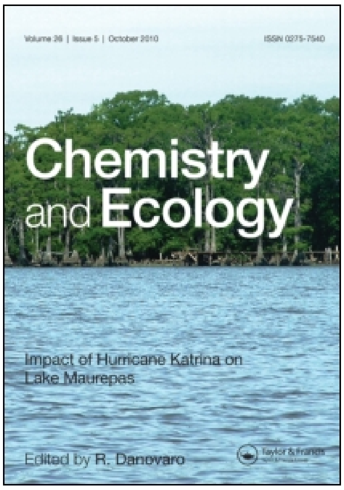

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GAS AND ORGANIC MATTER IN LAST GLACIAL AND HOLOCENIC SEDIMENTS OF VENICE LAGOON

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Two drills (MBM1* and MBM2) provided at "Bocca di Malamocco" gave environmental and palaeo-environmental information on sedimentation for the last 50,000 years. The MBM2 supplies textural, gas and organic matter studies of sediment and principal ion content of pore water. Two main palaeo-environments, divided in six cycles, are recognized. Marine environment characterizes the sediment above 12.80 metres below sea level (mbsl) and continental environment dominates the sediments below.

The concentration/depth profiles of dissolved ammonia, phosphates and gases are related to the occurrence of a relatively high organic content in the sediment core. Carbon dioxide to methane ratio shows a constant value below 20 mbsl, while above that level only carbon dioxide was detected. A sulphate gradient in the transition zone between the marine to fresh water interval suggests a methane oxidation. These findings indicate that diffusive transport of methane from marine sediments to the atmosphere may be considered minimal. The sedimentary cycles are related to the oxygen isotopic stages. They suggest a variable hydraulic regime occurred during the last Glacial time in the palaeo-plain corresponding to the present Venice lagoon.

Keywords: Gas; organic matter; holocenic sediments; Venice lagoon; sedimentary late quarternary; palaeoenvironment interstitial waters; ammonium and sulphate gradients

INTRODUCTION

The lagoon ecosystem, as well as most of the coastal zones, present a delicate and sensible equilibrium. As a consequence any anthropic activity must be managed carefully. The evolution of coastal areas, and particularly the lagoon ones, depends on phenomena which can

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*Second sample at site MBM1.

occur both over a short or a long time span. The methods and type of information related to the short time phenomena (e.g. seasonal measurement of environmental parameters) are well known. On the contrary, the study in coastal areas of long time events is quite new (Curzi, 1992) and requires the ecological, palaeo-ecological and geo-sedimentological characterization of Holocenic and last glacial sediments. This, in turn, provides an environmental and palaeo-environmental definition of sedimentary bodies involved and the reconstruction of their evolution at least over the late Quaternary.

According to the EEC 271/71 directive, the Venetian lagoon and whole the northern Adriatic Sea are considered areas sensitive to eutrophic phenomena, since they receive land runoff from a relatively large area, atmospheric inputs and eventually also some polluted groundwater from agriculture and aquaculture.

Two drills (MBM1* and MBM2) at "Bocca di Malamocco", one of the ports of the Venice lagoon, were provided in December, 1995, with the aim to define environmental and palaeo-environmental sedimentation for the last 50,000 years. This event gave an opportunity to extend the study also on the gas and organic matter in the sediment and principal ions in the pore water.

GEO-SEDIMENTOLOGICAL SETTING

The reconstruction of sedimentary evolution of the Venetian lagoon during last Glacial-Holocene time is to be set geologically in central-northern Adriatic Sea, because it represents an Adriatic margin zone where the sedimentation effects were sooner or later recorded respectively during the regressions or the transgressions occurring within the frame of the glacio-eustatic variations of the sea level.

The central-northern Adriatic Sea is considered a subsiding continental shelf. The detritus, coming from the Po river and many torrential streams, was deposited mostly as a progradation of the slope-shelf system from the north. The Meso-Adriatic Depression is essentially the toe of prodelta slope, partly emphasized by subsidence and compaction (Ciabatti *et al.*, 1987).

De Marchi (1922) first pointed out that central-northern Adriatic Sea was an alluvial plain during the latest glacial period. More recently, many palaeo-channels, over-consolidated clays, peat and fresh water faunas lying below the thin veneer of Versilian transgression sand have been found (Colantoni *et al.*, 1978; Curzi and Tomadin, 1987; Curzi *et al.* 1988; Lenaz and Taviani, 1983).

In the last 6,000 years (Holocene) the transport and distribution mechanism should be considered similar to the present one. The accumulation of finer material during the last 6,000 years constitutes the Holocene mud belt, whose origin and location result from an interaction between the river inputs and dispersal system controlled by Adriatic anti/clockwise circulation pattern. Its thickness is a few centimeters east of the Po river delta (Colantoni *et al.*, 1979) and strongly increases southward, reaching values over 40 m off Ancona and Pescara. Offshore, this belt is arranged in irregular strips somewhat parallel to the coast.

