SUBMARINE ACCUMULATIONS OF METHANE HYDRATES IN ADJACENCES OF SEYMOUR ISLAND (ISLA MARAMBIO), ANTARCTICA AND ITS PROBABLE ENVIRONMENTAL INCIDENT

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SUBMARINE ACCUMULATIONS OF METHANE HYDRATES IN ADJACENCES OF SEYMOUR ISLAND (ISLA MARAMBIO), ANTARCTICA AND ITS PROBABLE ENVIRONMENTAL INCIDENT

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Key words: GAS HYDRATES, METHANE ESCAPES, CLIMATIC CHANGE, SEYMOUR ISLAND (ISLA MARAMBIO), NW WEDDELL SEA, ANTARCTICA

Abstract: The presence of aliphatic hydrocarbons in sediments at the bottom of the platform and the continental margin of the northeastern tip of the Antarctic Peninsula and its natural escapes, leads us to infer about the likely effects they may have on the Antarctic environment, particularly on changes off average in surface temperatures and seawater. Methane leaks recorded in shallow waters of the region are compatible with the destabilization of gas hydrates in the marine substrate and with changes in average surface temperatures and seawater, suggesting a probable environmental impact such as As a consequence of this process, based on the hypothesis of the "*clathrate rifle*", the scientific theory of Gerry Dickens and James Kennet, which argues that the rise in sea temperature can lead to a sudden release of methane from the clathrate deposits located in the ocean bottoms, as happened in the Eocene.

1. Introduction

Gas hydrates are crystalline cells of ice where molecules mainly of methane and other gases (e.g. ethane, propane, carbon dioxide, hydrogen sulfide) are trapped. Natural hydrate deposits occur in two types of environments: within the "permafrost" (permanently frozen soil) of the polar regions and within the marine substrate of the world's oceans. The methane that forms hydrates recognizes two origins: 1) biogenic, generated by biological activity within sediments, and 2) thermogenic, caused by geological processes deep within the earth's crust. It can also be of mixed origin. The global amount of carbon contained in these types of accumulations is conservatively estimated as twice the carbon contained by all known fossil fuels on Earth plus all biomass, calcareous rocks, oceans and atmosphere.

Atmospheric greenhouse gases absorb and emit radiation within the thermal infrared range. In this context, methane (CH_4) together with water vapor, CO_2, nitrogen oxides (N_XO), chlorofluorocarbon gases (CFC) and ozone (O_3) are the main greenhouse gases. CH_4 is the simplest aliphatic alkane hydrocarbon, but it has a potential greenhouse effect on the global climate which is c. 25 times greater than CO_2 (Shine *et al*. 1990).

2. Situation in Antarctica

In Antarctica, accumulations of methane hydrates were inferred by seismic studies (Camerlenghi and Lodolo, 1994; Camerlenghi *et al*., 1994), on the continental margin of

the South Shetland Islands, north of the Antarctic Peninsula, where the depth del mar is c. 1,850 m. Jin *et al*. (2003). Silvia Busso *et al*. (2013) inferred the existence of methane hydrates in the area by indirect methods through seismic studies and electrical surveys.
Methane bubble emissions were detected in an extensive underwater area of the northern shelf of the South Georgia Islands and the continental margin to the northeast of the Antarctic Peninsula (Römer *et al*. 2013, Loreto *et al*. 2010, Marín Moreno *et al*. 2015, Loreto *et al*. 2012, Solovyov *et al*. 2011). Hydroacoustic surveys and video-based observations of the seabed document the presence of individual gas bubble emissions ("plumes"), which were limited to glacial fjords and valleys. The effective methane transport of these emissions to the hydrosphere was tested by relative enrichments of dissolved methane in the waters near the bottom of the bubble columns ("plumes"), where the isotopic composition of carbon indicates its biogenic origin.
On the other hand, in shallow waters of the Bouchard Strait (Admiralty Sound), off the coast of Marambio Island (*Seymour Island*, Antarctica), del Valle *et al*. (1997, 2002) corroborated the presence of methane emanations between 1997-2015 and also observed the progressive increase in vent sites in the area. The shallow depth of the sea (between 5 and 10 m) in which the leaks occur allows their observation and direct access for study purposes, without the need for sophisticated equipment.

