Composition and fate of organic matter in submarine cave sediments; implications for the biogeochemical cycle of organic carbon

Organic matter
Biogeochemistry
Early diagenesis
Budget
Cave

Matière organique
Biogéochimie
Diagénèse précoce
Bilan
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ABSTRACT

The biochemical composition of the sediments in a Mediterranean submarine cave (Marseille, France) was studied, and a budget for the biogeochemical cycle of organic carbon was calculated. Chloropigment and lipid levels were markedly lower in sediments from the dark inner section of the cave compared to the twilight outer section. These decreased levels were related to the decrease in the vertical inputs of particulate organic matter. Lower decreases were recorded in the sediment content of other organic constituents (organic carbon, organic nitrogen, carbohydrates, proteins). The analysis of carbohydrate and protein extracted from sediments (NaOH 1 N, 24 h, 4° C) yielded no significant information, demonstrating the ambiguous significance of such a chemical approach in sediments low in organic matter.

A biogeochemical budget for the cycling of organic compounds in the sediment was achieved using previous studies on suspended particle composition and vertical flux. Benthic degradation processes were highly efficient, ~ 90 % of the sedimenting organic carbon was degraded in the top 15 cm sediment layer, and only ~ 10 % of this input was buried. Lipids , with ~ 100 % used in the top layer, proved to be highly degradable compounds. Despite a high degradation rate of proteins and carbohydrates, respectively ~ 3 and ~ 8 % of their initial inputs were still present at 15 cm depth showing that some of these compounds are stable and may resist diagenetic decomposition. Complex organic matter was a significant source of organic carbon in these sediments, and, despite the high energetic investment required, must be considered as a potential resource, especially in oligotrophic environments.

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RÉSUMÉ

Composition et devenir de la matière organique sédimentaire dans une grotte sous-marine ; conséquences sur le cycle biogéochimique du carbone organique

Une étude de la composition biochimique des sédiments d'une grotte sous-marine méditerranéenne (Marseille, France) a été effectuée en 1985-1987, dans

le but de définir les caractéristiques du sédiment et de réaliser un bilan du cycle biogéochimique du carbone organique. Les fortes diminutions de concentrations en chloropigments et lipides dans le sédiment enregistrées entre la zone semi-obscure et la zone obscure de la grotte coïncident avec la diminution connue des apports verticaux de matière organique particulaire. La diminution des autres constituants organiques est beaucoup moins marquée. Le dosage des glucides et protéines séparés par extraction alcaline (NaOH 1 N, 24 h, 4°C) n'offre que peu d'intérêt et souligne les difficultés d'interprétation envers cette approche chimique, tout au moins dans de telles conditions de faible concentration en matière organique sédimentaire.
Le bilan biogéochimique du cycle des composés carbonés est réalisé en associant les résultats de cette étude avec ceux de travaux antérieurs sur la composition de la matière particulaire en suspension et le flux vertical de particules. Les processus de dégradation sont très efficaces dans le sédiment puisque ~90 % du carbone organique atteignant l'interface eau-sédiment sont dégradés dans les 15 premiers cm du sédiment, alors que seulement ~10 % sont enfouis en dessous de ce niveau. Les lipides utilisés à 100 % dans les quinze premiers centimètres représentent les composés les plus dégradés. Malgré le taux de dégradation élevé des protéines et des glucides, respectivement ~3 et ~8 % de leurs apports initiaux sont encore reconnus à 15 cm de profondeur. La matière organique complexe constitue une source importante de carbone organique dans les sédiments étudiés et, malgré le fait que la dégradation de ce matériel exige un important investissement énergétique, elle doit être considérée comme une ressource potentielle, particulièrement dans le cas d'environnements oligotrophes.

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INTRODUCTION

The biogeochemistry of organic compounds in sediments provides an approach to understanding degradation and recycling processes of organic matter by benthic micro- and macro-organisms in the top few cm of the sediment. Such processes, defined as early diagenesis, are directly related to the amount and nature of the inputs of particulate material at the sediment-water interface (Emerson *et al.*, 1985; Mann, 1986). The aim of this work is to study the composition and fate of the particulate organic matter (POM) in conditions of low organic matter inputs and to establish a budget for the biogeochemical cycle of the organic carbon.

In Mediterranean submarine caves, faunal density and biomass revealed strongly decreasing gradients from the entrance to the inner dark parts, both in hard substrata (Pérès, 1982; Harmelin *et al.*, 1985; Gili *et al.*, 1986) and sediment (Monteiro-Marquès, 1981; Fichez, 1989) communities. Previous studies on environmental conditions in Trémies cave (Marseille, France; *see* Fichez, 1991 *a*; 1991 *b*) demonstrated close interrelations between the decrease in fauna biomass and density, and the impoverishment in suspended and sedimenting particulate organic matter. The decline of POM inputs at the sediment-water interface affects the processes of benthic degradation. This influence, already studied through the metabolic pathways (Fichez, 1991 *b*), is studied here by following the fate of the main constituents of the POM (carbon, nitrogen, carbohydrates, proteins, lipids, chloropigments) in the sediment in order to determine their respective diagenetic transformations.