MATERIALS AND METHODS (EXPERIMENTAL SECTION)

Sampling

The analyses of sedimentological and chemical properties of porewater and sediments were provided only in the MBM2 drill. The sediment was recovered by an undisturbed piston sampler from a platform located at site shown on Figure 1. The drilling was then

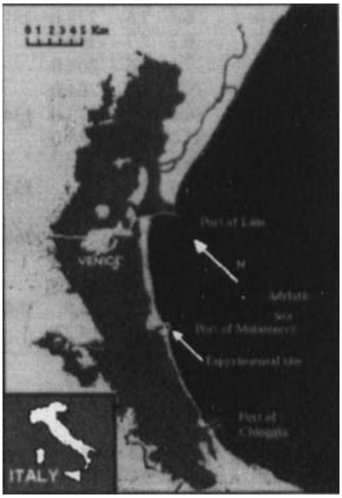


FIGURE 1 Location map.

segmented on ship giving 11 core samples spaced in such a way to represent the most important palaeo-environment features as suggested by preceding available lithological informations. The segmented core samples were immediately frozen and stored at −18°C and sent to the laboratory for chemical analyses. When at the laboratory, each of these samples was horizontally subsampled with a 3 cm i.d. plastic piston sampler to give three regularly spaced subsamples. A combined total of 33 point samples were at the end available for the study characterisation (Tab. I).

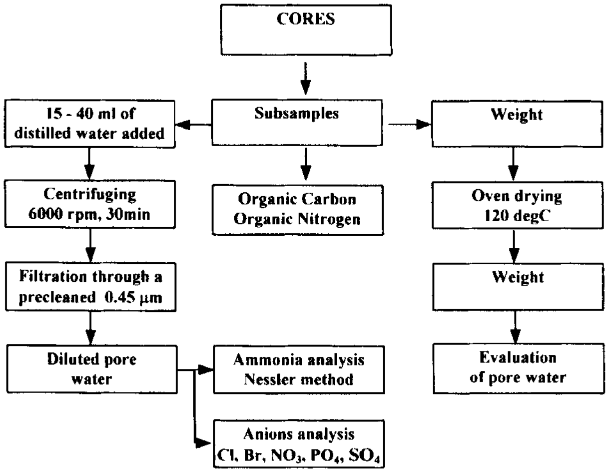
TABLE I Concentrations of the principal ions detected in the sediment samples

Depth mbsl	*Cl mg/l*	*Br mg/l*	*NO_3 mg/l*	*PO_4 mg/l*	*SO_4 mg/l*	*pH*	*NH_4 mg/l*	*Mn μg/l*	*Fe μg/l*	*CO_2 ppm/g*	*CH_4 ppm/g*
5.77	18474.9	60.6	0.7	1.2	2999.8	7.8	7.2	1943	29121	245	0.1
5.90	16045.3	52.7	3.7	1.1	2594.2	7.9	10.5	1375	28342		
6.03	19650.0	64.5	1.4	2.9	3119.7	7.7	7.7				
6.16	197.6	1.4	4.3	0.5	27.6	7.8	4.5				
6.29	4591.8	54.3	1.2	2.3	2042.0	7.9	4.0				
6.42	19920.4	66.7	2.0	0.1	2478.4	8.0	3.8			218	0.2
11.82	19640.9	66.7	4.5	31.1	1912.6	7.6	19.7				
11.90	21940.1	72.9	5.3	31.1	2603.0	7.9	13.0				
11.98	14486.3	47.4	1.3	13.2	1439.0	8.0	15.2	186	9319		
12.06	17228.3	54.6	1.9	8.2	1647.0	8.0	16.6	715	1624	820	2.4
16.27	5414.6	19.3	0.0	0.6	41.8	7.7	23.7			281	15
16.53	1745.0	17.3	0.1	0.0	52.7	7.7	33.2			178	8
19.77	1380.3	13.5	0.4	0.4	6.5	7.6	228.0	281	6762		
19.90	1010.7	11.2	0.4	3.7	6.2	7.7	200.0				
20.03	1337.3	12.3	0.4	2.3	7.1	7.6	208.0			404	47
24.17	1188.2	11.3	0.7	3.1	39.0	7.9	224.0				
24.30	1400.9	12.7	1.0	7.2	36.6	7.9	273.0	134	1579		
24.43	1401.3	12.4	0.7	17.7	33.0	8.1	276.0			1027	110
26.12	583.8	10.1	1.0	3.7	46.0	8.0	0.1			82	3
26.25	297.7	8.1	0.4	4.7	9.5	8.2	0.1	192	3639		
26.38	249.0	6.3	0.3	3.1	6.8	8.1	0.1				
34.82	629.4	2.4	0.4	0.4	12.6	7.6	144.0	266	14307		
34.95	660.2	2.5	0.5	31.1	12.3	7.8	149.0				
35.08	678.1	2.5	0.5	0.5	19.9	7.9	154.0				
44.62	152.7	0.7	0.9	1.1	46.8	8.2	8.0	164	1374		
44.75	123.0	0.5	4.0	1.7	19.5	8.4	4.2				
44.88	128.1	0.5	4.3	0.9	22.5	8.5	0.9			372	18
53.87	627.5	7.2	1.2	3.6	257.1	8.0	15.3			106	0.4
54.00	9770.0	30.4	0.0	5.9	1729.2	8.0	11.3	623	1631		
54.13	540.7	6.3	0.6	4.9	320.5	8.1	11.7			2	0.3
60.72	41.1	1.3	0.8	19.2	33.0	7.8	8.2	91	2453	41	0.5
60.85	15.5	0.1	0.5	13.3	12.8	8.1	10.2				
60.98	23.9	0.1	0.9	19.9	19.1	8.1	8.0			150	8