According to Xianyao Chen & Ka-Kit Tung (2014), the apparent slowdown in warming of the Earth's surface in the last 15 years could be due to the fact that heat was trapped in the depths of the Atlantic Ocean and the southern seas. This study suggests that such cycles have tended to occur in the last 20 to 35 years, and that global warming will sharpen again once heat rises to the surface of the water. According to these authors (*op. Cit*. 2014), in 1999 the warming of oceanic waters began to increase to a depth of 2000 m, just when the rapid climate warming of the 20th century began to decline. The fact that heat moves deep into the waters explains why the surface continues to have stable temperatures, in the same way that greenhouse gases trap more of the Sun's heat on the Earth's surface.

3. Objectives

This work aims to show, based on available historical data, the correlation between the increase in seawater temperature in the area and the increase in gaseous emanations into the atmosphere from accumulations of methane gas on the seabed in front of to the coasts of Marambio Island and the extreme NW of the Weddell Sea (Fig. 1), and briefly discuss their origin and their relationship to increases in surface temperature in the Antarctic Peninsula.

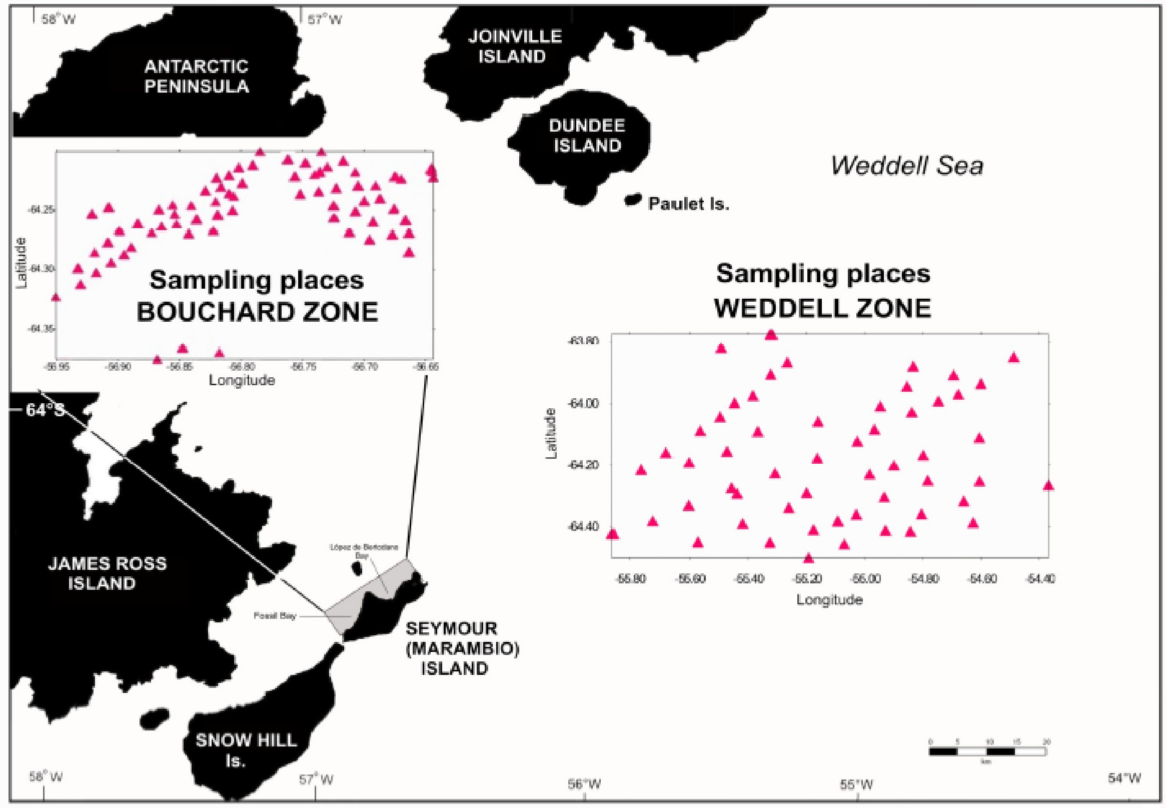

Fig. 1. Study zone

4. Work area

The investigations were carried out in two sectors with different characteristics; one with shallow waters, located in the Bouchard Strait, off the northern coast of Marambio Island and the other with deeper waters, located offshore about 70 km to the NE of said island (Fig. 1). The sector called “Zona Bouchard” comprises approximately 100 km^2 and the sector called “Zona Weddell” about 3,000 km^2. Field activities took place during the southern summers of 1994, 1995, 1997, 1998, 2011 and 2015, when the region was mostly covered by sea ice and icebergs, which made systematic sampling difficult in both sectors. . Methane gas emanations into the atmosphere were sampled in the shallow waters of the "Bouchard Zone", which is where the bubbles and flares from the seabed were visualized.

5. Geological setting

The work area (Fig. 1) is located within the sedimentary accumulation site called the James Ross Basin (Elliot, 1988), which is a “*sub-basin*” that comprises the northern part of a larger basin, called the Larsen Basin (del Valle *et al*., 1992) that developed behind a volcanic arc (back-arc basin), during much of the Mesozoic and Cenozoic. Within it, more than 6,000 meters thick clastic sediments were deposited, mostly of volcanic origin (*op. cit.* 1992).

