FACULTAD DE CIENCIAS DEL MAR

UNIVERSIDAD DE LAS PALMAS DE GRAN CANARIA

STUDY OF DISSOLVED OXYGEN ANOMALIES DURING THE ERUPTIVE STAGE OF THE SUBMARINE VOLCANO TAGORO, EL HIERRO ISLAND

Izar Callery Arranz

Curso 2016/2017

Dr. Eugenio Fraile Nuez

Prof. Dra. J. Magdalena Santana Casiano

Trabajo Fin de Título para la obtención del título del Grado de Ciencias del Mar

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Student's personal information:

Izar Callery Arranz
Grado en Ciencias del Mar
Curso 2016/2017
Universidad de Las Palmas de Gran Canaria, Facultad de Ciencias del Mar
Study carried out through the VULCANO-II and BIMBACHE projects in The Spanish Institute of Oceanography (IEO)

Personal information of the tutor and co-tutor:

Prof. Dra. J. Magdalena Santana Casiano

Departamento de Química. Facultad de Ciencias del Mar. Universidad de Las Palmas de Gran Canaria

QUIMA - Instituto Universitario de Oceanografía y Cambio Global (IOCAG)

Dr. Eugenio Fraile Nuez

Instituto Español de Oceanografía (IEO), Centro Oceanográfico de Canarias Santa Cruz Tenerife.

05/07/2017

Izar Callery Arranz

Tutora Académica: J. Magdalena Santana Casiano

Tutor de empresa: Eugenio Fraile Nuez

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1 ABSTRACT

The eruptive process that took place in October 10th 2011 at the island of El Hierro (Canary Islands), gave rise to the novel submarine volcano Tagoro, at 1.8 km south of the island of El Hierro in the marine reserve of "El Mar de las Calmas" (Canary Islands). In order to monitor the impact of the eruption on the marine ecosystem, several multidisciplinary oceanographic cruises were carried out in the affected area. Here we present a detailed study of the dissolved oxygen parameter with data collected in two oceanographic cruises during the eruptive stage. The findings highlight how the emission of reduced species produced by the submarine volcano Tagoro during the eruptive stage generated dissolved oxygen concentrations close to anoxic levels. Maximum oxygen depletion of 86.2% and 92.4% were found in Leg3 and Leg5 cruises respectively. These perturbations affect not only the marine reserve off El Hierro Island but also affect further areas, as it is transported by local currents to the north of the island producing a depletion of 17.7%. Moreover, our results show a volcanic plume with low dissolve oxygen concentration being trapped and transported by an anticyclonic eddy for tens of kilometres (oxygen depletion of approximately 5%). Finally, the Apparent Oxygen Utilization (AOU) parameter by definition should not be taken into account regarding submarine volcanic areas and the interpretation of this parameter should be made with caution.

Keywords: dissolved oxygen; hydrothermal vent; submarine volcano; Tagoro submarine volcano.

2 MOTIVATION

Low dissolved oxygen concentrations in open marine environments are mostly located close to Oxygen Minimum Zones (OMZs). While these areas are well studied, oxygen concentration anomalies caused by submarine volcanic eruption are poorly documented. It's rare appearance makes submarine volcanoes a unique opportunity for science to study how these systems can modify one of the most primordial marine environment variable in the ocean. During the eruptive stage of the submarine volcano Tagoro, very low dissolved oxygen concentrations were measured causing anoxia phenomena. This brought changes in the marine biota in an area of vital importance, "El Mar de las Calmas" marine reserve located at southwest of El Hierro Island.

This way, the study of the variability of dissolved oxygen, affected by an underwater volcanic eruption, will provide the possibility to describe and quantify how this parameter varies and how local currents can transport its perturbation or even interact with mesoscale structures such as anticyclonic eddies.

3 BACKGROUND

The past 10th of October 2011, a shallow submarine volcano (Tagoro) gave rise as a consequence of an underwater eruption located at 1.8 km off-shore of the southern coast of El Hierro Island, the westernmost and youngest island of the Canary Archipelago (Atlantic Ocean). During the eruption, large quantities of mantle-derived gases, solutes and heat were released into the surrounding waters (Fraile-Nuez et al., 2012). Under those circumstances, the material emitted reacts with the seawater and consequently important physical-chemical changes took place in the water column.

Many investigations have been carried out since July 2011 where an unusual seismic activity was recorded at the seismic stations deployed by the National Geographical Institute (IGN) in El Hierro (Fraile-Nuez, et al., 2012; Santana-Casiano et al., 2013), suggesting the outset of volcanic unrest. In order to being able to study the impact of the physical-chemical anomalies produced by the submarine volcano Tagoro on the marine environment, more than 23 multidisciplinary oceanographic cruises have been performed since the volcanic activity started.

Extreme physical-chemical perturbations caused by this event were shown in the whole water column (Fraile-Nuez et al., 2012). CTD measurements revealed maximum temperature anomalies of +18.8ºC obove the crater at 210 m depth. In the same study, water acidification up to 2.8 units within the first 100 m depth and 2 km from the volcano due to the high CO_2 release is measured. On November 17th, maximum values of 476 µmol/kg and 50 µmol/kg of dissolved reduced sulphur species and Fe(II) respectively, were observed close to the volcano at a depth of 75 m (Santana-Casiano et al., 2013). In the same study, in November 5th and 16th, patches of anoxia at 100 m depth were determined in the volcanically affected area. According to Fraile- Nuez et al. (2012), the most affected part of the water column was the layer from 75 m to 125 m depth, which experienced oxygen depletion near to anoxic levels.

4 INTRODUCTION

Changes in the oceanic content of dissolved oxygen have increasingly gained attention in recent years (Stendardo et al., 2015). Oxygen has been identified as a very sensitive indicator of both, physical and biological change in the ocean (Joos et al., 2003). Low dissolved oxygen concentrations in worldwide marine environments are known to be located mainly within the Oxygen Minimum Zones (OMZs). The horizontal distribution of oxygen shows major large-scale open ocean subsurface OMZs in the eastern parts of the Tropical Atlantic and Pacific oceans as well as in the northern Indian Ocean (Brandt et al., 2015). As described by Stramma et al. (2008), these layers with particularly low oxygen concentrations have lower concentrations in the Pacific, were suboxic concentrations are found (oxygen content falls below 4.5 µmol/kg), than in the Atlantic, were hypoxic concentrations are found (range >4.5 and < about 80 µmol/kg). While OMZs are well documented (e.g., Brandt et al., 2015; Fischer et al., 2013; Stramma et al., 2008; Stramma et al., 2009), dissolved oxygen anomalies caused by a submarine volcanic eruption is poorly studied.

Moreover, oceanic oxygen distribution is generally characterised by slightly supersaturated oxygen levels in the surface layer, an intermediate oxygen minimum, and higher oxygen levels at depth (Brandt et al., 2015). This vertical structure is a consequence of the delicate balance between the supply of oxygen through ventilation and circulation, oxygen production by photosynthesis, and oxygen consumption by remineralisation of sinking organic matter (Brandt et al., 2015). Changes in these primary drivers have been the main responsible for the evident global O_2 decline after the 1980s (Ito et al., 2017). Submarine volcanoes are also known to contribute to oxygen concentration decline (e.g. Vogt, 1989; Erba, 1994; Leckie et al., 1998, 2002; Stetter, 1982). Oxygen depletion up to anoxic levels in volcanically affected areas are observed over the years (e. g. Kilias et al., 2013; Malahoff et al., 2006; Resing et al., 2009). The impact of submarine volcanic eruptions and associated hydrothermal activity is a mechanism for ocean anoxia that has received special attention (Snow, et al., 2005).

In this term, is well known that hydrothermal vents affect the chemical composition of seawater (Resing et al., 2015). Submarine volcanoes inject large amounts of material of variable size, texture and chemical composition into the oceans (Mantas et al., 2011). Their emissions react with seawater leading to important physicals-chemical anomalies that may strongly impact the marine ecosystem (Resing et al., 2009). Moreover, the emission of reduced species, contribute to the decrease in the amount of dissolved oxygen in the system (Santana-Casiano et al., 2013). One of the reasons why this occurs it's because, after a hydrothermal emission, Fe (II) is oxidized under the presence of dissolved oxygen (Santana-González et al., 2017), making oxygen consumption a consequence. Dissolved oxygen present in seawater is also necessary for the oxidation of sulphide by sulphur-oxidizing bacteria, found in hydrothermal vents (Ruby et al., 1982). Oxygen consumption after a hydrothermal emission can be such, that oxygen levels in hydrothermal effluents decrease from normal ocean bottom water values to zero at the still warm temperature of <20ºC (Jannasch and Mottl, 1985; Edmond et al. 1979).

Here we present a complete study of quantification, distribution and transportation of dissolved oxygen anomalies caused by the emission of the submarine volcano Tagoro at the island of El Hierro. The phenomenon was analysed during the eruptive stage of the volcanic activity. After a compressed introduction of the study, the data and methods used for the quantification, distribution and transportation of dissolved oxygen anomalies are described. Afterwards, the results obtained are presented, followed by the discussion and conclusions to which have been reached.

5 DATA AND METHODS

5.1 Study location and cruises

The present study was carried out around the area of the submarine volcano Tagoro at El Hierro Island (Canary Islands, Spain, at 27º37'07''N – 017º59'28''W, Fig. 1-A). For this study, data from two different cruises were used, Bimbache_leg3 (Nov. 4^{th}-09^{th} 2011) at the southern area of El Hierro Island, and Bimbache_leg5 (Nov. 16^{th}-20^{th} 2011) focused on the northern area of the island but also with several stations at the vicinity of the submarine volcano Tagoro (Fig. 1-B). Both cruises were accomplished on board of R/V *Ramón Margalef*, from the Spanish Institute of Oceanography (IEO). Hereafter, Bimbache_leg3 and Bimbache_leg5 are going to be called Leg3 and Leg5 respectively.

