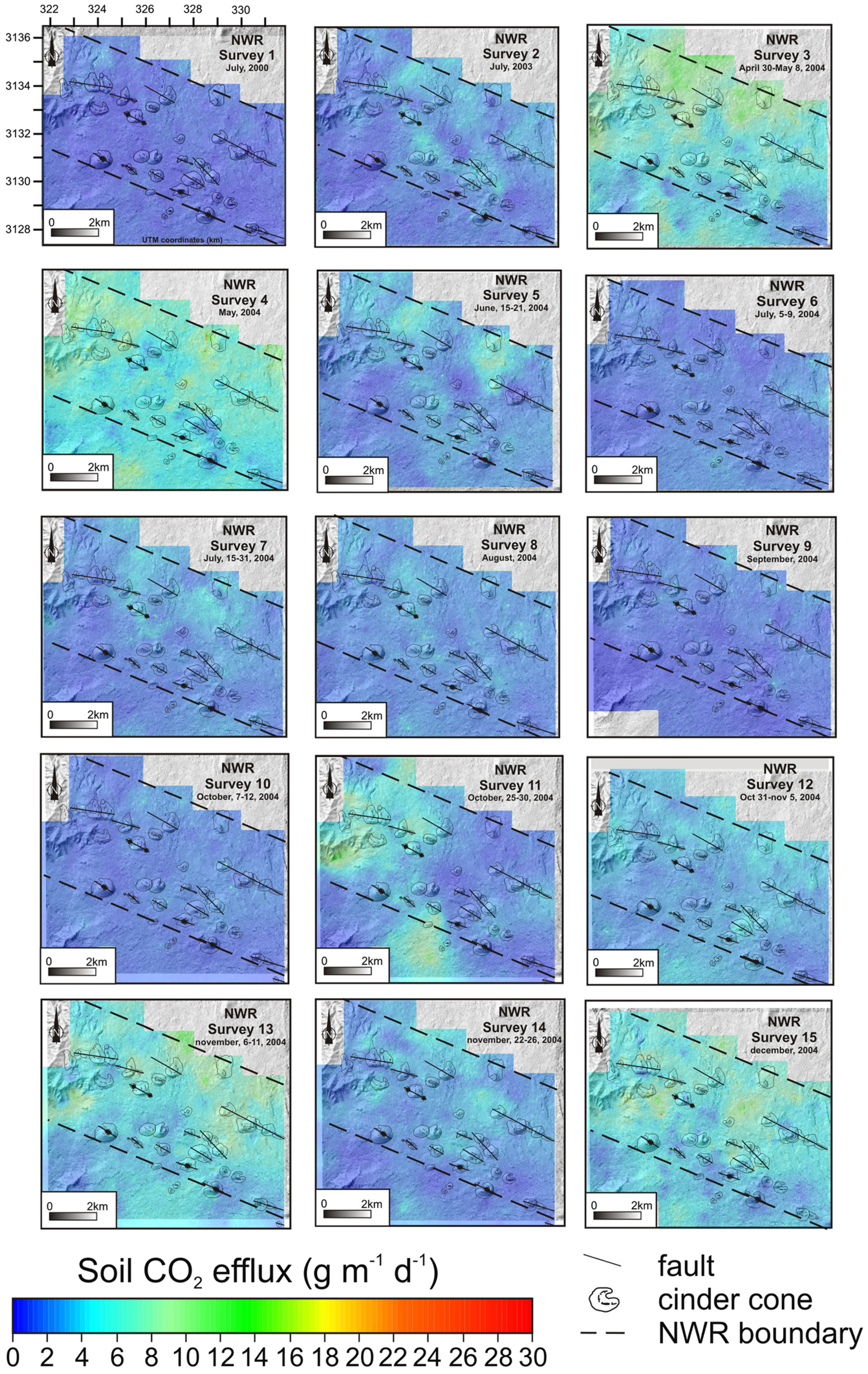