In the shallow waters near Marambio Island (Bouchard Zone, Fig. 1), where methane escapes occur (del Valle *et al*. 1997, 2002), the Cretaceous and Paleogene sediments predominate, belonging to the Marambio stratigraphic groups. and Seymour respectively. These sediments correspond to the so-called *"shallow play zone"* described by Macdonald *et al*. (1988), who inferred, by indirect geophysical methods (*eg* seismic reflection profiles) that in this area "shallow hydrocarbon reservoirs would be potentially small and would contain mainly gas, although the quality of the reservoirs would be higher there than at the levels deeper" (*op. cit*. 1988).

On Marambio Island, the *permafrost* reaches a thickness of *c.* 250 m (Borzotta and Trombotto, 2004). There, Fukuda *et al*. (1992) defined three levels of marine/glacimarine terraces: 1) The Plateau, 2) Sub-Plateau and 3) Larsen Terrace. The latter is the lowest, with 30-35 m asl and the cited authors assign it an age of 2,910 + 120 years B.P. ("Before the Present", conventionally considered as the year 1950), obtained in a layer of algae from the lower part of this terrace, located at *c*. 3 m asl.

According to Sloan *et al*. (1995), in the deep marine substratum of the Weddell Zone (Weddell Zone, Fig. 1) two seismo-stratigraphic entities would be present: 1) the so-called "U3" (*Reflections dipping* 3° -5° E-SE, *Cretaceous-Oligocene*?) and 2) "U4" (*Chaotic reflections, Jurassic vulcanites?*). The samples from the deepest seabed (289-556 m bnm), analyzed in this work, were obtained indistinctly in the domain of these two substrate units, inferred through high-resolution reflection seismic studies (*op. Cit*. nineteen ninety five).

From the structural point of view, the study area is located to the N of an important left-handed passing fault zone, located *c*. 25-35 km SE of the eastern coast of the Cerro Nevado and Marambio islands (Sloan *et al*. 1995, del Valle & Miller 2001). This fracture zone is parallel to the eastern edge of the Antarctic peninsula and its origin is attributed to tectonic movements that probably occurred during the Oligocene (Sloan *et al*. 1995). Due to its great relative antiquity, this structure would have no influence on the present work.

