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Sedimentation rate and early diagenesis of particulate organic nitrogen and carbon in Aydat Lake (Puy de Dôme, France)

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ABSTRACT

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A core of low-compacted sediment from a eutrophic lake (Aydat Lake) was extracted in order to study the early diagenesis of particulate organic carbon and nitrogen. We use a simple model where the advection rate was estimated with the classical ^{210}Pb method. We show that the ^{210}Pb data are not sufficient by themselves to provide a correct estimation of this parameter, but a model which includes the sediment compaction leads to a better understanding of the sedimentation process. Compaction is also taken into account in the diagenetic model which allows us to make an estimation of the carbon and nitrogen mineralization rates.

1. Introduction

Early diagenesis of particulate organic matter (POM) of different origins (marine or continental) has been extensively studied by many workers (e.g., Waksman, 1933; Arrhenius, 1950; Bader, 1955; Rosenfeld, 1981; Gaillard et al., 1987, 1989). However, the principal geochemical process which occur during organic matter mineralization have mainly been depicted through the chemical composition of pore water. Obviously, the pore-water medium is chemically much more sensitive and better reflects the nature of chemical reactions than the solid phase of the sediment.

The modelling of early diagenesis processes, since the initial publication of Berner (1964), has been improved in many details but always

uses, as a data base, concentration profiles of different soluble and reactive species: CO_2, NH_4^+, SO_4^{2-}, SiO_2, pH, alkalinity, etc., obtained from the analysis of pore water. Furthermore, by taking compaction into account (i.e. variable sediment porosity) the complexity of the mathematical resolution of diagenetic equations dealing with pore-water concentrations can be greatly enhanced. This process is currently neglected (e.g., Rosenfeld, 1981) or adjusted to a constant value even if this assumption is not experimentally supported (Murray et al., 1978). Therefore, when the sedimentation rate is estimated either by geomorphological observations or by radioactive decay methods (Rosenfeld, 1981), this parameter has not been related to compaction (Martin, 1985; Wilken et al., 1990).

We will show here that ^{210}Pb measurements, interpreted without taking compaction into account, may lead to a rather incorrect estimation of the sedimentation rate. On the other

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hand, we show that the assumption of an average (and constant) sedimentation rate does not appreciably affect the results concerning the mineralization rates of particulate organic carbon (POC) and nitrogen (PON).

2. Location and general features of Aydat Lake

Aydat Lake is located in the Massif Central, France, 25 km NW from Clermont-Ferrand (Puy de Dôme) (Fig. 1). The elevation is 850 m above mean sea level. The lake originates from the damming of the River La Veyre (the only tributary) by a basaltic flow which occurred 7000 yr ago. Its surface is $6 \cdot 10^5$ m^2, the average depth is 7 m and the maximum depth 15 m (Fig. 2). The water residence time is ~ 1 yr.

The lake is typically eutrophic and developes from May to October an anoxic hypolimnion.

3. Methods

A sediment core was manually extracted by a diver from the deepest part of the lake (15-m depth, point A, Fig. 2). This was done very carefully in order to prevent any disturbance of the upper part of the sedimentary column where the porosity is very high (98%). A 40-cm-length core was extruded and sliced within half an hour after retrieval. Samples were carried back to the laboratory in a freezer and freeze-dried thereafter.

The porosity was obtained by weighing the samples before and after desiccating.

Analyses of carbon and nitrogen were done by conventional CHN technique after samples were checked to be free of solid carbonates.

Results are summarized in Table 1. The precision is $\pm 1\%$ (at the 2σ confidence level).

