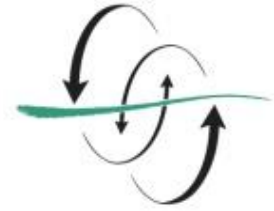


FACULTAD
DE CIENCIAS
DEL MAR



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DE GRAN CANARIA

ESTIMATING THE CONTRIBUTION OF
TERRESTRIAL ORGANIC MATTER IN
THE SOUTH-WESTERN MARGIN OF
BAJA CALIFORNIA DURING THE LATE
HOLOCENE

Galileo Rodríguez Amador

Curso 2013/2014

M^a Dolores Gelado Caballero

Alberto Sánchez González

Trabajo Fin de Título para la obtención
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Datos personales del estudiante:

Galileo Rodríguez Amador (galileo.rodriguez101@alu.ulpgc.es)

Estudiante de Grado de Ciencias del Mar

Curso 2013/2014

Facultad de Ciencias del Mar, Universidad de Las Palmas de Gran Canaria.

Participante en el programa de movilidad EEUU-América Latina, en la Universidad Autónoma de Baja California Sur (UABCS) y el Centro Interdisciplinario de Ciencias marinas, Instituto Politécnico Nacional (CICIMAR-IPN).

Datos personales del tutor y cotutor:

M^a Dolores Gelado Caballero

Universidad de Las Palmas de
Gran Canaria

Facultad de Ciencias del Mar

Departamento de Química

Alberto Sánchez González

CICIMAR-IPN

Departamento de Oceanología

Laboratorios de Biogeoquímica

Ambiental

X

Galileo Rodríguez Amador
Estudiante

X

M^a Dolores Gelado Caballero
Tutor

X

Alberto Sánchez González
Cotutor

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Abstract

The organic matter in the water column and sediment in transitional and marine environments in the ocean is described by a binary mixture of marine and terrestrial sources. The C:N ratio and $\delta^{13}\text{C}$ of samples and sources is used in a linear equation to estimate the fraction of organic matter (OM) from land in aquatic and sedimentary environments. However, terrestrial OM is relatively depleted in N and this fraction has been seriously and systematically underestimated by this misinterpretation of the C:N ratio and $\delta^{13}\text{C}$. Additionally, the composition of the Earth's organic matter is not well known in the region of Magdalena, as is the case in many studies in arid areas with little or no input from rivers. In this work new data for reason N:C and $\delta^{13}\text{C}$ core are shown severity collected at 700 m depth in order to evaluate the contribution of different sources of OM in the south-western Baja California margin, characterized by extensive oxygen minimum zone and high primary productivity. The N:C ratio suggests that the contribution of various land-based MO of between 19 and 57% during the late Holocene. The binary mixture the N:C ratio and $\delta^{13}\text{C}$ of OM appears indicate that marine source remains the dominant source.

Key Words: Sediment, N:C ratio, $\delta^{13}\text{C}$, Organic Matter, OMZ, Holocene

Introduction

Understanding the dynamics of biogeochemical cycles of organic matter (OM) requires knowledge of both the processes that control the distribution of the same as its source. At the bottom of the ocean margin sediments found that are rich in organic matter, both of marine origin and terrestrial origin (Smith et al., 2008). During the passage of the years, sedimentation buries this matter gradually, forming a register in which every centimeter of sediment may reflect from decades to centuries of information, depending on the area and its rate of sedimentation. In places with a high rate of sedimentation, sedimentary records have higher resolution, where every centimeter shows very few years (van Geen et al., 2003). This lets us know what changes occurred in short time scale.

The Holocene is the current geological period, comprising almost the last 12.000 years. Its onset is characterized by climate change that marked the end of the last glaciation (Wanner et al., 2008). This work is focus on the late Holocene which started 3,000 years ago.

The oceans are an important part of the carbon flux. Variations of carbon flux on a planetary scale ranging from millions of years for processes related to the earth's crust, to seconds or days for those related to the atmosphere-ocean interface and the photosynthesis (Sanchez and Carriquiry 2007). It is well known that photosynthetic organisms fix atmospheric CO₂ to form organic molecules for vital development which are incorporate in their tissues. After the death of organisms, the organic matter is degraded being the sequestered C return as CO₂ to the atmosphere. Occasionally in the marine environment, this process does not occur in the same way. The died organisms remains sink and are partially degraded in the water column and sediment. Finally they become part of the sediment, thus being trapped organic matter formed by photosynthetic processes (Zonneveld et al., 2010).

It should be note, the organic matter in the sediment is a combination of marine and terrestrial inputs. One of the major sources is the primary production emerged in the water column, which after the death of the organisms and their fall to the bottom, will be part of the sediment. On the other hand, the rivers provide huge amounts of organic matter from the continental basins sweep along their course (Zonneveld et al., 2010). Moreover in arid regions where there is no river source, the contribution of organic matter from land may be dominated by wind pathway (Sánchez et al., 2013).

Marine sediments can be used as temporary records that reflect real climate and global change (Ortiz et al., 2004). In the particular case of Magdalena margin, an exceptionally sedimentary high rate allow high resolution of temporary record because every centimeter of

sediment responds to a variation between 10 and 30 years of sedimentation (van Geen et al., 2003).