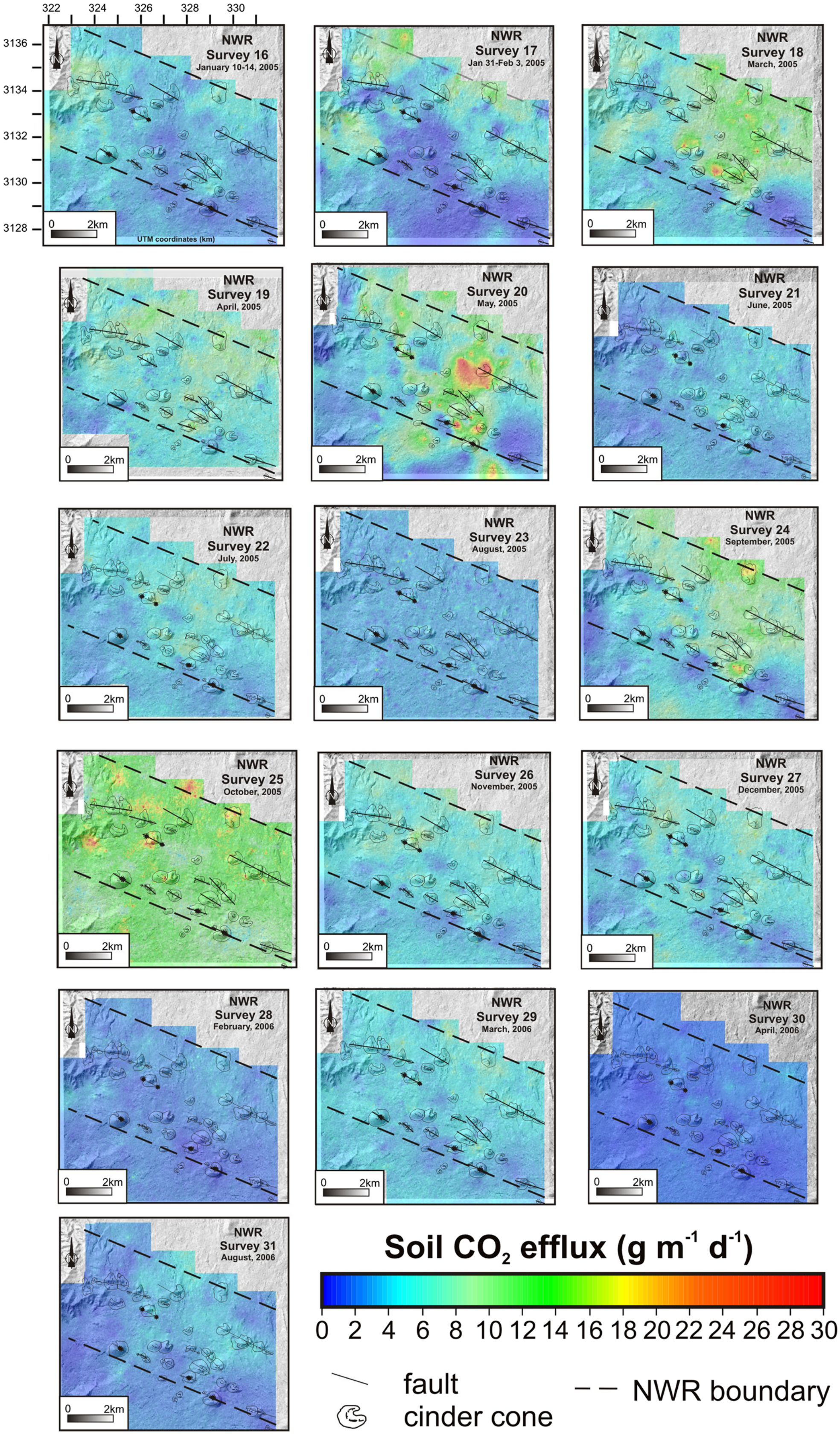


