Early diagenesis and vertical distribution of organic carbon and total nitrogen in recent sediments from southern Chilean fjords (Boca del Guafo to Pulluche Channel)

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ABSTRACT. Eleven surface sediment cores were taken with a Rumohr corer during the oceanographic cruise Cimar 8 Fiordos (July 2002; between the Corcovado Gulf and Pulluche Channel). These cores were used to determine the vertical distribution of organic carbon, total nitrogen, and their atomic ratio (C/N) for use as a diagenesis indicator. The grains observed were mostly clay-silt in four of the sediment cores and more heterogeneous in the other seven cores. Organic carbon and total nitrogen concentrations were higher in the four clay-silt cores than in the sandy cores, although in terms of their vertical distribution, both concentrations were relatively homogenous at most stations. Nevertheless, exponential decreases characteristic of first-order diagenetic degradation were observed in cores from three stations. The C:N ratio fluctuated between 7 and 10, indicating that the organic material in the sediments was mostly marine in origin. Values were lower at more oceanic stations and greater at more coastal stations; the contribution of terrigenous materials was greater at the latter. We inferred a slower break down of organic carbon as compared to total nitrogen from a steady-state first-order degradation kinetics model, that was applied to stations where both fractions had exponential vertical distributions. Remineralization percentages were between 23 and 34% (organic carbon) and 33 and 43% (total nitrogen) and accumulation percentages were between 77 and 66% (organic carbon) and 67 and 57% (total nitrogen).

Key words: sediments, grain size, carbon, nitrogen, C:N, diagenesis, estuaries, fjords, Chile.

Diagénesis temprana y distribución vertical de carbono orgánico y nitrógeno total en sedimentos recientes de los fiordos del sur de Chile (Boca del Guafo hasta canal Pulluche)

RESUMEN. Durante el crucero oceanográfico Cimar 8 Fiordos (julio 2002), entre golfo Corcovado y canal Pulluche, con un Rumohr corer se obtuvo 11 testigos de sedimentos superficiales. Con éstos se determinó la distribución vertical de carbono orgánico, nitrógeno total y sus relaciones atómicas (C:N) para ser usados como indicadores de la presencia de procesos diagenéticos. En cuatro testigos o "cores", la textura se caracterizó por estar compuesta principalmente por sedimento limo-arcilloso y en los otros siete la composición de textura fue más heterogénea. Las muestras limo-arcillosas presentaron mayores concentraciones de C-org y N-tot, que aquellas más arenosas. En cuanto a la distribución vertical de C-org y N-tot, sus concentraciones fueron relativamente homogéneas en la mayoría de las estaciones. Sin embargo, tres estaciones presentaron disminuciones de tipo exponencial características de procesos de degradación diagenética de primer orden. Valores de la razón C:N, entre 7 a 10, indican, en una primera aproximación, que la procedencia de la materia orgánica del sedimento es mayormente de origen marino. Los menores valores se registraron hacia el océano y los mayores valores hacia el continente, donde el aporte fluvial y terrígeno, es mayor. La aplicación de un modelo de diagénesis de primer orden a estaciones con distribuciones verticales exponenciales de C-org y N-tot, permitió inferir que el C-org se degrada más lentamente que el N-tot, obteniéndose porcentajes de remineralización entre 23 y 34%, y 33 y 43% para el C-org y N-tot y de acumulación entre 77 y 66%, y 67 y 57%, respectivamente.

Palabras clave: sedimentos, textura, carbono, nitrógeno, C:N, diagénesis, fiordos, Chile.

INTRODUCTION

Estuarine systems are areas that are subject to a large contribution of both autochthonous organic material from planktonic productivity and allochthonous particulate organic material transported by rivers and surface runoff. These coastal areas, including the estuarine ones, can be differentiated from oceanic areas by, amongst others, their high sedimentation rates ($0.1\text{--}10\text{ cm}\cdot\text{year}^{-1}$ v/s $0.1\text{--}10\text{ cm}\cdot 1000\text{ year}^{-1}$) (Berner, 1980). The gradual accumulation of sedimentary material, leaves the organic matter that is deposited on the sediment surface exposed to bacterial degradation in an oxidizing environment for long periods of time. Some authors suggest that processes such as adsorption into the sediments of material in the mineral phase, favors the preservation of compounds that, otherwise, might be easily degradable (Müller & Suess, 1979; Hedges & Keil, 1995).