The analysis of the constituents of sedimentary organic matter had been previously used to evaluate the nutritional value of the sediment (Buchanan and Longbottom, 1970) and to discriminate between the organic compounds which are readily biodegradable and those which are non-biodegradable (Liu, 1976). Nevertheless, the organic carbon present in the sediment is often considered to be resistant to decomposition (Marshall, 1972; Wilson *et al.*, 1985; Grant and Hargrave, 1987) and the lack of connections between the organic matter content of sediment and the benthic metabolism has been mentioned (Smith, 1978; Van Es, 1982). Moreover, the importance of degradation processes at the benthic boundary layer demonstrates that transformation processes on freshly sedimented material are of major significance for the benthic metabolism (Hargrave, 1980; Khripounoff *et al.*, 1985; Officer *et al.*, 1985). Consequently, the second part of this article considers the differences in organic matter content of suspensions (Fichez, 1991 *b*) and sediments in Trémies cave. This approach discriminates between diagenetic processes that occurred at the interface and in the sediment, and gives an estimate of the annual degradation rate of the main organic compounds at the benthic boundary layer. The combination of degradation rates with previous results on the vertical fluxes of particles (Fichez, 1990 *b*) yields a budget for the cycle of organic carbon and its main compounds (carbohydrate, protein, lipid, complex organic matter) in the top 15 cm sediment layer.

MATERIALS AND METHODS

Sediments were sampled in Trémies cave (Mediterranean Sea, Marseille, France) on four occasions (10 September 1985, 24 September 1985, 28 October 1986, 6 February 1987) at four sampling stations. Trémies cave (Fig. 1), previously described by Fichez (1991 *a*), is topographically separated in two sections. Station TR2 (17 m depth) is located in the twilight outer section, extending 0 m to ~30 m from the entrance. Stations TR3, TR4 and TR5 (8, 7 and 6 m depth, respectively) are located in the dark inner section, extending ~ 30 to ~ 50 m from the entrance and separated from the twilight section by a 8 m rocky rise. The average residence time of the water mass increased from 1 d in the twilight section to 8 d in the dark section (Fichez, 1989; 1991 *a*), resulting in a strong decrease in suspended chloropigments (Fichez, 1990 *a*), suspended POM (Fichez, 1991 a), vertical inputs (Fichez, 1990 *b*) and benthic metabolism (Fichez, 1990 *c*; 1991 *b*).

Sediment sampling was effected by SCUBA diving using a Plexiglas corer (length 30 cm, diameter 2.6 cm). Sediment cores were cut into 0-1 cm, 5-6 cm, 10-11 cm, and 15-16 cm sections; all samples were analysed for organic carbon and nitrogen, only 0-1 cm and 14-15 cm layers were analysed for the other compounds. One subsample of each section was transfered to a preweighted centrifuge tube and frozen until chloropigment titration. The remaining part of the sample was oven-dried at 60° C, ground in a mortar and stored in a desiccator until analysis. The water content of the sediment was determined by the weight lost during drying. Sediment carbon and nitrogen contents were analysed on a CHN analyser. The organic fraction was calculated following the difference-on-ignition (DOI) technique (Hirota and Szyper, 1975): analysis of untreated and calcinated (16 h, 500° C) subsamples respectively gave the total and inorganic content, the difference yielding the organic content. The DOI technique was proved to be more suitable than the HCl-acidification technique for determining organic carbon in sediments (Byers *et al.*, 1978; Kristensen and Andersen, 1987). The methods used for the titration of the sediment content in total carbohydrate (Dubois *et al.*, 1956) adapted to sediment (Artem'yev, 1969; 1970; Gerchakov and Hatcher, 1972; Le Coz, 1985), total protein (Lowry *et al.*, 1951) adapted to sediment (Le Coz, 1985), and total lipid (Marsh and Weinstein, 1966) were similar to the methods used in the study of the suspended POM in the same environment (Fichez, 1991 *a*) in order to allow comparison. After alcaline extraction on sediment (NaOH 1 N, 24 h, 4° C) protein and carbohydrate contents were analysed, both in the supernatant and in the remaining sediment. The soluble fraction (supernatant) has occasionally been regarded as representative of the biodegradable fraction of the considered organic compounds (Khripounoff *et al.*, 1985; Le Coz, 1985); this concept must be treated very cautiously, however, due to the absence of a relationship between the chemical extraction and any biological degradation process (Etcheber *et al.*, 1985).