The sedimentation rate was measured by using the radioactive disequilibrium of ^{210}Pb. Particles counting was made by β counting of
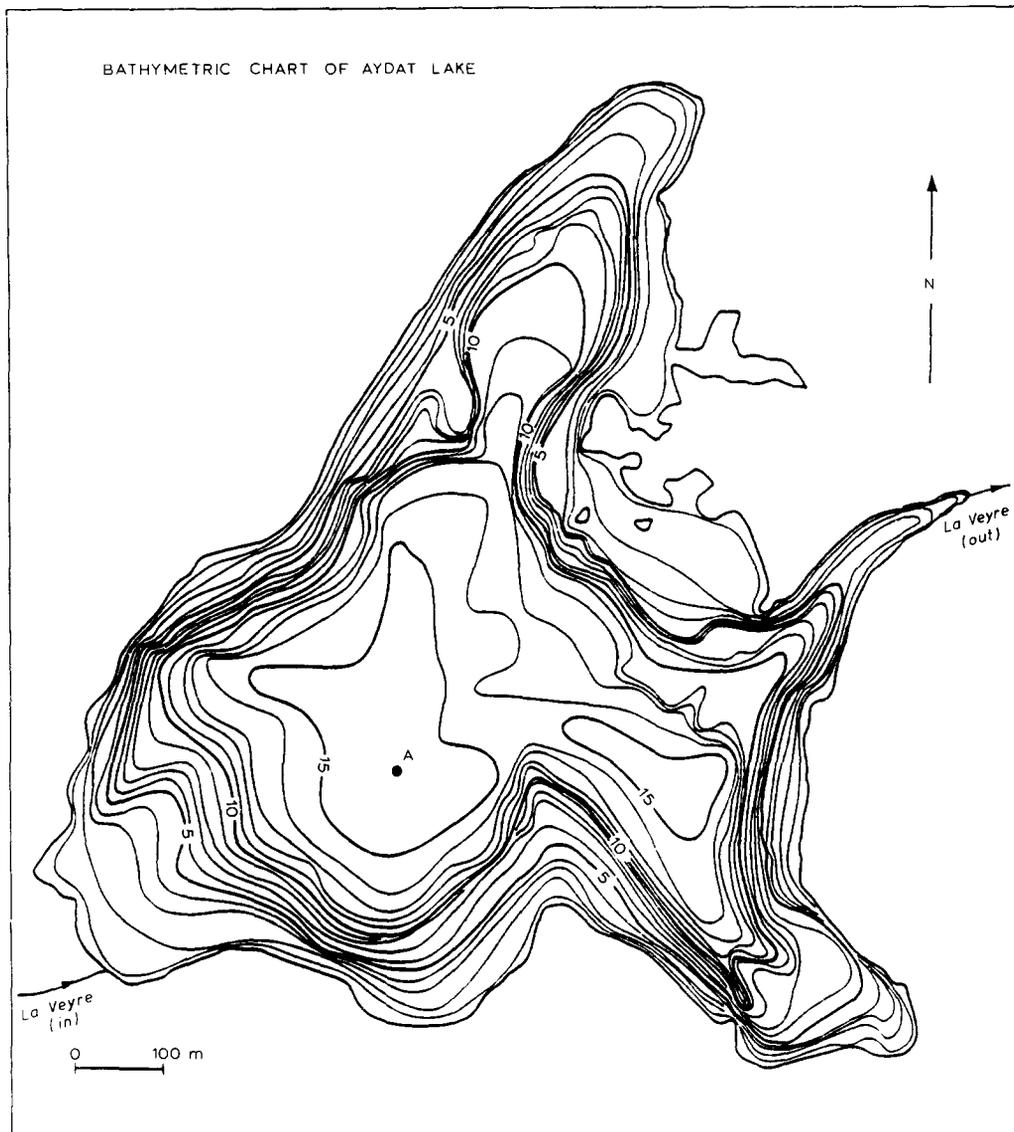

Fig. 1. Location of Aydat Lake.

Fig. 2. Bathymetric chart of Aydat Lake (from J.F. Gaillard and C. Rabouille, unpublished data, 1987). Depth contours are indicated in metres.

[210]Bi after radioactive equilibrium was reached. The results, expressed in desintegrations per minute in 1 g of sediment are reported in Table 2.
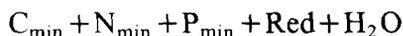
4. Results

The concentration profiles $C = f(z)$ and $N = f(z)$ are represented in Fig. 3a and b, re-

spectively. The z-axis (sediment depth in cm) is positively oriented downward.

5. Discussion

5.1. Equations of the model

The POM mineralization can be summarized by the reaction:

$$POM(C,H,O,N,P) + Ox \rightarrow$$

$$C_{min} + N_{min} + P_{min} + Red + H_2O$$

where C_{min}, N_{min} and P_{min} are the dissolved mineral species of carbon (dissolved CO_2, HCO_3^- and CO_3^{2-}), nitrogen (NH_4^+ and NH_3) and phosphorus ($H_2PO_4^-$ and HPO_4^{2-}), respectively. Ox is the available electron acceptor. It has been shown elsewhere (Philippe,

TABLE 1

Carbon and nitrogen concentrations in mole% of dry sediment

Depth (cm)	C (mole%)	N (mole%)
1– 2	1.383	0.150
6– 8	1.008	0.107
17–20	0.692	0.071
20–23	0.708	0.057
23–25	0.700	0.057
25–30	0.633	0.050
32–37	0.467	0.043