During sedimentation in the water column, autochthonous and/or allochthonous particulate organic material undergoes intense degradation and only a small fraction reaches the surface sediments (Wakeham & Lee, 1993). Having reached the bottom, the sediment is again submitted to decomposition as a result of a series of diagenetic reactions, which can either release or affix elements and compounds between the interstitial water and the overlying water column (Berner, 1980; Klump & Martens, 1987; Farías *et al.*, 1994, 1996). A variety of factors determine the quantity, vertical distribution, and chemical composition of the organic material found in the sediments. These factors include primary production, contributions of allochthonous material, adsorption of organic material in mineral phases, water column depth, sedimentation rates, bioperturbation, and the concentration of dissolved oxygen (Stumm & Morgan, 1981; Jorgensen *et al.*, 1990; Cowie & Hedges, 1992; Hedges & Keil, 1995; Fütterer, 2000).

Studies of the vertical distribution of components like organic carbon (C-org), total nitrogen (N-tot), and their atomic ratio (C/N) could be used to indicate diagenesis (Wakeham, 2002). C-org and N-tot decrease with increasing depth of burial as organic matter is being remineralized.

Eleven surface sediment cores, taken between Boca del Guafo and Pulluche Channel, were analyzed in order to determine the vertical distribution of C-org and N-tot and to elucidate the presence of diagenetic processes and the intensity

of their degradation based on a steady-state first-order degradation kinetics model.

MATERIALS AND METHODS

Leg one of the Cimar 8 Fiordos cruise was carried out between Boca del Guafo ($43^{\circ}47'S$) and Pulluche Channel ($45^{\circ}49'S$), from 5 to 20 July 2002, on board of the research vessel AGOR Vidal Gormaz.

Physical and chemical analysis

Sediment samples were taken from 11 stations with a Rumohr corer (70 cm long) (Fig. 1). The cores (max. length 50 cm) were stored vertically and frozen at -20°C until their analysis in the laboratory. The cores were cut into sections: 1 cm thick for the first three cm, 2 cm thick for the next 14 cm, and 3 cm thick from 17 cm to the core bottom. Each section was divided in two subsamples for physical (grain size) and chemical (carbon and nitrogen) analysis.

Sediment grain size (granulometry) was determined by wet sieving each section, separating the fractions according to the Udden Wentworth scale (Φ).

For the chemical analysis, each section was dried at 60°C in a vacuum oven and then ground to a very fine dust with an agate mortar and pestle. The analyses were done for C-org and N-tot. Total carbon was determined with a carbon elemental analyzer (LECO CR-12). C-org by burning in the LECO CR-12 a sample that had been pretreated with hydrochloric acid to eliminate the inorganic carbon. N-tot was determined by using the Kjeldahl technique indicated in Willard *et al.* (1956) and adapting it to a Micro-Kjeldahl device.

The equipment used in both, carbon and nitrogen analyses, was calibrated with soil standards with the carbon and nitrogen concentrations within the ranges of the samples. These standards are certified by the National Institute of Standards and Technology (NIST).

Diagenesis model

In the stations where the vertical C-org and N-tot distribution decreased exponentially with depth, a steady-state first-order degradation kinetics model was applied (Berner, 1980). This model separates sedimented organic material (G_o) into two fractions: the labile or metabolizable fraction (G_m) that is degraded and the residual refractory fraction (G_r) that is buried, where:

Figure 1. Geographic location of surface sediment sampling stations, Cimar 8 Fiordos cruise.

Figura 1. Posición geográfica de las estaciones de muestreo de sedimento en la expedición oceanográfica Cimar 8 Fiordos.

$$G_o = G_m + G_\infty \quad (1)$$

According to the Berner model (1980), sedimentation and burial rates are assumed to be constant over time and in steady state.

The remineralization of labile organic material is estimated according to:

$$G_Z = G_{mo} \exp[(-k/\omega) \cdot Z] + G_\infty \quad (2)$$

where: G_Z is the concentration of C-org or N-tot ($\text{mg} \cdot \text{g}^{-1}$) at depth Z (cm); G_{mo} is the labile fraction that is deposited initially ($\text{mg} \cdot \text{g}^{-1}$); G is the quantity of the residual refractory material ($\text{mg} \cdot \text{g}^{-1}$); k is a constant representing the rate of first-order decay (year^{-1}); and ω is the sedimentation rate ($\text{cm} \cdot \text{year}^{-1}$). The constant k was obtained from the slope of equation (2), which involves the sedimentation rate, in which decay is a function of time.

