



Oxidation and Origin of Organic Matter in Surficial Eastern Mediterranean Hemipelagic Sediments

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Abstract. Aerobic mineralisation of C_{org} in surface sediments of the deep (>2000 m water depth) eastern Mediterranean Sea has been quantified by analysis of detailed box core C_{org} concentration versus depth profiles and the modelling environment for early diagenetic problems MEDIA. The reactive fraction comprises 60–80% of the total C_{org} reaching the sediments and is largely oxidised within the surficial 10 cm. A non-reactive C_{org} fraction (G_{NR}) dominates at depths >10 cm, and makes up 20–40% of the total C_{org} flux to the sediments. First-order rate constants for decomposition of the reactive fraction calculated from the C_{org} profiles range from 5.4×10^{-3} to $8.0 \times 10^{-3} \text{ y}^{-1}$ to $8.0 \times 10^{-3} \text{ y}^{-1}$. Total mineralization rates in the surface sediment are between 1.7 and $2.6 \mu\text{mol C cm}^{-2} \text{ y}^{-1}$ and thus are typical for oligotrophic, deep-sea environments. The low fluxes and rapid remineralisation of C_{org} are accompanied by $^{210}\text{Pb}_{excess}$ surface mixed layers which are only 2 cm deep, among the thinnest reported for oxygenated marine sediments. Model results indicate a mismatch between the C_{org} profiles and O_2 microprofiles which were measured onboard ship. This can be attributed to a combination of decompression artefacts affecting onboard measurement of the O_2 profiles or the leakage of oxygen into the core during handling on deck. Furthermore, the used D_b values, based on ^{210}Pb , may not be fully appropriate; calculations with higher D_b values improve the O_2 fits. The surficial sediment $\delta^{13}\text{C}_{org}$ values of $\sim -22\text{‰}$ become less negative with increasing depth and decreasing C_{org} concentrations. The major $\delta^{13}\text{C}$ change occurs in the top 3 to 4 cm and coincides with the interval where most of the organic carbon oxidation takes place. This indicates that the reactive fraction of organic matter, commonly assumed to be marine, has a more negative $\delta^{13}\text{C}_{org}$ than the refractory fraction, usually held to be terrestrial. Palaeoproductivity estimates calculated from the sediment data by means of literature algorithms yield low surface productivities ($12\text{--}88 \text{ gC m}^{-2} \text{ y}^{-1}$), which are in good agreement with field measurements of primary productivity in other studies. Such values are, however, significantly lower than those indicated by recent productivity maps of the area derived from satellite imagery ($>100 \text{ gC m}^{-2} \text{ y}^{-1}$).

Key words: organic carbon, eastern Mediterranean, oxidation, production, ^{210}Pb , diagenesis, $\delta^{13}\text{C}$

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Introduction

Eastern Mediterranean sediments record two different sedimentation regimes: short (few thousand year) episodes of organic-rich deposition characterised by sapropel sediments with >2 wt.% C_{org} , interbedded with longer (tens of thousands of years) periods of organic-poor, hemipelagic sediment deposition. These contrasts in C_{org} concentrations indicate the singular character of the eastern Mediterranean basin, because on the one hand, low sediment C_{org} contents (<0.5 wt.%) are expected under oligotrophic areas or in slowly-accumulated open ocean sediments such as red clays, while on the other hand, high values (>2 wt.%) only occur in highly productive, upwelling continental margin areas (e.g., compilation by Müller and Suess, 1979).

Geochemical research on eastern Mediterranean sediments has mainly focused on the sapropels and the transitions between sapropels and the organic-poor sediments (e.g., Sigl et al., 1978; Anastakis and Stanley, 1986; De Lange et al., 1989, 1999; Pruyers et al., 1993; Higgs et al., 1994; Thomson et al., 1995; Van Santvoort et al., 1996a). The C_{org} -poor, deep-water sediments have been largely ignored, despite the fact that they compose most of the sedimentary column. The inorganic geochemical composition of the hemipelagic sediments of the basin are usually explained by differences in lithological source and the relative contribution of biogenic carbonate (Pruyers et al., 1991; Dekkers et al., 1994; Van Os et al., 1994, Nijenhuis et al., 2001). Oxidic sediments immediately above sapropels can exhibit high concentrations of redox-sensitive (trace-)elements, but these are generally sapropel sediments which have been oxidised after deposition (e.g., Thomson et al., 1995; Van Santvoort et al., 1996a; De Lange et al., 1999; Thomson et al., 1999). Sediment C_{org} concentrations between sapropel units are low and fairly constant, ranging between 0.1 and 0.2 wt.%. This concentration range seems to be independent of depth in core, sedimentation rate and water depth (e.g., Pruyers et al., 1991; this study).

This study focuses on the process of C_{org} oxidation in the top layer of eastern Mediterranean sediments. The aerobic mineralisation of C_{org} is quantified using the modeling environment for early diagenetic problems MEDIA (Meysman, 2001; Meysman et al., in press), with sediment $^{210}Pb_{excess}$ data utilised to quantify bioturbation. $\delta^{13}C$ values of the sedimentary organic carbon are discussed. Finally, based on the organic carbon data in the sediment, primary production rates are calculated.

Material and Methods

Three sub-cores are studied from box cores UM15, UM26 and UM35, recovered during the 1994 Palaeoflux cruise with R.V. Urania (Figure 1 and Table I). Pore water analyses of these cores have been reported elsewhere (Van Santvoort et al., 1996a). Sediment oxygen profiles were measured within 3 hours after core recovery by means of an oxygen electrode mounted on a computer-controlled micro

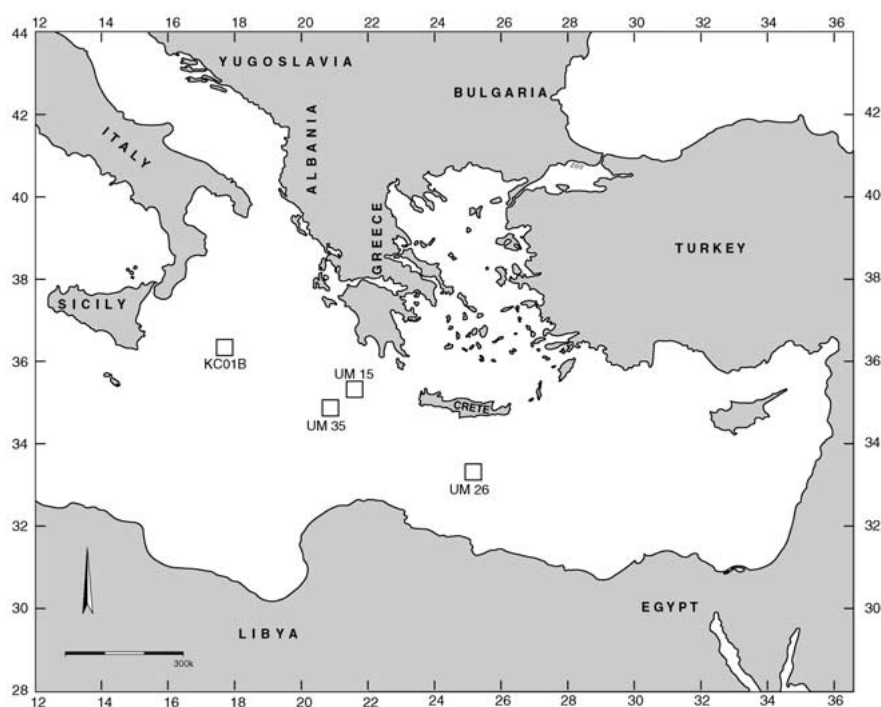


Figure 1. Sample locations of the cores used in this study. Position, water depth and sediment accumulation rates (for the UM boxcores) are listed in Table I.

manipulator (Cussen et al., 1994), and showed that the sediments are oxic down to the top of the most recent sapropel (S1), present at 22.3–28.5 cm depth in the different cores.

Table I. Summary of the cores studied. Accumulation rates for the UM boxcores were calculated from the base of the sapropel, assuming an age of 9.0 ky and a constant sedimentation rate since then. In the absence of the base of the sapropel in the core, the sediment accumulation rate for UM15 is calculated on the basis of the depth of the upper Mn-peak alone (see Van Santvoort et al., 1996a for details).

Core	Location	Water depth (m)	Sediment accumulation rate (cm ky ⁻¹)
UM15	35°17.4'N, 21°24.8'E	3308	4.7
UM26	33°23.6'N, 25°00.9'E	2161	3.1
UM35	35°11.0'N, 21°12.5'E	2672	3.3
KC01B	34°22.0'N, 20°02.7'E	3289	–

Sub-cores for C_{org} analyses were sampled at high resolution (2–3 mm). Samples were freeze-dried and finely ground in an agate mortar. Organic carbon was determined on a Fisons Instruments NCS NA 1500 analyser using dry combustion at 1030 °C. Inorganic carbon (carbonate) was removed before analysis by shaking 1 g samples twice for 24 hours in 1 M HCl. After drying at 80 °C, the sample was ground in an agate mortar. CO_2 gas released upon combustion from 30 mg acid-treated samples was cryogenically separated from the other gases and the $\delta^{13}\text{C}_{\text{org}}$ was measured with a VG SIRA 24 mass spectrometer. The precision was $<0.1\%$, and international and in-house standards were used to check the accuracy of the method. Standard deviations were always $<1.5\%$.