However it should also be considered another factor, the low oxygen concentration which limits the degradation of organic matter falling into the water column and down in the sediment (Guíñez et al., 2010). That is the reason because the oxygen minimum zones (OMZ) play a crucial role in the preservation of organic matter in marine sediment. In addition, these low oxygen concentrations inhibit the presence of benthic organisms which produce the bioturbation of sediments. In consequence, the formation of distinct bands in the layers of accumulated particles and the preservation these sediments is realized (Soutar and Crill, 1977).

To determine the source of the organic matter present in the sediment, the elemental and isotopic composition is analyzed. Knowing the $\delta^{13}\text{C}$ and N: C ratio, is possible to infer the source of organic carbon and nitrogen since each source has a characteristic isotopic signature (Hu et al., 2006.). Traditionally, C: N ratio has been used to the determination of the sources of organic matter in the sediment. However, the fraction of terrestrial OC is underestimated by the C:N ratio because the terrestrial organic matter is relatively depleted in nitrogen. Some authors have suggested the use of atypical N:C ratio in order to correct this mentioned error (Koprivnjak and Perdue, 2007).

Usual values reported for $\delta^{13}\text{C}$ of organic matter from terrestrial plants varies between -26 ‰ and -28 ‰ with an average of -27 ‰ and for organic matter of planktonic organisms the values ranging from -20 ‰ to -22 ‰ (Hu et al 2009). In the other hand, the C: N ratio of the organic material of marine origin have values between 5 and 8 in OM with a terrestrial origin they are > 15

Study case

In this work we study the core samples collected with gravity in the margin of Magdalena, a region influenced by OMZ and characterized by a high rate of sedimentation (van Geen et al., 2003). Several studies have addressed the characterization of carbon fluxes and organic matter during the last 50000 (Sanchez and Carriquiry 2007) in this region. Despite that not many have achieved reliably determine the source of organic matter in this area remaining yet to establish whether its origin lies in land-based or marine sources.

Moreover some data obtained in this area might not have been properly interpreted as C:N ratio was used to origin proxy which, as already noted above, likely underestimates the

contribution of terrestrial organic matter because nitrogen levels are quite low in that OM (Koprivnjak and Perdue, 2007).

Justification, hypothesis and objectives

Although it is true that the quantitative and qualitative description of accumulation rates Organic Carbon, Organic Nitrogen, Organic Phosphorous, etc. which have been made in previous work in this region to characterize the OM has relevance, more efforts are still needed to establish the origins of OM and for better understanding of the variables that control the fluxes of carbon in this region.

Furthermore, the composition of marine sediment and the quantitative differences between the sources of each of the components of the OM should be established to use as a temporal recording of climate changes at regional and global scale and establish future scenarios based on that knowledge.

Depending on the origin of organic matter found in sediments and its variation over time relationships with changes in climate and marine production, and fluvial and dust OM input could be ascertained

Our hypothesis is based on the fact that the biogeochemical tracers used for characterization of marine sediment in the region of Magdalena so far have been insufficient to establish totally the cycle of organic matter during the Holocene.

The study of sedimentary records gravity cores collected in the southwestern margin of the peninsula of Baja California during the last 5000 years should reveal the influence of the contribution of terrestrial material through the combined application of techniques for elemental and isotopic analysis of the N: C ratio. The proposed objectives are:

1. Concluding the sources of organic matter $\delta^{13}\text{C}$ based on and N: C ratio in the range of Magdalena.
2. Differentiate between sources of organic matter from land and sea in the range of Magdalena.
3. Estimate the contributions of organic matter from land in the range of Magdalena.

Material and Methods

Study Area

This work was carried out with samples from the margin of Magdalena region located on the peninsula of Baja California on the Pacific Ocean side (Figure 1). This area is affected by hydrographic features that determines the California Current that extends approximately between 48 ° and 23 ° N. Its circulation is controlled by the cell of high atmospheric pressure in the North Pacific and the cells of low pressure in the Aleutians. The average speed of the current is less than 25 cm s⁻¹, the average surface temperature in winter is ~ 13 ° C, while in summer is about 20 ° C. The wind system promotes the appearing of upwelling which promotes high primary productivity along the stream (Lynn and Simpson, 1987).

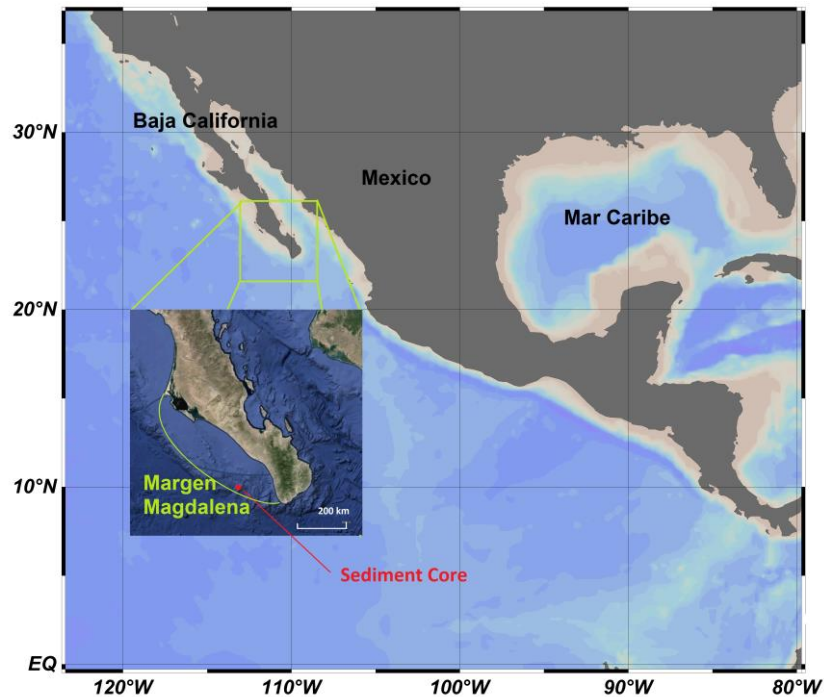


Figure 1. Study area showing the margin of Magdalena.