Study of dissolved oxygen anomalies during the eruptive stage of the submarine volcano Tagoro, El Hierro Island

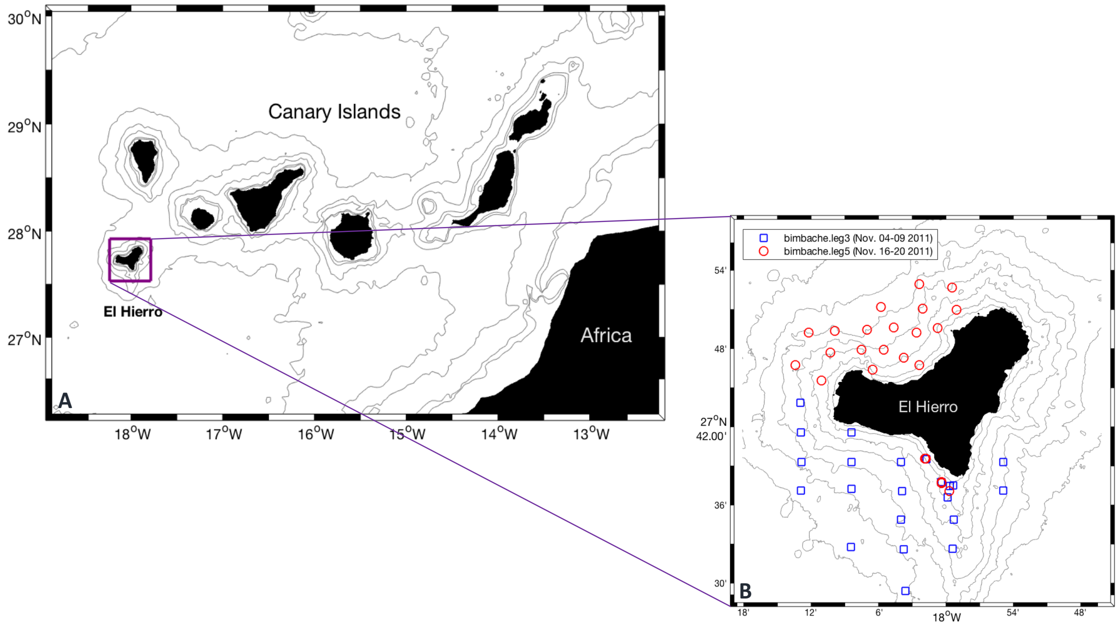

Figure 1. Study location and cruises. (A) Location of El Hierro Island within the Canary Archipelago. (B) El Hierro Island and the stations sampled during Leg3 (blue squares) and Leg5 (red circles) cruises.

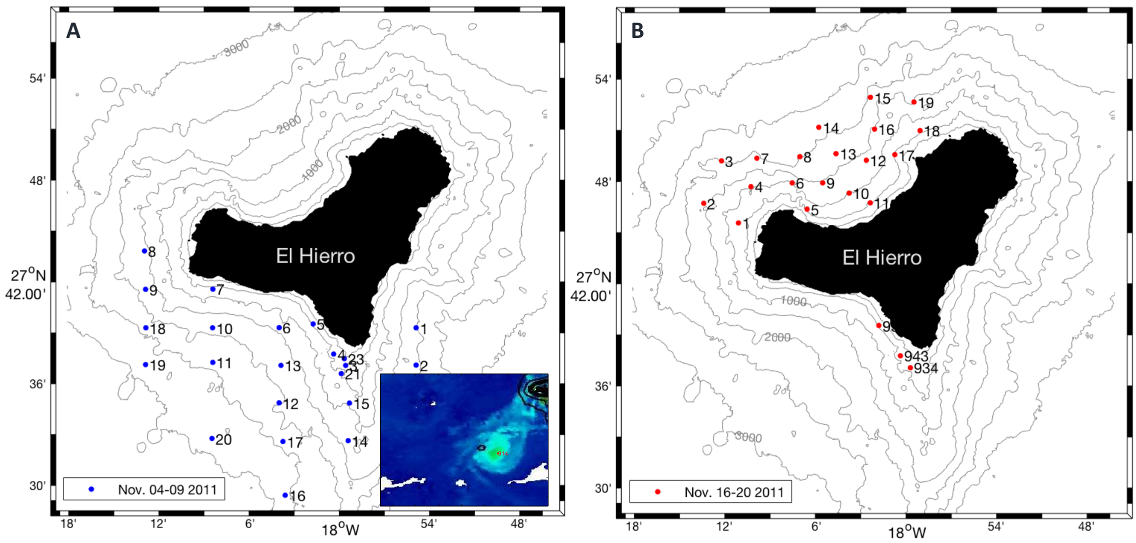

Figure 2. El Hierro Island and the CTD stations carried out through the study. (A) Location of the CTD stations sampled from November 4th-9th (2011) during Leg3 cruise at the southern area of El Hierro Island. The inset map shows the location of St. 914 together with the chlorophyll concentration on November 6th, 2011. Image acquired by NASA Terra MODIS and processed by the Marinemet project. (B) Location of the CTD stations sampled from November 16th-20th (2011) during Leg5 cruise in the northwest and the south of El Hierro Island.

5.2 Hydrography

Vertical profiles of conductivity, temperature and pressure were collected using a SeaBird 911-plus CTD equipped with dual conductivity and temperature sensors. A SBE43 dissolved oxygen sensor and a ECO FL fluorescence sensor were coupled to the CTD. The system collets data in a continuous mode at 24 Hz (24 samples per second), giving us a high vertical resolution. Sensors were calibrated at the SeaBird laboratory before the cruises. The accuracy of the temperature, conductivity and oxygen sensors are 0.001 °C, 0.0003 S/m and ± 2% of saturation, respectively. Water samples with a 24–10L bottle carousel were carried out at 24 stations for Leg3 and 25 stations for Leg5 for the measurements of dissolved oxygen concentrations at specific depths (see Fig. 2).

5.3 Bathymetry

Two datasets of bathymetry were used to generate maps in this study, Topo15.1, created by Smith and Sandwell (1997) to perform the overview of El Hierro (Fig. 1-A) and a multi-beam bathymetry dataset obtained during one of the last cruises carried out in the area (Vulcano_0316) used to produce detailed maps of the bathymetry of the volcano (Fig. 1B-2). The bathymetric data of the monitoring cruise was acquired using a Konsberg Simrad EM-710 echosounder, which operates at sonar frequencies in the 70 to 100 kHz range, the data was processed with CARIS HIPS and SIPS and yields a bathymetric grid resolution of 1 m with 100% coverage.

5.4 Dissolved Oxygen

Dissolved oxygen samples collected by niskin bottles at different depths were measured using a modification of the original Winkler method (Winkler, 1888; Carpenter, 1965). Oxygen determination was measured on board in the wet laboratory. Samples from Leg3 were processed manually, while during Leg5 cruise, samples were analysed using an automated potentiometric titrate. Results are giving in µmol/kg of seawater.

5.5 Dissolved oxygen calibration

Through scatter function in Matlab, dissolved oxygen concentrations given by the SBE 43 sensor and dissolved oxygen concentrations of the niskin water samples are compared in order to obtain the best linear approximation by least-squares.

Once all the data is represented and the regression line is obtained, a confidence level is generated to expose the data belonging to the outlier. The regression line is defined as the line that best fits the square minimum at all points. The confidence level is defined as the percentage of data that adapts to the least-squares regression line.

The values in the outlier correspond to data that for some reason (SBE43 sensor error, miscalculation Winkler method, etc.) is faulty and has a value numerically distant to the rest. Therefore, outlier data should not be taken into account for calibration.

In order to obtain a good calibration, a R^2 as close to the value of 1 as possible must be obtained. Once outlier data is left aside, the value of R^2 increases and the calculation of the equation of the regression line can be performed. Once the values of the slope (a) and the value intersecting the y coordenate (b) of the regression line equation are obtained (y=ax+b), the calibration of dissolved oxygen concentrations for the SBE 43 sensor can be executed.

5.6 Differential Oxygen Anomaly (DOA)

The Differential Oxygen Anomaly (DOA) calculation allows to study the differences between the dissolved oxygen concentration values affected by the perturbation caused by the submarine volcano against the non-affected ones providing the quantification of the deoxygenation of the water mass (Simpson et al., 1984; Simpson and Lynn, 1990). The non-affected values correspond to stations with no perturbation in the dissolved oxygen field (reference St.).

5.7 Apparent Oxygen Utilization (AOU)

The Apparent Oxygen Utilization (AOU) is determined as the difference between the dissolved oxygen concentration in equilibrium with the atmosphere corrected to its value at the salinity, temperature, and pressure where the water samples were taken and the measured dissolved oxygen concentration. Dissolved oxygen values for seawater (saturated value) where obtained using Benson and Krause (1984) equation.

5.8 Matlab

All data is analysed and processed in the numerical computing and programming language Matlab (version R2016a). Several Toolbox and functions have been used to be able to perform the analyses mentioned. The toolbox used for the development of this project includes UNESCO seawater library and M_Map. The UNESCO seawater library toolbox (Version 3.3, 22/Sep/2010) was written by Phil Morgan and Lindsay Pender from CSIRO. The M_Map package (Version 1.3, 20/Dec/1998) is a mapping toolbox written for Matlab v5 generated by Rich Pawlowicz. This toolbox includes routines to project data in 18 different spherical projections, a grid generation routine, a coastline database, a global elevation database and the possibility to hook into freely available high-resolution coastlines and bathymetry/topography.

6 RESULTS

6.1 Oxygen calibration

In this study, dissolved oxygen data is gathered in two different ways, through the niskin bottles of the rosette and by a SBE43 dissolved oxygen sensor. Samples collected by the niskin bottles are more accurate and are collected at specific depths, while data gathered by SBE43 sensor is collected in a continuous mode vertically. In order to study the water column with the highest resolution possible, the continuous variable should be adjusted with the more precise variable. Therefore, in order to keep the data supplied by the sensor, we must calibrate this data with the one provided by the niskin bottles.