The recycled or degraded fraction is equal to the difference between the total concentration at the

sediment surface, G_o ($\text{mg}\cdot\text{g}^{-1}$), and the concentration at depth where the remaining organic material is residual or refractory, G_∞ ($\text{mg}\cdot\text{g}^{-1}$):

$$G_{mo} = G_o - G_\infty \quad (3)$$

In a stationary state, the fractions G_o , G_{mo} , and G_∞ are constants and the remineralized and accumulated percentages are given by:

$$\% \text{ Remineralization} = \frac{G_{mo}}{G_o} \cdot 100 = \frac{G_o - G_\infty}{G_o} \cdot 100 \quad (4)$$

$$\% \text{ Accumulation} = \frac{G_\infty}{G_o} \cdot 100 \quad (5)$$

RESULTS

Distribution of physical and chemical sediment characteristics

Grain sizes in four cores were nearly homogenous, with clay-silt fractions over 80% (St. 8, 9, 17a and 53; Fig. 2). Four other cores were somewhat heterogeneous, with a preponderance (50-60%) of one fraction, usually very fine sand or clay-silt (St. 6, 14, 51 and 54; Fig. 2). The remaining three cores were highly heterogeneous, having more dispersed grain sizes and no single fraction over 50% (St. 11, 72, and 76; Fig. 2).

Vertical distribution values for C-org and N-tot were greatest ($> 2.0\%$ and $> 0.3\%$, respectively) throughout the entire sediment column at stations 8 and 9, whereas the lowest values ($< 0.5\%$ and $< 0.1\%$) throughout the column were found at stations 11, 14, and 72 (Fig. 3).

The greatest variations in the vertical distribution of the C:N ratio were observed at stations 14 and 76 (6.8-14.1); lesser variations were observed at stations 8 and 9 (7.1-8.6) (Fig. 4).

Diagenetic model

In general terms, the vertical C-org and N-tot distribution was almost homogenous in some cores (St. 14, 54) and abruptly varied in others (St. 51). In a reduced group, the vertical distribution of the C-org and N-tot concentration resembled an exponential distribution (St. 6, 9, and 53); because of this, a steady-

state first-order degradation kinetics model was applied (Berner, 1980) in order to estimate the respective decay rates and remineralization and accumulation percentages. This model requires a sedimentation rate, which had to be estimated since the cores used were not dated. In order to estimate the sedimentation rate, the different values known for the area were considered: Rojas (2002) estimated sedimentation rates between 0.26 and 0.33 $\text{cm}\cdot\text{year}^{-1}$ for Aysén Fjord and 0.28 $\text{cm}\cdot\text{year}^{-1}$ for Costa Channel; Salamanca & Jara (2003) estimated 0.15 $\text{cm}\cdot\text{year}^{-1}$ for Cupquelán Fjord, between 0.29 and 0.36 $\text{cm}\cdot\text{year}^{-1}$ for Aysén Fjord, and 0.67 $\text{cm}\cdot\text{year}^{-1}$ for Quitralco Fjord; and Sepúlveda *et al.* (2005) estimated 0.25 $\text{cm}\cdot\text{year}^{-1}$ for Puyuhuapi Channel. Unfortunately, sedimentation rates were not available for oceanic channels (St. 53, King Channel), although these rates could differ from those of the interior channels.

Based on the previous sedimentation rates for Aysén Fjord and the Costa and Puyuhuapi channels, and taking into account that these channels showed oceanographic characteristics similar to those of Moraleda Channel (Silva *et al.*, 1998), an average sedimentation rate of 0.29 $\text{cm}\cdot\text{year}^{-1}$ was calculated as representative of all the inner channels. Since information was not available for areas similar to the oceanic station 53, this station was assigned the same sedimentation rate as the others. C-org and N-tot remineralization and accumulation percentages (Table 1) were estimated using this sedimentation rate and applying Berner's (1980) steady-state first-order degradation kinetic model.

DISCUSSION

Relationship between grain size and concentrations of C-org and N-tot

Stations 8, 9 and 53 are characterized by being made up of a high percentage of clay-silts ($> 80\%$), which were the sediments with the greatest concentrations of C-org and N-tot ($> 2\%$ and $> 0.2\%$) (Figs. 2 and 3). This well known characteristic (Hedges & Keil, 1995; Fütterer, 2000; Hedges, 2002; Wakeham, 2002) has also been observed in the Chilean fjord zone where the organic material content was higher in fine than in coarse sediments (Silva *et al.*, 1998; Silva & Ortiz, 2002; Rojas & Silva, 2003).