Several tests have been carried out to check the removal of refractory carbonates such as dolomites by the HCl treatment. Test results show that all carbonates are removed from the sample so that the $\delta^{13}\text{C}$ measurements are not influenced by these components.

Dissolved organic carbon (DOC) analyses of the HCl fractions after shaking revealed that negligible amounts of C_{org} were removed from the sample. These tests were not only performed on the samples but also on standards. The obtained DOC concentrations are below the detection limits of 0.5 ppm. Based on these results it can be assumed safely that the method for the removal of inorganic carbon as described above, only affects the inorganic carbon fraction of the sample.

The $^{210}\text{Pb}_{\text{excess}}$ method was employed to quantify bioturbation at the top of the cores (Nozaki et al., 1977; Soetaert et al., 1996). Samples (1 g) were leached with 6 M HCl in the presence of a ^{209}Po tracer. The Po isotopes were then plated on Ag planchettes by the method of Flynn (1968) for proxy determination of ^{210}Pb via ^{210}Po by alpha spectrometry.

Results and Discussion

OXIDATION OF ORGANIC MATERIAL

C_{org} profiles (Figure 2a) have highest concentrations near the sediment surface, and decrease with depth to achieve asymptotic values between 0.13 to 0.16 wt.% within the upper 5–10 cm of the sediment. The corresponding pore water O_2 profiles from the three box cores studied (Figure 2a) suggest that O_2 consumption, as revealed by the concave curvature in the profiles, is intense over the uppermost 2–3 cm. Between this surface zone and the top of the oxidized sapropel only minor additional O_2 is consumed. O_2 is fully removed at a greater depth (22.3–28.5 cm) where it is used to oxidise the most recent sapropel, S1 (Van Santvoort et al., 1996a). The sediments of all three cores are therefore oxic down to the S1 unit.

C_{org} oxidation by O_2 in the upper layer of the core was reproduced using the object-oriented modeling environment MEDIA (Modelling Early DIAgenesis) (Meysman 2001, Meysman et al., in press). This general-purpose software package for early diagenetic problems provides both transient and steady-state model description of reactive transport processes affecting organic matter, nutrients,

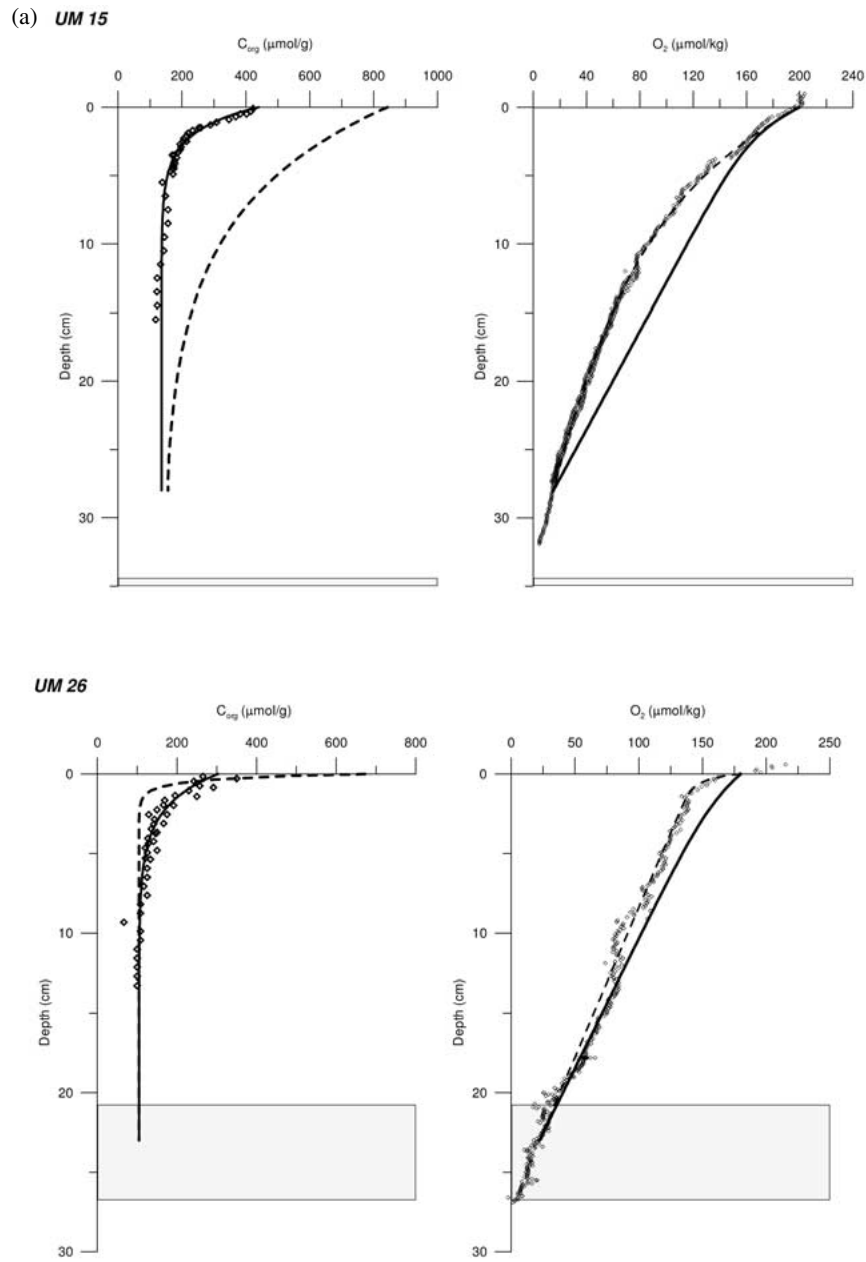
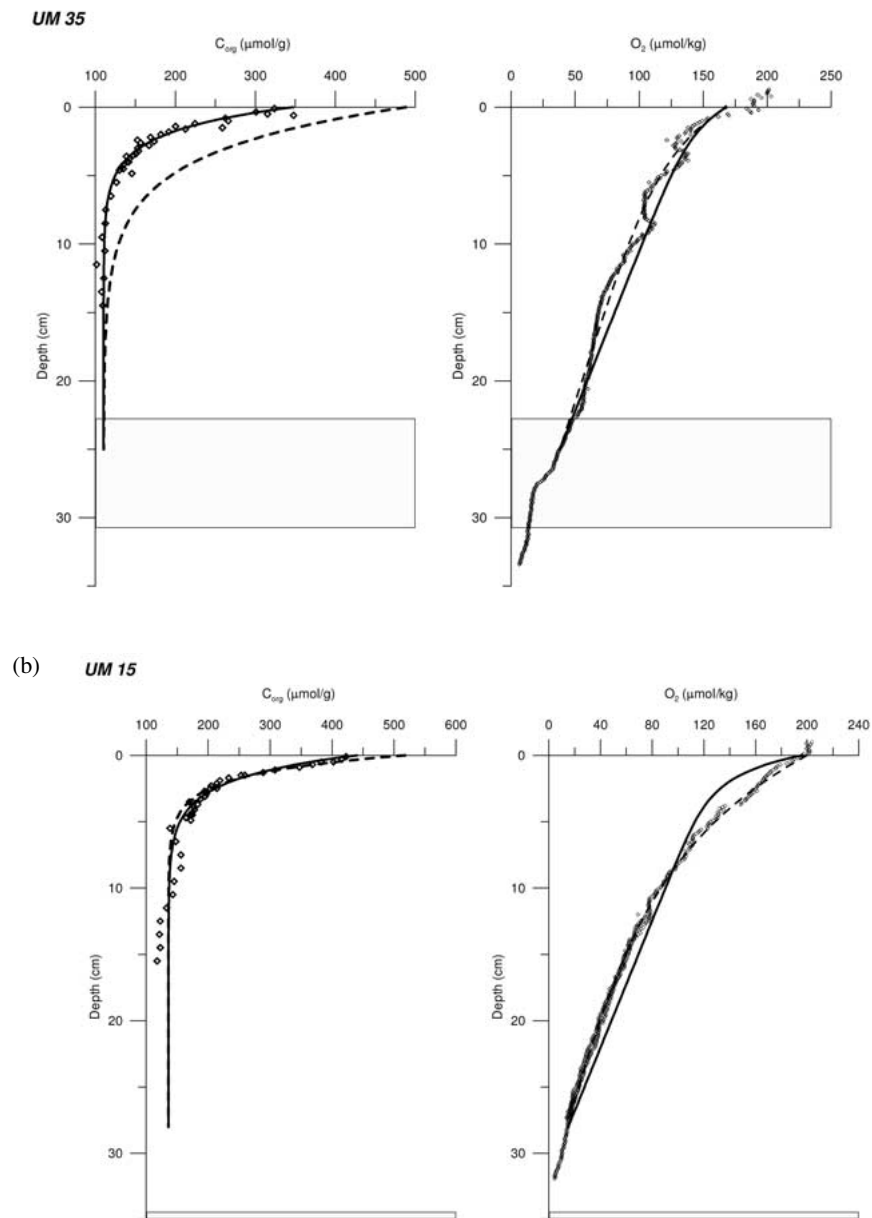


Figure 2. Organic carbon concentration and oxygen concentration versus depth profiles for cores UM15, UM26 and UM35. Part of the O_2 profile of UM15 was re-profiled at a different position in the core at 12 cm, which explains the overlap in the profile. The S1 sapropel (>2 wt.% organic carbon) is indicated by the shaded area. Solid lines are the fits of MEDIA to the C_{org} data and the corresponding O_2 profiles. Dotted lines are the fits of MEDIA to the O_2 profiles and the corresponding C_{org} profiles. (a) ^{210}Pb derived D_b values are used for the fits. (b) MEDIA derived D_b values are used.