From the biogeochemical point of view, Magdalena margin are characterized by high primary productivity, favouring the development of OMZ ($O_2 < 2\mu\text{mol/kg}$) (Fig. 2) located between 400 and 800 m depth (van -Geen et al., 2003; Carriquiry and Sánchez, 2007). This OMZ has been well described in the work of accumulation of organic carbon and calcium carbonate by Sanchez et al. (2013)

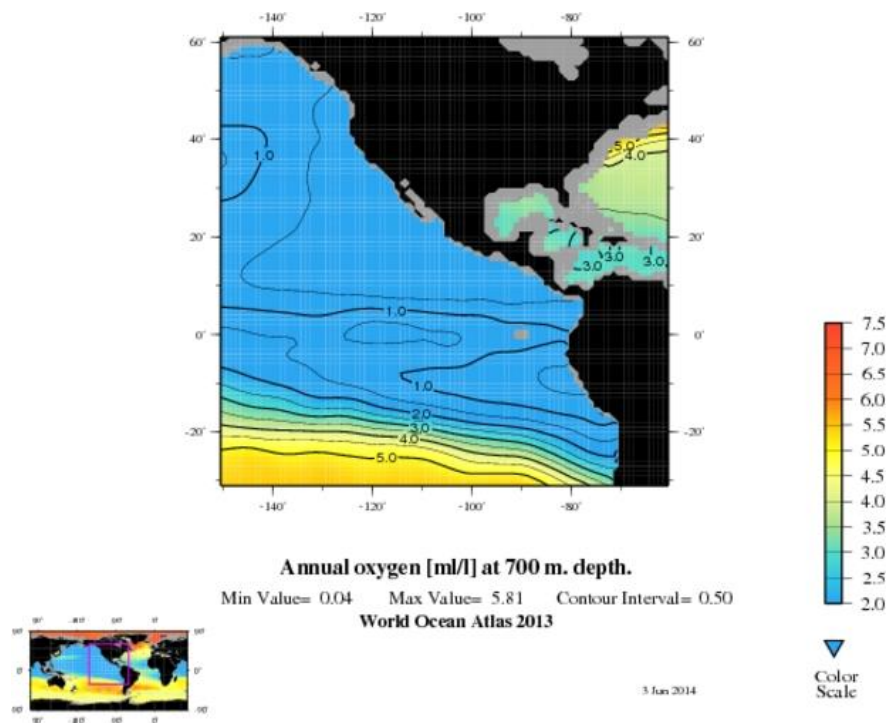


Figure 2. OMZ on the Pacific Coast of Mexico. Image taken from the web nodc.noaa.gov.

These characteristics make this area an ideal region for the study of the fluxes of carbon as it represents a high sedimentation rate, one oxygen minimum zone and is also a region with a high frequency of upwelling because of its mentioned wind regime. In this work, a model to estimate the age of studied core and its temporal variation was based on previous reported data (van Geen et al., 2003; Marchitto et al., 2007) using different cores which had dated showing the age of the sediments in the area (Figure 3):

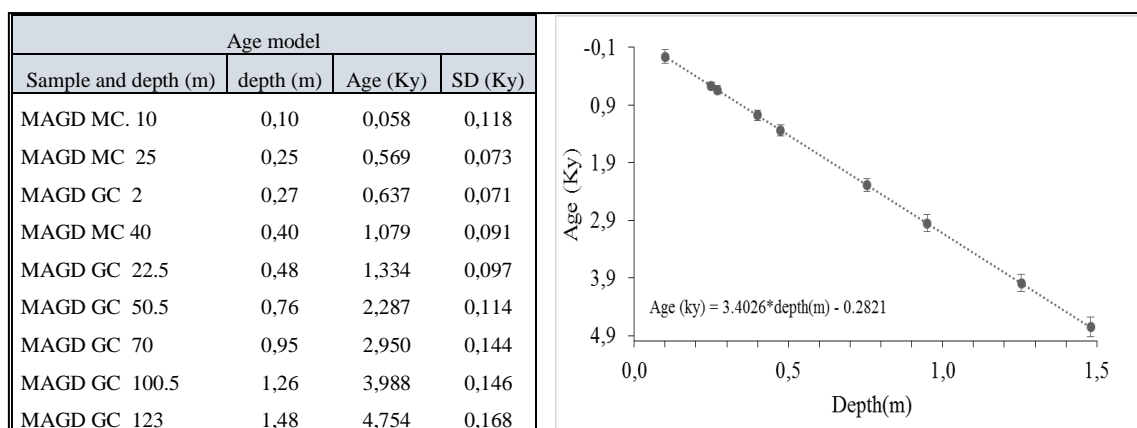


Figure 3. Age Model adapted from van Geen et al 2003 and Marchitto et al 2007.