This can be explained by the fact that fine, clay silt particles have larger surface areas than sand particles and tend to have associated negative

Figure 2. Grain size fraction and organic carbon vertical distribution for Cimar 8 Fjords sediment columns, where: [fine granule + very fine granule] = $\circ$, [very coarse sand + coarse sand + medium sand] = $\square$, [fine sand + very fine sand] = Δ , [silt + clay] = $\circ$ and organic carbon = $\bullet$.

Figura 2. Distribución vertical de la textura y carbono orgánico para las columnas de sedimento de Cimar 8 Fjords, donde: [grava fina + grava muy fina] = $\circ$, [arena muy gruesa + arena gruesa + arena mediana] = $\square$, [arena fina + arena muy fina] = Δ , [limos + arcillas] = $\circ$ y carbono orgánico = $\bullet$.

Figure 3. Vertical distribution for Cimar 8 Fiordos sediment columns. ● Organic carbon (%) and □ total nitrogen (%).

Figura 3. Distribución vertical de ● carbono orgánico (%) y □ nitrógeno total (%) para las columnas de sedimento de Cimar 8 Fiordos.

Table 1. Parameters of the kinetic model of first-order diagenesis for vertical profiles of C-org and N-tot from stations 6, 9 and 53.**Tabla 1. Parámetros del modelo cinético de primer orden de diagénesis en estado de equilibrio, aplicado a la distribución vertical de C-org y N-tot de las estaciones 6, 9 y 53.**

Parameters	Organic Carbon			Total Nitrogen		
	St. 6	St. 9	St. 53	St. 6	St. 9	St. 53
Z (cm)	24.5	16	14	24.5	14	14
ω (cm·year ⁻¹)	0.29	0.29	0.29	0.29	0.29	0.29
α (cm ⁻¹)	0.064	0.131	0.160	0.119	0.159	0.205
k (year ⁻¹)	0.019	0.038	0.046	0.035	0.046	0.059
$\tau = 1/k$ (year)	54	26	22	29	22	17
$t_{1/2}$ (year)	37	18	15	20	15	12
G_{mo} (mg·g ⁻¹)	2.30	10.39	5.51	0.61	1.56	1.57
G_o (mg·g ⁻¹)	10.06	30.20	20.84	1.67	4.76	3.67
G (mg·g ⁻¹)	7.76	19.81	15.33	1.06	3.20	2.10
% Remineralization	22.85	34.41	26.44	36.41	32.77	42.78
% Accumulation	77.15	65.59	73.56	63.59	67.23	57.22

where:

Z (cm) = depth of the sediment column; the model assumes that no more changes from degradation (early diagenesis) take place from this point in the sediment column and that the remainder consists of only refractory material.

τ = $1/k$ (year); time of residence of the labile fraction.

$t_{1/2}$ = $\ln 0.5 / k$ (year); half-life of the labile fraction.

α (cm⁻¹) = k/ω ; attenuation coefficient or best fit coefficient.

k (year⁻¹) = $\alpha \cdot \omega$; constant rate of decay of organic material, also known as the constant rate of first-order decay.

charges. Therefore, upon entering the sea water, their surfaces are quickly coated with a layer of organic material. The ratio C-org/surface area is higher for finer than for coarser sediments, such as sand particles (Hedges & Keil, 1995; Hedges, 2002; Wakeham, 2002). Therefore, the finer sediments should have greater concentrations of organic material.

Station 17a is an exception to the above pattern, consisting largely of clay silt sediments but with intermediate concentrations of C-org and N-tot ($\blacktriangle$ 1% and $\blacktriangle$ 0.1%). This could be due to a greater inorganic fraction brought into the fjord's fine sediment by adjacent rivers (Aysén, Cuervo, and Cóndor). If the inorganic fine sediment fraction input is large and fast enough to reach the bottom quickly, it could increase the presence of very fine particles without necessarily increasing the sediment's organic content.