Fig. 8 Soil CO$_2$ efflux maps (surveys 1–15) of mean CO$_2$ efflux obtained from an average of 100 realizations (E-type estimates)

Fig. 9 Soil CO_2 efflux maps (surveys 16–31) of mean CO_2 efflux obtained from an average of 100 realizations (E-type estimates)



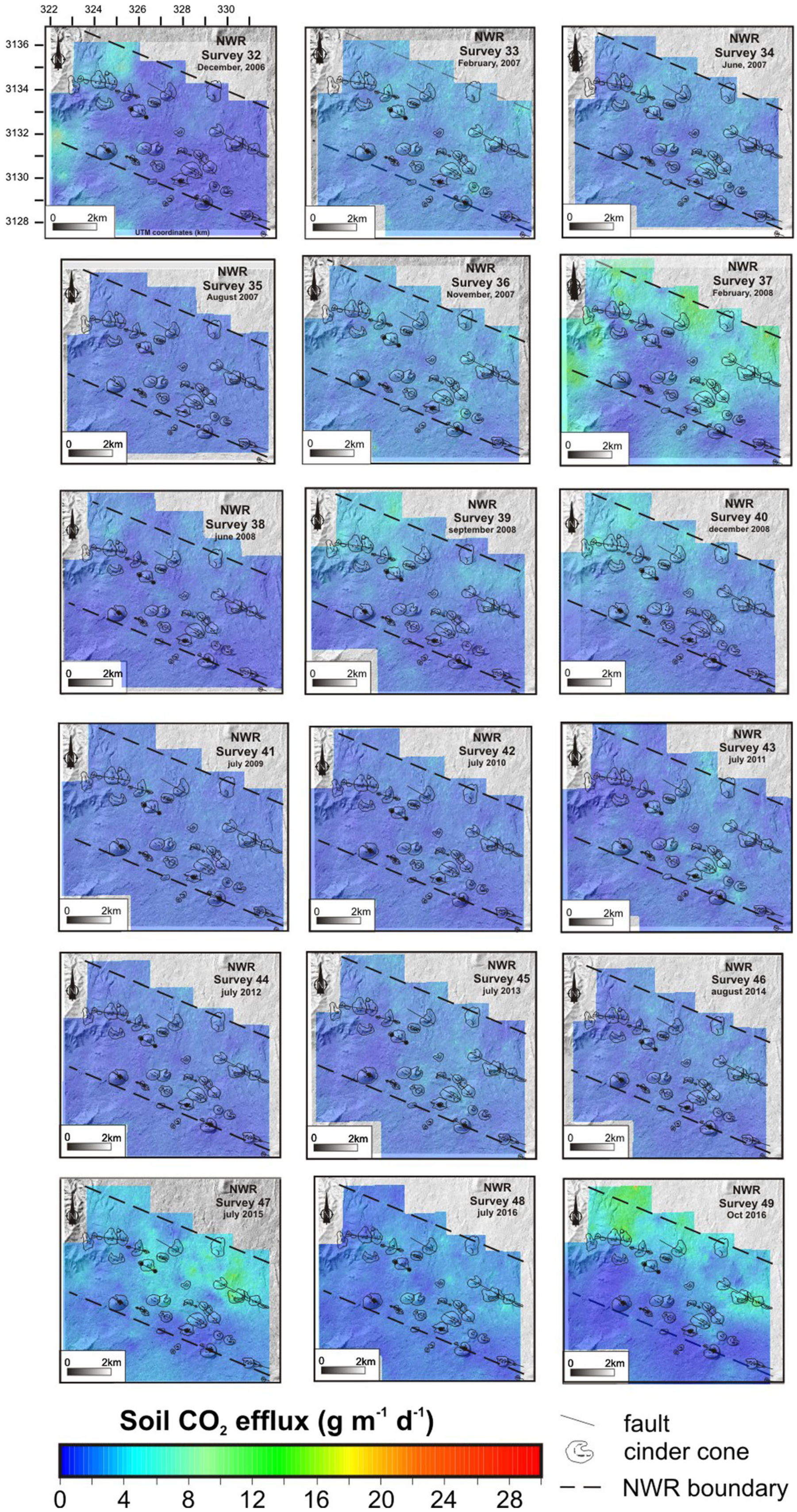


Fig. 10 Soil CO_2 efflux maps (surveys 32–49) of mean CO_2 efflux obtained from an average of 100 realizations (E-type estimates)