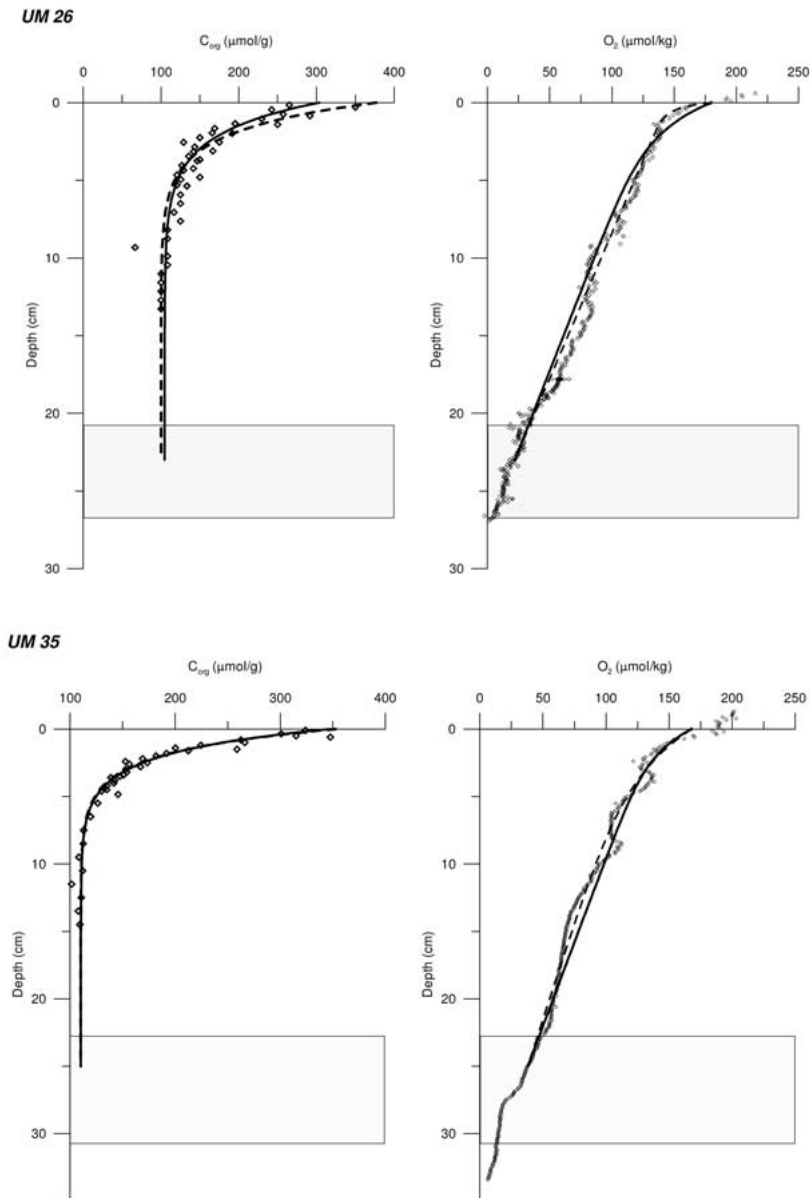


Figure 2. Continued.

oxidants and reduced by-products in aqueous sediments. In this study, the package was used to quantify aerobic C_{org} oxidation and to check the consistency of the C_{org} and O_2 profiles. To model the decreasing degradability of the organic matter, MEDIA implements the multi-G formulation of Westrich and Berner (1984). In this approach the total pool of sedimentary organic material G_T is subdivided into

several classes, each having a different reactivity towards oxidation (Jørgensen, 1978).

$$G_T = \sum_1^n G_i, \quad (1)$$

where G_T is the amount of total decomposable organic matter (wt.%) and G_i is the amount of organic matter in fraction i (wt.%). Each fraction degrades independently via different first-order kinetics.

$$\frac{dG_i}{dt} = -k_i G_i, \quad (2)$$

where t is time (y) and k_i is the first-order decay constant for organic matter in fraction i (y^{-1}).

Transport of solids is thought to be influenced by sediment accumulation and bioturbation. Sediment density was assumed to be equal to 2.6 g cm^{-3} . The porosity was fixed at 0.7, which is a typical value for deep-basin sediments in the eastern Mediterranean (Slomp et al., 2002), and was assumed constant with depth (no compaction). Advection velocities were calculated based on the depth location of the sapropel, i.e., either the base of the sapropel or the depth of Mn-peak (Table 1, see Van Santvoort et al., 1996a for details). Bioturbation is described via the analogy of Fickian diffusion (Goldberg and Koide, 1962; Boudreau, 1986). Biodiffusion coefficients D_b ($\text{m}^2 \text{ y}^{-1}$) were calculated from the ^{210}Pb profiles for each site (section 3, Figure 5, Table IV). The modelled sediment stratum ranged from the sediment water interface to the top of the sapropel, and appropriate boundary conditions were imposed. For organic matter, a fixed flux (Neumann condition) was assumed at the sediment water interface, while no gradient boundary condition was used at the top of the sapropel. For O_2 , fixed concentrations (Dirichlet conditions) were used at both the upper and lower boundary. At the lower boundary, being the top of sapropel S1, oxygen is absent, due to the oxidation of the sapropel. To verify the performance of MEDIA, simulated C_{org} and O_2 profiles were compared to the solutions of an (approximate) analytical model (as used e.g., by Hammond et al., 1996) and matching results were obtained.

C_{org} decomposition in the box cores was well-described by decay of one reactive fraction and a refractory fraction. Distinction of more fractions produced only marginal (less than a few percent) improvement to the fits and therefore the simplest model has been chosen. The model fits to the C_{org} profiles reveal that 85–90% of the organic matter reaching the sediment surface is reactive. Approximately 40–50% of the total organic material in the sediment is oxidised within the first 3 cm of the sediment in all cores (Figure 2a; Table II). Over the next 6–7 cm, a further 20–30% is degraded and below this depth only the refractory fraction persists (fraction G_{NR} , which constitutes ca. 30% of the total C_{org} present in surficial sediments). The fitted k_R values for the three locations range between 5.4×10^{-3} and $8.0 \times$

Table II. Organic matter fluxes at the sediment-water interface (G_T = total, G_R = reactive, G_{NR} = non-reactive) and the first-order rate constant for organic matter decomposition (k_R) obtained by fitting the C_{org} profiles with the model MEDIA. Corresponding model fits to the C_{org} and O_2 profiles are shown in Figure 2a. The organic matter concentrations at the sediment-water interface, the time needed to reach the 50% and 1% level of the reactive fraction ($t_{50\%}$ and $t_{1\%}$), and C_{org} -oxidation rates in the sediment above the sapropel are also listed. At the bottom of the table, the G_T flux is listed as obtained from the MEDIA fits. Values in brackets are percentages of the total organic matter flux or concentration.

	UM15	UM26	UM35
Flux ($\mu\text{mol cm}^{-2} \text{y}^{-1}$)			
$-G_T$	3.03	1.92	2.93
$-G_R$	2.53 (84%)	1.67 (87%)	2.64 (90%)
$-G_{NR}$	0.50 (16%)	0.25 (13%)	0.28 (10%)
Concentration (%)			
$-G_T$	0.56	0.38	0.43
$-G_R$	0.39 (71%)	0.26 (67%)	0.30 (70%)
$-G_{NR}$	0.16 (29%)	0.13 (33%)	0.13 (30%)
k_R (y^{-1})	6.0×10^{-3}	5.4×10^{-3}	8.0×10^{-3}
$t_{50\%}$ (G_R) (y)	116	129	87
$t_{1\%}$ (G_R) (y)	770	858	575
C-ox. Above S1 ($\mu\text{mol cm}^{-2} \text{y}^{-1}$)	2.53	1.67	2.64
Flux G_T (MEDIA) ($\mu\text{mol cm}^{-2} \text{y}^{-1}$)	9.23	4.43	3.52

10^{-3}y^{-1} . These values are within the range expected for oligotrophic, deep-sea low-sedimentation rate environments (e.g., Grundmanis and Murray, 1982; Boudreau, 1997), where the organic matter generally has a low reactivity. C_{org} -oxidation rates in the sediment above the sapropel vary from 1.7 to 2.6 $\mu\text{mol cm}^{-2} \text{y}^{-1}$ (Table II) and are typical for deep-sea environments where very little reactive organic matter survives transport through the water column before reaching the sediment (e.g., Emerson et al., 1985; Hammond et al., 1996).