Silva *et al.* (1998) observed a similar situation in the more southern Quitalco and Cupquelán fjords, where sediments were 100% clay-silt and had less

organic content (averaging 0.4% C-org and 0.04% N-tot) than did Station 17a. These authors explained the low concentration of organic matter by the huge presence of clay-silt sediments originating in the weathering of rocks from the Campo de Hielo Norte glacier. This material, which appears milky in the fjord waters, lowering the light penetration to a few centimeters, causes organic carbon to be "diluted" upon reaching the sediments with the results indicated above. The situation of Aysén Fjord is different because no large glaciers are found in the area and so no milky material is observed suspended in the fjord. Thus the contribution of fine inorganic material from the weathering of rocks in its hydrographic basin should be lower than Quitalco and Cupquelán fjords, resulting in less "dilution" of the organic components and, therefore, intermediate C-org and N-tot concentrations.

Stations 11, 14, 51, 54, 72, and 76 had more heterogeneous grain size, with sandy fractions predominating over clays and silts (Fig. 2). Thus, these stations had low concentrations of C-org and N-tot (< 1% and < 0.1%; Figs. 2 and 3).

Vertical distribution of C-org and N-tot

In general, vertical C-org and N-tot distributions did not show exponential type decay in the first 20-30 cm (Fig. 3). At times, the profiles of these variables were relatively homogenous, insinuating that the sediments may be affected by mixing from physical and/or biological processes (St. 14 and 54). This is possible because bacterial and animal activities are most intense and electron acceptors more energetic in the surface layer of the sediments (Aller, 1982). This uniform distribution could also be the result of rapid sedimentary deposition (*i.e.*, high sedimentation rates), in which organic material is quickly moved below the more diagenetically active zone and, therefore, suffers less degradation. Moreover, rapid deposition quickly protects the sedimented organic material from contact with the main oxidizing agents found in the overlying sea water such as oxygen, nitrate, and sulfate (Hedges & Keil, 1995).

The situation at stations 11, 51, and 72 is more complex. The column presented nearly homogenous strata of C-org and N-tot in the upper sections, typical of bioperturbed activity. C-org and N-tot increased at depth along with clay-silts (Fig. 2). These changes in grain size and C-org and N-tot concentrations with depth can be related to different chemical and physical compositions of the sediments as opposed to those previously accumulated or with changes in the material's degradation.

At stations 6, 9 and 53, C-org and N-tot concentrations were similar to an exponential distribution with depth. This type of distribution allows us to assume scarce or null bioperturbation activity and diagenetic decomposition of the organic material with a first-order kinetic (Berner, 1980).

C:N ratio

The C:N ratio for marine phytoplankton is 6.6, for fresh marine sediments is 7 to 10, and for terrestrial plants is over 20 (Deevy, 1973; Rullkötter, 2000). Because of this, it is possible to use the C:N ratio as a "proxy" for an initial inference as to the origin of the material that composes the sediments. The combined use of the C:N ration and the stable carbon isotope ratio ($\delta^{13}\text{C}$), with higher values in marine (-15 to -19‰; Emerson & Hedges, 1988), than in terrestrial material (-19 to -22‰; Fontugne & Jouanneau, 1987), has also been used frequently to the same purpose (Meyers, 1994, 1997; Thornton

& McManus, 1994; Müller, 2001; Ruiz-Fernández *et al.*, 2002).

When using only the C:N ratio, it is important to keep in mind that, as the organic material falls to the bottom, the nitrogen-containing compounds are preferentially used relative to carbon-containing compounds (Burdige & Martens, 1988; Jorgensen, 1996; Wakeham, 2002). This can partially alter the relationship's indication as to the organic material's origin.

The C:N ratio observed in the study area (Fig. 4) fluctuated between 6 and 8 (station 72) and between 7 and 10 (stations 6, 8, 9, 11, 17a, 53 and 54). Stations 14, 51, and 76 had a few C:N values over 10, although in general, values remained between 7 and 10. Similar C:N values were observed by Silva & Prego (2002), throughout the entire Chilean fjord area, from Puerto Montt (41°S) to Cape Horn (56°S).

However, this southern Chilean fjord area has abundant vegetation with native forests, and an important part of the organic residues and terrigenous material is transported by rivers and runoff from the nearby coast (the Aysén River basin drainage provides an average annual flow of 5000 m³·s⁻¹ and has an average annual rainfall of 3000 mm; Guzmán, 2004). Thus, allochthonous organic material is eventually deposited in the sediments along with autochthonous marine material.