6. Materials and methods

The historical analysis of the variation in surface temperatures was made based on the data provided by the National Meteorological Service (Argentina) of 3 (three) Antarctic bases, Marambio Base (Arg.), Esperanza Base (Arg.) And Base Eduardo Frei (Ch.). The historical analysis of the variation of seawater temperatures was carried out with data extracted from the databases of the French operational oceanography program CORIOLIS, of the United States National Oceanic and Atmospheric Administration (NOOA for its acronym in English) and the ARGOS International Network.
Reconnaissance of seabed morphology was performed with EdgeTech Discover 4150 portable side scan sonar. Substrate profiles up to c. 210 m depth below the seabed were obtained with the EdgeTech Discover SB-3200-XS portable seabed profiler (*"sub bottom profiler"*). The sediment samples were obtained with a 10/20 Kg *Benthic snapper and piston & gravity corer*.
To verify the variation of methane gas emissions into the atmosphere, a series of videos recorded by the Argentine Antarctic Institute in the Campaigns was used.

7. Results

7.1 Analysis of surface temperatures

The climatology of Antarctica has suffered in recent years variations in terms of temperatures. From the analysis carried out based on the data obtained from the National Meteorological Service for three Antarctic bases in the study area, it can be extracted that there were variations by making an interpretation regarding the periods analyzed and their length. The trend lines of the temperatures do not remain constant depending on the periods analyzed and their length, since the same periods are not available for the three bases. In this regard, each database is analyzed individually in its available periods and then comparisons are made in similar periods in order to obtain homogeneous conclusions from the study area.

The first comparison is made taking into account the totality of the available periods of each Meteorological Station, analyzing first the extreme months (January and July) and then the annual periods taking the maximum, average and minimum temperatures. In all cases, the slope of the Trend Lines is analyzed in order to obtain conclusions.

7.1.1 Comparison between Stations for the available periods

Due to the little variation in the slopes of the Trend Lines of the analyzed periods, it was decided to take them "per thousand" and not "percent" to avoid confusion with the number of zeros.

In the following Table (Table 7.1.1), the slopes of the Trend Lines of the Maximum, Average and Minimum Temperatures of the three stations in the months of January and July are analyzed and then the annual period and for the periods available for each Weather Station.

Table 7.1.1 Comparative table of trends of Maximum, Average and Minimum Temperatures

Note: The values "per thousand" (‰) indicate the slope of the trend line of the Maximum, Average and Minimum Temperatures for the available periods of each Station. The numbers in red indicate the negative slopes, that is, there was a decrease in temperature.

Bases (Weather Stations)	January			July			Annual		
	Temperatures			Temperatures			Temperatures		
	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum
(1)	Pend. LT	Pend. LT	Pend. LT	Pend. LT	Pend. LT	Pend. LT	Pend. LT	Pend. LT	Pend. LT
Esperanza	0,12‰	0,08‰	0,06‰	0,03‰	0,03‰	0,10‰	0,10‰	0,10‰	0,10‰
Marambio	0,18‰	0,13‰	0,07‰	-0,01‰	-0,11‰	-0,04‰	0,10‰	0,10‰	0,10‰
Eduardo Frei	-0,08‰	-0,08‰	-0,12‰	0,10‰	0,25‰	0,10‰	-0,01‰	-0,01‰	-0,02‰

For the months of January, July and Annual, for the available periods of each Base. Source: self made.

(1) Pend. LT: slope of the Trend Lines of Maximum, Average and Minimum Temperatures.

In the month of January from 1961 to 2014 for the Esperanza Base Station and from 1971 to 2014 for the Marambio Base Station, the slopes of the Trend Lines for maximum temperatures are double the minimum. Regarding the month of July, for a period of 54 years the slopes are gentle but positive for the Esperanza Base Station and negative for a period of 44 years for the Marambio Base Station. With respect to the annual periods, for both seasons they are positive and equivalent. Regarding the Eduardo Frei Base Station (Chile), the data are for a period of 20 years, giving negative slopes for the months of January and the annual periods (although softer) and positive for the month of July.