Sampling and Sample treatment

The sediment core that is used in this study (MAGD09) was collected aboard the research vessel New Horizon during a cruise in 2009 in the margin of Magdalena, Baja California Sur, Mexico. The core was collected (23 ° 27.67 'N 111 ° 34.69' W) at a depth of 680 m in the OMZ. It was refrigerated at 4 ° C until analysis in the laboratory.

Laboratory

For determination of Nitrogen and Organic Carbon (OC) and the stable isotopes of Carbon was carried out a pretreatment and treatment of samples prior to elementary analysis in line with Sanchez et al., 2013. The details of these processes are summarized below:

- Determination of Nitrogen. Samples of gravity sediment core were separated by centimeter according to the depth and frozen immediately after collection (137 samples). Once in the laboratory, they were defrosted and placed in a drying oven at 50 ° C for three days. After drying, they were homogenized with mortar and then were weighed (approximately 5 mg) and tin packed into capsules for further analysis.

- Determination of Carbon: samples after drying, a fraction in test tubes (plastic) to which was added 1 ml of 3.7% hydrochloric acid daily during three consecutive days to achieve the elimination of separated associated carbon carbonates. After that, the samples were washed with distilled water and centrifuged twice. Finally, they were dried at 40 ° C in an oven for two days. Once dry, the samples were weighed approximately 1mg and packaged in tin capsules.

The analysis of Carbon and Nitrogen elemental and isotopic analysis of $\delta^{13}\text{C}$ was performed by using elemental analyzer coupled to COSTECH4010 to a Finigan Delta V Plus mass spectrometer in the CICIMAR-IPN .. The elemental Carbon and Nitrogen are expressed in weight percent $\delta^{13}\text{C}$ data are expressed in units of parts per thousand (‰), which in the case of Carbon data is a value relative to the reference standard Peedee Belemnite Vienna. Thus $\delta^{13}\text{C}$ values are obtained using the equation:

$$\delta X(\text{‰}) = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 10^3$$

Where X is the $\delta^{13}\text{C}$ and R is the isotopic ratio ($^{13}\text{C}/^{12}\text{C}$). Accuracy standards for elemental analysis of Carbon and Nitrogen were 0.3% and 0.03%, respectively. For the analysis accuracy $\delta^{13}\text{C}$ standard was 0.01 ‰.

Finally, to make a quantitative estimate of terrestrial inputs, the equations proposed by Schultz and Calder, (1976) and Minoura et al., (1997) are used:

$$\text{Terrestrial inputs (\%)} = (\delta^{13}\text{C}_{\text{marine}} - \delta^{13}\text{C}_{\text{sample}} / \delta^{13}\text{C}_{\text{marine}} - \delta^{13}\text{C}_{\text{terrestrial}}) \times 100$$

And Perdue and Koprivnjak, 2007:

$$\text{Terrestrial inputs (\%)} = ((\text{C:N}_{\text{sample}} - \text{C:N}_{\text{marine}}) / (\text{C:N}_{\text{terrestrial}} - \text{C:N}_{\text{marine}})) \times 100$$

$$\text{Terrestrial inputs (\%)} = ((\text{N:C}_{\text{sample}} - \text{N:C}_{\text{marine}}) / (\text{N:C}_{\text{terrestrial}} - \text{N:C}_{\text{marine}})) \times 100$$

Resolution of the above equations need to introduce the marine and terrestrial standards for the area which were calculated from published data from terrestrial plants found in the peninsula of Baja California and submarine sediment traps (Table 2).

Table 1. Marine and terrestrial standards of $\delta^{13}\text{C}$ and N:C and C:N ratios.

standard	Marine	Terrestrial
$\delta^{13}\text{C}$	-20,5	-25,6
N:C	0,09	0,06
C:N	11,19	20,6

Results

Estimated amount MO content in the sediment.

After analysis of the samples, the average values of OC, N and $\delta^{13}\text{C}$ were estimated using an integration of the different values found in the sediment core (Table 2). Temporal variation of OC and N values variation along the sediment core are presented in Figure 4.

Table 2. Organic Carbon and Nitrogen sediment composition (%) and $\delta^{13}\text{C}$ values found in Magdalena margin.

Study Area	%OC	%N	$\delta^{13}\text{C}$
M. Magdalena (680m)	11.85± 1.55	1.08±0.18	-20.38±0.7