SAMPLE PREPARATION AND ANALYTICAL METHODOLOGY

Pore Water

Since centrifuging and/or squeezing did not recover sufficient pore water from all the samples, the extraction procedure selected followed the strict protocol summarized on Scheme 1 to ensure uniform handling.



Scheme 1 Extraction procedure for obtaining interstitial water.

The anion levels of the extraction waters were subsequently used to represent a surrogate of the pore water characteristics. Analyses were provided with a Dionex ion Chromatograph mod. 4500i Conductivity Detector (column Ion Pac AS9-SC4 mm), eluent sodium carbonate 1 mM and sodium bicarbonate 0.75 mM, flow rate 1 ml min^{-1}; anions considered were chlorides, bromides, phosphates, nitrates, sulphates.

Cation analyses on the extraction waters were made with inductively coupled plasma (ICP) emission spectrometry (Perkin Elmer mod I 5000). Metals measured were manganese, iron and others (Cd, Zn, Pb, Cu, Hg).

Sediments

Organic carbon content of the sediments was estimated as the sum of the carbohydrate (CHO), protein (PRT) and lipid (LIP). Carbon fraction equivalents were calculated using conversion factors, respectively of LIP 0.75, PRT 0.49 and CHO 0.45. LIP were analyzed following the Bligh and Dye (1959) method applied to sediments: tripalmetine solutions have been used as standards. PRTs were extracted with sodium hydroxide 0.5 N (4°C, 3 h) and analysed according to Hartree and Rice (1982) using bovine albumin as a standard. Total carbohydrates (CHO) were analysed according to Gerchakov and Hatcher (1972), using D(+) glucose as standard. Concentrations reported are considered as glucose equivalent units. Sediments treated in a muffle furnace (450°C, 2 h) were used as a blank as described in details by Danovaro and Fabiano (1990).

The sediment gas estimate (methane and carbon dioxide) was provided with the headspace technique on samples collected independently from the core. In brief, about 200 ml of the sediment brought on ship was immediately sealed in a 500 ml glass bottle, frozen at −18°C and sent for the successive gas chromatographic analyses (Carlo Erba mod. MF500, FID and Thermal Detector, 100/200 carbosieve S-II column).

From a sedimentological point of view, the total core was split in half and described with the help of the Munsell chart for colours. The description was verified by grain size analysis, executed with ASTM sieves for the coarser fraction and with the sedigraph for the finer ones. Samples were prepared following the standard procedure (Gallignani and Magagnoli, 1978) in about 56 m of sediments recovered below sea bottom (mbsb), located at a water depth of 61 m below sea level (mbsl).

RESULTS AND DISCUSSION

The MBM1* and MBM2 were drilled at a distance of a few tens of metres. The MBM1* provided textural, mineralogical, microfauna and absolute age analyses; the MBM2 supplied textural, mineralogical analyses coupled with a gas and organic matter study of sediment and principal ion content of pore water.

A close relationship between the sedimentary successions of two drills has been found. The horizontal relation is very clear on continental-marine boundary and less on continental-continental boundary, but sufficient to allow correlations.

The lithological and textural description of the MBM2 drill are reported on Figure 2. The presence of two main palaeo-environments is suggested by the sedimentological evidence (Curzi *et al.* in press.) and by microfaunal analyses correlated from MBM1* drill (Borsetti *et al.*, in press). Marine environment characterizes the sediment above 12.80 mbsl and below 51.70 mbsl; continental environment dominates the sediments included between the levels mentioned.