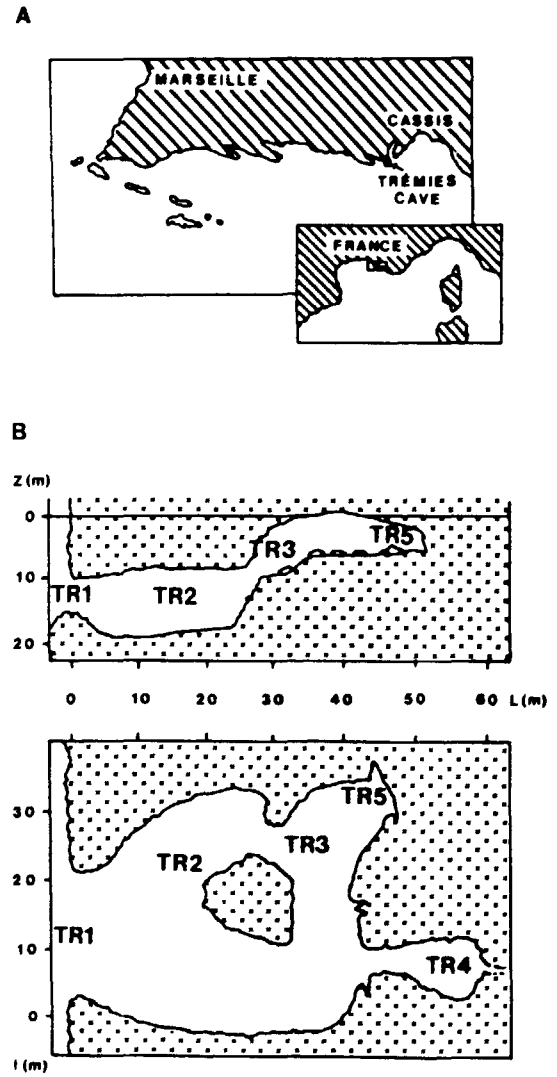

Figure 1

Location (A) and topography (B) of Trémies cave with position of the four sampling stations (TR2, TR3, TR4, TR5). Topography is shown through a vertical view in the top and a side view in the bottom drawing (Z = water depth, L = length, l = width).

Position et topographie de la grotte des Trémies et position des quatre stations d'échantillonnage (TR2, TR3, TR4, TR5). La topographie est représentée en coupe horizontale en haut et en coupe verticale en bas (Z = profondeur, L = longueur, l = largeur)

Chlorophyll *a* and phaeopigments were titrated on wet sediment by fluorimetric analysis of the acetonic extract (~95 % final concentration of acetone; Holm-Hansen *et al.*, 1965; Daemen, 1986). After analysis, the sample was oven-dried and the weight of dry sediment measured. Pigment concentrations were related to the corresponding dry weight of sediment and expressed as $\mu g\ g^{-1}$ dry sediment. Concentrations of only total chloropigment were considered here due to the relatively low amount of chlorophyll *a* compared to phaeopigments.

For each biochemical titration, blanks were made by subjecting previously calcinated (600° C, 48 h) sediments to the corresponding analytical procedure.

RESULTS

The profiles of organic carbon (OC) and organic nitrogen (ON) contents of sediment showed a clear decrease with depth from the surface to 15 cm depth (Fig. 2). The highest OC concentrations (15.8 mg g^{-1} at 0 cm, 7.0 mg g^{-1} at 15 cm) were recorded in the twilight outer section (TR2). OC concentrations decreased in the dark inner section, reaching minimum values at TR3 (6.9 mg g^{-1} at 0 cm, 3.0 mg g^{-1} at 15 cm), whereas ON showed few differences between stations.

The composition of sediments at 0 and 15 cm depth is presented in Table 1. Water content was 50 to 60 % at the sediment surface and 30 to 40 % at 15 cm. The OC:ON (weight) ratio usually ranged from between 10 and 12, except at TR3 where low values of ~7 were recorded. The concentrations of the organic compounds always declined from 0-1 cm to 14-15 cm. Considering the evolution of concentrations from the twilight outer section (TR2) to the dark inner section (TR3, TR4, TR5), the OC, ON, carbohydrate and protein contents of sediment displayed moderate decreases, while lipid and chloropigment contents strongly decreased, with values in the dark section generally ~10 % of those in the twilight section. The ratio of insoluble to soluble carbohydrates (ICH:SCH) showed small variations both in sediment depth and in space. The corresponding ratio for proteins (IPR:SPR) varied only slightly from the twilight section to the dark section in the 0-1 cm layer, whereas it increased strongly at 15 cm depth with maximum values of 23.0 at TR4 and 25.5 at TR5, these two stations being the most remote sampling points. Very low concentrations of chloropigments were recorded, especially in the dark inner section (TR3, TR4, TR5), where pigment contents ranged from 0.43 to 0.55 µg g^{-1} at 1 cm and were not detectable at 15 cm.