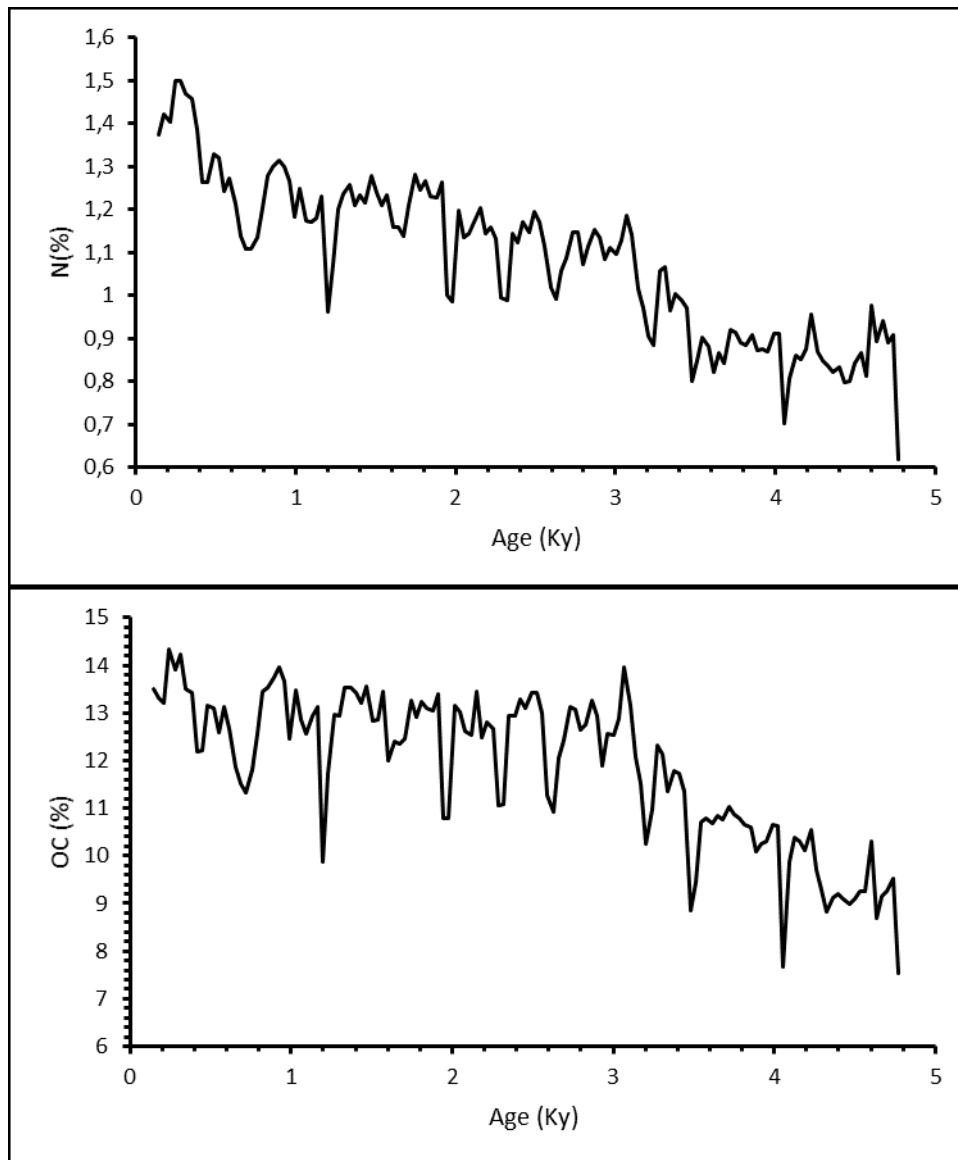


Figure 4. Temporal variation of organic carbon (top) and nitrogen (bottom) expressed as % in the marine sediment Magdalena margin during the last 5000 years.

Characterization of OM Sources in the area.

To estimate sediment MO sources, $\delta^{13}\text{C}$ relations between carbon and C:N ratio have been firstly examined (Figure 5). According to these results it can be seen that most of the MO found in samples correspond to a marine origin. However, a number of samples presented values that were differed from the range previously described for the organic matter of marine origin (Hu et al., 2009). Correspondingly, relationships between $\delta^{13}\text{C}$ and the N:C ratio have been established. As described above for C:N ratio a similar behavior was found with a large

portion of the sample values within the range of marine organic matter. However, the N:C ratio presented a significantly better agreement with the expected values for the marine OM.