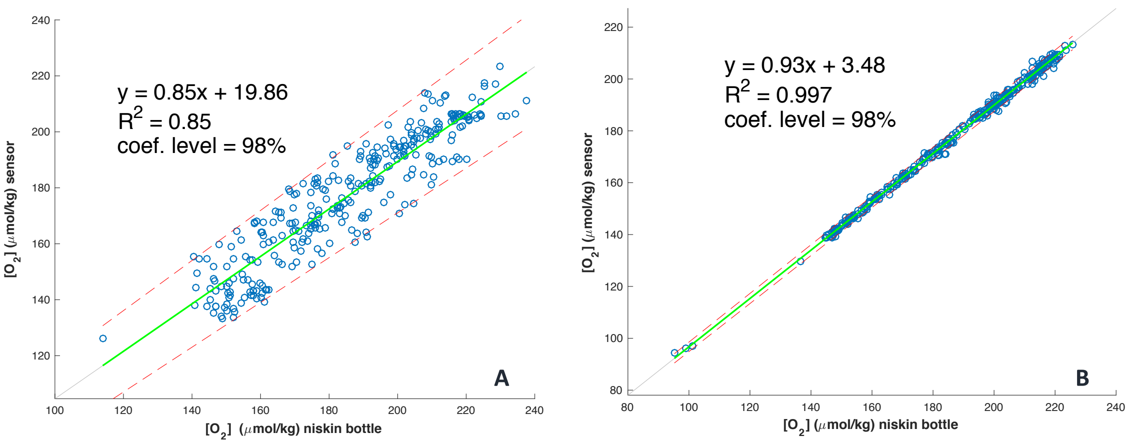

Figure 3. Comparison of dissolved oxygen concentration data of niskin bottles versus continuous data provided by the SBE43 dissolved oxygen sensor for Leg3 (A) and Leg5 (B) oceanographic cruises. Straight green line refers to the regression line. Red discontinuous line shows the confidence level for each oceanographic cruises at 98%. In both graphs the respective regression line equation and R^2 is shown.

Figure 3 shows the comparison of the dissolved oxygen concentration data of niskin bottles versus continuous data provided by the SBE43 dissolved oxygen sensor for both oceanographic cruises (Leg3 and Leg5, Fig. 3-A and Fig. 3-B respectively). A regression line using least squares that better fits to the data together with its confidence level interval were represented to obtain the regression line equation and R^2. The result obtained for the regression line equation that corresponds to Leg3 is y=0.85x+19.86 (Fig. 3-A). The R^2 obtained for this calibration is 0.85. On the other hand, the equation of the regression line that corresponds to the Leg5 cruise is y=0.93x+3.48 (Fig. 3-B). This second cruise has a R^2 of 0.997. Knowing that the value obtained for R^2 depends on how good the agreement between both data sets is, we can observe how the R^2 obtained for Leg5 is more adequate than the one in Leg3. The percentage of data used for the Leg3 cruise is 85.5%. The percentage of data used for Leg5 cruise is higher, 91.8%. These differences might be due to the fact that during the Leg3 cruise oxygen data was processed by manual techniques totally visualized by an observer, while in Leg5 cruise, data was processed using an automatized method by a potentiometric titration. In both regressions, the confidence level is 98%.

Hereafter, all figures performed and results obtained have been carried out with the corrected dissolved oxygen concentration values obtained from the sensor after the calibration.

6.2 Vertical dissolved oxygen concentration profiles

In order to study how dissolved oxygen concentrations are affected by the perturbation caused by the submarine volcanic eruption, vertical profiles have been performed (Fig. 4).

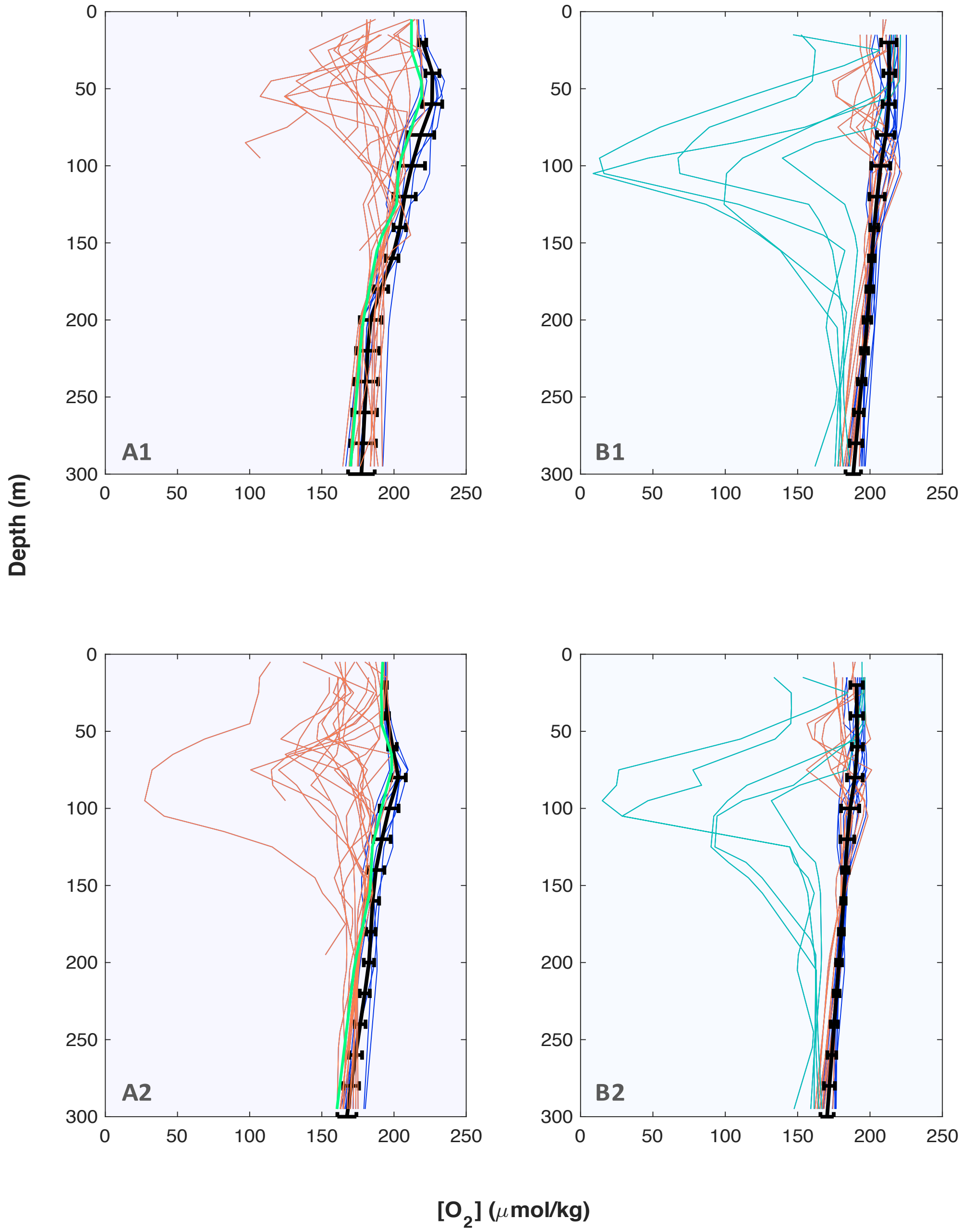

Figure 4. Vertical profiles of dissolved oxygen concentrations of Leg3 (A) and Leg5 (B) cruises. A1 and B1 refer to dissolved oxygen concentrations of niskin bottles. A2 and B2 refer to dissolved oxygen concentrations of calibrated SBE43 sensor. Black bolted line shows the mean profile of non-affected stations with its correspondent standard deviation. Green line in (A) subplots represent St. 914 located 90 km southwards from the island of El Hierro. Light blue lines in B1 and B2 refer to stations located over Tagoro in Leg5 cruise.

Figure 4 shows vertical profiles of dissolved oxygen concentrations of Leg3 (Fig. 4-A) and Leg5 (Fig. 4-B) oceanographic cruises. Vertical profiles of dissolved oxygen concentrations obtained by punctual samples of niskin bottles are shown in figures 4-A1 and 4-B1. By contrast, vertical profiles of dissolved oxygen concentrations obtained by SBE43 sensor are shown in figures 4-A2 and 4-B2. The reference stations or stations with a vertical distribution of dissolved oxygen concentrations non-affected by the perturbation of the submarine volcano Tagoro, are shown in dark blue. A mean profile of dissolved oxygen concentration for the unaffected stations was obtained along with it's correspondent standard deviation for each cruise (black bolted line). The reference stations for Leg3 cruise are St. 2, 8, 9, 18 and 19. However, St. 9, 10, 11, 12 13, 14, 16, 17, 18 and 19 are the ones used as reference stations for Leg5 cruise. Stations affected by perturbation are indicated in red. In figures 4-A1 and 4-A2, St. 914 of Leg3 cruise, located 90 km southward of the El Hierro Islands coast, is shown in green coloured line. Stations located in the vicinity of the Tagoro submarine volcano during the Leg5 cruise are shown in light blue lines in figures 4-B.

Figure 4-A2 shows how dissolved oxygen concentrations manifested a perturbation with respect to the mean reference profile in the first 200 m approximately. The lowest dissolved oxygen concentration shown in this figure is a value of 30.5 µmol/kg. For stations located north westwards of El Hierro Island (Fig. 4-B2), the perturbation in the dissolved oxygen concentrations by Tagoro submarine volcano is also observed within the first 100 m depth of the water column (red lines). The lowest dissolved oxygen concentration for these stations is 174.9 µmol/kg. Stations located in the vicinity of the submarine volcano in Leg5 cruise show high perturbation in the oxygen parameter from the surface to approximately 300 m depth. The lowest dissolved oxygen concentration caused exclusively by the volcanic disturbance in this area is quantified as 15.02 µmol/kg.

Both figures (Fig. 4-A2,B2) show perturbation on stations near the submarine volcano Tagoro within the surface and 150 m depth. However, stations located north-westwards of El Hierro Island in Leg5 cruise, present also a significant perturbation in the dissolved oxygen parameter that might be due to the transportation of the physical-chemical perturbation generated by the submarine volcano caused by local currents (Fig. 5).