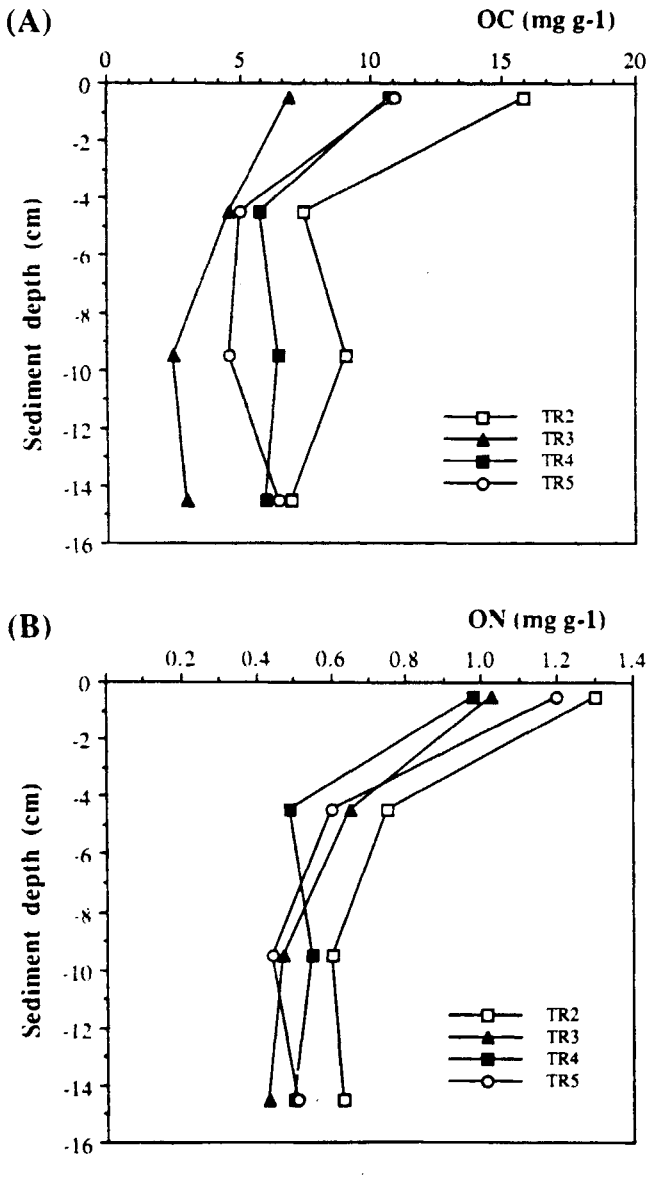

Figure 2

Profiles of (A) organic carbon and (B) organic nitrogen concentrations in the fifteen centimetres top layer of sediment of Trémies cave.

Profils verticaux des concentrations en carbone organique (A) et azote organique (B) dans les quinze premiers centimètres du sédiment dans la grotte des Trémies

DISCUSSION

Sediment composition

The general decrease in concentrations of organic compounds with sediment depth corresponded with the classical feature of the decline of organic matter with depth and age due to aerobic and anaerobic microbial decomposition processes (Jørgensen, 1983). Nevertheless, a large amount of organic constituents was still present at 15 cm, demonstrating that a significant fraction of organic matter in sediment is refractory to degradation (Marshall, 1972; Grant and Hargrave, 1987). Chloropigments and lipids were a very good index of the biodegradable fraction of organic matter as they clearly decreased in depth as well as from the twilight to the dark (TR3, TR4, TR5) section. The strong decrease in lipid contents demonstrated the importance of this highly energetic compound (Brody, 1945; Salonen *et al.*, 1976) as a nutritional resource for the heterotrophic metabolism in the sediment. The carbohydrate and protein contents decreased as well, but these compounds were still present at 15 cm depth demonstrating that even a part of these simple organic constituents is difficult to degrade. The ability of some biogenic carbon compounds to resist diagenetic decomposition is well known, especially for carbohydrates (Artem'yev, 1970). The study of the decomposition of organic compounds in sediments from the Bay of Biscay (Khripounoff *et al.*, 1985) yielded convergent results, demonstrating lipid degradation to be highly efficient when a fraction of sedimenting carbohydrate and protein resisted degradation.

No significant change was observed in the carbohydrate ICH:SCH ratio. The variations of the protein IPR:SPR

Table 1

Sediment composition in the twilight outer section (TR2) and the dark inner section (TR3, TR4, TR5) of Trémies cave (OC organic carbon, IC inorganic carbon, ON organic nitrogen, CH carbohydrates, PR proteins, LI lipids). Values are mean and standard deviation (four samples).