Corresponding model-calculated O_2 profiles show a concave curvature in the surface sediment, and near-linear profiles down to the top of the sapropel (Figure 2a). Calibrating the model to the C_{org} profiles, the measured O_2 profiles show a stronger decrease with depth than the modelled profiles for all three cores. Additional simulations showed that this discrepancy between the modelled and measured O_2 values is not the effect of nitrification. Due to low nitrate concentrations, its inclusion in the model has a negligible effect on the O_2 profiles. Therefore, it is most likely the result of a decompression artefact in the on-deck O_2 -measurements. The occurrence of such pressure-related artefacts in O_2 -microprofiles of deep-

sea sediments measured on-deck was demonstrated earlier by Glud et al. (1994) who showed that measurements on recovered sediment cores showed lower O_2 penetration depths and higher diffusive uptake rates than *in situ* measurements. The differences increased with increasing water depth and were ascribed to three factors: (1) expelling of porewater due to the release of the hydrostatic pressure; (2) transiently-increased temperature during core recovery and handling on deck, causing an increase of respiration processes which increases the O_2 uptake and (3) a combination of both processes could be lethal to some species of bacteria and meiofauna. The availability of more organic compounds will increase the O_2 uptake.

To assess the magnitude of the change in respiration rates needed to explain the O_2 profiles in our cores, we fitted the model to the O_2 profiles and calculated the corresponding C_{org} profiles. The results are shown as dotted lines in Figure 2a and again clearly show the mismatch between the C_{org} and O_2 profiles. In all cores, much higher surface concentrations and fluxes of C_{org} are required than those that were actually measured. Corresponding respiration rates were up to a factor 12 (UM26) higher than those calculated based on the measured C_{org} profiles. This clearly demonstrates the need for either (1) *in situ* O_2 measurements or (2) C_{org} profiles in combination with accurate sediment transport rates (D_b , ω) when assessing organic matter decomposition in deep-sea surface sediments.

In the above discussion the implicit assumptions were made that the calculated D_b values (based on the ^{210}Pb profiles) are correct and that the mismatch between calculated and measured O_2 concentrations is the result of incorrect O_2 measurements. A different approach is the assumption that the O_2 data are correct but that the D_b values as calculated from the ^{210}Pb profiles are not accurate. Soetaert et al. (1998) showed that mixing rates based on C_{org} can be one order of magnitude higher than mixing rates based on ^{210}Pb . The organic (reactive) particles are mixed faster than the inorganic (non-reactive) ^{210}Pb particles resulting in different mixing rates. Therefore, calculations were carried out with different (higher) D_b values (Table IV). This improves the O_2 fits as shown in Figure 2b.

A final remark about the O_2 profiles is that some oxygen may have leaked into the core during coring and handling of the cores on deck. It is not possible to quantify this effect. The eventually measured profiles are the result of the possibilities mentioned before. We consider the pressure effect as the most important factor. *In situ* measurements of oxygen could clarify the observed mismatches.

In the absence of sapropels or turbidites at shallow depth, oxygen penetration into Eastern Mediterranean sediments would be much deeper than observed. This is expected because in most non-sapropel intervals C_{org} concentrations are similar to the G_{NR} values observed for the surface sediment (Table II) and rates of C_{org} decomposition are low. For example, results for a long core profile from the eastern Mediterranean (Figure 3), mostly show a range of C_{org} values between 0.1 and 0.2 wt.% for depths of 2.5–37 m below the sea floor, corresponding to ages of 20 ky–1.1 My (Van Santvoort et al., 1996b). Note that the lowest C_{org} values in

Figure 3, down to 0.05 wt.%, correspond to ash layer horizons, i.e., are due to admixture with C_{org} lean allochthonous material. The lack of a consistent decrease of non-sapropel organic carbon with depth in core KC01B indicates that little or no degradation of the remaining organic carbon takes place under oxygen-deficient conditions.

ORGANIC MATTER $\delta^{13}\text{C}$ SYSTEMATICS

The quantity of organic matter represented by each component in the multi-G model is a modelfit parameter rather than a distinguishable class of compounds, and the model yields no information on organic matter sources. In an enclosed basin like the eastern Mediterranean, sedimentary C_{org} in principle may be expected to consist of both marine material produced in the photic zone and land-derived (terrestrial) material. $\delta^{13}\text{C}_{\text{org}}$ systematics are often used to differentiate between these sources, with values of -27‰ and -20‰ generally cited for terrestrial and marine C_{org} , respectively (Degens, 1969; Emerson and Hedges, 1988; Prahl et al., 1989). Naturally, these are average values for terrestrial and marine C_{org} , different compounds may have different $\delta^{13}\text{C}_{\text{org}}$ values (e.g., Jasper and Hayes, 1993). The most striking example for this is the difference between C_3 and C_4 plants. The $\delta^{13}\text{C}$ values of C_3 plants, which include trees, shrubs and cool-climate grasses, range from -22 to -32‰ . In contrast, C_4 plants, which include many tropical grasses, sedges and seagrasses, usually exhibit $\delta^{13}\text{C}$ values in the range of -9 to -16‰ . Several studies showed (e.g., Goñi et al., 1998; Huang et al., 2000) that the C_3/C_4 ratio can change over time by changes in climatic and atmospheric conditions. Furthermore, individual marine cores may record factors such as changes in aeolian transport pathways and wind strength (Sarnthein et al., 1981).

The marine fraction is commonly assumed to be subject to more rapid oxidation (Emerson and Hedges, 1988; Prahl et al., 1980), whereas the terrestrial fraction is thought to be relatively resistant to further remineralisation in the marine environment since it has already been exposed to degradation on land and during transport (Prahl et al., 1989; Hedges et al., 1994; Hedges and Keil, 1995). Our model calculations clearly indicate that the organic matter decomposition systematics can be adequately described using two fractions, namely a refractory and a reactive fraction. Concurring with commonly taken assumptions, we will tentatively assume that these fractions correspond to a predominantly 'terrestrial' and 'marine' component respectively. If in line with our model results, the organic matter remaining in sediments below 10 cm is assumed to be the refractory terrestrial component alone. Then from the model-calculated relative proportions of refractory and reactive fractions in the topmost sediment (avg. 30 and 70%; Table II), and the C_{org} and $\delta^{13}\text{C}_{\text{org}}$ values for these respective sediments (Figure 4), an average $\delta^{13}\text{C}_{\text{org}}$ of -20.8 ± 0.2 and -22.6 ± 0.4 for terrestrial and marine components is calculated (Table III). These values being more negative for the marine than for the terrestrial component deviate from what is commonly reported for oceanic sediments. How-

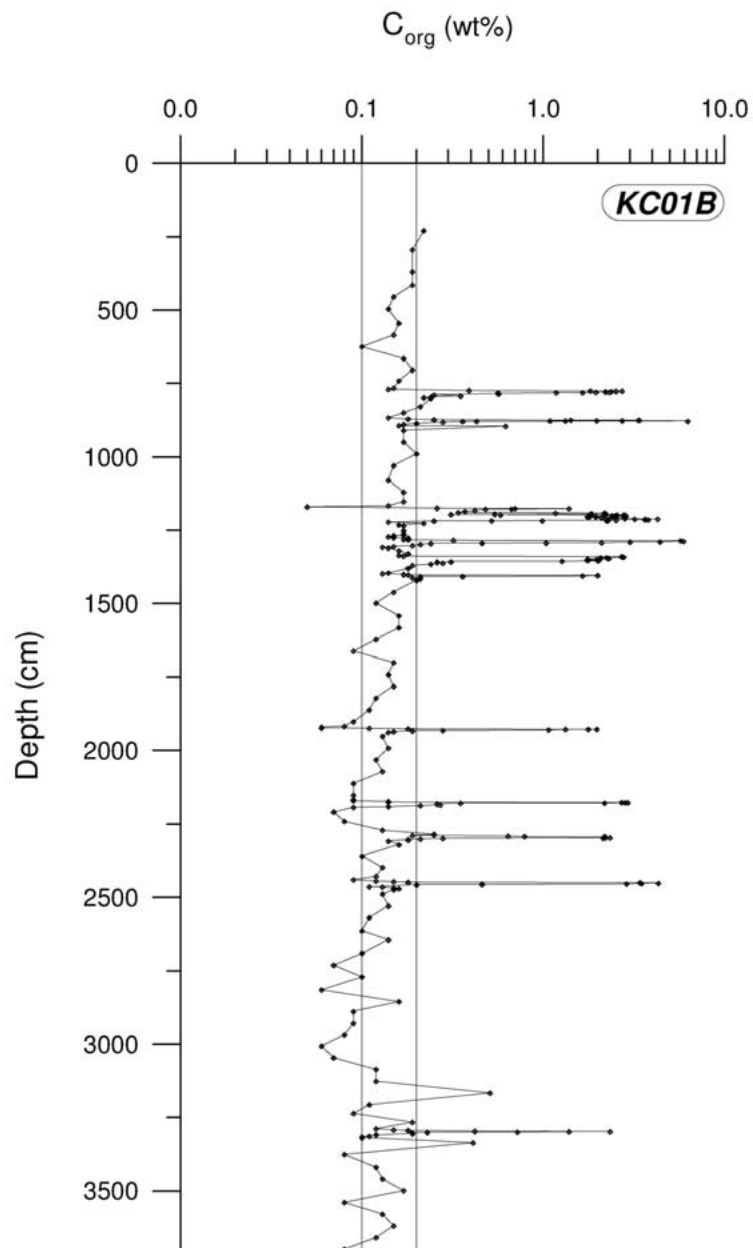


Figure 3. Organic carbon versus depth profile in piston core KC01B. Solid lines are drawn at 0.1 and 0.2 wt.% C_{org} . Organic carbon concentrations are mostly between these values, except in the sapropel(ic) intervals (much higher) and ash layers (lower). Note the logarithmic x-axis.