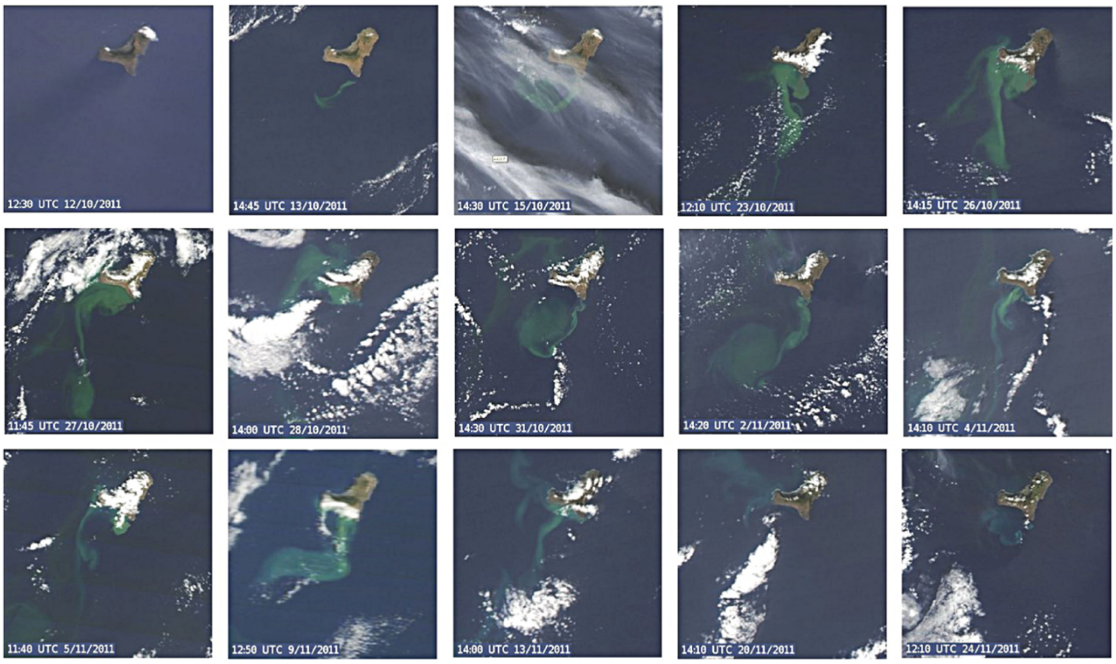

Figure 5. NASA MODIS RGB multitemporal images monitoring El Hierro's submarine volcano (October–November, 2011; Eugenio et al., 2014).

The satellite images sequence in figure 5 shows the evolution of the disturbance generated by the eruption of the submarine volcano Tagoro from the 12th of October to 24th of December 2011. A plume of anomaly extends from the eruption area towards the northwest and the southwest of El Hierro Island by local currents and mesoescale activity.

6.3 Dissolved oxygen concentration contours

By performing contours of dissolved oxygen concentrations, we have the possibility of quantifying this variable, and hence, the results obtained can be studied and interpreted. Figure 6 shows two dissolved oxygen concentration vertical contours versus distance for specific transects of Leg3 and Leg5 oceanographic cruises.

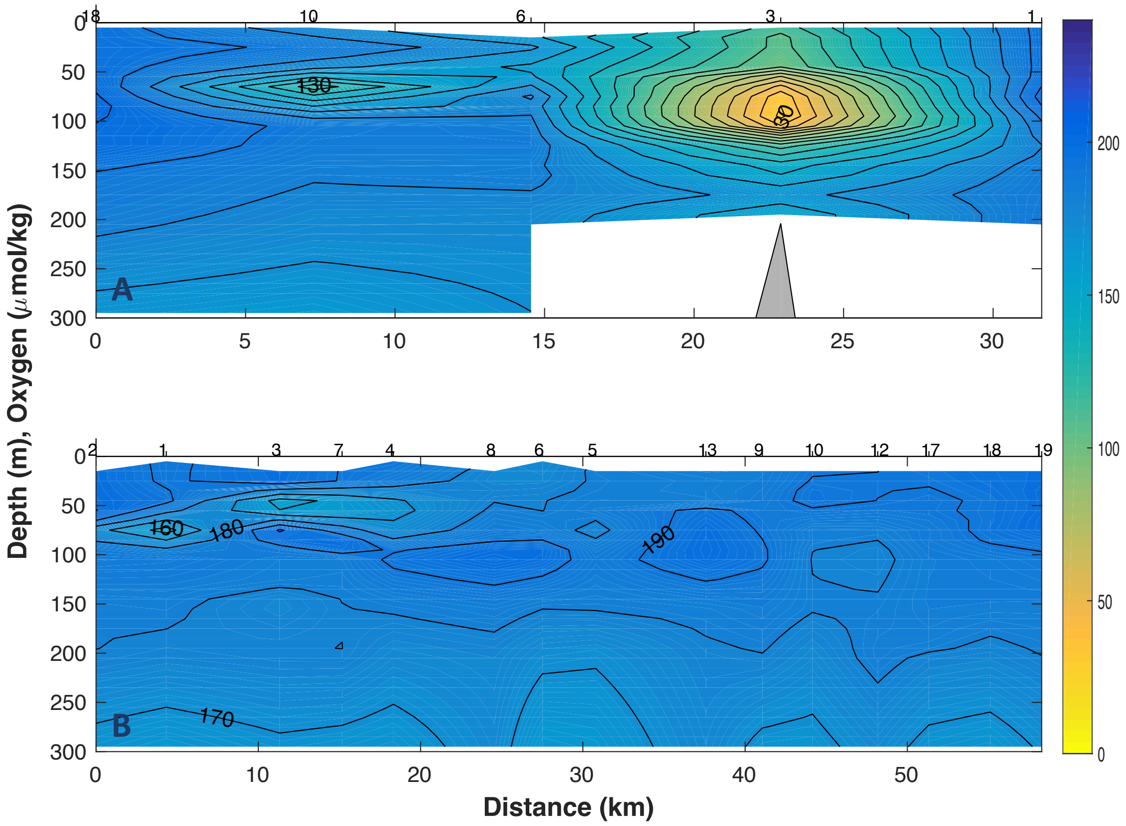

Figure 6. Vertical contours of dissolved oxygen concentration versus distance from specific transects of Leg3 (A) and Leg5 (B).

Figure 6-A corresponds to Leg3 cruise carried out in the south of El Hierro Island. The stations that correspond to this specific transect are St. 18, 10, 6, 3 and 1 (see Fig. 2-A), which trace a line from the west of the island of El Hierro towards the east, passing over Tagoro (St. 3). Figure 6-A shows a large plume centred between the surface to approximately 150 m depth that covers practically the whole distance of the transect (25 km). Within this plume, it is observed how there are two differentiated nuclei, of which the one with lowest concentration (27.3 µmol/kg, see Table 1) is just above the submarine volcano (St. 3) at approximately 95 m depth. Further westwards at St. 10, at a depth of 65 m, lies a second nucleus. The concentration of dissolved oxygen found in this nucleus is 124.62 µmol/kg.

Figure 6-B shows a specific contour of Leg5 cruise. As in the previous case, the contour shows a plume that expands from the north-western part of the island towards the north with an extension of approximately 20 km. The stations that form part of this contour are St. 2, 1, 3, 7, 4, 8, 6, 5, 13, 9, 10, 12, 17, 18 and 19 (see Fig. 2-

B). In comparison to the dissolved oxygen concentrations obtained for Leg3 cruise, those of Leg5 are significantly smaller. The first differentiated nucleus, with the lowest dissolved oxygen concentration, is located around St. 1 at approximately 75 m depth. This nucleus has a dissolved oxygen concentration of 156.5 µmol/kg (Table 1). Under St. 3, at a depth of approximately 47 m, there is a second nucleus with a concentration value of 156.08 µmol/kg.

Table 1 Dissolved oxygen concentration statistics (Mean, standard deviation, maximum and minimum) for Leg3 and Leg5 cruises.

Cruise	Location study area	Date	$[O_2]$ mean (µmol/kg)	Std. (µmol/kg)	Max. $[O_2]$ (µmol/kg)	Min. $[O_2]$ (µmol/kg)	Depth min. $[O_2]$	St. number min. $[O_2]$
Leg3	south	Nov. 4th-9th 2011	161.12	17.8	209.8	27.3	95	3
Leg5	south	Nov. 16th-20th 2011	149.05	32.8	196.65	15.03	95	943
	north		180.12	7.92	201.15	156.5	75	1

6.4 Differential oxygen anomaly (DOA) contours

DOA offers the possibility to study and quantify dissolved oxygen anomalies in the study area. The calculation of DOA helps to study how dissolved oxygen concentrations have been perturbed by the eruption of the submarine volcano Tagoro and how this perturbation has spread.

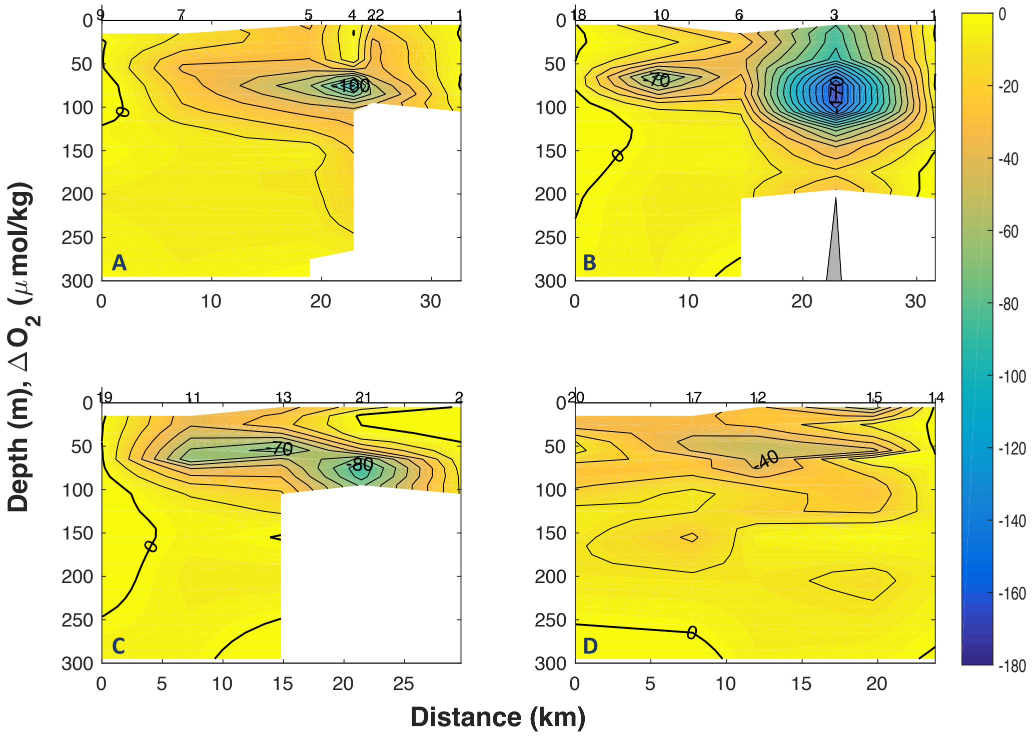

Figure 7. Vertical contours of differential oxygen anonalies (DOA) versus distance were represented for Leg3 cruise in 4 different zonal transects (A-D) from north to south (see Fig. 2-A).