TABLE 2

Concentrations of ^{234}U, $^{210}Pb_{total}$ and $^{210}Pb_{excess}$

Depth (cm)	^{234}U (dpm g^{-1})	$^{210}Pb_{total}$ (dpm g^{-1})	$^{210}Pb_{excess}$ (dpm g^{-1})
0– 1	4.31	22.34	18.03
1– 2	4.07	21.56	17.49
2– 3	3.78	19.94	16.16
3– 4	2.42	19.96	17.54
4– 5	3.04	18.65	16.61
5– 6	3.56	18.02	14.46
6– 7	2.57	15.49	12.92
7– 8	3.06	17.63	14.57
8– 9	2.26	12.09	9.83
9–10	2.57	12.72	10.15
10–11	2.61	10.33	7.72
11–12	1.82	11.03	9.21
12–13	2.02	11.38	9.36
13–14	2.21	11.37	9.16
14–15	2.05	10.98	8.93
15–16	1.98	9.29	7.31
16–17	2.42	7.27	4.85
17–18	1.91	8.16	6.25
18–19	1.97	7.87	5.90
19–20	1.88	6.90	5.02
20–21	2.48	7.70	5.22
21–22	2.28	6.32	4.04
22–23	2.10	5.38	3.28

1989) that for Aydat Lake, Ox can be represented by oxidized forms of Fe (mainly amorphous ferric hydroxides) and by the organic matter itself which is disproportionated into equivalent amounts of CO_2 and CH_4. Methanogenesis is here the most efficient process of mineralization. As the sediment has always been completely depleted in oxygen, O_2 never appears as an oxidant. Red is the reduced conjugate form of the oxidant, i.e. CH_4 and soluble forms of $Fe(II)$, mainly Fe^{2+}.

The consumption rate of an element X from the POM (here C or N) can be represented by a kinetic law of the form:

$$dX/dt = -K_x X^n$$

where K_x is the kinetic constant; and n the order of the reaction.

On the other hand, the input rate of the same element X brought to the lake bottom by sedimentation can be described by the equation:

$$dX/dt = -\omega \cdot \partial X/\partial z$$

where ω is the sedimentation rate expressed in cm yr^{-1}.

The asymptotic pattern of the profiles (Fig. 1a and b) suggests a chemical reaction where the order $n = 1$ with respect to the organic matter (Berner, 1980).

If, as a hypothesis, we suppose steady state was achieved, then $dX/dt = 0$ and the following global equation represents equal rates of advection and chemical reactions:

$$-\omega \cdot \partial X/\partial z - K_x X = 0 \qquad (1)$$

The simplest case would suppose ω to be constant along with sediment depth, i.e. compaction would be neglected. But, when looking at the porosity profile (Fig. 4) it is obvious that the hypothesis of negligible compaction cannot be supported here; therefore, ω is also a function of depth and eq. 1 becomes:

$$-\omega(z) \cdot \partial X/\partial z - K_x X = 0 \qquad (2)$$

If we make the hypothesis of steady-state compaction of the sediment, then we can write an
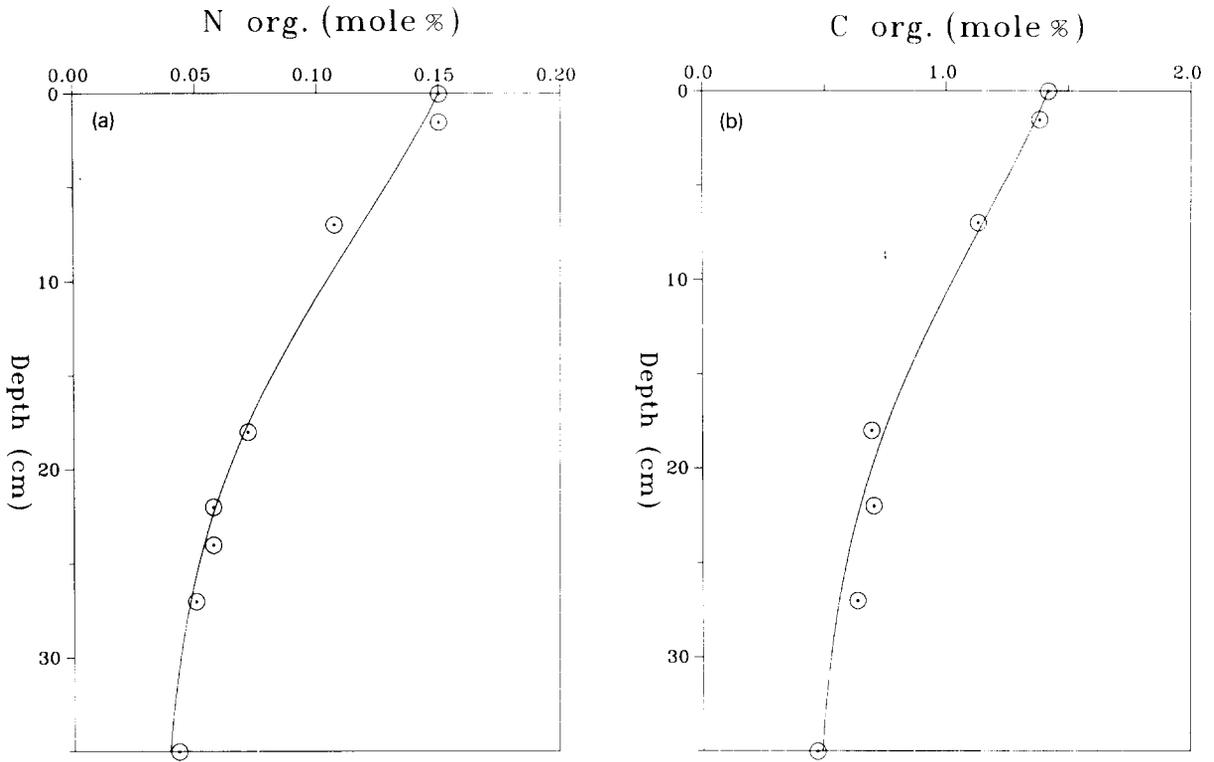
Fig. 3. a. Profile of particulate organic carbon. The *continuous line* represents the calculated profile using eq. 10.
b. Profile of organic nitrogen. The *continuous line* represents the calculated profile using eq. 10.