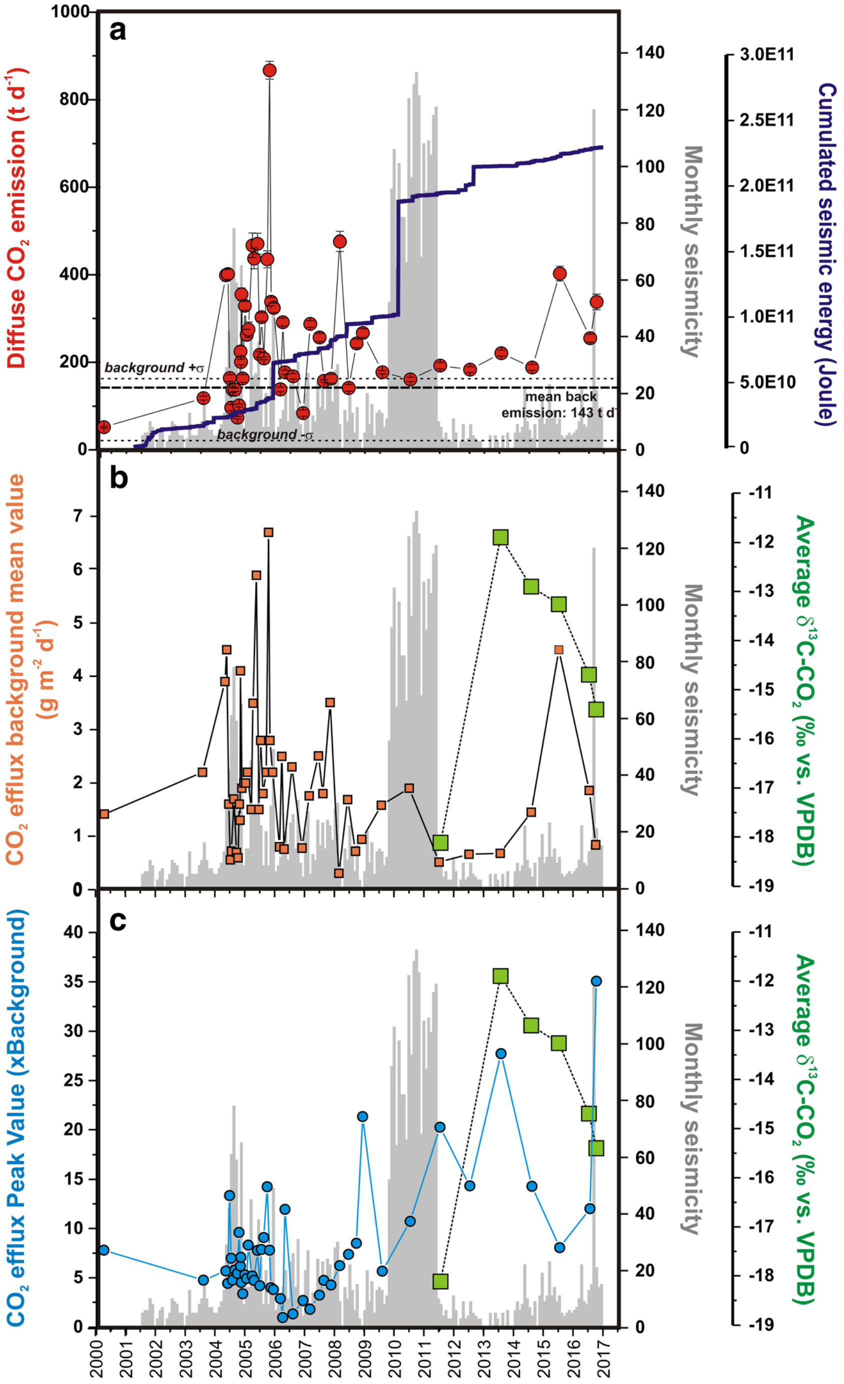


Fig. 11 **a** Time series of diffuse CO_2 output for the 2000–2016 NWR zone surveys. *Horizontal line* indicates the mean value of the background CO2 output from NWR zone of Tenerife and the standard deviation of this mean value. *Blue line* shows cumulative released seismic energy (calculated based on the Gutenberg and Richter law—1956). **b** Time series of CO_2 efflux background mean values for the 2000–2016 NWR zone surveys. In green are average δ13C(CO_2) values for 2011, 2013, 2014, 2015, and 2016 surveys. **c** Time series of CO_2 efflux peak values for the 2000–2016 NWR Zone surveys. In *green* area verage δ13C(CO_2) values for 2011, 2013, 2014, 2015, and 2016 surveys. **a**–**c** Histograms represent monthly seismicity during the period 2000–2016 (source IGN)

(476.2 ± 22.7 t day^{-1}) and was followed by an almost constant diffuse CO_2 output. These observations are consistent with those made at Teide volcano (Pérez et al. 2012).

Since 2006, an increasing trend in the total CO_2 emission from the Teide summit cone has been recorded. In 2009 (second period, B in Fig. 2b) a CO_2 emission value similar to that measured in 2004–2005 was reached. This increase matched the increase in onshore microseismicity recorded by IGN in 2009–2010, probably caused by fluid injection and/or movements that entailed shear and tensile failure of the reservoir rocks. The increase occurred along with an increase in the CO_2/CH_4 ratio in the Teide fumarolic gases, thus indicating episodes of magmatic gas injection within the Teide volcanic-hydrothermal system (Pérez et al. 2013).