Figure 7 shows four vertical zonal contours of DOA versus distance at four different transects of Leg3 cruise. The contour sequence is distributed from the north to the south (Fig. 7A-D) covering the entire study area. Figure 7-A presents a differentiated nucleus at St. 4, at a depth of 75 m. In contrast, in the second contour (Fig. 7-B) there are two differentiated nuclei. These nuclei are located between 50 m and 120 m depth, under St. 10 and 3. The nucleus located at St. 3 is the one with the lowest minimum DOA value (maximum anomaly of dissolved oxygen concentration) and with the greatest expansion of all the contours shown in Figure 7. The structure presented in figure 7-C has a similar shape to the ones observed in previous contours, but located at different stations (St. 11, 13 and 21) and with weaker DOA. The final contour (Fig. 7-D) shows the highest DOA value (minimum affection of dissolved oxygen concentration) of the four studied in figure 7, located at St. 17, 12 and 15, around 50 m depth.

Figure 8 shows similarities with Figure 7, four vertical zonal DOA contours versus distance are shown, which in this case correspond to the Leg5 oceanographic cruise. The sequence is distributed from the northwest towards the north (Fig. 8A-C). Figure 8-D presents a contour in the vicinity of the submarine volcano Tagoro, in the south of

El Hierro Island during the same cruise (Leg5). The entire northern and southern area of the island of El Hierro is studied with these transects (see Fig. 2-B).

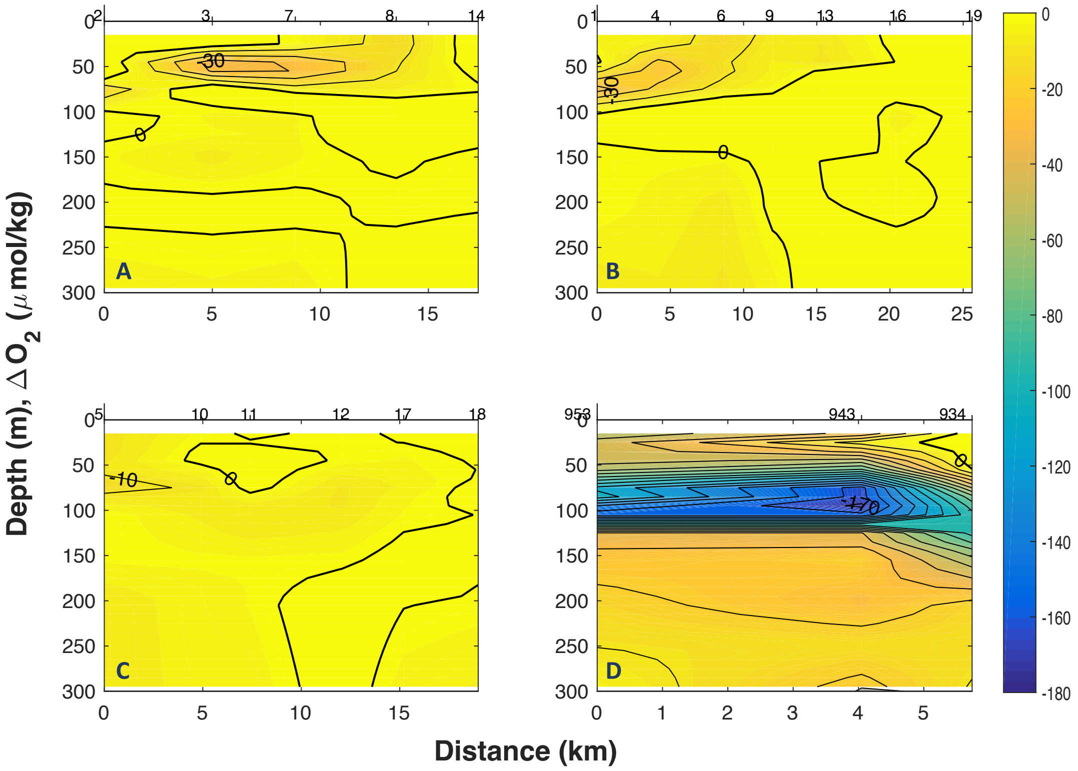

Figure 8. Vertical contours of differential oxygen anonalies (DOA) versus distance were represented for Leg5 in 4 different zonal transects (A-D).

Figure 8-A shows a north-eastward propagation of DOA with a single differentiated nucleus between St. 3 and 7 at a depth of approximately 50 m. Figure 8-B shows the lowest value of DOA of the northern area at St. 1 (around 75 m depth) representing the maximum anomaly of the dissolved oxygen parameter. Figure 8-C presents the nucleus with highest DOA of figure 8. This nucleus is located at St. 5 at depth of 75 m approximately. The contour shown in the last figure (Figure 8-D) shows the lowest values of DOA shown in figure 8 (maximum anomaly of dissolved oxygen concentration). This anomaly is concentrated at St. 943, at a depth of 95 m.

Figure 9 shows two DOA vertical contours versus distance of specific transects for both oceanographic cruises, Leg3 (Fig. 9-A) and Leg5 (Fig. 9-B). The stations that conform the transects in figure 9 are the same than the ones shown in figure 6 for the quantification of the dissolved oxygen concentration.

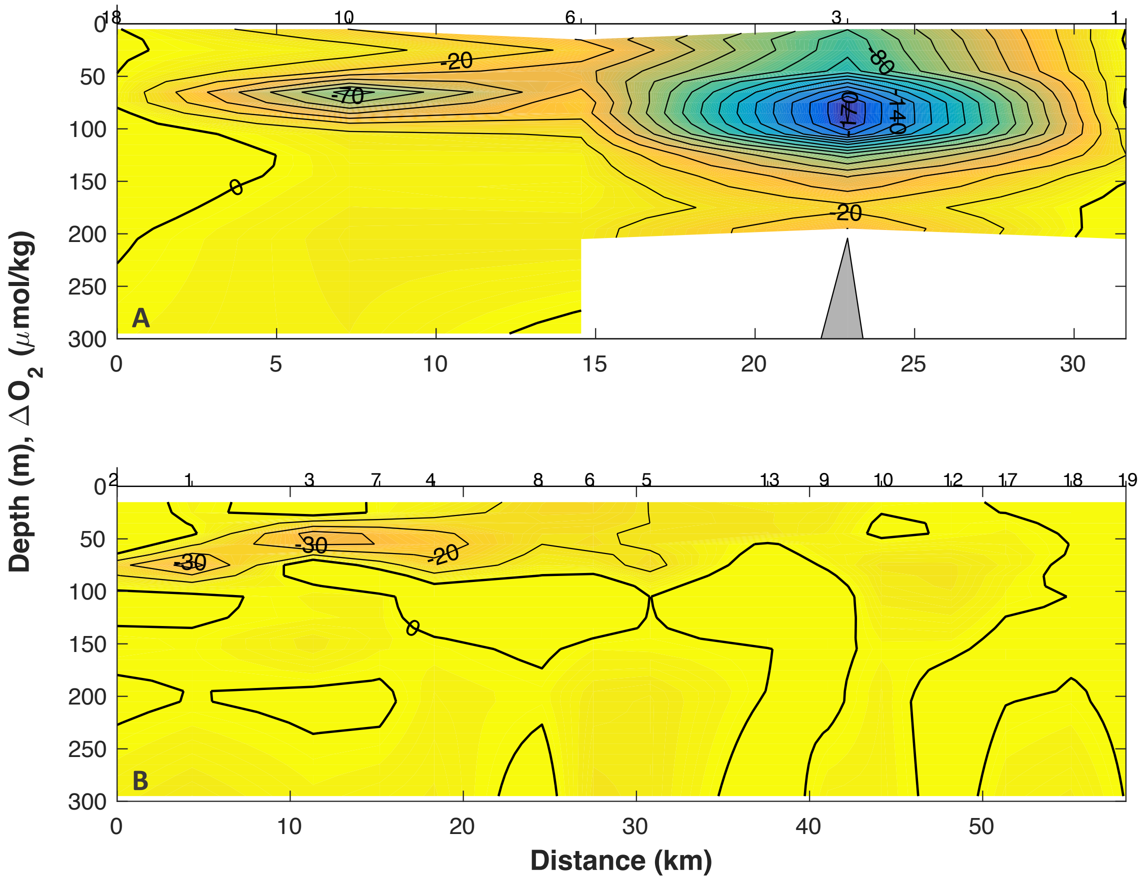

Figure 9. Vertical contours of differential oxygen anonalies (DOA) versus distance of specific zonal transects for Leg3 (A) and Leg5 (B) oceanographic cruises.

Figure 9-A presents a contour that corresponds to a specific transect of Leg3 cruise carried out at the southern area of El Hierro Island. A large plume of 25 km of extension that expands from the submarine volcano (St. 3) towards the west to St. 10 is shown. This plume, with low DOA values, expands from surface to 150 m depth. Within the plume, two differentiated nuclei are observed. The nucleus with lowest minimum DOA, maximum anomaly of dissolved oxygen concentration value (-170.9 µmol/kg, see Table 2), is located just above Tagoro at St. 3, at 95 m depth. The second nucleus located at St. 10 at a depth of 65 m, has a DOA value of -73.7 µmol/kg. The contour shown in figure 9-B corresponds to a specific transect of Leg5 oceanographic cruise. A plume with smaller extension is shown. As in the previous contour two differentiated nuclei are observed. This time the anomaly is concentrated from 20 m to 100 m depth. The nucleus with maximum anomaly of dissolved oxygen concentration (-34.3 µmol/kg, see Table 2) nucleus is found at St.1 at 75 m depth. The second nucleus is located at St. 3 and 7 at an approximate depth of 50 m, with a value of -34.2 µmol/kg.

Table 2. DOA statistics (Mean, standard deviation, minimum, mean oxygen concentration of the reference stations and maximum oxygen depletion percentage) for Leg3 and Leg5 cruises.