Pinto & Bonert (2005), using the $\delta^{13}\text{C}$ measurements from sediment samples taken in Moraleda Channel and Aysén Fjord (Cimar 4 Fiordos cruise, September 1998), observed that Moraleda had high values (-15 to -17‰) characteristic of marine material, whereas the head of Aysén had low values (-22 to -25‰), which were associated with increased allochthonous content toward the head of the fjord. Stations 6, 11, 14, and 17a (Cimar 8 Fiordos), coincided in position with those of Cimar 4 Fiordos and, therefore, the sediment's chemical characteristics should be similar. In this area, the $\delta^{13}\text{C}$ of the surface sediments fluctuated between -15.9 and -21.7‰ (Pinto & Bonert, 2005) and the C:N ratio fluctuated between 7 and 9 (Fig. 4).

Therefore, using the database of calculated C:N values from this study and the $\delta^{13}\text{C}$ observations of Pinto & Bonert (2005), it can be concluded that the surface sediments in the study area are mostly marine in origin with contributions from terrestrial materials that increase towards the continental extremes of the fjords.

Figure 4. C:N ratio (μg-atC·g⁻¹/μg-atN·g⁻¹) vertical distribution for Cimar 8 Fjords sediment columns.

Figura 4. Distribución vertical de la relación C:N (μg-átC·g⁻¹/μg-átN·g⁻¹) para las columnas de sedimentos de Cimar 8 Fiordos.

The only station where the vertical distribution of the C:N ratio increased gradually with depth (from 7.1 to 8.6) throughout the column was station 53. This increase in the C:N ratio (Fig. 4) and decrease of C-org and N-tot (Fig. 3) was caused by the selective degradation of the nitrogen-containing compounds, as previously indicated by Klump & Martens (1987), Farías & Salamanca (1990); and Jorgensen *et al.* (1990), amongst others.

Diagenesis

In the cores from stations 6, 9 and 53, the C-org and N-tot concentrations decreased practically exponentially with depth. This was attributed to diagenetic degradation and, therefore, the steady-state first-order degradation kinetics model proposed by Berner (1980) could be applied. Of these three cores, only the core from station 53 smelled of H₂S, indicating anaerobic conditions in the sediments. Berner (1980) and Boudreau (1997) indicated that the exponential diagenetic profile tends to be more defined with anaerobic degradation than with aerobic degradation, which agrees with the observations of station 53.

The decay constants (*k*) or first-order kinetic decompositions for stations 6, 9 and 53 were estimated to be 0.02, 0.04 and 0.05 year⁻¹ for C-org and 0.04, 0.05, and 0.06 year⁻¹ for N-tot, respectively (Table 1). Their estimated half lives were 37, 18 and 15 years (C-org) and 20, 15 and 12 years (N-tot). These results indicate that, in general, C-org decomposes more slowly than N-tot in the sediment column.

The low remineralization and high accumulation percentages of C-org and N-tot calculated for stations 6, 9, and 53 (Table 1) could be explained by a rapid sedimentation rate that did not favor bacterial degradation of organic material, but rather its accumulation in the sediments.

The differences observed in these percentages indicate, furthermore, that the remineralization of N-tot is faster than that of C-org, so the buried organic material contains more C-org than N-tot. This is due to the fact that the nitrogen-containing compounds (*e.g.*, proteins) are more labile than carbon compounds (*e.g.*, fats) and therefore break down more rapidly (Burdige & Martens, 1988; Wakeham, 2002). Louchouart *et al.* (1997) also showed, in the St. Lawrence Estuary (Canada), a diagenetic selectivity in the sediments, obtaining a *k* = 0.035 year⁻¹ and a half-life of 20 years for C-org and a *k* = 0.054 year⁻¹ and a half life of 13 years for

N-tot. Although this selective remineralization between C-org and N-tot is quite common in sediments, it is not always the case. Louchouart *et al.* (1997), in the same St. Lawrence Estuary, observed equal reactivity rates for C-org and N-tot at one station. The selective degradation and decay rates observed in this Chilean fjord area are similar to those of the Canadian fjords.