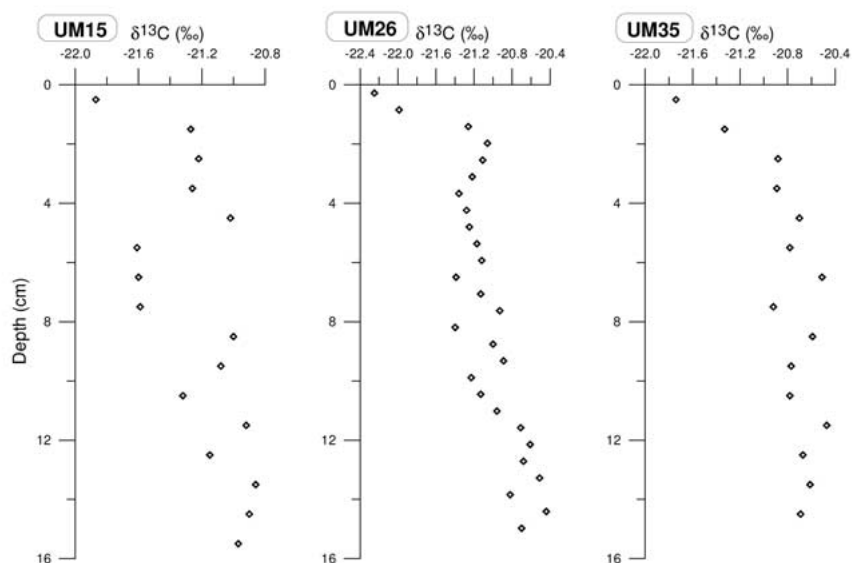


Figure 4. $\delta^{13}\text{C}$ (‰) versus depth profiles for UM15, UM26 and UM35. Values become less negative with increasing depth in all three cores.

ever, in eastern Mediterranean sediments clearly a prominent decrease in reactive organic carbon concurs with a change to less negative $\delta^{13}\text{C}$ values (Figure 4). This cannot but indicate that the reactive fraction of organic matter, commonly assumed to be marine, has a more negative $\delta^{13}\text{C}_{\text{org}}$ than the refractory fraction, usually held to be terrestrial. Although these average $\delta^{13}\text{C}_{\text{org}}$ values, being more negative for marine than for terrestrial organic matter, deviate from the oceanic values usually reported, they fall within the respective range of average values reported for terrestrial and for marine organic matter. A similar $\delta^{13}\text{C}_{\text{org}}$ change was observed by Gacia et al. (2002) in the western Mediterranean, reporting values of -25‰ for organic material in the water column and of -20‰ for C_{org} in the underlying sediments.

This deviation in relative marine and terrestrial $\delta^{13}\text{C}_{\text{org}}$ values found in the Mediterranean may be due to the highly oligotrophic nature of this semi-enclosed basin, where a major part of the primary production flows to the microbial food-web (e.g., Turley, 1999). A detailed organic geochemical and ecological study, combined with compound-specific $\delta^{13}\text{C}_{\text{org}}$ work is needed to elucidate detailed background information for the sources and behaviour of the $\delta^{13}\text{C}_{\text{org}}$ in the eastern Mediterranean.

Table III. Calculated $\delta^{13}\text{C}_{\text{org}}$ values for the reactive and refractory organic carbon fractions. The non-reactive fraction is the organic material that remains deeper than 10 cm in the sediment, all other organic matter is assumed to be reactive. The calculated $\delta^{13}\text{C}_{\text{org}}$ is obtained by using the following equation:

$$\delta^{13}\text{C}_{\text{org}}(R) = \frac{\%C_{\text{org}}(T) \cdot \delta^{13}\text{C}_{\text{org}}(T) - (\%C_{\text{org}}(NR) \cdot \delta^{13}\text{C}_{\text{org}}(NR))}{\%C_{\text{org}}(R)}$$

where (R), (NR) and (T) represent the reactive, non-reactive and total fractions respectively.

	UM15	UM26	UM35
Total C_{org} (%)	0.56	0.38	0.43
Total $\delta^{13}\text{C}_{\text{org}}$ (‰)	-22.0	-22.4	-22.0
Non-reactive C_{org} (%)	0.16	0.13	0.13
Non-reactive $\delta^{13}\text{C}_{\text{org}}$ (‰)	-20.6	-20.9	-20.9
Reactive C_{org} (%)	0.39	0.26	0.30
Reactive $\delta^{13}\text{C}_{\text{org}}$ (‰) (calculated)	-23.1	-22.3	-22.5

$^{210}\text{Pb}_{\text{excess}}$ SYSTEMATICS: MIXED LAYERS, BIOTURBATION INTENSITIES AND INVENTORIES

$^{210}\text{Pb}_{\text{excess}}$ is a useful short-term proxy tracer for C_{org} fluxes in the deep sea (Moore and Dymond, 1988). Following ^{222}Rn emanation from the continents to the atmosphere, a fraction of the ^{222}Pb then produced by ^{222}Rn decay is deposited on the surface ocean (Turekian et al., 1977). Biological scavenging processes remove this ^{210}Pb from the surface ocean to the underlying sediments (Moore and Dymond, 1988; Fisher et al. 1988), along with additional ^{210}Pb produced from dissolved ^{226}Ra present deeper in the water column (Cochran et al., 1990). The activity supplied to the sediments in this way is termed $^{210}\text{Pb}_{\text{excess}}$ because it is additional to the ^{210}Pb present in radioactive equilibrium with ^{226}Ra in detrital materials.

Due to the bioturbative effects of sediment infauna, $^{210}\text{Pb}_{\text{excess}}$ is mixed downwards into the sediments from the sediment/water interface, resulting in a surface mixed layer (SML) in deepsea sediments. The observed SML distributions of $^{210}\text{Pb}_{\text{excess}}$ may then be modelled to quantify bioturbation intensity and depth, where these measures are average values applicable to the past 100 y (Nozaki et al., 1977). Like C_{org} concentration/depth profiles, surficial sediment $^{210}\text{Pb}_{\text{excess}}$ profiles are assumed at steady-state, i.e., a constant tracer supply balances consumption by radioactive decay ($t_{1/2} = 22.3$ y). Assuming steady-state supply and decay, fluxes are related to inventory according to:

$$J = \lambda I, \quad (3)$$

where J is the $^{210}\text{Pb}_{\text{excess}}$ flux ($\text{dpm cm}^{-2} \text{y}^{-1}$), λ is the decay constant of ^{210}Pb (y^{-1}) and I is the inventory (dpm cm^{-2}).

Table IV. $^{210}\text{Pb}_{\text{excess}}$ inventory and bioturbation coefficients (D_b) of the UM box cores. Dpm = disintegrations per minute. The estimated bioturbation coefficients for MEDIA fits (last row) were used in the exercise where it was assumed that the measured oxygen data are correct. An alternative D_b value was used to improve the fits as shown in Figure 2b.

	UM15	UM26	UM35
$^{210}\text{Pb}_{\text{excess}}$ inventory (dpm cm^{-2})	24.2	10.2	13.8
Bioturbation coefficient ($\text{cm}^2 \text{y}^{-1}$) as calculated from ^{210}Pb profiles	0.010	0.015	0.019
Estimated bioturbation coefficient for MEDIA fits ($\text{cm}^2 \text{y}^{-1}$)	0.037	0.038	0.026

The inventory (I) is evaluated as

$$I = \sum (A_i \rho_i \Delta z_i), \quad (4)$$

where A_i is the $^{210}\text{Pb}_{\text{excess}}$ activity in dpm g^{-1} for sample i (dpm g^{-1}), ρ_i is the dry bulk density (g cm^{-3} ; assumed constant = 0.7 g cm^{-3}) and Δz_i is the thickness (cm).

Assuming a constant biodiffusion constant D_b ($\text{cm}^2 \text{y}^{-1}$), a constant sedimentation rate ω (cm y^{-1}) and constant density ρ (g cm^{-3}) in the mixed zone, D_b is evaluated by fitting the following equation directly to the ^{210}Pb profiles using a least squares minimization routine:

$$A = A_0 \exp\left(\frac{\omega - \sqrt{\omega^2 + 4\lambda D_b}}{2D_b} z\right) \quad (5)$$

with boundary conditions $A = A_0$ and $A \rightarrow 0$ as $z \rightarrow \infty$.

Assuming no bioturbation, an advective velocity of 4 cm ky^{-1} (Table 1) and a timespan of 4 times the ^{210}Pb half-life (i.e., about 100 y), ^{210}Pb would penetrate the sediment only to around 4 mm. Hence, any deeper ^{210}Pb is due to mixing, and the zone over which significant non-zero ^{210}Pb activities are found, determines the thickness of the SML. The ^{210}Pb data from the three box core sub-cores (Figure 5) indicate shallow SMLs and low bioturbation intensities (Table IV). Like the overall sediment accumulation rate (Table I) and C_{org} contents and fluxes (Table II), the $^{210}\text{Pb}_{\text{excess}}$ inventory data of UM15 are greater than those of the other two cores (Table IV).