additional relation (Berner, 1980):

$$\partial(1-\phi)\omega/\partial z=0$$

or

$$(1-\phi)\cdot\partial\omega/\partial z-\omega\cdot\partial\phi/\partial z=0 \qquad (3)$$

where ϕ is the interconnected porosity of the sediment. The porosity profile can be fitted to a linear relation:

$$\phi=\phi_0-\alpha z$$

with $\phi_0=0.98$, $\alpha=2\cdot10^{-3}$ cm^{-1} and a correlation coefficient $\rho=0.97$.

Substituting the ϕ expression in eq. 3, we obtain after integration:

$$\omega=\omega_0[(1-\phi_0)/(1-\phi_0+\alpha z)] \qquad (4)$$

which represents the analytical expression $\omega(z)$ of eq. 2. This equation can now be inte-

grated and will provide a calculated profile $X=f(z)$.

5.2. Evaluation of the sedimentation rate

The sedimentation rate was evaluated by the classical method of the ^{210}Pb "excess" present in the solid phase of the sediment. We present hereafter a brief overview of the method which is extensively described in Goldberg (1963) and Koide et al. (1972).

^{210}Pb originates from the radioactive decay of ^{214}Po which belongs itself to the radioactive series of ^{238}U. The half-lives of the first terms of this radioactive chain are far much longer than the half-lives of the descendants. The radioactive disequilibrium which is the base of the method is due to the occurrence, within the radioactive chain, of a gaseous component, ^{222}Rn (α-emitter, half-life$=3.8$ days), which
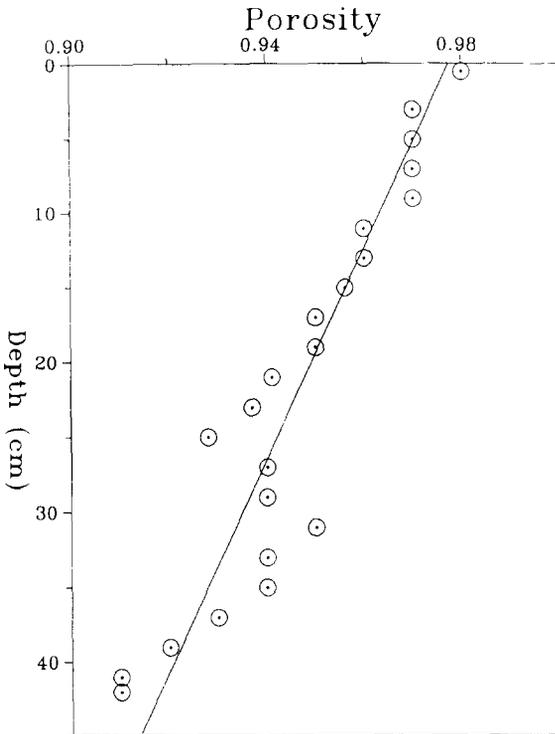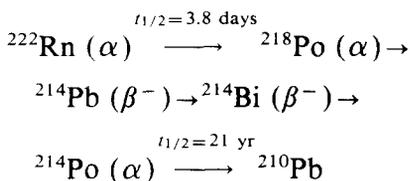
Porosity

Fig. 4. Porosity profile adjusted to a linear function:
$\phi = 0.98 - 2 \cdot 10^{-3} z$ $(\rho = 0.97)$

diffuses into the atmosphere and is converted into a solid aerosol of ^{210}Pb through the chain:

$$^{222}\text{Rn} \ (\alpha) \ \xrightarrow{t_{1/2} = 3.8 \text{ days}} \ ^{218}\text{Po} \ (\alpha) \rightarrow$$

$$^{214}\text{Pb} \ (\beta^-) \rightarrow ^{214}\text{Bi} \ (\beta^-) \rightarrow$$

$$^{214}\text{Po} \ (\alpha) \ \xrightarrow{t_{1/2} = 21 \text{ yr}} \ ^{210}\text{Pb}$$

This aerosol of ^{210}Pb enters the lacustrine ecosystem. Being separated from the radioactive chain it decays according to its own half-life and can be used for absolute geochronological purposes.