7.1.2 Comparison between Stations for the periods 1994-2014

If we make the comparison for the three stations in comparable periods, that is, from 1994 to 2014 (Table 7.1.2), for the annual periods the slopes of the Trend Lines are negative, being more pronounced for the Esperanza and Marambio Base Stations.

Table 7.1.2 Comparative table of trends of Maximum, Average and Minimum Temperatures

Note: The values "per thousand" (‰) indicate the slope of the trend line of the Maximum, Average and Minimum Temperatures for the available periods of each Station. The numbers in red indicate the negative slopes, that is, there was a decrease in temperature.

Bases	Annual Temperature		
	Maximum	Average	Minimum
(1)	Pend. LT	Pend. LT	Pend. LT
Esperanza	-0,10‰	-0,10‰	-0,10‰
Marambio	-0,10‰	-0,10‰	-0,10‰
Eduardo Frei	-0,01‰	-0,01‰	-0,02‰

For the Period 1994-2014 of each Base. Source: self made.

(1) Pend. LT: slope of the Trend Lines of Maximum, Average and Minimum Temperatures.

7.1.3 Comparison between Stations for the periods 1971-2009

If we compare the periods in which there was an increase in the average temperature in the Antarctic Peninsula, according to the data available for equal periods, we can compare the data from the Esperanza and Marambio Base Stations from 1971 to 2009 and for the Eduardo Frei Base Station from 1994 as of 2009 (Table 7.1.3). In all cases the slopes are positive, steeper for the first two stations (38-year period) and softer for the last (15-year period).

Table 7.1.3 Comparative table of trends of Maximum, Average and Minimum Temperatures

Note: The values "per thousand" (‰) indicate the slope of the trend line of the Maximum, Average and Minimum Temperatures for the available periods of each Station.

Bases	Annual Temperature		
	Maximum	Average	Minimum
(1)	Pend. LT	Pend. LT	Pend. LT
Esperanza	0,10‰	0,10‰	0,10‰
Marambio	0,10‰	0,10‰	0,10‰
Eduardo Frei	0,03‰	0,07‰	0,09‰

For the Period 1971-2009 of each Base. Source: self made.

(1) Pend. LT: slope of the Trend Lines of Maximum, Average and Minimum Temperatures.

On the other hand, a study, published in the journal Science (Science, August 22, 2014: vol. 345 No. 6199 pp 897-903), says that an apparent slowdown in the warming of the Earth's surface in the last 15 years could This is because the heat is trapped in the depths of the Atlantic Ocean and the southern seas.

The study suggests that such cycles have tended to occur in the last 20 to 35 years, and that global warming will sharpen again once heat rises to the surface of the water.

Tung and Xianyao Chen (2014), from the Ocean University of China, studied temperatures from water samples up to 2,000 m deep. They concluded that in 1999 the water began to get warmer, just as the rapid warming of the 20th century began to decline. The fact that heat moves deep into the waters explains why the surface continues to have stable temperatures, in the same way that greenhouse gases trap more of the Sun's heat on the Earth's surface.

This agrees with the comparison made, where the slopes of the Trend Lines for the 1994-2014 Period are negative. It can be concluded then, that in long periods (50 years or more) there was a considerable increase in temperature, which was declining in recent years with the beginning of the new century.