MBM2 sediments can be assembled in six sedimentary cycles. Each cycle is characterized by a base generally presenting a coarser texture and a top with prevalently finer sediments alternated locally with peat levels. The top of the cycle appears generally eroded and overconsolidated at the contact with the basal sands of the overlying cycle. The first cycle, between 61.30 and 51.70 mbsl, usually sandy, points out a beach environment at about 54 mbsl that links the continental (superior) and the marine (inferior) environments. Its age can be refered to about 50,000 years. The second cycle ends at 37.4 mbsl and can be divided in three further subcycles whose boundaries are located at 48.3 and 42.3 mbsl. The third cycle reaches 30.5 mbsl while the fourth and the fifth are found at 24.5 and 12.8 mbsl. The sixth cycle, 5.3 mbsl, presents a sandy texture. This last Holocenic cycle started depositing the sediments around 6000 years ago. The microfaunal analyses, still in progress, suggest a clear connection with a marine environment only within the sixth cycle and to a lesser extent. The other cycles consist certainly of continental sediments affected by flooding and subsiding. The continental sedimentary variations are attenuated at the boundary of the second and the third cycle (37.4 mbsl) or the boundary of the third and the fourth cycle (30.5 mbsl). The fifth cycle (24.5 mbsl) presents a well marked base of coarse textured and a thick strata of clay (17.0–12.8 mbsl) extended mostly over the Venetian lagoon (Gatto and Previatello, 1974). This sediment, called "Caranto", overconsolidated roughly in the upper 1.5 m, is sealing the fifth cycle. A well evident erosional surface, indicating the Versilian Transgression, marks the limit between continental (II, III, IV, V cycles) and marine conditions (VI cycle).

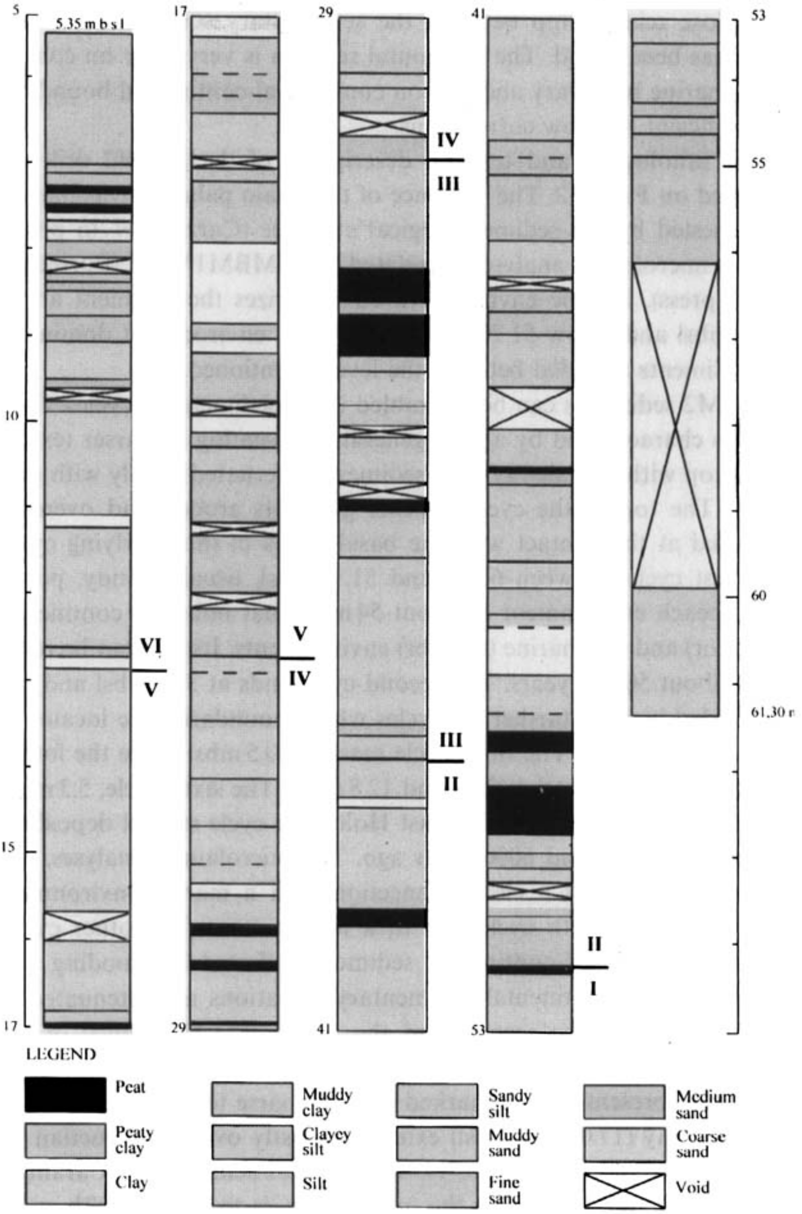


FIGURE 2 Sedimentological log of MBM2 drill.