The total activity of ^{210}Pb can be separated into two components:

(1) a component by in situ production (within the sediment) which is in radioactive equilibrium with ^{234}U. The activity of this nuclide is used to calculate the ^{210}Pb production.

(2) An "excess" component which originates from the atmosphere. That fraction is

only taken into account to estimate the sedimentation rate.

We have supposed that the in situ production of ^{210}Pb is in radioactive equilibrium with ^{234}U (or ^{230}Th). This assumption is not totally correct because, in such a sedimentary reduced environment, Ra is a relatively mobile chemical element. Therefore, one of the links of the chain (^{226}Ra, which is located between ^{230}Th and ^{210}Pb) is perhaps in a situation of radioactive disequilibrium. However, this disequilibrium affects mainly the top level of the core. In reducing sediments from lakes and fjords (Petit, 1974; Von Damm et al., 1979; Smith and Walton, 1980) the ^{226}Ra/^{230}Th activity ratio is never higher than 1.2–1.3, thus the correction of the in situ component of ^{210}Pb must be low.

5.2.1. Evaluation of the average sedimentation rate (linear model).

The radioactive decay of ^{210}Pb can be written according to the classical first-order law:

$$\log(\text{Pb}_0/\text{Pb}) = (\log 2 / T) t \qquad (5)$$

where Pb_0 is the present activity at the sediment–water interface; Pb the activity which remains after a given elapsed time; and T the half-life of ^{210}Pb.

If the sedimentation rate is supposed to be a constant $\bar{\omega}$, the thickness of the deposited sediment during time t is $z = \bar{\omega} t$ and eq. 5 becomes:

$$\log(\text{Pb}_0/\text{Pb}) = (\log 2 / T) \cdot z / \bar{\omega} \qquad (6)$$

This is a linear relation where the slope is $1/\bar{\omega}$ (Fig. 5). Analytical results of Table 2 are used to calculate $\bar{\omega} = 0.46 \pm 0.07$ cm yr^{-1} with a correlation coefficient $\rho = 0.97$.

5.2.2. Non-linear model.

This previous evaluation of the sedimentation rate ω does not take into account the sediment compaction, i.e. the relation which links ω to the porosity. Let us write $dt = dz/\omega$. If ω is expressed as in eq. 4, then the time t which is necessary to deposit a

Log (Pb_0/Pb)

Fig. 5. Determination of $\bar{\omega}$ (linear model).
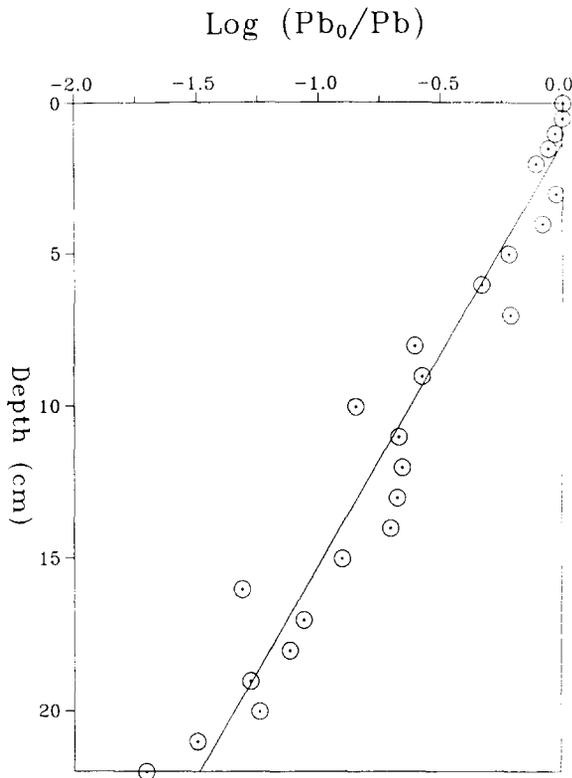
A(z) (cm)

Fig. 6. Determination of ω_0 (non-linear model).

sediment layer of a given thickness z can be obtained by integration:

$$t = \int_0^z \frac{(1-\phi_0) + \alpha z}{\omega_0(1-\phi_0)}\, dz \qquad (7)$$

The result can be expressed as:

$$t = A(z)/\omega_0$$

where

$$A(z) = z + \alpha z^2/2(1-\phi_0) \qquad (8)$$

The time t can be calculated independently with the ^{210}Pb profile and eq. 5, while $A(z)$ can be calculated at every depth z. Fig. 6 shows the linear relation $A(z) = \omega_0 t$ from which it is possible to calculate $\omega_0 = 0.90 \pm 0.09$ cm yr^{-1} with a correlation coefficient $\rho = 0.97$.