Composition des sédiments dans la zone semi-obscure (TR2) et dans la zone obscure (TR3, TR4, TR5) de la grotte des Trémies (OC carbone organique, IC carbone inorganique, ON azote organique, CH carbohydrates, PR protéines, LI lipides). Les valeurs représentent la moyenne et l'écart-type (quatre répliquats)

	Station TR2		Station TR3		Station TR4		Station TR5	
	Mean	(SD)	Mean	(SD)	Mean	(SD)	Mean	(SD)
0-1 cm layer								
Porosity (%)	62.0	(7.5)	53.3	(10.2)	55.9	(8.7)	61.9	(9.3)
IC (mg g^{-1})	53.4	(4.0)	77.1	(7.1)	48.9	(2.0)	67.3	(4.9)
OC (mg g^{-1})	15.8	(2.8)	6.9	(1.2)	10.7	(1.7)	10.9	(4.9)
ON (mg g^{-1})	1.30	(0.10)	1.03	(0.30)	0.98	(0.40)	1.20	(0.10)
OC:ON	12.15		6.70		10.92		9.08	
IC:OC	3.38		11.17		4.57		6.17	
Total CH (mg g^{-1})	4.12	(0.66)	3.10	(1.12)	2.40	(0.67)	3.26	(1.00)
Soluble CH (mg g^{-1})	0.34	(0.09)	0.25	(0.06)	0.18	(0.08)	0.26	(0.14)
Insoluble CH (mg g^{-1})	3.78	(0.68)	2.85	(1.12)	2.22	(0.65)	2.94	(0.91)
ICH:SCH	11.12		11.40		12.33		11.31	
Total PR (mg g^{-1})	2.62	(0.67)	1.03	(0.35)	1.11	(0.43)	1.51	(0.56)
Soluble PR (mg g^{-1})	0.51	(0.20)	0.29	(0.10)	0.27	(0.09)	0.35	(0.12)
Insoluble PR (mg g^{-1})	2.11	(0.79)	0.74	(0.37)	0.84	(0.41)	1.16	(0.48)
IPR:SPR	4.51		2.51		3.07		3.37	
LI (mg g^{-1})	0.66	(0.17)	0.07	(0.04)	0.07	(0.05)	0.11	(0.05)
Chloropigments (µg g^{-1})	5.90	(1.48)	0.43	(0.25)	0.54	(0.36)	0.55	(0.31)
14-15 cm layer								
Porosity (%)	43.2	(6.9)	30.9	(6.4)	38.8	(4.1)	37.9	(5.6)
IC (mg g^{-1})	58.3	(8.4)	72.0	(9.2)	51.2	(3.7)	67.7	(4.4)
OC (mg g^{-1})	7.0	(3.5)	3.0	(2.1)	6.0	(3.4)	6.5	(2.0)
ON (mg g^{-1})	0.63	(0.15)	0.43	(0.09)	0.50	(0.12)	0.51	(0.25)
OC:ON	10.95		6.98		12.00		12.75	
IC:OC	8.33		24.00		8.53		10.62	
Total CH (mg g^{-1})	1.52	(1.07)	0.88	(0.90)	0.87	(0.46)	0.91	(0.35)
Soluble CH (mg g^{-1})	0.11	(0.07)	0.05	(0.05)	0.06	(0.03)	0.06	(0.03)
Insoluble CH (mg g^{-1})	1.41	(1.21)	0.83	(1.02)	0.81	(0.35)	0.85	(0.38)
ICH:SCH	12.82		16.60		13.50		14.17	
Total PR (mg g^{-1})	1.07	(0.34)	0.60	(0.22)	0.48	(0.16)	0.53	(0.20)
Soluble PR (mg g^{-1})	0.13	(0.05)	0.06	(0.02)	0.02	(0.01)	0.02	(0.01)
Insoluble PR (mg g^{-1})	0.94	(0.33)	0.54	(0.22)	0.46	(0.17)	0.51	(0.18)
IPR:SPR	7.23		9.00		23.00		25.50	
LI (mg g^{-1})	0.11	(0.03)	0.01	(0.01)	0.01	(0.01)	0.01	(0.01)
Chloropigments (µg g^{-1})	0.12	(0.08)	0.00	(0.00)	0.00	(0.00)	0.00	(0.00)

ratio are difficult to interpret, except for its tendency to increase with depth which could demonstrate some links between the insoluble fraction and the non-biodegradable state of the buried proteins. Nevertheless, for sediments with low organic content such ratios provide no valuable information and may be considered as inaccurate tools for the study of the nutritional value of sedimentary organic matter.