7.1.4 Comparison between the maximum and mean annual temperatures of the Marambio Station for the period 2000-2019

If now the comparison is made from the beginning of this century to 2019 for the Marambio Base Station, it can be seen that the slope of the maximum annual temperatures is positive and that of the mean annual temperatures is negative for that period (Fig. 2)

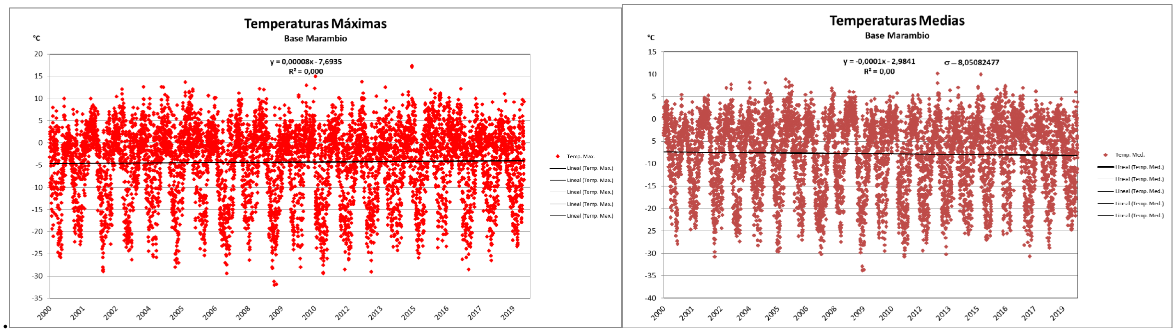

Fig. 2. Graph of annual average surface temperatures. Marambio Base 2000-2019

7.2 Analysis of sea water temperatures

For the analysis of the temperature in the depths of the sea, the ARGO International Network coordinated by the Argo Information Center (AIC) located in Toulouse (France) was used, as part of the monitoring and monitoring system. coordination of the Joint WMO-IOC Technical Commission on Oceanography and Marine Meteorology (JCOMMOPS) for operational ocean observations. The Argo Program deploys floats that measure the temperature and salinity of the surface layer and in the depth of the oceans. More than 3,000 floats have been deployed across the oceans, and each float is programmed to sink to 2,000 m deep. At greater depths, the temperature and salinity measurements are carried out through a CTD instrument (CTD = Conductivity, Temperature, Depth in English), which is submerged from a boat or platform. These instruments are used by the Bermuda Institute of Ocean Sciences (BIOS), which has been taking ocean measurements, such as temperature, salinity, and oxygen concentration, for more than 55 years.

For historical data, the French Operational Oceanography Program, CORIOLIS, and the World Database of the United States National Oceanic and Atmospheric Administration (NOAA) were used, from which they could be obtained from the study area, data from 1902.

For the study area restricted to the area where the methane emissions were located, the month of January was taken as the sampling month, due to the fact that being the central month of the southern summer, there is more abundance of data due to the decrease in the frozen areas, a fact that later makes it possible to make a comparison and draw a conclusion regarding temperatures at depth.

Regarding the historical graphs, it can be concluded that in the first 55 years of the 20th century, the surface and depth temperatures of the sea in the study area, 73% on average of the temperatures were below 0°C. Between 1958 and 1976, an increase in surface temperature was noted in most of the buoys (93.8%) and this was maintained until 1991 (85.7%). What is relevant is the increase in water temperature between 150 and 500 m depth from the XXI century (87%), which can have a considerable influence on methane emissions (Fig. 3). For subsurface temperatures up to 20 m depth, a slight increase in temperatures is also observed, as indicated by the trend line.