We can summarize and compare the results given by the two models: relations (5), (6) and (8) show that the time t can be related to the sediment depth z using two ways:
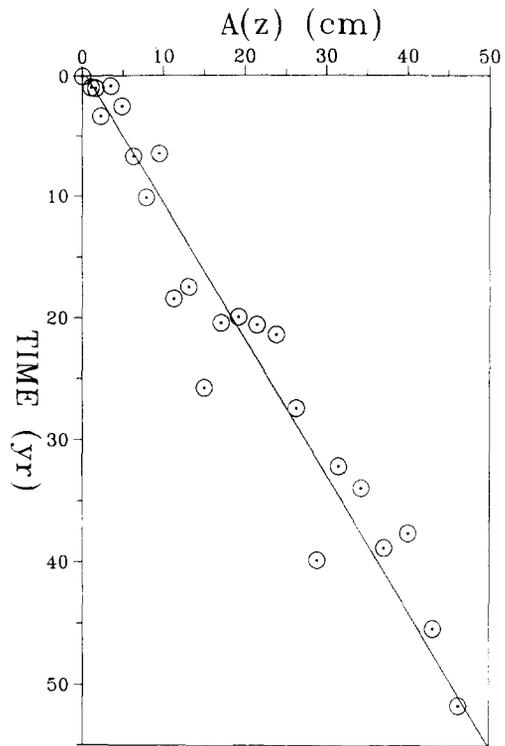
(1) $z = \bar{\omega} t$

(2) $A(z) = \omega_0 t$

Fig. 7 compares these relations. Taking into account the analytical dispersion, the linear and the non-linear model cannot be statistically discriminated. However, the observation of the sediment core shows that the last deposited annual layer (the sediment–water interface) exhibits two sublayers: (1) a brown-reddish sub-layer which represents the winter layer; and (2) a black sub-layer which represents the summer layer. The total thickness is ~ 1 cm. Therefore, the non-linear model provides a better description of the global sedimentation process.

Moreover, this model shows that a given sediment layer at a given depth z into the sediment core represents a very different time period according to the value of z. From its initial value $\omega_0 = 0.9$ cm yr^{-1} at the sediment–
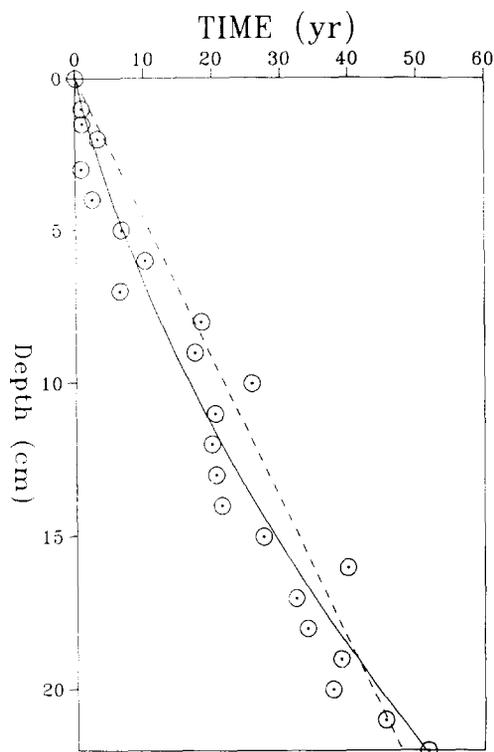
TIME (yr)

Fig. 7. Relations $t = f(z)$. The *dashed line* represents the linear model ($\bar{\omega} = 0.46$ cm yr^{-1}). The *continuous line* represents the non-linear model ($\omega_0 = 0.90$ cm yr^{-1}).

water interface, $\omega = 0.2$ cm yr^{-1} at 30-cm depth. This shows clearly that in a highly compacted sediment, the ^{210}Pb method cannot provide a correct estimation of the sedimentation rate by itself.