Cruise	Location study area	Date	DOA mean (µmol/kg)	Std. (µmol/kg)	Min. DOA (µmol/kg)	Depth min. DOA (m)	St. number min. DOA	Mean [O_2] of ref. St.*	Max. O_2 depletion %
Leg3	south	Nov. 4th-9th 2011	-22.15	18.43	-170.9	95	3	198.2	86.2
Leg5	south	Nov. 16th-20th 2011	-33.3	33.5	-171.9	95	943	198.2	92.4
	north		-1.96	5.15	-34.3	75	1	190.2	17.7

* The mean oxygen concentration of the reference stations is calculated at the same depth where the minimum DOA is found.

To be able to obtain the deoxygenation the submarine volcanic eruption has caused in each cruise, the maximum oxygen depletion percentage has been calculated. In the vicinity of the submarine volcano similar values are found for both cruises (86.2% for Leg3 and 92.4% for Leg5). Conversely, at the north-western area of El Hierro Island, an oxygen depletion of 17.7% is found in Leg5 cruise.

In order to visualize in detail, the DOA dispersion at a certain depth, horizontal contours have been performed. Figure 10 shows the localization of stations carried out during both oceanographic cruises along with a horizontal contour of the DOA affected area at 75 m depth.

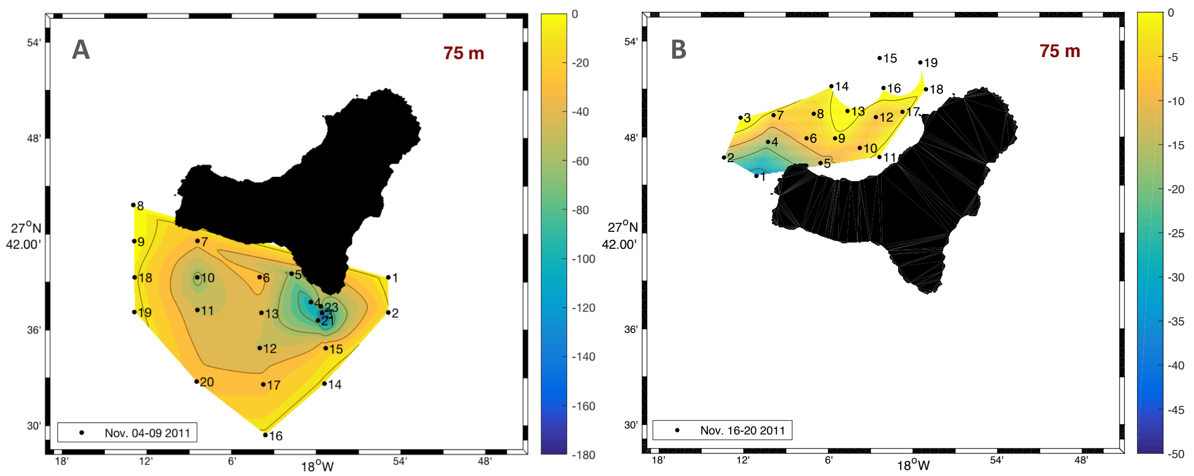

Figure 10. Horizontal contours of DOA affected area at 75 m depth for both oceanographic cruises, Leg3 (A) and Leg5 (B). Different scales are set for both cruises, [0:-180] for Leg3 and [0:-50] for Leg5.

Figure 10-A corresponds to Leg3 cruise. This figure shows how the lowest DOA values (maximum anomaly of dissolved oxygen concentration) at 75 m depth are located at stations just above the submarine volcano (St. 4, 23, 3 and 21). The anomaly expands towards the west, where low DOA values are also found at St. 10. Stations 10,

11, 13, 12, 5, 4, 3, 23 and 21 are the most affected by the anomaly at that depth. Figure 10-B corresponds to Leg5 cruise. It is observed how the lowest DOA value at 75 m depth is located at St. 1. An anomaly plume expands towards the north of the study area affecting mostly St. 2, 4 and 5. Other stations (St. 7, 8, 6, 9, 10, 12 and 17) are also affected but to a lesser degree.

6.5 Apparent Oxygen Utilization (AOU) contours

Another way of studying oxygen concentration distribution is by using the AOU parameter. Figure 11 shows two AOU vertical contours versus distance of specific transects for both oceanographic cruises, Leg3 (Fig. 11-A) and Leg5 (Fig. 11-B).

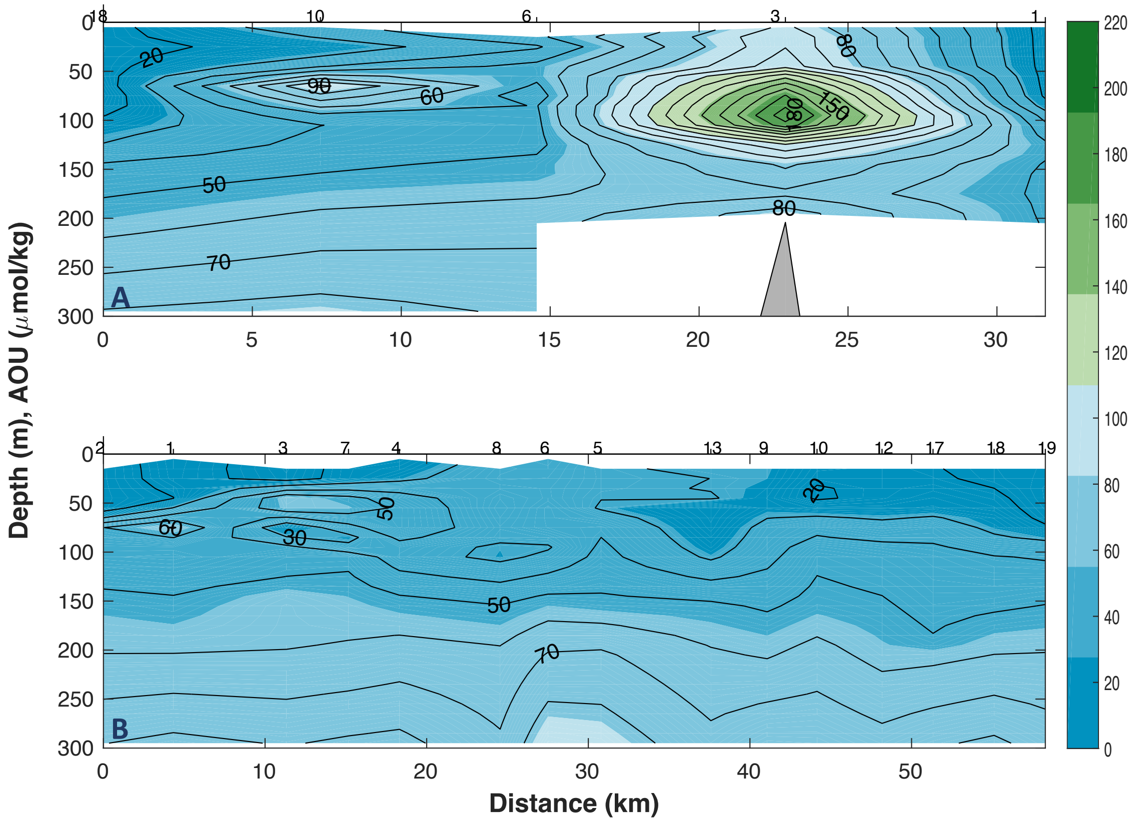

Figure 11. Vertical contours of Apparent Oxygen Utilization (AOU) versus distance of specific zonal transects from Leg3 (A) and Leg5 (B).

Figure 11-A shows a vertical contour that belongs to a specific transect of Leg3 oceanographic cruise. This contour draws a line from the southwest to the southeast of El Hierro Island. The stations that form this contour are the same as in figures 6-A and 9-A. Figure 11-A shows two differentiated nuclei with high AOU values that expands approximately along 25 km. The first nucleus is located just above the submarine volcano (St. 3), about 95 m depth. This nucleus presents the highest AOU

value, 186.6 µmol/kg (Table 3). The second nucleus is located towards the northwest of the previous nucleus, at a depth of approximately 65 m, at St. 10. The AOU value of this nucleus is 92.2 µmol/kg.

Figure 11-B shows a specific vertical contour from Leg5 cruise. The stations that form this contour (same as in Fig. 6-B and 9-B) cross the whole study area from northwest of El Hierro Island to the northernmost area. The contour shows an extension of approximately 20 km. The highest AOU values are found in two differentiated nuclei localised between 20 m and 100 m depth. The nucleus with greater AOU concentration (61 µmol/kg, see Table 3) is located in St. 1 at a depth of 75 m. Further north, at St. 3 and 7 at 50 m depth, the second differentiated nuclei is located with an AOU value of 58 µmol/kg.

Table 3. AOU statistics (Mean, standard deviation and maximum) for Leg3 and Leg5 cruises.

Cruise	Location study area	Date	AOU mean (µmol/kg)	Std. (µmol/kg)	Max. AOU (µmol/kg)	Depth max. AOU (m)	St. number max. AOU
Leg3	south	Nov. 4^{th}-9^{th} 2011	93.8	29.93	186.6	95	3
Leg5	south	Nov. 16^{th}-20^{th} 2011	82.7	36.4	211.65	95	943
	north		35.73	10.4	61	75	1

6.6 Fluorescence

In order to discard the possible effect of primary producers regarding the oxygen consumption, it is important to make an analysis of fluorescence in the same transects used for previous vertical contours (Fig. 6, 9 and 11). Figure 12 shows two fluorescence vertical contours versus distance of specific zonal transects for each cruise.

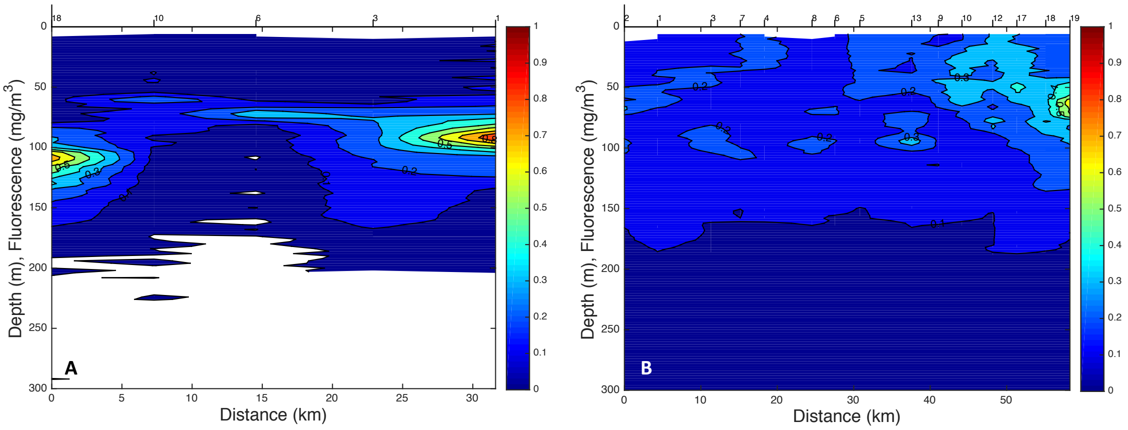

Figure 12. Vertical contours of fluorescence versus distance of specific zonal transects for Leg3 (A) and Leg5 (B) cruises.