Biogeochemical budget

The calculation steps and results for the biogeochemical budget of organic carbon compounds in the twilight outer section (station TR2) and the dark inner section (station TR5) are explained and displayed in Table 2. The composition of the suspended particles sampled a few metre above the sediment proved to be similar to the composition of particles collected by sediment traps 30 cm above the sediment-water interface (Fichez, 1989; 1990 *b*). Previous studies provided the composition of suspended particles (Fichez, 1991 a) and the vertical flux of organic carbon for TR2 (48.6 gC m^{-2} yr^{-1}) and TR5 (8.0 gC m^{-2} yr^{-1}; Fichez, 1990 *b*). Carbohydrate, protein, and lipid contents of particles were converted to carbon using conversion factors of 0.45, 0.50, 0.75 gC g^{-1}, respectively, according to the composition of the titration standards used (for natural composition *see* also Degens, 1970; Jeffrey, 1970; Saliot *et al.*, 1984; Fukami *et al.*, 1985). It must be emphasized that the use of average conversion factors is responsible for a major simplification bias, as it neglects the diversity in the composition of organic compounds. It is also possible to use a conversion factor based on energy equivalents (Brody, 1945; Salonen *et al.*, 1976), but such an alternative is responsible for a similar bias and lead to similar reserves (Lieth, 1975). This second method was first applied to biogeochemical cycling in the deep-sea (Khripounoff *et al.*,

Table 2

Calculation steps for the biogeochemical budget for the organic carbon compounds at TR2 and TR5. Vertical flux of POC and organic content of particles are from Fichez (1990 b; 1991b), respectively. Calculation modes are explained for each parameter; C-X symbol used in vertical flux calculations means the carbon content of the organic compound X which is related to the corresponding column (X = CH carbohydrates, PR proteins, LI lipids, COM complex organic matter).

Étapes de calcul du bilan biogéochimique des composés organiques carbonés à TR2 et TR5. Le flux vertical et la teneur en carbone organique des particules proviennent de Fichez (1990 *b* ; 1991*b*). Les modes de calcul sont expliqués pour chaque paramètre; le symbole C-X utilisé dans le calcul du flux vertical signifie la teneur en carbone du composé X correspondant à la colonne considérée (X pouvant être CH carbohydrates, PR protéines, LI lipides, COM matière organique complexe).

	Calculation mode	POC	C-CH	C-PR	C-LI	C-COM
Station TR2						
(1) Particles (mg g^{-1})		62.3	7.8	15.7	21.8	17.0
(2) Sediment 1 cm (mg g^{-1})		15.8	1.8	1.3	0.5	12.2
(3) Sediment 15 cm (mg g^{-1})		7.0	0.7	0.5	0.1	5.7
(4) Loss 0-1 cm (%)	100.[(1)-(2)]:(1)	74.6	76.9	91.7	97.7	28.2
(5) Loss 1-15 cm (%)	100.[(2)-(3)]:(1)	14.1	14.1	5.1	1.9	38.3
(6) Loss 0-15 cm (%)	(4)+(5)	88.7	90.9	96.8	99.6	66.5
(7) Burial > 15 cm (%)	100-(6)	11.3	9.0	3.2	0.4	33.5
(8) Vertical flux (gC m^{-2} yr^{-1})	(C-X:POC).(POC flux)	48.6	6.1	12.2	17.0	13.3
(9) Deg. 0-1 cm (gC m^{-2} yr^{-1})	(8).(4)	36.3	4.7	11.2	16.6	3.8
(10) Deg. 1-15 cm (gC m^{-2} yr^{-1})	(8).(5)	6.8	0.8	0.6	0.3	5.1
(11) Deg. 0-15 cm (gC m^{-2} yr^{-1})	(9)+(10)	43.1	5.5	11.8	16.9	8.9
(12) Burial > 15 cm (gC m^{-2} yr^{-1})	(8)-(11)	5.5	0.6	0.4	0.1	4.4
Station TR5						
(13) Particles (mg g^{-1})		49.7	5.3	11.4	14.9	18.1
(14) Sediment 1 cm (mg g^{-1})		10.9	1.5	0.8	0.1	8.5
(15) Sediment 15 cm (mg g^{-1})		6.5	0.4	0.3	0.0	5.8
(16) Loss 0-1 cm (%)	100.[(13)-(14)]:(13)	78.1	71.7	93.0	99.3	53.0
(17) Loss 1-15 cm (%)	100.[(14)-(15)]:(13)	8.9	20.8	4.4	0.7	14.9
(18) Loss 0-15 cm (%)	(16)+(17)	87.0	92.5	97.4	100.0	67.9
(19) Burial > 15 cm (%)	100-(18)	13.0	7.5	2.6	0.0	32.1
(20) Vertical flux (gC m^{-2} yr^{-1})	(C-X:POC).(POC flux)	8.0	0.9	1.8	2.4	2.9
(21) Deg. 0-1 cm (gC m^{-2} yr^{-1})	(20).(16)	6.2	0.6	1.6	2.4	1.6
(22) Deg. 1-15 cm (gC m^{-2} yr^{-1})	(20).(17)	0.7	0.2	0.1	~ 0.0	0.4
(23) Deg. 0-15 cm (gC m^{-2} yr^{-1})	(21)+(22)	6.9	0.8	1.7	2.4	2.0
(24) Burial < 15 cm (gC m^{-2} yr^{-1})	(20)-(23)	1.1	0.1	0.1	0.0	0.9

1985). It was also applied to Trémies cave in a previous work (Fichez, 1989), yielding conclusion similar to those from the carbon-equivalents method used in the present paper.