The indicated $^{210}\text{Pb}_{\text{excess}}$ SMLs in the studied cores are 2 cm thick (Figure 5) and are among the lowest reported for marine sediments (compare e.g., Trauth et al., 1997). They are similar to SML estimates made earlier from $^{210}\text{Pb}_{\text{excess}}$

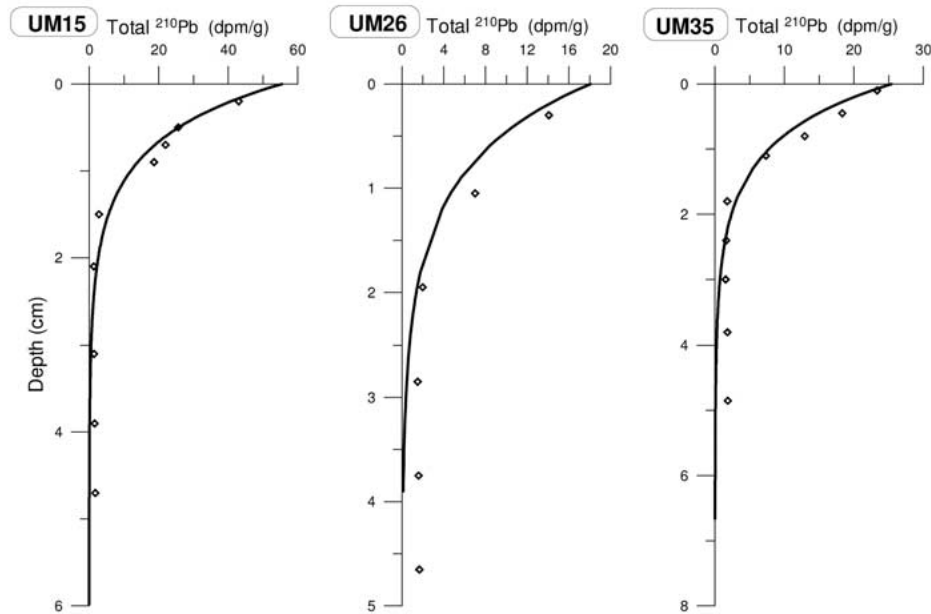


Figure 5. Specific activities of total ^{210}Pb versus depth for the three box cores studied. $^{210}\text{Pb}_{\text{excess}}$ is present only in the upper 2 cm, below these depths low levels of supported ^{210}Pb (mean 1.63 dpm g^{-1}) are present in detrital materials ($^{210}\text{Pb}_{\text{excess}} = \text{total } ^{210}\text{Pb} - \text{detrital } ^{210}\text{Pb}$). $^{210}\text{Pb}_{\text{excess}}$ persists for only ~ 100 y because of its short half-life. The observed $^{210}\text{Pb}_{\text{excess}}$ distribution is therefore not caused by sediment accumulation ($\sim 3 \text{ cm ky}^{-1}$; Table I), but rather by bioturbation in a surface mixed layer. Solid lines in the profiles are model fits to the data.

profiles from other deep-water eastern Mediterranean sites (Table 4, Thomson et al., 1995). The thin $^{210}\text{Pb}_{\text{excess}}$ SMLs correspond to the depth layer with the most marked decrease in C_{org} , and it is anticipated that thin $^{210}\text{Pb}_{\text{excess}}$ SMLs will prove to be characteristic of deep-water eastern Mediterranean sediments. The D_b values are at the low end of the range observed in low sedimentation rate, deep-sea environments (Boudreau, 1994). As a result of the oligotrophic conditions in the area, C_{org} fluxes reaching the sea floor are low, and as a consequence of the low food supply flux and its rapid remineralisation, the intensity of bioturbation is low and the bioturbated zone is small in these sediments. In a suite of well-dated, deep-water eastern Atlantic cores, Trauth et al. (1997) observed that SML thickness increased directly with food supply from a minimum SML thickness of ~ 2 cm, but no such relationship was found with overall sediment accumulation rate. Thin SMLs and low mixing intensities, similar to those observed here, were also noted at the oligotrophic end-member of a transect down the west African continental slope from eutrophic to oligotrophic conditions (Legeleux et al. 1994).

From the correlation between C_{org} and $^{210}\text{Pb}_{\text{excess}}$ fluxes observed in sediment traps by Moore and Dymond (1988), it might be expected that low C_{org} fluxes from

Table V. Calculation of the primary production ($\text{gC m}^{-2} \text{y}^{-1}$) using different equations. The upper value is calculated with the fluxes (F_C) calculated with the ^{210}Pb derived D_b values, the lower with the MEDIA derived D_b values and fluxes (F_C). Since the terrestrial component can not be quantified confidently, the total C_{org} fluxes as listed in Table II are used. Actual values will therefore probably be lower.

	Reference	UM15	UM26	UM35
$F_C = \frac{P}{0.0238 \cdot z + 0.212}$	Suess (1980)	28	12	22
		88	27	27
$F_C = \frac{P^{1.22}}{2.29 \cdot z^{0.5}}$	Sarnthein et al. (1992)	24	14	21
		60	27	25
$F_C = \frac{P^{1.41}}{2.44 \cdot z^{0.65}}$	Betzer et al. (1984)	34	21	28
		76	37	35

F_C is the organic carbon flux to the sediment, P is primary production, z is depth.

Eastern Mediterranean productivity could result in low $^{210}\text{Pb}_{\text{excess}}$ inventories in the underlying sediments. Direct wet and dry deposition measurements of $^{210}\text{Pb}_{\text{excess}}$ on the northern land margin of the Mediterranean Sea (Radakovitch et al., 1999) consistently yield values of $\sim 0.6 \text{ dpm cm}^{-2} \text{ y}^{-1}$, which is similar to the value expected from the model of Turekian et al. (1977). This corresponds to a steady state inventory or standing crop of $19 \text{ dpm cm}^{-2} \text{ }^{210}\text{Pb}_{\text{excess}}$. The other potential source of $^{210}\text{Pb}_{\text{excess}}$ to the sediments is ^{226}Ra in the water column, but we have been unable to locate eastern Mediterranean water column $^{210}\text{Pb}/^{226}\text{Ra}$ data to evaluate this source. The atmospheric input expected to the sea surface alone is matched and exceeded only by the sediment inventory in core UM15 (24 dpm cm^{-2}), whereas the UM26 and UM35 inventories are less than that expected from atmospheric input alone ($10\text{--}14 \text{ dpm cm}^{-2}$; Table IV). For comparison, Cochran et al. (1990) found a mean deep North Atlantic inventory of 31 dpm cm^{-2} , (minimum 11, maximum 51 dpm cm^{-2}). The UM26 and UM35 data therefore are consistent with an inefficient scavenging of ^{210}Pb by primary production in surface water.

ORGANIC CARBON FLUXES TO THE SEDIMENTS AND PRIMARY PRODUCTION

Previous studies have shown that the eastern Mediterranean is an area where the production of organic material is (very) low and is therefore classified as oligotrophic (e.g., Dugdale and Wilkerson, 1988). Using the model-calculated organic carbon fluxes (Table II) it is possible to calculate estimates of the primary production (Suess, 1980; Betzer et al., 1984; Sarnthein et al., 1992). Equations and results are listed in Table V and range from 12 to $34 \text{ gC m}^{-2} \text{ y}^{-1}$ for the ^{210}Pb derived D_b values and from 21 to $88 \text{ gC m}^{-2} \text{ y}^{-1}$ for the MEDIA derived D_b values which all confirms the oligotrophic character of the eastern Mediterranean.

A different approach to make an estimate of the primary production is the utilisation of oxygen. For this, some assumptions must be made: (1) the average depth of the eastern Mediterranean is 1791 m; (2) deep water is water below 200 m water depth; Levantine Intermediate Water and water from other source areas is found below this depth (e.g., Bryden and Stommel, 1984; Roether and Well, 2001); (3) the residence time of the deep water is 100 y, which means that 1% of the deep water is refreshed every year (Roether and Well, 2001); (4) 90–98% of the export production is remineralised; (5) the primary production is ten times the export production (e.g., Müller and Suess, 1979); (6) the oxidation of organic carbon is the only process that utilises oxygen. Oxygen concentrations of 220 μM for the surface water (unpublished data) and 200 μM for the outflowing deep water (Roether and Well, 2001; unpublished data) were found. The surface water concentration used is slightly lower than the normally used concentration of 240 μM which is the equilibrium concentration with the atmosphere. Using the Redfield equation for the oxidation of organic matter results in an upper estimate for primary production of 30–33 $\text{gC m}^{-2} \text{y}^{-1}$. The most important parameters in this calculation are the deep water residence time and the primary/export production ratio. On the basis of detailed hydrographic data and using sophisticated modelling, Roether and Well (2001) made an accurate assessment based on the same principle, resulting in a new productivity of 16 $\text{gC m}^{-2} \text{y}^{-1}$.