Figure 12-A shows a fluorescence vertical contour that corresponds to a specific zonal transect of Leg3 cruise. Two differentiated fluorescence nuclei are shown. The nucleus with highest fluorescence value (>0.8 mg/m^3) is located at St. 1 at a depth of 100 m approximately. The second nucleus, located at St. 18 at 115 m depth, has the second maximum fluorescence concentration values (>0.7 mg/m^3). St. 1 and 18 coincide with the non-affected DOA and AOU stations. Conversely, at St. 10, 6 and 3 minimum or cero fluorescence concentrations are shown. These stations coincide with the ones where DOA and AOU anomalies are found.

Figure 12-B shows a vertical contour of fluorescence that corresponds to a specific zonal transect of Leg5 cruise. A single differentiated nucleus is found at St. 19 at 60 m depth with a fluorescence concentration of >0.6 mg/m^3. This nucleus seems to expand towards the south with lower fluorescence concentrations (St. 18, 17, 12 and 10). Figure 12-B shows a similar pattern as figure 12-A, stations with minimum or cero fluorescence concentration are the ones affected by the submarine volcanic eruption in previous DOA and AOU contours (St. 2, 1, 3, 7, 4, 8, 6, 5, 13 and 9), and vice versa.

6.7 Approximate affected area

In order to clearly visualize and quantify the approximate deoxygenation area produced by the submarine volcano Tagoro during both cruises, a illustration has been performed using the information obtained at the previous DOA and AOU contours. Figure 13 shows the location of the stations carried out along with the approximate affected area caused by the submarine volcano Tagoro regarding the dissolved oxygen parameter in both Leg3 (A) and Leg5 (B) cruises.

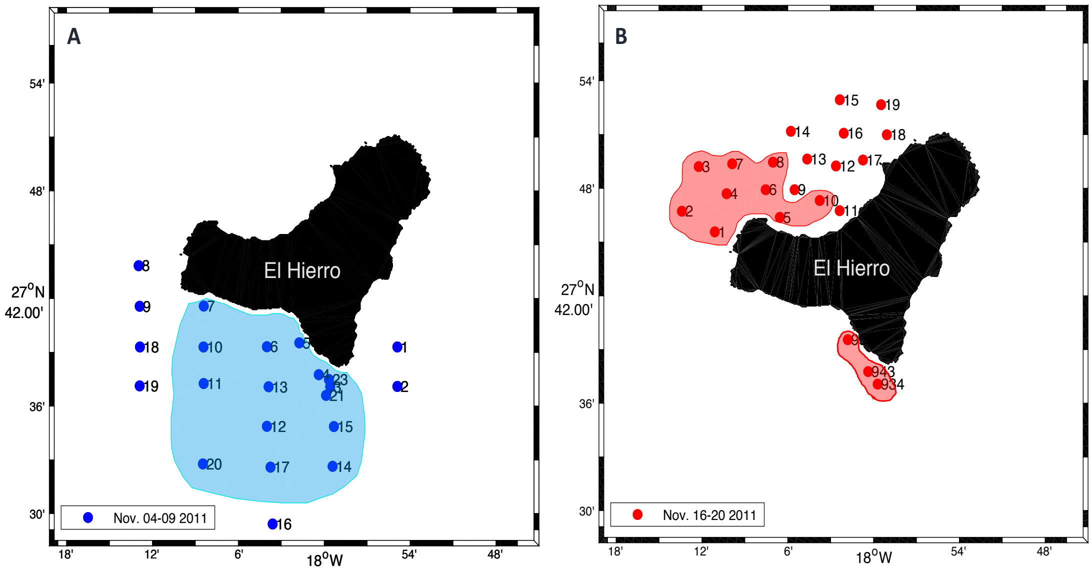

Figure 13. Approximate affected area caused by the submarine volcano Tagoro regarding the dissolved oxygen parameter in both Leg3 (A) and Leg5 (B) cruises.

The first figure (Fig. 13-A) corresponds to Leg3 cruise. Figure 13-A shows how the oxygen perturbation expands through the south of El Hierro Island and mainly affects the stations in the vicinity the submarine volcano. The approximate affected area of Leg3 cruise is 372 km^2 (Table 4). However the figure that corresponds to Leg5 cruise (Fig. 13-B), shows how oxygen perturbation affects the stations located just above the submarine volcano and the northwest of the El Hierro Island. The approximate affected area off the northern coast of El Hierro Island for Leg5 cruise is less, 112 km^2 (Table 4). The approximate affected area on the south of Leg5 cruise has not been calculated because the few stations carried out in that area do not represent the complete perturbation the submarine volcano has caused. However, these stations are located just above the submarine volcano and show maximum oxygen anomalies (see Fig.4).

Table 4. Approximate affected area of both cruises (Leg3 and Leg5).

Cruise	**Date**	**Affected area (km^2)**
Leg3	Nov. 4^{th}-9^{th} 2011	372
Leg5 north	Nov. 16^{th}-20^{th} 2011	112

6.8 Interaction with mezo-scale structures (anticyclonic-eddy – St. 914)

Volcanic origin plumes are rarely trapped by a mezo-scale structure. The interaction of a mezo-scale structure, an anticyclonic-eddy respectively, with a plume of volcanic origin has never been studied before. During Leg3 cruise, a St. at the furthest southwest of El Hierro Island located approximately 90 km from St. 1, was carried out (St. 914). This St. gives the possibility to study the affection over long distances the submarine volcano Tagoro has caused and how this is diluyed. Figure 14 provides detailed information about St. 914.

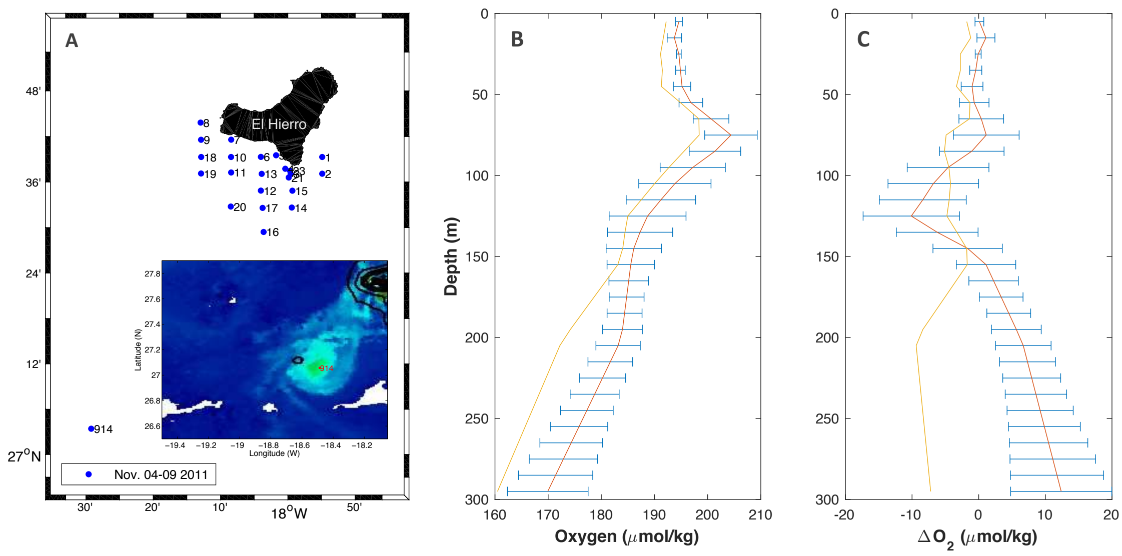

Figure 14. A closer look at St. 914 of Leg3 oceanographic cruise. (A) shows all stations carried out in the south of El Hierro Island in Leg3 cruise. The inset map shows the location of St. 914 together with the chlorophyll concentration on November 6th, 2011. Image acquired by NASA Terra MODIS and processed by the Marinemet project. Figure 14-B shows a vertical profile of oxygen concentration distribution of St. 914. Figure 14-C shows a vertical profile of DOA distribution of St. 914. In both, yellow line refers to St. 914. Red refers to a non-affected St. with its correspondent standard deviation.

Figure 14-A shows all stations carried out during the Leg3 cruise, including a chlorophyll concentration inset map of the farthest St. (St. 914). Oxygen vertical distribution in Figure 14-B, shows how oxygen concentrations at St. 914 are significative lower than the ones used as reference stations for the Leg3 cruise within the first 50 m. In that layer, oxygen depletion has been calculated between 2-4%. Lower oxygen concentrations are also found between 150 m and 300 m depth but more study should be done in order to corroborate is this anomaly is caused or not by the volcanic plume. The DOA vertical distribution shown in figure 14-C shows a similar pattern, dissolved oxygen anomaly is found in the first 50 meters (2-4 μmol/kg) and between 150 m and 300 m depth.

7 DISCUSSION

The hydrothermal emissions of the submarine volcano Tagoro affect the dissolved oxygen concentrations of the surrounding waters. The low oxygen values caused by the submarine volcanic perturbation are lower than the ones found in the "shadow zone" at the eastern boundary in the subtropical North Atlantic (Stramma et al., 2008). However, even lower oxygen values are observed in the Pacific, where suboxic zones (<4.5 µmol/kg) are found (Morrison et al., 1999). Low dissolved oxygen concentrations values reach up to 27.3 µmol/kg and 15.03 µmol/kg at the St. just above the submarine volcano during Leg3 and Leg5 cruises respectively. In such reduced oxygen concentrations, it makes it hard for life in marine ecosystems to survive. In a study by Fraile-Nuez et al. (2012), no fish schools were acoustically detected within the volcano affected area, and many dead fish were observed floating at the surface. These low oxygen concentrations contrast with the measurements that are expected to be found in the Canary Island region as described by Pérez et al. (2001), were values of 195 µmol/kg are observed for the Eastern North Atlantic Central Water (ENACW), confirming the measurements found for the oxygen concentration at the reference stations.