The third period started in 2015 (C in Fig. 2b) before the sharp increase in seismicity recorded in and around Tenerife island, and reached a maximum value of 403 ± 17 t day^{-1} of CO_2 from the studied area. This anomalous seismicity was characterized by an intense seismic swarm on 2 October 2016, with more than 400 recorded long-period events although only about 83 were located by IGN. This anomalous seismicity occurred together with a sharp increase in diffuse CO_2 emission at the summit crater of Teide (unpublished data), suggesting the release of hydrothermal fluids from a magmatic-hydrothermal reservoir.

If we compare the time evolution of the diffuse CO_2 output with the monthly seismic time series, some positive correlations are observed. Peaks in diffuse CO_2 output in April–May 2004, March–May 2005, and October 2005 coincide with peaks of seismic activity. Marrero et al. 2005, observed a considerable increase in the partial pressure of CO_2 (pCO_2) in the groundwater system during the period of volcanic unrest 2001–2004. They interpret this increase was due to movement of magma or other fluids at depth, triggering pressure changes in the volcanic-hydrothermal system located under the western side of Las Cañadas Caldera. The observed increases in diffuse CO_2 emission seem to be the surface expression of the strain-stress changes that occurred at depth during the anomalous seismic activity. A deep magma injection, which might have occurred beneath the northwest flank of Teide-Pico Viejo in April–May 2004 at a depth of about 13–15 km (Almendros et al. 2007), is the most plausible cause to explain the observed variation in the total CO_2 output in the NWR zone. Since the deep magma injection in 2004 did not end in a volcanic eruption and arrested mafic dykes remained at a certain depth (several km), a widespread increase in the level degassing linked to the degassing structures in the area would be expected, explaining the observed changes in the CO_2 release, with values clearly above the background value.

During the period 2004–2005, at the peak of seismic activity, the chemical composition of Teide's fumaroles changed significantly, this time indicating a deep perturbation of the Teide hydrothermal-magmatic system (Melián et al. 2012). However, the very low values of SO_2 values together with the stable $^3He/^4He$ isotopic ratios measured in the fumarolic discharges and the geothermometry data (270–300 °C) (Pérez et al. 2004a) do not support the hypothesis that new basaltic magma was injected from depth into the phonolitic chamber of Teide as was suggested by other researchers (Martí et al. 2009).

Soil CO_2 efflux mean background values as well as peak values (xBackground) showed also a correlation with observed seismicity, seismic energy release and mean $\delta^{13}C(CO_2)$ values (Fig. 11b, c). Epicenters of located events (Fig. 2c) show that during the period of study, most of earthquakes were recorded underneath Tenerife Island (northwest and towards the southeast) and between Tenerife and Gran Canaria Islands. Dominguez Cerdeña et al. 2011 applied different techniques to improve the seismic catalog of volcano-tectonic events detected during the 2004 seismic-volcanic unrest of Tenerife. They classified seismicity into a small number of families by means of cross-correlation analysis and relocated the seismic events. Relocation revealed two seismogenic zones separated by more than 10 km and located at different depths, one NW of the Teide–PicoViejo complex and the other on the SW border of Las Cañadas caldera. Mean background values showed a similar behavior to that registered by the CO_2 emission rates, with a clear tendency of increasing from 2014. Peak values (xBackground) showed a first peak on December 2008, 10 months before the start of the seismic activity and followed later by a continuous increase to the value computed on July 2015. This parameter is a geochemical expression of the magnitude of the anomalous degassing, and the observed change in the trend may indicate an increase in future seismic-volcanic activity.