The six cycles evidenced initially by both sedimentological and microfaunal analysis (Borsetti *et al.*, in press) are now confirmed and detailed by anion profiles. Chlorides, bromides and sulphates (described below) support a clear marine environment in the sixth cycle and the continental environment in all other cycles with the exception of the 54.00 mbsl level. Particularly, the first one shows continental evidence, but a clear marine ingression occurred during the 54.00 mbsl level deposition. The boundary between the V and VI cycles, while it is marked by lithological and sedimentological structures, presents a diffusion interval of the anions below the Versilian erosional surface (12.77 mbsl). Considering the 14C absolute age of 19,900 ± 400 and 29,635 ± 800 years, from the peat located at 17.80–1711 and 31.06–32.01 mbsl in the correlated MBM1* (Borsetti *et al.*, in press) and supposing a constant sedimentation rate, a tentative age of around 45,000 years for 54.00 mbsl, marine ingression could be inferred. Emiliani (1955) defined the oscillations of O_{18}/O_{16} in different groups (oxygen isotopic stages) and first pointed out the relationship between these oscillations and variations of glacio-eustatic temperatures. In the Emiliani scenario, the sedimentary cycles are related to the temperature fluctuation of the last 50,000 years. In other words, the first sedimentological cycles could be related to the base of the 3rd oxygen isotopic stage, where the temperature is the highest of the whole stage and similar to that reached during the last deglacial time (18,000–12,000 years ago). Finally the first, second and third cycles were likely to be deposited during the third isotopic stage (64,000 –32,000 years ago), the IV and V cycles during the II stage (32,000–13,000 years ago) and the VI during the first stage (13,000–0 years ago).

Support to this scenario could come from the sediment and porewater chemical composition. Concentration/depth profile of organic matter, biogenic gases and ammonia together with that of the ions considered are reported on Table I, and in Figures 3 to 10.

All the measured anions provide higher values beyond about 20 mbsl. Chlorides reach concentrations typical of sea water between 5.30 and 12.06 mbsl (average around 18600 mg l^{-1}). The singularity of the value found at 6.16 mbsl is to be attributed to the occurrence of reworked shell fragments prevailing on this level. Between 12.53 and 16.53, the level decrease is gradual. From 16.53 to 60.98 mbsl their

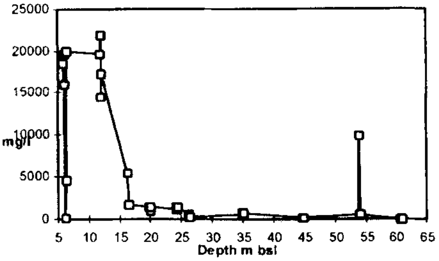


FIGURE 3 Cl Concentration/Depth.

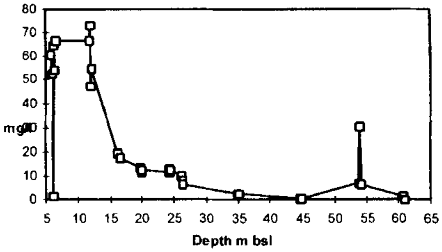


FIGURE 4 Br Concentration/Depth.

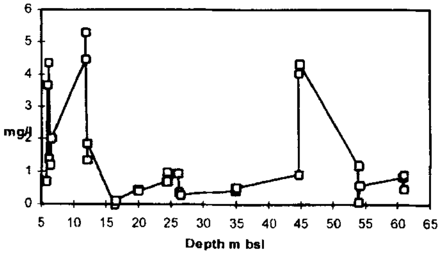


FIGURE 5 NO_3 Concentration/Depth.

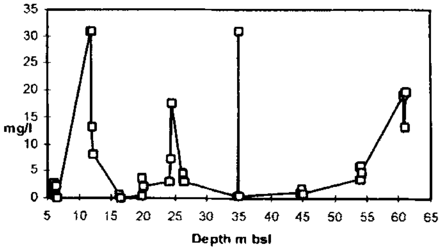


FIGURE 6 PO_4 Concentration/Depth.

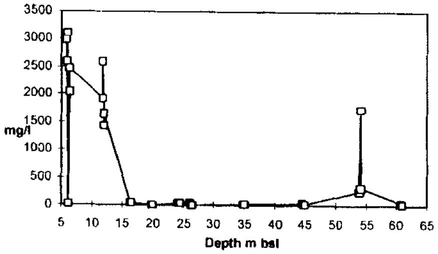


FIGURE 7 SO_4 Concentration/Depth.