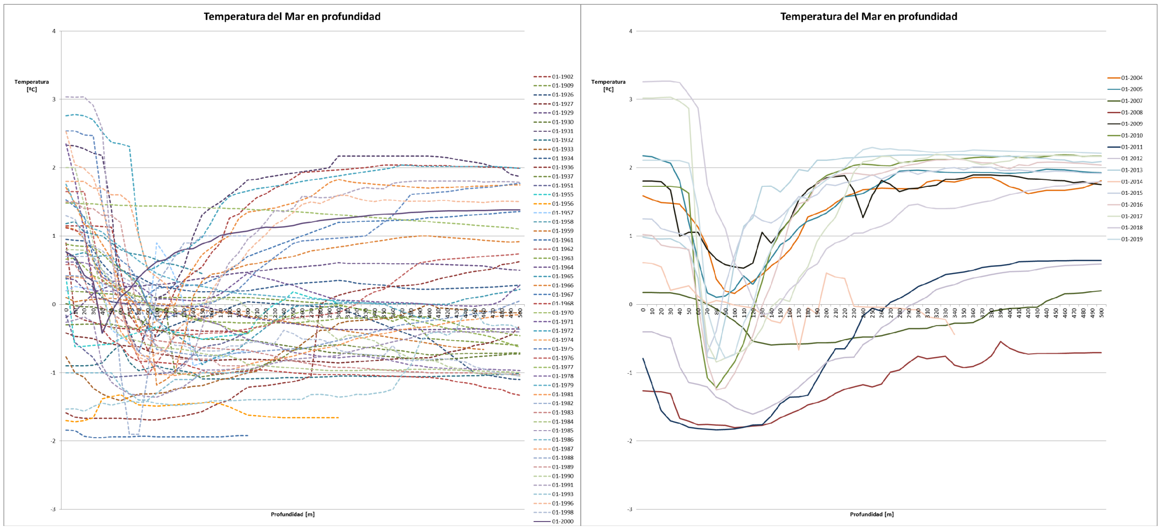

Fig. 3. Seawater temperature-depth graph in the study area. Period 1902-1999 and 2000-2019

7.3 Analysis of Methane released into the atmosphere

In the Bouchard Zone, 88 samples of superficial bottom sediments were analyzed, obtained at water depths between 0.5 m and 37 m. Methane contents vary between 115 ppm and 9,995 ppm, with 423 ppm as a general average. Likewise, small amounts of more complex hydrocarbons, from ethane to pentane, were detected in all samples (del Valle *et al.*, 2015). Numerous gas leaks were detected (del Valle et al. 1997, 2002), whose composition on a total of 6 samples yielded c. 160,000 ppm of CH_4 on average together with traces of SH_2 and CO_2. The samples were obtained in shallow waters, between 10-15 m deep.
The methodology, to analyze the probable environmental effect produced by the methane gas bubbles that emanate into the atmosphere, consisted of estimating the concentration of that methane using the mass balance equation, the radiative forcing produced by the methane using the formulas in the Document Technical II of the year 1997, prepared by the Intergovernmental Panel on Climate Change (IPCC for its acronym in English) and its relationship with the variation of temperature through the Stefan-Boltzmann law, making a calculation of the probability of occurrence. From this law the effective parameter of climate sensitivity is obtained, in the available period of quantifiable data on methane emissions (10 years). It was also assumed in that period, that what happened in the bubbles available through videos, is similar for the entire area, therefore the available data were extrapolated to the 88 methane leaks surveyed in the Bouchard Zone (shallow depth zone) by the team of researchers from the Argentine Antarctic Institute.
The results were the following:

Table 7.3 Results of Methane Bubbling Sampling in the Bouchard Zone

Measured Parameter	Year 2002	Year 2012	Difference in 10 years
Average ascent speed	0,23 m/s	0,41 m/s	78%
Surface volume	$3{,}35 \times 10^{-8}$ m^3	$9{,}04 \times 10^{-7}$ m^3	27 veces
Cantidad de burbujas que llegan a superficie	566 burb/min	2054 burb/min	362%
Number of bubbles reaching the surface	0,58 Tn/año	56,7 Tn/año	97 veces
Concentration of methane released into the atmosphere	1746,66 ppbv	1860,54 ppbv[(1)]	6,5%
Greenhouse effect produced by methane emissions	0,2072 w/m^2	0,2327 w/m^2 [(2)]	0,0254 w/m^2
Temperature variation due to radiative forcing			0,015 K [(3)]
Probable Environmental Incidence			3%

(1) The unit of concentration ppbv (parts per trillion volume is 1000 million) is equivalent to nmol / mol.
(2) Radiative forcing in watts per square meter.
(3) Temperature difference in degrees Kelvin.