Insights into the causes of the 2004 seismo-volcanic crisis in Tenerife

Considering the data on the historical eruptions, the volcano-tectonic structure of the NWR zone, the seismic activity, and results from study of diffuse gas emissions, three hypotheses can be proposed to explain the period of anomalous seismic-volcanic activity: (1) regional tectonic reactivation, (2) magmatic reactivation, and (3) a combination of both. Volcanic systems are natural sources of CO_2 to the atmosphere. In low temperature volcanic systems, CO_2 from the mantle is easily absorbed, mainly by aquifers, decreasing its emission to the atmosphere (Allard 1992). The presence of faults and/or deep fractures with high permeability encourages the transport of endogenous CO_2 to the atmosphere (Irwin and Barnes 1980). In some volcanic systems, the existence of CO_2 reservoirs formed by release of this gas from the volcanic-hydrothermal system has been reported (Allard et al. 1991; Giggenbach and Glover 1992; McGee et al. 2000). Changes in the stress field caused by energetic seismic events can trigger migration of these deep-seated gases to shallower environments, as has been suggested for the anomalous period of diffuse CO_2 emission that took place at Mammoth Mountain (California) in December 1997 (McGee et al. 2000) and other volcanic areas (Pérez et al. 2007; Salazar et al. 2002).

The stratigraphic sequence of the NW rift zone comprised a pile of mafic lavas and pyroclastic rocks with some felsic interbedded ignimbrites from the Central Volcanic Complex. The permeability changes between these rock layers might favor the accumulation of deep-seated gases, but all these deposits are cut by numerous sub vertical dykes that constitute discontinuities and greatly increase the vertical permeability of the upper crust. The high dike-induced vertical permeability of the NWR zone does not favor the accumulation of gas pockets at depth and facilitates the continuous outgassing process.

The increased number of seismic events observed between 2001 and 2003 seems to be related to the active fault between Tenerife and Gran Canaria islands. Stress changes induced by seismic waves from mid-2001 might have slightly affected the volcanic-hydrothermal system of Tenerife from 2001 as was proposed by Pérez et al. 2013. This hypothesis is supported by some geochemical evidence such as a pulse in the total CO_2 output at the summit cone of Teide (Melián et al. 2012; Pérez et al. 2004a, 2013), an increase of ^{222}Rn activity and partial pressure of CO_2 (pCO_2) in groundwater before the anomalous seismic activity (Pérez et al. 2004a, 2007; Marrero et al. 2008). Hill et al. 2002, reported that pressure changes in a magma body induced by the isotropic, compressional component of a stress field in the vicinity of a volcanic system are possible, promoting additional melting and the exsolution of gases and other volatiles from the magma. There is evidence that stress changes associated with large earthquakes ($M > 6.5$) occurring relatively far from a volcanic system are capable of triggering volcanic unrest. This took place at Long Valley Caldera in response to the Landers earthquake (1992) in the USA, with the eruption of Mount Fuji, Japan, in 1707, and the eruption of Mount Pinatubo in the Philippines in 1991. Even though the magnitudes of the earthquakes between Tenerife and Gran Canaria after 2001 were relatively low ($M < 3.0$), stress changes induced by seismic waves might have triggered small pressure changes in the volcanic-hydrothermal system of Teide, enhancing advective overpressure and favoring the release of volcanic gases to the surface. Among these volcanic gases, carbon dioxide is, after water, the most abundant volatile in magmas and the dominant gaseous component in hydrothermal systems (Stolper and Holloway 1988; Pan et al. 1991). The geochemical changes identified above could be the surface expression of these stress changes induced by the anomalous seismic activity.

The significant pulse observed in total CO_2 emission at Teide summit cone in 2001 (Pérez et al. 2013) occurred simultaneously with an increase in the continuously recorded diffuse CO_2 efflux at the TFE01 geochemical station located at the summit of Teide (Pérez and Hernández 2008). This provided the first volcanic unrest alert in 2004 to the local government of Tenerife. During the period 2004–2005, at the peak of seismic activity, the chemical composition of Teide's fumaroles changed significantly, confirming a deep perturbation of the Teide hydrothermal-magmatic system (Melián et al. 2012).

From April 2004, a change in location of the epicenters of the earthquakes took place and they concentrated mainly in the northwestern sector of the island. Almendros et al. (2007) reported that this new scenario resulted from a deep magma injection beneath the west flank of Teide-Pico-Viejo. Domínguez et al. (2011) agreed with this hypothesis and proposed a model of a single magma intrusion affecting the central part of the island with lateral dikes driven along the rifts to the northwest and southwest. The magmatic processes that have occurred throughout the geologic history of the NWR zone have been always related to the intrusion of mafic dykes. Although no intrusions have been inferred in the area through geodetic studies (Sagiya et al. 2007), several studies have confirmed that dykes do not usually reach the surface, and in 90% of cases, they are arrested at depth (Gudmundsson and Brenner 2004). In fact, these studies suggest that the different properties of rocks in a rift zone encourage dyke arrest and that several intrusions have to occur before the stress field is homogenized and a new intrusion can reach the surface and cause an eruption.