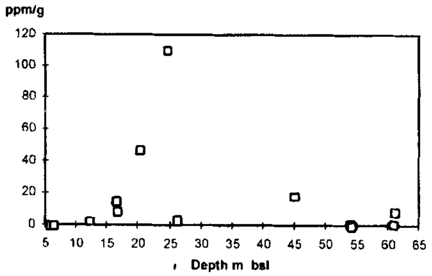


FIGURE 8 CH_4 Concentration/Depth.

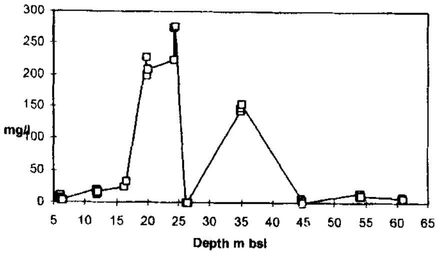


FIGURE 9 NH_4 Concentration/Depth.

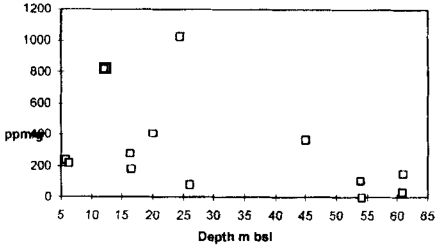


FIGURE 10 CO_2 Concentration/Depth.

level is lower (average around 400 mg l^{-1} and in the fresh water range. However, at 54 mbsl a sharp increment to ≈ 9700 mg l^{-1} indicates a new marine influx even if its absolute level is around the half of that of sea water. The transition from the sea chlorinity to fresh water is detected between 12.06 and 16.53 mbsl with a gradual concentration decrement that can be represented by a Fickian diffusion model. Gieskes (1983) has pointed out that if it is assumed that only vertical transport through interstitial waters is important, then the flux of chemical constituents can be described by the equation (1) where J_z is the mass flux, p the porosity, z the depth coordinate in metres (positive downwards), u the interstitial water velocity relative to the sediment/water interface (ms^{-1}), C the mass concentration and D_b the diffusion coefficient.

$$J_b = p \cdot D_b \cdot \frac{\partial C}{\partial z} + p \cdot u \cdot C \tag{1}$$

$$\frac{\partial pC}{\partial t} = \frac{\partial}{\partial z}(J_z) + R \tag{2}$$

The mass balance is given by equation (2) where R is a chemical source-sink term. If we consider $R=0$, $u=0$, then we can evaluate D_b from the available experimental samples. Chosing a porosity value of 0.5, bulk density of 1.2 g cm^{-2} and a time of 6000 years, we found the ion diffusion coefficient D_b values relative to that of chlorides (Tab. IV). The difference between relative D_b ratios for the ions selected may be well understood, keeping in mind the overall stoichiometric equations for the sequence of oxidants during an organic matter decomposition as summarized on Table II (De Lange 1986, Froelich *et al.* 1979). Nitrates and sulphates are consumed during the diagenetic sequence, hence their diffusivity results are lower and their profiles steeper. The soluble fraction of both manganese and iron, on the contrary, increases during the oxidation of organic matter and this leads to an apparent higher diffusivity.

Bromides and sulphates show a concentration/depth profile similar to that described for chlorides; their ion to chloride ratios are approximately 0.0019 ± 0.000014 and 0.048 ± 0.00049, values characteristic of sea water (0.0015 for Br/Cl and 0.05 for SO_4/Cl reported for $S=35\%$).

TABLE II Oxidaton reactions of organic matter in marine sediments (De Lange, 1986)

1. **Oxygen reduction**

$138\,O_2 + C_{106}H_{263}O_{110}N_{16}P + 18\,HCO_3^- \rightarrow 124\,CO_2 + 16\,NO_3^- + HPO_4^{2-} + 140\,H_2O$

2. **Nitrate reduction**

$94.4\,NO_3^- + C_{106}H_{263}O_{110}N_{16}P \rightarrow 13.6\,CO_2 + 92.4\,HCO_3^- + 55.2\,N_2 + HPO_4^{2-} + 84.8\,H_2O$

3. **MnO_2 reduction**

$236\,MnO_2 + C_{106}H_{263}O_{110}N_{16}P \rightarrow 364\,CO_2 + 470\,HCO_3^- + 8\,N_2 + HPO_4^{2-} + 104\,H_2O + 236\,Mn^{2+}$

4. **Fe_2O_3 reduction**

$212\,Fe_2O_3 + C_{106}H_{263}O_{110}N_{16}P + 740\,CO_2 + 316\,H_2O \rightarrow 846\,HCO_3^- + 424\,Fe^{2+} + 16\,NH_3 + HOP_4^{2-}$