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REFERENCES

- Aller, R. 1982. The effects of macrobenthos on chemical properties of marine sediments and overlying water. In: P.L. McCall & M.J.S. Tevesz (eds.). *Animal-sediments relations*. Plenum Press, New York, pp. 53-102.
- Berner, R. 1980. *Early diagenesis: a theoretical approach*. Princeton University Press, New York, 421 pp.
- Boudreau, B. 1997. *Diagenetic models and their implementation: modelling transport and reactions in aquatic sediments*. Springer-Verlag, Berlin, 414 pp.
- Burdige, D. & C. Martens. 1988. Biogeochemical cycling in an organic rich coastal marine basin: 10. The role of amino acids in sedimentary carbon and nitrogen cycling. *Geochim. Cosmochim. Acta*, 52: 1571-1584.
- Cowie, G. & J. Hedges. 1992. Sources and reactivities of amino acids in the coastal marine environment. *Limnol. Oceanogr.*, 37: 703-724.

- Deevy, E. 1973.** Sulfur, nitrogen and carbon in the biosphere. In: G.M. Woodwell & E.V. Peacan (eds.). Carbon and the biosphere. USAEC, Washington D.C., pp. 182-190.
- Duinker, J. 1980.** Suspended matter in estuaries: adsorption and desorption processes. In: E. Olausson & I. Cato (eds.). Chemistry and biogeochemistry of estuaries. John Wiley & Sons, New York, 452 pp.
- Emerson, S. & J. Hedges. 1988.** Processes controlling the organic carbon content of open ocean sediments. *Paleoceanography*, 3: 621-634.
- Farías, L. & M. Salamanca. 1990.** Distribución vertical de sulfato, cloruro y amonio en el agua intersticial de sedimentos de bahía de Concepción, Chile. *Cienc. Tecnol. Mar*, 14: 33-44.
- Farías, L., L. Chuecas & M. Salamanca. 1996.** Effect of coastal upwelling on nitrogen regeneration from sediments and ammonium supply to the water column in Concepción bay, Chile. *Estuar. Coast. Shelf Sci.*, 43: 137-155.
- Farías, L., M. Salamanca & L. Chuecas. 1994.** Variaciones estacionales del flujo de partículas y contenido de materia orgánica a la interfase agua-sedimento en bahía Concepción, Chile Central. *Cienc. Tecnol. Mar*, 17: 15-31.
- Fontugne, M. & J. Jouanneau. 1987.** Modulation of the particulate organic carbon flux to the ocean by macrotidal estuary-evidence from measurements of carbon isotopes in organic matter from the Gironde system. *Estuar. Coast. Shelf Sci.*, 24: 377-387.
- Fütterer, D.K. 2000.** The solid phase of marine sediments In: H.D. Schulz & M. Zabel (eds.). Marine Geochemistry. Springer-Verlag, Berlin, pp. 1-25.
- Guzmán, D. 2004.** Caracterización hidrográfica y oceanográfica y balance biogeoquímico de nitrógeno y fósforo en el fiordo Aysén. Tesis Magíster en Oceanografía. Pontificia Universidad Católica de Valparaíso y Universidad de Valparaíso. 74 pp.
- Hedges, J. 2002.** Sedimentary organic matter preservation and atmospheric O₂ regulation. In: A. Gianguzza, E. Pelizzetti & S. Sammartano (eds.). Chemistry of marine water and sediments. Springer, Berlin, pp. 105-123.
- Hedges, J. & R. Keil. 1995.** Sedimentary organic matter preservation: an assessment and speculative synthesis. *Mar. Chem.*, 49: 81-115.
- Jorgensen, B. 1996.** Material flux in the sediment. In: B. Jorgensen & K. Richardson (eds.). Coastal and Estuarine Studies. American Geophysical Union, pp. 115-135.
- Jorgensen, B., M. Bang & T. Blackburn. 1990.** Anaerobic mineralization in marine sediments from the Baltic Sea-North Sea transition. *Mar. Ecol. Prog. Ser.*, 59: 39-54.
- Klump, J. & C. Martens. 1987.** Biogeochemical cycling an organic-rich coastal marine basin. 5. Sedimentary nitrogen and phosphorus budgets based upon kinetic models, mass balances, and the stoichiometry of nutrient regeneration. *Geochim. Cosmochim. Acta*, 51: 1161-1173.
- Louchouart, P., M. Lucotte, R. Canuel, J. Gagné & L. Richard. 1997.** Sources and early diagenesis of lignin and bulk organic matter in the sediments of the Lower St. Lawrence estuary and the Saguenay fjord. *Mar. Chem.*, 58: 3-26.
- Meyers, P. 1994.** Preservation of elemental and isotopic identification of sedimentary organic matter. *Chem. Geol.*, 144: 289-302.
- Meyers, P. 1997.** Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. *Org. Geochem.*, 27: 213-250.
- Müller, A. 2001.** Geochemical expressions of anoxic conditions in Nordasvannet, a land-locked fjord in western Norway. *Appl. Geochem.*, 16: 363-374.
- Müller, P. & E. Suess. 1979.** Productivity, sedimentation rate and sedimentary organic matter in the oceans. 1. Organic carbon preservation. *Deep-Sea Res.*, 26 A: 1347-1362.
- Pinto, L. & C. Bonert. 2005.** Origen y distribución espacial de hidrocarburos alifáticos en sedimentos de seno Aysén y canal Moraleda, Chile Austral. *Cienc. Tecnol. Mar*, 28(1): 35-44.
- Rojas, N. 2002.** Distribución de materia orgánica, carbono y nitrógeno, y diagénesis temprana en sedimentos de la zona de canales australes entre los golfos Corcovado y Elefantes, Chile. Tesis de Oceanografía. Escuela de Ciencias del Mar. Universidad Católica de Valparaíso, 80 pp.
- Rojas, N. & N. Silva. 2003.** Distribución espacial de textura, C y N en sedimentos recientes en canales y fiordos chilenos. Golfo Corcovado (43°50'S) a