The variability observed in total CO_2 emission from the NWR zone of Tenerife from 2004 to 2006 is well explained in terms of strain-stress changes in response to earthquakes related to intrusion of mafic dykes, which affected the volcanic-hydrothermal system and release of gases and other volatiles from the rising basaltic magma. Changes in diffuse gas emission have been observed in other volcanic areas in relation to periods of seismic and/or volcanic unrest. At Usu volcano (Japan), an increase in diffuse CO_2 emission rate was registered 6 months before the March 2000 eruption, and decreased quickly after the eruption (Hernández et al. 2001). In Cerro Negro volcano (Nicaragua), the same process was observed, with a high CO_2 emission during the eruptive period (August 1999) and low CO_2 emissions during the surveys carried out in 2002–2006, clearly located in an inter-eruptive period (Salazar et al. 2001). The quick changes registered in the soil CO_2 efflux values and their spatial distribution in the NWR zone in 2004 and 2005 suggest an increase in vertical permeability triggered by strain-stress changes in the subsurface related to movement of magma and related fluids. Temporal variations in diffuse CO_2 output are related to changes in the soil CO_2 efflux, which correspond to changes in both background and peak populations. Considering these observations and the seismic data, it is likely that the intrusion of a dyke/s at deep levels in the NWR Zone caused the 2004 volcanic unrest in Tenerife and the observed geochemical anomalies in diffuse CO_2 emission at the NWR zone of Tenerife.

Conclusions

The data presented here show that the increased seismicity episodes registered in and around Tenerife Island between 2004 and 2005, 2010–2011, and 2016 were preceded by geochemical anomalies produced by an increasing release to the surface of soil CO_2 at the NWR zone. The first anomaly was recorded between October 2004 and March 2006 coinciding with the highest measured diffuse CO_2 emission (October 2005; 876 t day^{-1}) and preceding an earthquake of M 4.0 registered in November 2005. The second anomaly occurred in February 2008, with maximum value of 476 t day^{-1}, and before anomalous seismicity was registered between 2010 and 2011. The third anomaly occurred in 2015, 1 year before the increased seismicity observed in and around Tenerife Island during 2016. These anomalous periods in the diffuse CO_2 emission suggest the occurrence of subsurface magma degassing and magmatic fluid injection, perhaps due to strain-stress changes beneath the NWR zone.

The diffuse CO_2 emissions, and the isotopic composition of soil CO_2, indicate different contributions to this gas released from NWR zone. Biological processes such as degradation of organic matter seem be the main source of CO_2 to the observed surficial effluxes at the NWR zone during the study period, although a slight contribution of deep-seated CO_2 cannot be neglected. This endogenous CO_2 is mainly diffusively released at several sites along the central and north sector of NWR zone.

The recorded data demonstrate the importance of measuring these parameters to identify and evaluate changes in volcanic activity and allowed us to define background levels for NWR zone of Tenerife and to establish thresholds useful for future monitoring. Regular surveys of soil CO_2 efflux seem to be an effective geochemical surveillance tool at the NWR zone of Tenerife Island, able to detect changes in the CO_2 emission rate that might presage future episodes of volcanic unrest.

Acknowledgements This research was financially supported by (i) project MAKAVOL from MAC 2007–2013 Transnational Cooperation Program of the European Union, (ii) projects ALERTA and ALERTA II from INTERREG IIIB Azores-Canaries-Madeira, (iii) project CGL2005-07509 from the Spanish Ministry of Science and Technology, (iv) Canary Islands Government Research Agency, ACIISI (SolSubC200801000385), and (v) the Cabildo Insular de Tenerife (Spain). We thank a significant number of undergraduate students from The University of La Laguna for their enthusiastic collaboration during fieldworks. We also want to thank to Civil Protection of Santa Cruz de Tenerife for providing two vehicles during the soil gas surveys performed in 2004 as well as municipal governments of the northwestern side of Tenerife Island (La Guancha, Garachico, El Tanque, Santiago del Teide and Guía de Isora) for their logistic collaboration. The comments and critical reviews provided by two anonymous reviewers as well as by Luca D'Auria and James D.L. White have significantly improved the quality of this paper.

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