These estimates concur with those from the sediment data of this study, but differ from the mean annual values shown on satellite images (Longhurst et al., 1995 and Antoine et al., 1995). The Longhurst map shows productivities $>100 \text{ gC m}^{-2} \text{y}^{-1}$ for the eastern Mediterranean, while Antoine et al. (1995) give an average productivity value for the Ionian Basin of 104 $\text{gC m}^{-2} \text{y}^{-1}$, also considerably higher than field values measured by others and the estimates made here (Table V). According to the satellite derived values, more C_{org} is produced than is expected from the fluxes recorded at depth. To obtain these values in our calculation, the deep water residence time should be 2–3 times faster or the primary/export production ratio should be reduced by a similar factor of 2–3. Both possibilities are not very likely and therefore more in-depth investigations are necessary.

The process(es) that lead to sapropel formation are still not fully understood. This study contributes to this ongoing effort in that it clarifies some of the boundary conditions using subrecent sediments. Clearly, present-day primary production and water column conditions can not lead to sapropel formation. This is in good agreement with sapropel observations which indicate enhanced primary production and/or enhanced preservation due to suboxic water column conditions.

Conclusions

Organic carbon profiles for surficial sediments of the eastern Mediterranean can be modelled by the multi-G model using only two fractions, namely a reactive and a refractory one. In the uppermost 2–3 cm of the sediments approximately 40–50%

of the total organic matter is oxidised; 20–30% is degraded over the next 6–7 cm and below this a refractory fraction persists. The k_R values are within the range expected for oligotrophic, deep-sea low-sedimentation rate environments that supply degraded C_{org} to the seafloor. All reactions in the sediments above sapropel S1 take place under oxic conditions and oxygen is never limiting in these intervals.

Unusual $\delta^{13}C$ values are observed: the values in the surface sediments are more negative than deeper in the core. The major changes take place in the top 3–4 cm where most of the organic carbon oxidation occurs. This indicates that the reactive fraction of organic matter, commonly assumed to be marine, has a more negative $\delta^{13}C_{org}$ than the refractory fraction, usually held to be terrestrial. A detailed organic geochemical study using compound specific $\delta^{13}C_{org}$ is needed to elucidate the more precise background information for the sources and behaviour of $\delta^{13}C_{org}$ in the eastern Mediterranean.

The surface mixed layers, the layer where $^{210}Pb_{excess}$ is present, are only 2 cm thick in these cores and are likely to be characteristic of deep-water eastern Mediterranean sediments. The most intense organic matter degradation takes place in the SMLs and is another confirmation of the low bioturbation depth in these sediments.

Estimates based on organic carbon fluxes and oxygen utilisation show low primary production values, ranging from 12 to 34 $gC\ m^{-2}\ y^{-1}$ for the ^{210}Pb derived D_b values and from 21 to 88 $gC\ m^{-2}\ y^{-1}$ for the MEDIA derived D_b values. These values are in good agreement with values found in other studies, but are low compared to satellite derived data. These data emphasize that the present primary production and water column conditions can not lead to sapropel formation.

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Appendix

Abstract from the Computers & Geosciences paper by Meysman et al. (in press):

The MEDIA (Modelling Early DIagenesis) software package comprises a flexible and extensible software system that provides problem-solving assistance for simulating 1D reactive transport in surface sediments. MEDIA allows multiple diagenetic models to be built by extending a model template with new model

components from a toolbox of available objects (elements, species, parameters, reactions). A detailed review is given of the transport and reaction components available for model construction. Upon assemblage, the model is channelled to the numerical subunit of the MEDIA package. Via a canonical transformation, the user-defined mixed kinetic equilibrium model is rearranged into a proper set of Differential Algebraic Equations (DAE), for which both steady-state and transient solutions can be calculated. Steady-state profiles are obtained either directly using a Newton–Raphson method, or alternatively, as the asymptotic result of a dynamic simulation. Dynamic simulations involve a global implicit procedure based on the stiff-ODE solver package VODE, employing a Direct Substitution Approach (DSA) to reduce the number of equations in the DAE system. Verification of the MEDIA code was accomplished (1) by comparison with analytic models and (2) by emulating the model formulation and output of the existing diagenetic model code STEADYSED. As an example application, a diagenetic model was constructed to analyse an extensive dataset collected from a marine sediment in the Santa Barbara Basin (California). The different pathways of organic matter mineralization were modelled, and the coupling among the biogeochemical cycles of C, O, N, S, Mn and Fe was investigated. Depth profiles of both porewater and solid-phase constituents could be reproduced with great accuracy.

References

- Anastasakis, G. C. and Stanley, D. J. (1986) Uppermost sapropel, eastern Mediterranean: Paleoceanography and stagnation, *Nat. Geogr. Res.* **2**, 179–197.
- Antoine, D., Morel, A., and André, J.-M. (1995) Algal pigment distribution and primary production in the eastern Mediterranean as derived from coastal zone scanner observations, *J. Geoph. Res.* **100**, 16193–16209.
- Betzer, P. R., Showers, W. J., Laws, E. A., Winn, D., DiTullio, G. R. and Kroopnick, P. M. (1984) Primary productivity and particle fluxes on a transect of the equator at 153°W in the Pacific Ocean, *Deep Sea Res.* **31**, 1–11.
- Boudreau, B. P. (1986) Mathematics of tracer mixing in sediments: I. Spatially dependent, diffusive mixing, *Am. J. Sci.* **286**, 161–198.
- Boudreau, B. P. (1994) Is burial velocity a master parameter for bioturbation?, *Geochim. Cosmochim. Acta* **58**, 1243–1249.
- Boudreau, B. P. (1997) *Diagenetic Models and their Implementation. Modelling Transport and Reactions in Aquatic Sediments*, Springer, 414 pp.
- Bryden, H. L. and Stommel, H. M. (1984) Limiting processes that determine basic features of the circulation in the Mediterranean Sea, *Oceanol. Acta* **7**, 289–296.
- Cochran, J. K., McKibbin-Vaughan, T., Dornblaser, M. M., Hirschberg, D., Livingston, H. D., and Buessler, K. O. (1990) ^{210}Pb scavenging in the North Atlantic and North Pacific Oceans', *Earth Planet. Sci. Lett.* **97**, 332–352.
- Cussen, H., Braithwaite, A. C. and Wilson, T. R. S. (1994) A robust, pressure-tolerant, low oxygen demand, dissolved oxygen electrode for profiling into deep ocean sediment, *Underw. Techn.* **20**, 3–7.
- De Lange, G. J., Middelburg, J. J., and Pruyssers, P. A. (1989) Discussion: Middle and late quaternary depositional sequences and cycles in the eastern Mediterranean', *Sedimentology* **36**, 161–158.

- De Lange, G. J., Van Santvoort, P. J. M., Langereis, C., Thomson, J., Corselli, C., Michard, A., Rossignol-Strick, M., Paterne, M., and Anastasakis, G. (1999) Palaeo-environmental variations in eastern Mediterranean sediments: A multidisciplinary approach in a prehistoric setting', *Progress in Oceanography* **44**, 369–386.
- Degens, E. T. (1969) Biogeochemistry of stable carbon isotopes, In: *Organic Geochemistry* (eds. E. Eglinton and M. T. J. Murphy), Springer Verlag, New York, pp. 304–329.
- Dekkers, M. J., Langereis, C. G., Vriend, S. P., Van Santvoort, P. J. M., and De Lange, G. J. (1994) Fuzzy *c*-means cluster analysis of early diagenetic effects on natural remanent magnetisation acquisition in a 1.1 My piston core from the central Mediterranean, *Phys. Earth Planet. Int.* **85**, 155–171.
- Dugdale, R. C. and Wilkerson, F. P. (1988) Nutrient sources and primary production of the south-eastern Mediterranean, *Oceanologica Acta* **9**, 179–184.
- Emerson, S., Fischer, K., Reimers, C., and Heggie, D. (1985) Organic carbon dynamics and preservation in deep-sea sediments, *Deep-Sea Research* **32**, 1–12.
- Emerson, S. and Hedges, J. I. (1988) Processes controlling the organic carbon content of open ocean sediments, *Paleoceanography* **3**, 621–634.
- Fisher, N. S., Cochran, J. K., Krishnaswami, S., and Livingston, H. D. (1988) Predicting the ocean flux of radionuclides on sinking biogenic debris, *Nature* **335**, 622–625.
- Flynn, W. W. (1968) The determination of low levels of polonium-210 in environmental materials, *Anal. Chim. Acta* **43**, 221–227.
- Gacia, E., Duarte, C. M., and Middelburg, J. J. (2002) Carbon and nutrient deposition in a Mediterranean seagrass (*Posidonia oceanica*) meadow, *Limnol. Oceanogr.* **47**, 23–32.
- Glud, R. N., Gundersen, J. K., Jørgensen, B. B., Revsbech, N. P., and Schulz, H. D. (1994) Diffusive and total uptake of deep-sea sediments in the eastern South Atlantic Ocean: in situ and laboratory measurements, *Deep-Sea Res.* **41**, 1767–1788.
- Goldberg, E. D. and Koide, M. (1962) Geochronological studies of deep-sea sediments by the ionium/thorium method, *Geochim. Cosmochim. Acta* **26**, 417–450.
- Goñi, M. A., Ruttenger, K. C., and Eglinton, T. I. (1998) A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico, *Geochim. Cosmochim. Acta* **62**, 3055–3075.
- Grundmanis, V. and Murray, J. W. (1982) Aerobic respiration in pelagic marine sediments, *Geochim. Cosmochim. Acta* **46**, 1101–1120.
- Hammond, D. E., McManus, J., Berelson, W. M., Kilgore, T. E., and Pope, R. H. (1996) Early diagenesis of organic material in equatorial Pacific sediments: Stoichiometry and kinetics, *Deep-Sea Res. II* **43**, 1365–1412.
- Hedges, J. I., Cowie, G. L., Richey, J. E., Quay, P. D., Benner, R., Strom, M., and Forsberg, B. R. (1994) Origins and processing of organic matter in the Amazon River as indicated by carbohydrates and amino acids, *Limnol. Oceanogr.* **39**, 743–761.
- Hedges, J. I. and Keil, R. G. (1995) Sedimentary organic matter preservation: An assessment and speculative synthesis, *Mar. Chem.* **49**, 81–115.
- Higgs, N. C., Thomson, J., Wilson, T. R. S., and Croudace, I. W. (1994) Modification and complete removal of eastern Mediterranean sapropels by postdepositional oxidation, *Geology* **22**, 423–426.
- Huang, Y., Dupont, L., Sarnthein, M., Hayes, J. M., and Eglinton, G. (2000) Mapping of C₄ plant input from North West Africa into North East Atlantic sediments, *Geochim. Cosmochim. Acta* **64**, 3505–3515.
- Jasper, J. P. and Hayes, J. M. (1993) Refined estimation of marine and terrigenous contributions to sedimentary organic carbon', *Glob. Biogeochem. Cycles* **7**, 451–461.
- Jørgensen, B. B. (1978) A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments. 2. Calculations from mathematical models. *J. Geomicrobiol.* **1**, 29–51.