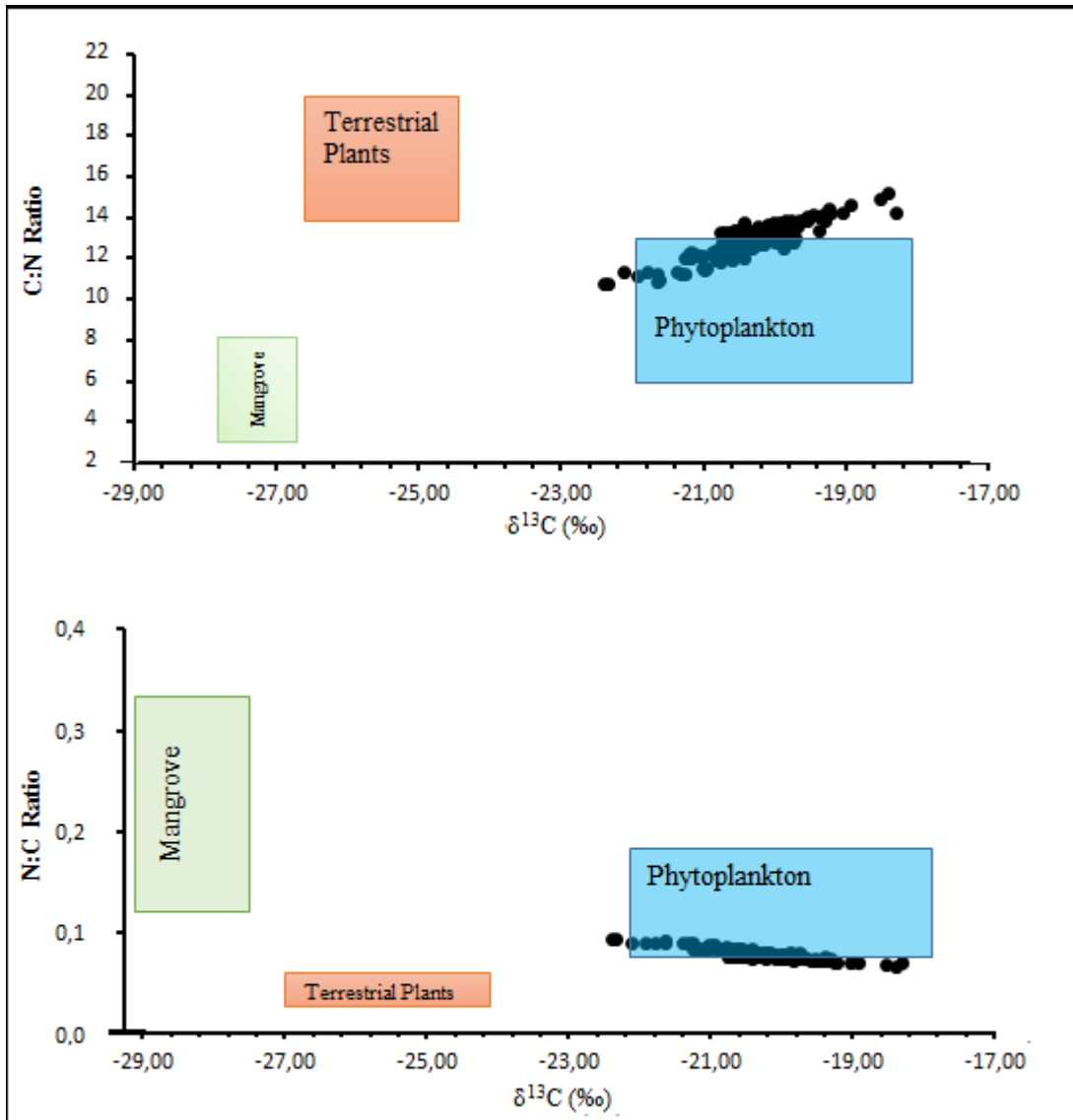


Figure 5. C:N ratio (top) and N:C ratio (bottom) and $\delta^{13}\text{C}$ (‰) values in the samples (black points) and reported range of C:N and N:C ratios and $\delta^{13}\text{C}$ for marine and terrestrial OM in the boxes are presented.

Terrestrial OM inputs

The results of terrestrial inputs obtained using the equations proposed by Schultz and Calder, (1976); Minoura et al., (1997); and Perdue and Koprivnjak, (2007) have inconsistencies. Terrestrial input calculated from $\delta^{13}\text{C}$ data reveal two major increase in amount of OM, one at 280 years ago (37 %) and another at 4600 (32 %) years ago. In contrast, the results from the C:N ratio and N:C ratio show an inverse pattern to that resulting from $\delta^{13}\text{C}$ with a minima

instead of the maximum mentioned before. Moreover there are differences in the magnitude of the values obtained from C:N or N:C ratio being highest for the case of the N:C ratio.