5.3. Modelling the concentration profiles of particulate organic carbon and nitrogen

Eq. 2 can now be rewritten in a new form which includes the analytical expression of $\omega(z)$:

$$-\omega_0\left(\frac{1-\phi_0}{1-\phi_0+\alpha z}\right)\frac{\partial X}{\partial z} - K_x X = 0 \qquad (9)$$

with the following boundaries conditions:

$z = 0 \quad \rightarrow \quad X = X_0$

and

$z \rightarrow \infty \quad \rightarrow \quad X \rightarrow X_\infty$

where $X\infty$ corresponds to the amount of organic carbon and nitrogen refractory to any further mineralization (i.e. the burial term). Integration of eq. 9 gives:

$$X = (X_0 - X_\infty)\left[\exp-\left\{\frac{K_x}{\omega_0}\right.\right.$$

$$\left.\left.\times\left(z + \frac{\alpha z^2}{2\omega_0(1-\phi_0)}\right)\right\}\right] + X_\infty \qquad (10)$$

The experimental profiles provide numerical values required to adjust the previous boundaries conditions:

(1) For POC: $C_0 = 1.42$ mole% and $C_\infty = 0.46$ mole%

(2) For PON: $N_0 = 0.15$ mole% and $N_\infty = 0.036$ mole%

A non-linear regression method (Nash, 1979) is used to fit the theoretical profiles. The best adjustment is obtained when: $K_C = K_N = 3.0 \cdot 10^{-2}$ yr^{-1}.

Experimental uncertainties related to ω_0, ϕ_0 and α are propagated in the estimation of the K_x-values; therefore, the global error range likely is not $< \pm 15\%$. Consequently, K_C and K_N must represent the same first-order constants related to the mineralization of the POM which may lie within the range: $K_{POM} = (3.0 \pm 0.5) \cdot 10^{-2}$ yr^{-1}.

This result is not appreciably affected if the same calculation is done when we use the average sedimentation rate $\bar{\omega} = 0.46$ cm yr^{-1}. The values for K_x are $4.7 \cdot 10^{-2}$ and $3.6 \cdot 10^{-2}$ yr^{-1} for C and N, respectively, which, obviously, is close to the error range of the K_{POM} calculated with the non-linear model. This result shows that kinetic constants deduced from modelization of diagenetic processes are not very sensitive to large variation of porosity. This is probably the reason why Murray et al. (1978) are able to generate a set of consistent values for K_C, K_N and K_S (where the subscript N and S refer to ammonia and sulfate, respectively), assuming a constant porosity, while this assumption is not supported by the sedimentary context.
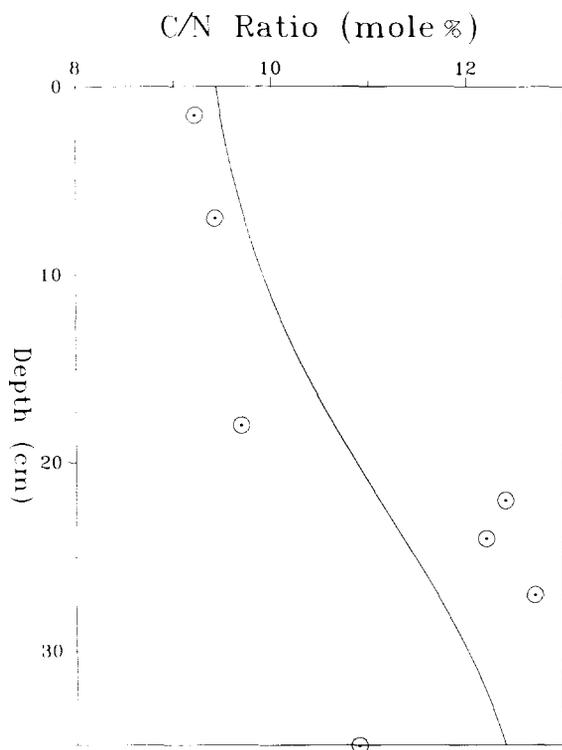
Fig. 8. Evolution of the ratio C/N. The *continuous line* represents the calculated C/N ratio with eq. 10.

The similarity observed in the mineralization rate constant for POC and PON may look amazing because it suggests identical reaction rates for quite different organic compounds such as cellulose polymers, glucosides and fatty acids on one hand and proteins and amino-sugars on the other hand. Such a similarity has already been mentioned by Murray et al. (1978).

It is well established that nitrogen-rich compounds are more labile than carbohydrates. This is obvious if we compare the evolution of the calculated and observed C/N ratio along the sediment core (Fig. 8): the residual organic matter becomes more and more depleted in nitrogen. However, our results imply the same rate for different reactions where the elementary processes are likely very different. That contradiction can be resolved if we make the assumption of a multi-step mechanism:

(1) A slow breakdown of the macromolecules.