5. **Sulphate reduction**

$53\,SO_4^{--} + C_{106}H_{263}O_{110}N_{16}P \rightarrow 39\,CO_2 + 67\,HCO_3^- + 16\,NH_4^+ + HPO_4^{2-} + 53\,HS^- + 39\,H_2O$

Nitrates and phosphates, on the contrary, show different patterns. Considering the high variability and level of nitrates from the sea bottom down to 12.06 mbsl (1–6 mg l^{-1}) and the location of the second maximum at 44.88 mbsl, shifted near 10 m upwards than the other anions, but an obvious explanation is lacking. However, this occurrence must be analyzed also in the light of the manganese and iron ions profile (Tab. I). Their maxima are observed at the sediment floor andthen they decrease immediately downward with a diffusional trend. The mobility of dissolved manganese (Mn^{2+}), its ability to consume oxygen and the almost identical redox potential with respect to nitrates could easily change the sequence in the classic diagenetic reactions presented on Table II, so consenting the presence of nitrates (Burdige and Gieskes, 1983).

Still a new-fashioned suggestion merits attention: the icy pore-water and snow melt can contain higher levels of this anion (Biederbeck and Campbell 1971). Even if nitrate concentrations generally decrease with soil depth, the snowmelt period has the highest nitrate levels in soil depth (Stoddard, 1994). On this basis, it is possible to conceive that the variability and level of nitrates may be related to climate variations which occurred during sedimentation.

The phosphate pattern is more complex showing at least four relative maxima located at 11.90, 24.43, 34.95, 60.98 mbsl (from 13 to 31 mg l^{-1}). Associated to the phosphate, maxima of bacterial biomasses reported on Table III may be compared. Their link can be inferred

TABLE III Organic matter (OC) and bacterial biomass (BBM) on sediment samples

Depth mbsl	*OC mg/l*	*BBM*
5.35	1933	17.8
12.12	595	16.18
16	2027	190.97
20.2	6099	1540.85
23.95	915	4.75
25.9	1832	4.46
34.6	4471	24.16
44.53	559	2.72
53	889	3.49
61.05	4889	98.8

TABLE IV Chloride ions and relative diffusion coefficients

Ion selected	*Range of depth (mbsl)*	*Relative Diffusivity (Ion/Cl)*
Chloride	12.06–26.38	1
Nitrate	11.82–16.53	0.13
Sulphate	11.90–20.03	0.37
Manganese	5.77–24.03	3.40
Iron	5.77–12.06	2.53

from the diagenetic succession reported on Table II, where phosphate is always released from the first through to the last oxidation reaction. The low values found within the upper 6.42 mbsl are possibly to be attributed to a chemical precipitation of insoluble salts. In effect, the presence of reduced species of iron and manganese shows maxima down to 12.06 mbsl, as illustrated on Table I, thus offering the possibility of a precipitation of phosphate of manganese, iron, besides other insoluble salts.

The organic matter profile (Tab. III) is characterized by three maxima located at 20.20, 34.60 and 61.05 mbsl. The first and the second are paired with an elevated concentration of ammonia (Tab. I, Figure 9) and could correspond to the IV or V reaction of the diagenetic succession (Tab. II). The third one shows the same correlation with ammonia even if with a different relative ratio. Aside the hypothesized diagenetic succession, both the maxima localization of methane and the carbon dioxide pattern do require more insight. Actually, the maxima of carbon dioxide observed at 12.06, 24.43 and 44.88 (Tab. I) are shifted upwards from the sea floor with respect to those of the organic carbon. A bubble gas rising from the generation point (maximum of organic carbon) to the first encountered encapsuling zone can explain this circumstance. Moreover, the methane profile does follow the corresponding carbon dioxide, with the only exception for the peak located at 12.06 mbsl, within the salinity transition zone. This absence could be explained by a sulphate oxidation process. As a matter of fact, sulphate ions are rapidly fading around 16.27 mbsl at the same depth where methane starts to increase confidently. It has already been documented that sulphate may be consumed during anaerobic methane oxidation as methane diffuses upwards into the sulphate bearing zone. Cranston (1994) hypothesizes a theoretical ratio between sulphate consumption and ammonia release, labeled S/N, equal to 13.5. He suggests the following summary equation to describe the methane oxidation: $CH_4 + SO_4^{2} = HS^- + HCO_3^- + H_2O$.