The three main biochemical classes of organic compounds (carbohydrates, protein and lipid) do not account for the whole organic matter; the residual fraction being described as heterogeneous, polyfunctionalised and macromolecular in nature (Cough and Mantoura, 1990). The large number of terms used in the litterature to identify this fraction (*i.e.* heteropolycondensate, complex molecules, geopolymers, marine humics) reflects that little is known of its detailed molecular composition. As the formation of such substances is not yet clarified the term complex organic matter (COM) was used in this study. It is possible to estimate the amount of carbon associated with COM by calculating the difference between the overall particulate organic carbon (POC) and the carbon content of the three simple compounds (CH, PR, LI). When combined with a carbon-budget, this approach, based on the fractionation of the POC into its main compounds, provides an assessment of the nature and rate of the biogeochemical degradation processes. The degradation coefficient for each organic constituent is represented by the difference in concentrations between two successive sediment layers related to the initial concentration in the suspended particles and is expressed as percentages.

For each constituent, the degradation coefficients are very similar from one station to another. The percentage of sedimenting POC lost through early diagenesis is 75 % at TR2 and 78 % at TR5 in the first centimetre and reaches 89 % at TR2 and 87 % at TR5 in the top 15 cm sediment layer, just more than 10 % being thus buried below 15 cm. The biological degradation (which proved to account for most of the benthic decomposition processes in the cave: Fichez, 1991 *a*) shows high efficiency when degrading the POM

reaching the sediment at both stations (~90 % degraded), in agreement with other results from various environments (Reimers and Suess, 1983; Hammond *et al.*, 1985; Khripounoff *et al.*, 1985; Hargrave and Phillips, 1986). The degradation coefficients for carbohydrates were slightly lower than for POC resulting in the burial below 15 cm depth of 9.0 % (TR2) and 7.5 % (TR5) of the initial input. This confirms that a non-negligible part of the carbohydrates is refractory to degradation. Proteins were more efficiently used as 92 % (TR2) and 93 % (TR5) of the input was degraded in the first centimetre while burial below 15 cm depth only accounted for ~3 % at TR2 and TR5. Lipids are the most biodegradable compounds in the sediment, with ~100 % being degraded in the top 15 cm sediment layer and 98 to 99 % of the decomposition processes occurring in the first centimetre at both stations. As far as simple organic compounds were concerned, lipids, proteins and carbohydrates displayed decreasing nutritional values. Originately assumed to be highly refractory to decomposition, COM was largely degraded in the top 15 cm sediment layer (67 % at TR2, 68 % at TR5). Despite the energetic investment necessary to fractionate COM polymers into simple degradable organic compounds (Tenore *et al.*, 1984), the importance of COM in benthic degradation processes had been progressively revised as it may account for a potential source of carbon to heterotrophic metabolism (Khripounoff *et al.*, 1985). Concurrently, it is possible to wonder if the depolymerization of the COM, which is mainly composed of carbohydrate-protein aggregates (Hatcher, 1978; Mayer, 1989), may be responsible for the presence of some of the simple compounds identified at 15 cm depth.

It must be emphasized that considering similar sediment depths (15 cm) introduces a bias in the comparison between the two stations (TR2, TR5). The time scale for the benthic processes occuring through the 15 cm top layer of the sediment is greater in the dark section than in the twilight section. If we assume approximate values for vertical sediment fluxes (1200 g m^{-2} yr^{-1} at TR2 and 230 g m^{-2} yr^{-1} at TR5: Fichez 1990 *b*) and porosity (50 % at TR2 and TR5), and an *in situ* density of 1.1 for the sediment, then the rough estimate for the sedimentation time corresponding to the settlement of a 15 cm sediment layer is 70 year at TR2 and 360 year at TR5. Nevertheless, the calculation of the budget clearly demonstrates that the large majority of the degradation processes takes place in the first cm of the sediment (corresponding sedimentation time of 3.7 year at TR2, 19 year at TR5 for a porosity of 60 %) and that long term processes only account for a very weak part of the overall degradation of the organic compounds.