The lowest DOA values (maximum anomaly of dissolved oxygen concentration) for both cruises have been estimated in -170.9 µmol/kg and -171.9 µmol/kg at the stations just above the submarine volcano for Leg3 and Leg5, respectively. These values are extremely low compared to open ocean water. But in reference to OMZ zones, these are almost half of the perturbation with values between -80 µmol/kg (above 200m depth) and -50 µmol/kg (below 200 m depth) for the study by Brandt et al. (2015) at the eastern tropical North Atlantic. Conversely, for a study carried out at Lōʻihi volcano (Hawai'i), 100% of oxygen depletion was observed (Malahoff et al., 2006), closer to the values obtained in this work where oxygen depletion percentage during Leg3 and Leg5 were 86.2% and 92.4 %, respectively. Moreover, lower oxygen depletion percentage were described by Staudigel et al. (2006), where oxygen depletion percentage varies between 14.3 % to 28.6 % within the crater. This last value is in concordance with the obtained in our work for the plume transported by the volcano Tagoro off the northern coast of El Hierro Island during Leg5 cruise (17.7 %).

Satellite images sequence provided by NASA show ‹ how the perturbation caused by the submarine volcano Tagoro is dispersed in different directions around the island of El Hierro. Plumes of discoloured water of volcanic origin were also observed by satellite imagery in Tonga, Southwest Pacific Ocean (Mantas et al., 2011). This plume experienced big variations in flow direction and size, extending at times over more than 50 km. Discoloured seawater was also observed about 1.5 km off the western coast of the volcanic island of Miyakejima Volcano (Japan) in June 2000 (Kaneko et al., 2005). In the present study, part of the perturbation it is observed to surround the island of El Hierro towards the northwest transported by local currents. The stations carried out in Leg5 cruise at the northwest of El Hierro Island, confirm that the perturbation caused by Tagoro has reached that side of the island. The lowest dissolved oxygen anomaly found in that area is -34.3 µmol/kg at 75 m depth at St. 1. On the satellite images, it is also observed that the perturbation reaches the furthest southwest of El Hierro Island trapped by an anticyclonic-eddy. This phenomenon can be observed in a station carried out in Leg3 oceanographic cruise in that same area (St. 914), where dissolved oxygen anomalies are shown. Buoy trajectories shown in a study by Sangrá et al. (2005) suggest that anticyclonic eddies can interact with other structures as filaments with high chlorophyll concentrations. Other works studied these interactions as Arístegui et al. (1997), but never before has been studied an interaction with a volcanic plume.

In the present study, the highest AOU values obtained for each cruise are 186.6 µmol/kg and 211.6 µmol/kg respectively. In a study by Boyer et al. (1999), large-scale seasonal variability of AOU for the Atlantic and Pacific Oceans studies how biological activity and seasonal stratification in the summer gives the upper 50-75 m of the water column in each basin a lower AOU in summer than in winter. In general terms, in the mixing layer of the water column, oxygen concentration is typically close to saturation due to close contact with the atmosphere (low AOU values), but in our study high AOU values are obtained due to the oxygen depletion caused by the perturbation generated by the submarine volcano Tagoro. Lower AOU values are described in a study by Pérez et al. (2001) for the existent different water masses in the Canary Islands region. For instance, an AOU value of 37 µmol/kg is shown for the ENACW, extremely low in compared with our values, conversely, high AOU values closer than our finding are described in the same study (149 µmol/kg for the Antarctic Intermediate Water (AAIW)) but these are due to poor ventilation water masses at 1200 m depth. Pérez et al. (1998), it is said that AOU vertical distributions distinguishes the waters recently formed from those aged by their high AOU values. Deoxygenation caused by the submarine volcanic eruption by definition modified the interpretation of AOU parameter. Therefore, AOU values and the interpretation of this parameter should be made with caution for volcanic active regions.

8 CONCLUSION

There is clear and abundant evidence of the dramatic changes the submarine volcanic eruption of Tagoro has brought regarding the oxygen parameter in both oceanographic cruises (Leg3 and Leg5). Dissolved oxygen concentration up to anoxic levels were found at the vicinity of the submarine volcano (27.3 µmol/kg and 15.03 µmol/kg for Leg3 and Leg5, respectively). Oxygen depletion of 86.2% and 92.4 % was measured for both cruises respectively. This study shows how the area of dispersion of the perturbation caused by the submarine volcano Tagoro in its sorrounding area is 327 km^2, greater than the area of the island of El Hierro (268.7 km^2).

It has been found that the mentioned perturbation can not only affect the vicinity of the submarine volcano Tagoro, but can also be transported over long distances. Low dissolved oxygen anomalies have been found at the northwest of El Hierro Island (-34.3 µmol/kg). It has been proved that the affected area by the submarine volcanic eruption at the northwest of El Hierro (112 km^2), has no relation whatsoever with oxygen cunsumption regarding primary producers. The transportation of the dissolved oxygen anomalies to this area of the island of El Hierro are suggested to be due to local currents. Moreover, oxygen depleition has also been found at the furthest southwest of El Hierro Island transported by the interaction of an anticyclonic which conserves and transports this anomaly by more than 90 km, with a oxygen depletion between 2-4%.

The present study also suggets that the AOU parameter by definition should not be taken into account regarding submarine volcanic areas and its interpretation should be done with cauiton. The AOU values obtained in this study do not represent the age and biological response the water mass in the study area can have.

9 FUTURE WORKS

After the submarine volcanic eruption, extreme conditions were found on the marine environment on the southwest of El Hierro Island. In future works, in order to continue with the study carried out in this project, a more detailed study of the oxygen parameter can be made. For instance, more oceanographic cruises can be taken into account to create a longer time series. Moreover, oxygen parameter perturbation in the post-eruptive stage can also be studied to learn how its variability and transportation changes over time.

10 ACKNOWLEDGEMENTS

This study has been supported by funds from FEDER and the Spanish Ministry of Economy and Competitiveness through the VULCANO-II (CTM2014-51837-R) project and from the Spanish Institute of Oceanography through BIMBACHE (IEO, 2011-2012) project. I would like to thank the invaluable work of the Captain and crew of the *R/V Ramón Margalef* from the Spanish Institute of Oceanography (IEO) during both oceanographic cruises. I would also like to thank the University of Las Palmas de Gran Canaria (ULPGC) for the knowledge received at college, to the IEO for allowing me to pursuit my college work experience in their institution and, my supervisors, Dr. Eugenio Fraile Nuez and Prof. Dra. J. Magdalena Santana Casiano for their dedication and help.

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Additional information about the development of this study

- **Detailed description of the activities carried out.**

As shown in the timing of the TFG, these are the activities carried out during the development of the same:

- Initial meeting. Planning and timing
- Search and study of specific bibliography
- Data gathering, processing and graphing
- Realization of motivation, background, introduction and data and methods.
- Results and discussion
- Conclusion and abstract

All these activities were carried out in 180 hours of attendance and 270 hours of personal research. Each of the above points will be described in detail below.

<u>Initial meeting. Planning and timing</u>

During the first week, a series of meetings were carried out along with my co-tutor, where the timing and my stay in the centre (IEO) while I performed the TFG were planned. We came to an agreement and decided that I would go to the centre on weekdays from 9 am to 15 pm. It was also decided that the TFG was going to have a scientific papers structure.

<u>Search and study of specific bibliography</u>

The search and study of bibliography in the field that I am working on is of vital importance for being able to understand and develop this project. This activity was mainly carried out during two weeks. However, while working on the TFG, more bibliography was searched for.

<u>Data gathering, processing and graphing</u>

Taking into account that the development of this TFG is based on the work experience completed beforehand, the data and graphs developed during that time are the ones used for the this project.

<u>Realization of motivation, background, introduction and data and methods</u>

Once the bibliography was gathered and graphs made, I began with the development of the theoretical part of the TFG. This activity was supervised by my co-tutor at all time and was carried out in 3 weeks.

<u>Results and discussion</u>

The results obtained were analysed and interpreted along with my co-tutor. Subsequently, a selection of the graphs developed during my work experience was made for the study. The results obtained are satisfactory since they show and quantify the oxygen anomalies described in the title of this study. As for the discussion, with the help of the bibliography I already had, the results obtained were compared with those obtained by other scientists. This activity took 3 weeks to develop.

Conclusion and abstract

The conclusions were made taking into account the results and discussion already written. The abstract was the last thing to develop, were a summary of the study is embodied.

- **Training received**

During the TFG, I have acquired both theoretical and practical knowledge. As theoretical knowledge I have gained more insight about the variability of dissolved oxygen in the ocean, especially oxygen distribution in relation to hydrothermal activity and submarine volcanoes. As practical knowledge I have learnt and become more familiar about programming in Matlab. My co-tutor gave me a certified course of Matlab in the oceanography field.

- **Integration and involvement level in the department and relationship with personnel.**

The integration and involvement level within the department throughout my stay at the IEO was complete. I had total freedom to go to the office of my co-tutor to ask him any doubts I came across with. In addition, the rest of scientists in the department, were also willing to share their knowledge anytime. The work environment was very professional. Moreover, the relationship with members of all departments, including the staff, has been close at all times. The scientist with whom I shared the office with was very kind and we all helped each other whenever needed.

- **Positive and negative aspects related to the development of this study.**

There are several positives aspects related to the development of this study. First of all, I have been able to be part of one of the most outstanding institutions in the field of oceanography of this country during six months. Another positive aspect is that the development of this study has provided me with new knowledge about programing language and its use. It has also provided me with a greater vision about dissolved oxygen anomalies regarding submarine volcanoes.

The development of this study has also help me in at a personal level, as it has helped me gain confidence and patience when deciding how to best solve a problem that appear during an investigation.

- **Personal evaluation of the learning achieved during this study.**

The personal evaluation of the learning received throughout the TFG is positive. Thanks to the opportunity offered by Dr. Fraile, the IEO and consequently the ULPGC, I have had the chance to learn how to work in science. I have been able to learn new programming languages and to analyse big data sets. It has also helped me to strengthen the knowledge and techniques learnt during the degree and putting them into practice.