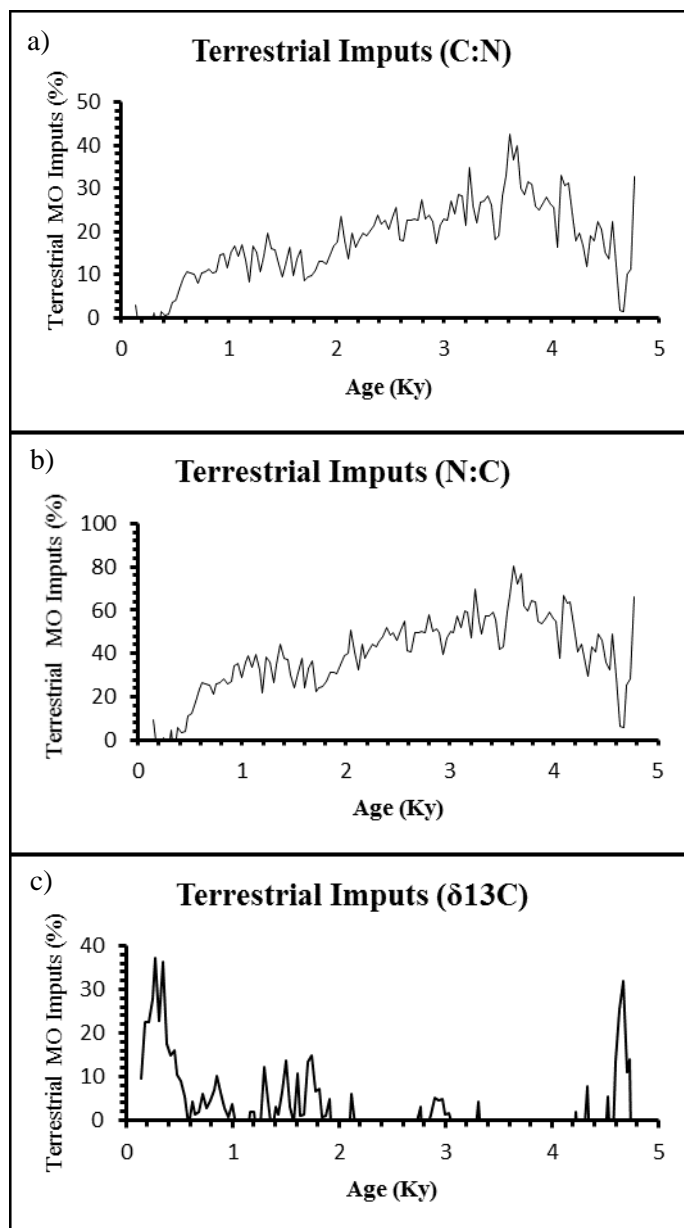


Figure 6. Temporal variations of the contributions of OM of terrestrial origin: a) calculated with the equation of Schultz and Calder values (1976), b) and c) calculated with Perdue and Koprivnjak (2007) equations values.

Discussion

At first, the sediments found in the margin of Magdalena have a composition characterized by an high amount of organic matter (Table 2) compared to other regions such as the Gulf of Tehuantepec or Alaska (Table 3) which are at the same depth. This feature could be

related with the occurrence of important phenomena of upwelling in this area (Lynn and Simpson, 1987). In the last 5000 years there has been an increase of OC and N, which is consistent with previous works (Carptanis et al 2011, Ortiz et al., 2004)

Table 3. Reported values of %C, %N and $\delta^{13}\text{C}$ in zones under influence of an OMZ.

References	Location (depth)	%OC	%N	$\delta^{13}\text{C}$
Pichevin (2010)	Nicaragua (863m)	7.5±0.4	0.8±0.06	-20.4 ± 0.3
	Tehuantepec (719 m)	5.2±0.5	0.56±0.08	-19.01±0.1
Arellano (2011)	Mazatlán (454 m)	6.3±1.0	0.67±0.1	
Hendy (2004)	Pta. Concepción (955 m)	2.5±0.2		
Ricuarte (2013)	Bahía de La Paz (415 m)	3.7±0.7	0.58±0.1	-20.6±0.9
		%OC	Max	Min
Addison (2012)	Alaska goulf (680 m)	0.5	0.9	0.3

One possibility for the inconsistent results using Schultz and Calder (based on $\delta^{13}\text{C}$) and Perdue Koprivnjak (based on C:N and N:C ratios) could be due to those terrestrial plants or phytoplankton organisms that are not included in the present estimations. Consequently, marine and terrestrial C: N, N:C and $\delta^{13}\text{C}$ standards should be revised.

Otherwise, efforts for producing a more precise determination of the origin of the organic compounds found in the sediments, could be necessary. For example, OM may be analyzed for the presence of long chain hydrocarbons typical in terrestrial plant tissues (Meyers et al., 2001)

Conclusions

In the present work the variations in the composition of the OM in sediments collected in the margin of Magdalena corresponding with the last 5000 years have been established. Moreover, it has been proved that the highest input of OM is from marine primary production and this source is the dominant trend observed through the time period.

Although an important part of the previous work in the area has been carried out using $\delta^{13}\text{C}$ and C:N ratio, new tracers including N:C ratio, quantification of chemical species as long chain hydrocarbons, etc. will be necessary in future works in order to clarify the variations of OM in a short time scale. More efforts are required to define properly methods to calculate the dominant sources of OM..

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Web:

World Ocean Circulation Experiment Global Data Resource

<<http://www.nodc.noaa.gov/woce/wdiu/>>

Memoria final del TFG

GRADO EN CIENCIAS DEL MAR. ASIGNATURA: 40630 – Trabajo Fin de Grado

1. Descripción de las actividades desarrolladas durante la realización del TFG

El trabajo fue realizado en el departamento de Oceanología, en los laboratorios de Química Orgánica y Química Inorgánica a cargo del Dr. Alberto Sánchez González. Durante mi estancia me encargué de:

- Pretratamiento y tratamiento de muestras de sedimento:
 - a) Secado de muestras en estufa a 50° C.
 - b) Homogenización de las mismas con mortero y almacenado en tubos de Eppendorf.
 - c) Digestiones ácidas con ácido clorhídrico al 3,7% (1 ml por cada 4 gramos de sedimento aproximadamente y dejar actuar un día a temperatura ambiente) para análisis de carbono. Se repetía 3 veces la adición de ácido y al cuarto día se pasaba al enjuagado con agua destilada en la centrifugadora (20 minutos a 4000 rpm a 25°C).
 - d) Por último pesado y empaquetado para el análisis, el cual consiste en el uso de cápsulas de estaño donde se introduce la cantidad de sedimento pertinente para el análisis, en mi caso 5 mg para nitrógeno y entre 1 y 3 mg para carbono. Luego se cierran esas cápsulas con sumo cuidado haciendo uso de pinzas y están listas para el análisis.
- Calibrado de equipos analíticos: siendo el espectrofotómetro del visible (modelo Spectronic 200, casa comercial Thermo Scientific), el espectrofotómetro de masas (modelo Delta V Plus, casa comercial Thermo Scientific y el analizador elemental de combustión (casa comercial Costech Instruments).
- Análisis de muestras por duplicado: un análisis para nitrógeno y otro para carbono. Almacenamiento de datos con Excel y procesamiento de datos con el software del analizador elemental (Isodat).
- Revisión bibliográfica de artículos científicos relacionados con la temática de mi TFG

2. Formación recibida:

Durante los meses de prácticas, fui capacitado en distintas técnicas de pretratamiento y tratamiento de muestras, al igual que en el calibrado de los aparatos analíticos como el espectrofotómetro de masas y el analizador elemental. También tuve la oportunidad de practicar técnicas aprendidas durante el Grado.