The calculation of the fluxes (sedimentation, degradation, burial) of organic compounds and the subsequent representation of the benthic pathways in the top 15 cm sediment layer (Fig. 3) reveals a large difference between the flux values in the twilight outer section (TR2) and the dark inner section (TR5); fluxes at TR5 were approximately 14

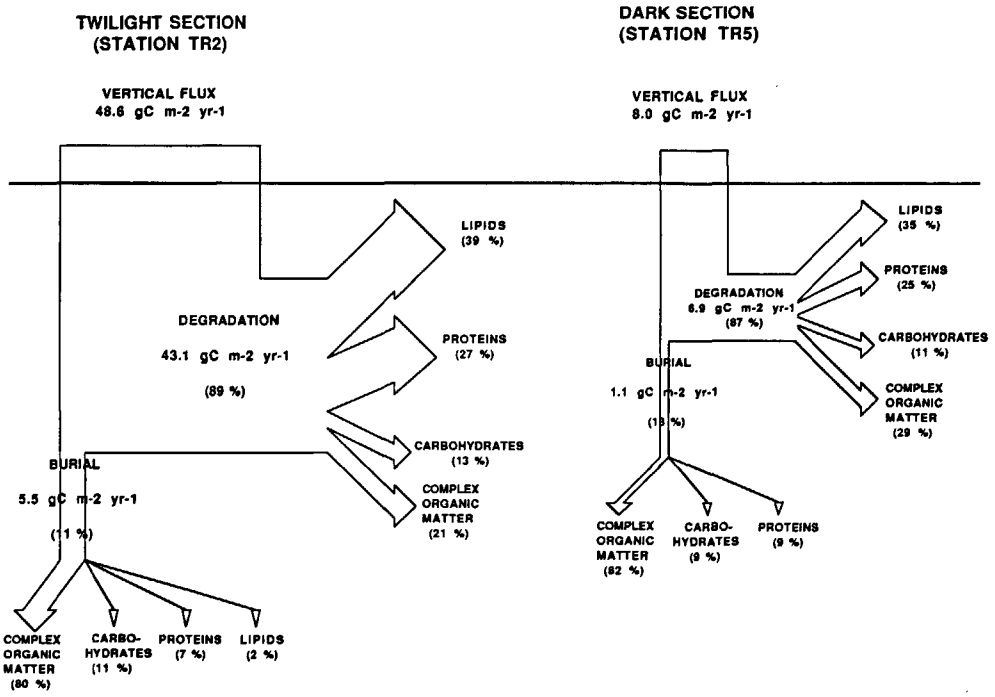

Figure 3

Biogeochemical budget for the organic carbon compounds in the fifteen centimetres top layer of sediment in the twilight area (TR2) and the dark area (TR5) of Trémies cave. Degradation and burial are expressed as percentage of the vertical flux, further biochemical fractionations are respectively expressed as a percentage of the degradation and the burial fluxes.

Bilan biogéochimique pour les composés organiques carbonés dans les quinze premiers centimètres de sédiment de la zone semi-obscure (TR2) et de la zone obscure (TR5) de la grotte des Trémies. La dégradation et la sédimentation permanente sont exprimées en terme de pourcentage du flux vertical, le fractionnement biochimique ultérieur au sein de chacun de ces deux flux est exprimé en terme de pourcentage du flux concerné.

to 23 % of those at TR2. Furthermore, TR2 and TR5 displayed some differences in the metabolic pathways (Fichez 1991 *b*) as anaerobiosis represented 12 % and aerobiosis 88 % of organic carbon degradation processes at TR2, while aerobiosis was the only process responsible for benthic degradation at TR5. Despite such differences in the amount of sedimenting organic material and the metabolic pathways between these two stations, benthic degradation processes are very convergent. This result shows the biogeochemical transformations to be largely influenced by the initial composition of the particles (the particulate material is provided to both sites (TR2, TR5) by a common source: the open sea waters entering the cave).

CONCLUSIONS

Our knowledge of the composition of organic matter in sea-water and marine sediments is still incomplete, especially for complex organic matter (Mayer, 1989), and analytical procedures for a simple characterization of the organic matter composition have to be improved (Carney, 1989; Rice and Rhoads, 1989). However, the approach developed in this study yielded some significant information on the cycling of POM and the biogeochemistry of organic carbon in sediments. This work on submarine caves and, more generally speaking, on carbon-limited environments, reveals the high biodegradability of lipids and the importance of COM as a carbon source, despite the possible low energetic profitability of the latter. Almost 90 % of the sedimenting POC was degraded in the 15 cm top layer proving decomposition processes in the sediment to be very efficient. This kind of study could be considered as a fundamental assessment of the budget of particulate organic carbon and as an interesting basis for the selection of further investigations such as choosing a suitable organic tracer or focusing on the detailed composition of a single class of organic compounds.

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