- golfo Elefantes (46°30'S), Chile. *Cienc. Tecnol. Mar*, 26(1): 15-31.
- Ruiz-Fernández, A., C. Hillaire-Marcel, B. Ghaleb, M. Soto-Jiménez & F. Páez-Osuna. 2002.** Recent sedimentary history of anthropogenic impacts on the Culiacán River Estuary, northwestern México: geochemical evidence from organic matter and nutrients. *Environ. Pollut.*, 118: 365-377.
- Rullkötter, J. 2000.** Organic matter: the driving force for early diagenesis. In: H.D. Schulz & M. Zabel (eds.). *Marine Geochemistry*. Springer-Verlag, Berlin, pp. 129-172.
- Salamanca, M. & B. Jara. 2003.** Distribución y acumulación de plomo (Pb y 210Pb) en sedimentos de los fiordos de la XI Región. Chile. *Cienc. Tecnol. Mar*, 26(2): 61-71.
- Sepúlveda, J., S. Pantoja, K. Hughen, C. Lange, F. González, P. Muñoz, L. Rebolledo, R. Castro, S. Contreras, A. Ávila, P. Rossel, G. Lorca, M. Salamanca & N. Silva. 2005.** Fluctuations in export productivity over the last century from sediments of a southern Chilean fjord (44°S). *Estuar. Coast. Shelf Sci.*, 65: 587-600.
- Silva, N. & P. Ortiz. 2002.** C y N, su distribución y estequiometría, en sedimentos superficiales de la región sur de la zona de fiordos y canales australes de Chile, 52°-56°S (Crucero Cimar Fiordo 3). *Cienc. Tecnol. Mar*, 25(1): 89-108.
- Silva, N. & R. Prego 2002.** Carbon and nitrogen spatial segregation and stoichiometry in the surface sediments of southern Chilean inlets (41°-56°S). *Estuar. Coast. Shelf Sci.*, 55: 763-775.
- Silva, N., J. Maturana, J.I. Sepúlveda & R. Ahumada. 1998.** Materia orgánica, C y N, su distribución estequiometría, en sedimentos superficiales de la región norte de los fiordos y canales australes de Chile (Crucero Cimar-Fiordo 1). *Cienc. Tecnol. Mar*, 21: 49-74.
- Stumm, W. & J. Morgan. 1981.** *Aquatic Chemistry. An introduction emphasizing chemical equilibria in natural water*. John Wiley & Sons, New York, 780 pp.
- Thornton, S. & J. McManus. 1994.** Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems: Evidence from the Tay Estuary, Scotland. *Estuar. Coast. Shelf Sci.*, 38: 219-233.
- Wakeham, S. 2002.** Diagenesis of organic matter at the water-sediment interface. In: A. Gianguzza, E. Pelizzeti & S. Sammartano (eds.). *Chemistry of marine water and sediments*. Springer. Berlin, pp. 146-164.
- Wakeham, S. & C. Lee. 1993.** Production, transport, and alteration of particulate organic matter in the marine water column. *Organic Geochemistry*. Plenum Press, New York, 6: 145-169.
- Willard, H., N. Furman & C. Bricker. 1956.** *Análisis químico cuantitativo*. Marín, Barcelona, 557 pp.

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