(2) A quick metabolization which converts the end-products of the first step into mineral species which are found in pore water. Therefore, K_{POM} should represent only the first slow step, i.e. the polymers break down. Moreover, the organic matter behaves like a two-component mixture [the "multi G" model of Berner (1980)]:

(1) a "low-energy" term which can be easily metabolized where the C/N ratio is equal to $(C_0 - C_\infty)/N_0 - N_\infty)$, i.e. C/N = 8.4.

(2) a "high-energy" term which, within the same time reaction range, is much more refractory to the mineralization processes (the burial fraction) where the C/N ratio is equal to C_∞/N_∞, i.e. C/N = 12.8.

6. Conclusions

We have shown that the ^{210}Pb method, commonly used to estimate the sedimentation rate, cannot be applied to a highly porous sediment if compaction is not considered. However, the experimental dispersion of ^{210}Pb data, inherent to the method, does not allow us to discriminate between the linear and the non-linear model.

While the solid fraction of the sediment is a much less chemically sensitive system than pore water, we show here that data obtained on the solid can be used to enlighten the geochemical processes occurring during the mineralization of particulate organic matter.

Acknowledgements

References

Arrhenius, G., 1950. Carbon and nitrogen in subaquatic sediments. Geochim. Cosmochim. Acta, 1: 15–21.

Bader, R.G., 1955. Carbon and nitrogen relations in surface and subsurface marine sediments. Geochim. Cosmochim. Acta, 7: 205–211.

Berner, R.A., 1964. An idealized model of dissolved sulfate distribution in recent sediments. Geochim. Cosmochim. Acta, 28: 1497–1503.

Berner, R.A., 1980. Early Diagenesis — A Theoretical Approach. Princeton University Press, Princeton, N.J., 241 pp.

Gaillard, J.F., Sarazin, G., Pauwels, H., Philippe, L., Lavergne, D. and Blake, G., 1987. Interstitial water and sediment chemistries of Lake Aiguebelette (Savoy, France). Chem. Geol., 63: 73–84.

Gaillard, J.F., Pauwels, H. and Michard, G., 1989. Chemical diagenesis in coastal marine sediments. Oceanol. Acta, 12: 175–187.

Goldberg, E.D., 1963. Geochronology with Pb-210. In: Radioactive Dating. IAEA (Int. At. Energy Agency), Vienna, 121 pp.

Koide, M., Soutar, A. and Goldberg, E.D., 1972. Marine geology with ^{210}Pb. Earth Planet. Sci. Lett., 14: 442–446.

Martin, J.M., 1985. The Pavin crater lake. In: W. Stumm (Editor), Chemical Processes in Lakes. Wiley-Interscience, New York, N.Y., pp. 169–188.

Murray, J.W., Grundmanis, V. and Smethie, Jr., W.M., 1978. Interstitial water chemistry in the sediment of Saanich Inlet. Geochim. Cosmochim. Acta, 42: 1011–1026.

Nash, J.C., 1979. Compact Numerical Methods for Computers: Linear Algebra and Function Minimization. Adam Hilger, Bristol, 227 pp.

Petit, D., 1974. ^{210}Pb et isotopes stables du plomb des sédiments lacustres. Earth Planet. Sci. Lett., 23: 199–206.

Philippe, L., 1989. Bilan géochimique du fer et du phosphore dans un écosystème lacustre eutrophe: le lac d'Aydat (Puy de Dôme). Thèse de Doctorat d'Université, Université Paris 7, Paris, 186 pp.

Rosenfeld, J.K., 1981. Nitrogen diagenesis in Long Island Sound sediments. Am. J. Sci., 281: 436–462.

Sarazin, G., Gaillard, J.F., Philippe, L., Rabouille, C. and Michard, G., 1988. Aydat Lake: Early diagenesis and related environmental aspects. In: European Association for Geochemistry. International Congress of Geochemistry and Cosmochemistry. Chem. Geol., 70: 115 (abstract; special issue).

Smith, J.N. and Walton, A., 1980. Sediment accumulation rates and geochronology measured in the Saguenay fjord using the ^{210}Pb dating method. Geochim. Cosmochim. Acta, 44: 225–240.

Von Damm, K.L., Benninger, L.K. and Turekian, K.K., 1979. The ^{210}Pb chronology of cores from Minor Lake, New Hampshire. Limnol. Oceanogr., 24: 434–439.

Waksman, S.A., 1933. On the distribution of organic matter in the sea bottom and the chemical nature and origine of marine humus. Soil Sci., 36: 125–147.

Wilken, M., Anton, K.K. and Liebezeit, G., 1990. Pore water chemistry of inorganic nitrogen compounds in the eastern Skagerrak (N.E. North Sea). Hydrobiologia, 207: 179–186.