8. Discussion

Gas hydrates are stable under the pressure and temperature conditions that occur in two natural environments: 1) the polar regions, where temperatures are low enough for permafrost to exist in both continental and marine areas. On the continental ones, where the surface temperature is below 0°C, the upper limit of stability of gas hydrates is estimated at 150 m depth and in marine sediments lying below 300 m depth, and 2) deep ocean regions, especially continental slopes and shelves and island margins, where there are very cold marine waters and depths exceeding 300-500 m (Kvenvolden 1993, a and b).
According to Mienert *et al*. (1998), in shallow waters, methane is transferred to the water column from destabilized methane hydrate deposits and can be incorporated into the atmosphere. This situation coincides with the observations made in shallow waters between 1994-2015 in the Bouchard Zone, where numerous gas vents occur, with a predominance of methane (c. 160,000 ppm, c. 16%) and traces of CO_2 and SH_2. These vents and the presence of gaseous hydrocarbons, mainly methane, in the sediments of the seabed are compatible with the speculation of Macdonald *et al*. (1988) on the existence of gas reservoirs in the substrate of the “shallow play zone” (see section 4- Geological Framework of this work).
It was possible to verify, based on the available data of the bubbling in the Bouchard Zone (see Table 7.3), an increase for a period of 10 years (2002-2012), of the measured parameters, which can be correlated with the increase of the deep sea temperatures since the beginning of the 21st century.

9. Conclusions

The release of methane from the frozen marine substrate in the vicinity of Marambio Island would be linked to the climatic instability of the late Cenozoic, when vast areas of the continental shelf of Antarctica were flooded during the transgression that occurred c. 18,000 years, following the last glacial maximum (LGM). In this way, the heat transferred by the sea to the substrate, now flooded, would have destabilized the hydrate accumulations originally formed within the subaerial permafrost during the LGM.

Additionally, the extraordinarily rapid rate of climate warming recently recorded in the extreme north of the Antarctic Peninsula (Fernandoy *et al*. 2015, Davies et al. 2012, Glasser *et al*. 2011, Turner *et al*. 2005, van der Broeke *et al*. 2004) would have contributed to accelerate the destabilization of hydrates in the area. The consequences of this warming can be observed to a great extent in the reduction of the ice sheet in this region of Antarctica and of the ice shelves (ice sheves) in the seas that surround it. Recent temperatures are extraordinarily high, setting a new record of +16.5 °C in March 2015 (Base Esperanza Meteorological Station, Argentina), this is unprecedented during the Holocene (Fernandoy *et al*. 2015).
Also based on the available data, it was obtained that the probability of occurrence of an environmental incidence of the emanations is very low (3%) and that they do not give a certainty of this environmental effect. But based on the Clathrate Rifle Theory (Dickens and Kennet, 2003) the episodic atmospheric emissions of CH_4 resulting from the instability of the hydrate deposits contributed significantly to the distinctive behavior of the climate change of the Paloecene-Eocene Thermal Maximum (PETM) on the one hand, and on the other, there are significant differences between the 21st century, the PETM and the potential of hydrates to abruptly emit methane. A fundamental difference is the presence of the polar ice sheet in the 21st century and the lack of polar ice at the end of the Paleocene. As a result of considerably cooler temperatures at the Poles in the 21st century than at the end of the Paleocene, there is 2.3 times more carbon stored in polar hydrates than existed during the PETM (Charles *et al*., 2007).
The demonstration of the climatic effects of hydrate dissociation in the PETM, the fastest rate of anthropogenic climate change compared to the Paleocene, suggests at least a moderate risk of hydrate dissociation that could have a significant impact on climate change current (MacWilliams, 2017). Furthermore, a moderate risk implies that the threat of the clathrate gun firing again in the coming decades is significantly sufficient for societies to prepare contingency scenarios for situations in which the clathrate gun actually triggers (MacWilliams, 2017).
In the study area, the palaeogeographic and paleoclimatic conditions for the formation of methane hydrates occurred and currently the geographic and geol conditions also exist.

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