Técnicas nuevas aprendidas durante el TFG:

- Homogenización con mortero

- Pesado y empaquetado de muestras solidas
- Uso de analizador elemental y espectrofotómetro de masas.

Técnicas aprendidas durante el Grado de Ciencias del Mar y aplicadas durante el TFG:

- Uso de espectrofotómetro
- Secado de muestras
- Enjuagado con centrifugadora
- Uso del material común del laboratorio
- Limpieza y esterilizado de material de laboratorio tras su uso.

También asistí semanalmente a seminarios impartidos en el centro de investigación con distintas temáticas relacionadas con el mar: pesquerías, migración de mamíferos marinos, distribución de elementos traza en el Golfo de California, dinámica de corrientes en el margen pacifico de Baja California, etc.

Bajo recomendación de mi tutor de empresa, acudí a 4 clases sobre isotopos estables centradas en el análisis de isótopos de ^{18}O , ^{13}C , ^{15}N en matrices orgánicas y sedimentarias. Estas clases eran impartidas por mi tutor de empresa y estaban relacionadas con mi trabajo de investigación ya que usaba el análisis de isótopos de ^{13}C , ^{15}N y la razón N:C en sedimentos para determinar el aporte terrestre de materia orgánica al margen de Magdalena en los últimos 4000 años aproximadamente.

3. Nivel de integración e implicación dentro del departamento y relaciones con el personal.

El nivel de integración e implicación con el personal del departamento y el laboratorio fue bastante satisfactorio. Todos se mostraron receptivos ante mis dudas y sugerencias, y fueron muy atentos formándome para las labores que realicé durante mi estancia.

El departamento se componía de aproximadamente 26 personas, pero sólo tuve una relación más estrecha con mi tutor y su grupo de investigación, la jefa de laboratorio, el técnico superior del laboratorio y alumnos de maestría (máster). Los descansos facilitaron la integración personal con los otros alumnos de maestría y las salidas de campo con los demás grupos de investigación. En los seminarios conocí a distintos profesores de otros departamentos y en las clases de isótopos entablé relación con otros alumnos de máster y doctorado. Gracias a ello pude conocer los distintos trabajos que realizaban y la variedad de usos que le daban al análisis de isotopos: análisis climáticos en matrices coralinas con ^{18}O , determinación de alimentación en tiburones y tortugas con isótopos de ^{15}N , determinación de fuentes de contaminación con isótopos de ^{15}N .

4. Aspectos positivos y negativos más significativos relacionados con el desarrollo de las prácticas.

Aspectos positivos: aprender sobre el trabajo que existe detrás del mundo de la investigación, y valorar dicho trabajo. El haber trabajado en equipo y de manera autónoma, con las responsabilidades que acarrearán ambas situaciones:

Trabajar en equipo me ha permitido relacionarme con el resto del laboratorio y con otros grupos de investigación y tener una visión más holística. Además, tienes la responsabilidad de que tu equipo de trabajo y tus superiores dependen de tu trabajo al igual que yo dependo del suyo.

En cambio trabajar solo me ha aportado más disciplina de trabajo y más responsabilidad a la hora de tratar muestras con las que desarrollas tu investigación, pues los despistes y descuidos pueden frenarte o incluso obligarte a reiniciar el trabajo. También te da más libertad a la hora de optimizar técnicas, siempre y cuando no alteren los resultados.

Aspectos negativos: me gustaría haber aprendido más variedad de técnicas experimentales durante el transcurso de mis prácticas.

5. Valoración personal del aprendizaje conseguido a lo largo de la práctica.

Me ha parecido una experiencia enriquecedora desde el punto de vista profesional, académico y personal:

- Profesional: conocer el trabajo que hay detrás de todos los resultados que vemos en el papel o presentaciones en pantallas y la dedicación y responsabilidad que requiere la producción de datos científicos de calidad.
- Académico: aprender técnicas de laboratorio y los principios teóricos en los que se basan, poder usar lo aprendido durante el curso en un ámbito más laboral y comprender el fin del trabajo realizado.
- Personal: El tratar con otras personas en el grupo de investigación y fuera de él, intercambiar conocimientos de nuestro trabajo y poder discutir acerca de ellos, y conocer las motivaciones y los objetivos que los impulsan a trabajar en el ámbito de la investigación marina. Además, al realizar las prácticas externas y el TFG en Baja California Sur, México me ha permitido conocer la cultura de este país, su forma de vida, su deliciosa gastronomía y la cantidad de vida salvaje que se observa cerca de la ciudad. Sus hermosas playas donde acampar y las aguas repletas de biodiversidad, desde pequeños peces globo hasta grandes tiburones ballena. Y por supuesto compartir todas estas experiencias con la encantadora gente de México que he conocido y con la que he entablado amistad.

Sinceramente gracias a la asignatura y lo aprendido en ella he adquirido una mayor confianza y seguridad a la hora de desempeñar el trabajo de laboratorio y de campo.