- Legeleux, F., Reys, J.-L., and Schindt, S. (1994) Particle mixing rates in sediments of the northeast tropical Atlantic: Evidence from $^{210}\text{Pb}_{\text{xs}}$, ^{137}Cs , $^{228}\text{Th}_{\text{xs}}$ and $^{234}\text{Th}_{\text{xs}}$ downcore distributions, *Earth Planet. Sci. Lett.* **128**, 545–562.
- Longhurst, A., Sathyendranath, S., Platt, T., and Caverhill, C. (1995) An estimate of global primary production in the ocean from satellite radiometer data, *J. Plankt. Res.* **17**, 1245–1271.
- Meysman, F. (2001) Modelling the influence of ecological interactions on reactive transport processes in sediments, Ph.D. Thesis, University of Gent, 213 pp.
- Meysman, F. J. R., Middelburg, J. J., Herman, P. M. J., and Heip, C. H. R. (in press) Reactive transport in surface sediments. II. MEDIA: An object-oriented problem-solving environment for early diagenesis, *Computers & Geosciences*.
- Moore, W. S. and Dymond, J. (1988) Correlations of ^{210}Pb removal with organic carbon fluxes in the Pacific Ocean, *Nature* **331**, 541–544.
- Müller, P. J. and Suess, E. (1979) Productivity, sedimentation rate, and sedimentary organic matter in the oceans – I. Organic carbon preservation, *Deep-Sea Research* **26A**, 1347–1362.
- Nijenhuis, I. A., Becker, J. J., and De Lange, G. J. (2001) Geochemistry of coeval marine sediments in Mediterranean ODP cores and a land section: Implications for sapropel formation models, *Palaeogeogr. Palaeoclimat. Palaeoecol.* **165**, 97–112.
- Nozaki, Y., Cochran, J. K., Turekian, K. K., and Keller, G. (1977) Radiocarbon and ^{210}Pb distribution in submersible-taken deep-sea cores from Project FAMOUS, *Earth. Planet. Sci. Lett.* **34**, 167–173.
- Prahl, F. G., Bennet, J. T. and Carpenter, R. (1980) The early diagenesis of aliphatic hydrocarbons and organic matter in sedimentary particulates from Dabob Bay, Washington, *Geochim. Cosmochim. Acta* **44**, 1967–1976.
- Prahl, F.G., De Lange, G. J., Lyle, M., and Sparrow, M. A. (1989) Post depositional stability of longchain alkenones under contrasting redox conditions, *Nature* **341**, 434–437.
- Pruysers, P. A., De Lange, G. J., and Middelburg, J. J. (1991) Geochemistry of eastern Mediterranean sediments: Primary sediment composition and diagenetic alterations, *Mar. Geol.* **100**, 137–154.
- Pruysers, P. A., De Lange, G. J., Middelburg, J. J., and Hydes, D. J. (1993) The diagenetic formation of metal-rich layers in sapropel-containing sediments in the eastern Mediterranean, *Geochim. Cosmochim. Acta* **57**, 257–536.
- Radakovitch, O., Cherry, R. D., and Heussner, S. (1999) ^{210}Pb and ^{210}Po : traces of particle transfer on the Rhône continental margin, *Deep-Sea Research I* **46**, 1539–1563.
- Roether, W. and Well, R. (2001) Oxygen consumption in the eastern Mediterranean, *Deep-Sea Research I* **48**, 1535–1551.
- Sarnthein, M., Pflaumann, U., Ross, R., Tiedemann, R., and Winn, K. (1992) Transfer functions to reconstruct ocean palaeoproductivity: A comparison, In: *Geol. Soc. Spec. Pub. No. 64* (eds. C. P. Summerhayes, W. L. Prell, and K. C. Emeis), pp. 411–427.
- Sarnthein, M., Tetzlaff, G., Koopmann, B., Wolter, K., and Pflaumann, U. (1981) Glacial and interglacial wind regimes over the eastern subtropical Atlantic and North-West Africa, *Nature* **293**, 193–196.
- Sigl, W., Charmely, H., Fabricius, F., D'Argoud, G., and Müller, J. (1978) Stratigraphy of late quaternary sediments in the eastern Mediterranean, In: *Init. Repts. DSDP 42A* (eds. K. J. Hsü, L. Montadert et al.), pp. 445–465.
- Slomp, C. P., Thomson, J., and De Lange, G. J. (2002) Enhanced regeneration of phosphorus during formation of the most recent eastern Mediterranean sapropel, *Geochim. Cosmochim. Acta* **66**, 1171–1184.
- Soetaert, K., Herman, P. M. J., Middelburg, J. J., De Stigter, H. S., Van Weering, T. E. W., Epping, E., and Helder, W. (1996) Modelling of ^{210}Pb -derived mixing activity in ocean margin sediments: Diffusive versus non-local mixing, *J. Mar. Res.* **54**, 1207–1227.

- Soetaert, K., Herman, P. M. J., Middelburg, J. J. and Heip, C. (1998) Assessing organic matter mineralization, degradability and mixing rate in an ocean margin sediment (Northeast Atlantic) by diagenetic modeling, *J. Mar. Res.* **56**, 519–534.
- Suess, E. (1980) Particulate organic carbon flux in the oceans – surface productivity and oxygen utilization, *Nature* **288**, 260–263
- Thomson, J., Higgs, N. C., Wilson, T. R. S., Croudace, I. W., De Lange, G. J., and Van Santvoort, P. J. M. (1995) Redistribution and geochemical behaviour of redox-sensitive elements around S1, the most recent eastern Mediterranean sapropel, *Geochim. Cosmochim. Acta* **59**, 3487–3501.
- Thomson, J., Mercone, D., De Lange, G. J., and Van Santvoort, P. J. M. (1999) Review of recent advances in the interpretation of eastern Mediterranean sapropel S1 from geochemical evidence, *Mar. Geol.* **153**, 77–89.
- Trauth, M. H., Sarntheim, M., and Arnold, M. (1997) Bioturbational mixing depth and carbon flux at the sea floor, *Paleoceanography* **12**, 517–526.
- Turekian, K. K., Nozaki, Y., and Benninger, L. K. (1977) Geochemistry of atmospheric radon and radon products, *Ann. Rev. Earth. Planet. Sci.* **5**, 227–255.
- Turley, C. M. (1999) The changing Mediterranean Sea – a sensitive ecosystem?, *Progress Oceanogr.* **44**, 387–400.
- Van Os, B. J. M., Lourens, L. J., Hilgen, F. J., and De Lange, G. J. (1994) The formation of Pliocene sapropels and carbonate cycles in the Mediterranean: Diagenesis, dilution or productivity. *Paleoceanogr.* **9**, 601–617.
- Van Santvoort, P. J. M., De Lange, G. J., Thomson, J., Cussen, H., Wilson, T. R. S., Krom, M. D., and Ströhle, K. (1996a) Active post-depositional oxidation of the most recent sapropel (S1) in sediments of the eastern Mediterranean, *Geochim. Cosmochim. Acta* **60**, 4007–4024.
- Van Santvoort, P. J. M., De Lange, G. J., Langereis, C. G., and Dekkers, M. J. (1996b) Geochemical and paleomagnetic evidence for the occurrence of ‘missing’ sapropels in eastern Mediterranean sediments, *Paleoceanography* **12**, 773–786.
- Westrich, J. T. and Berner, R. A. (1984) The role of sedimentary organic matter in bacterial sulfate reduction: The G model tested, *Limnol. Oceanogr.* **29**, 236–249.