In this case, if the solubility of calcium carbonate is exceeded, carbonates precipitation can occur and this is observed actually by sediment thermal analysis and reported on Figure 13. Also, the sulphate to chloride ratio when plotted against the depth core (Fig. 12) outlines the lower values in the discontinuity found between 16.77 and 34.5 mbsl. Moreover, if ammonia and sulphate gradients are plotted to show the relationship between sulphate consumption and ammonia release within the depth interval 11.98–16.27 mbsl (Fig. 11), a ratio of 0.04 against the theorized 0.08 is found. This represents the excess of sulphate depleted based on ammonia production that has been utilized for methane oxidation. The entire set of observations tend to confirm the diffusion-oxidation process hypothesized.

A linear correlation between the gas concentrations may be obtained selecting the values below 16.77 mbsl (lower sulphate level). Methane (CH_4) to carbon dioxide (CO_2) ratio is described by the linear relationship (ppm $CH_4\,g^{-1} = 0.102$ CO_2 ppm g^{-1} -10) with a correlation coefficient, $r^2 = 0.95$ as illustrated on Figure 14. The methane to carbon dioxide ratio of about 0.1 indicates a prevalence of the

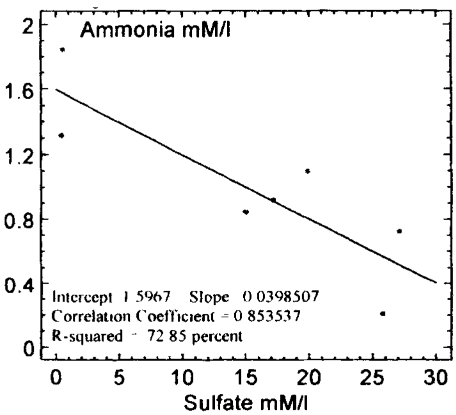


FIGURE 11 Sulphate/Ammonia relationship.

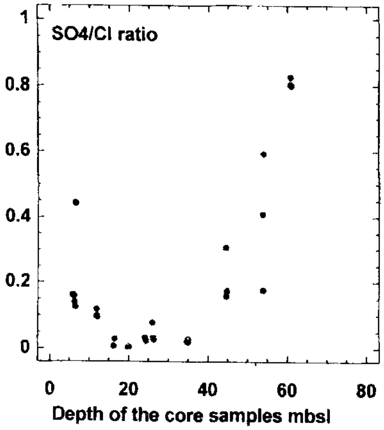


FIGURE 12 Plot of SO_4/Cl vs Depth mbsl.

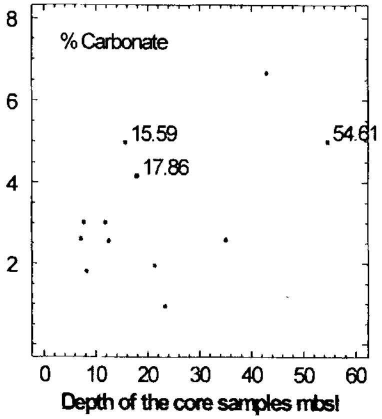


FIGURE 13 Carbonate content of the sediment cores.

oxidative reactions numbered 1 to 5 in the diagenetic scheme with respect to the methanogenic environment.

Methane, as expected, is also correlated to ammonia through the following relation:

ppm CH_4 $g^{-1} = 0.36$ ppm NH_4 $g^{-1} + 5.0$, with a correlation coefficient $r^2 = 0.81$ as illustrated on Figure 15. The loss of association in

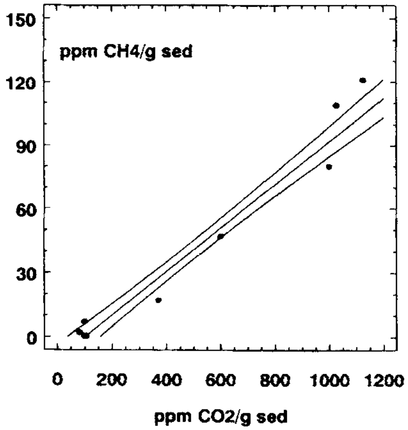


FIGURE 14 Methane vs Carbon Dioxide Depth below 17 mbsl.

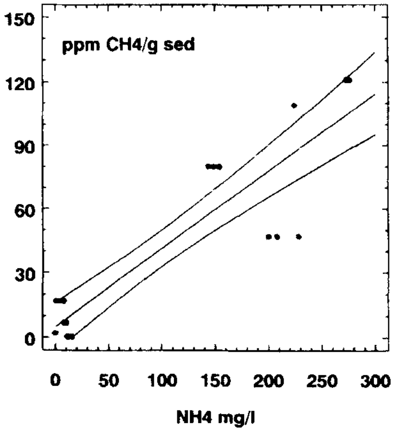


FIGURE 15 Methane vs Ammonia. Depth below 17 mbsl.

this case is probably to be ascribed to the different upward diffusion as discussed before. The higher water solubility of ammonia with respect to the other gases may justify this behaviour.

CONCLUSIONS

The interdisciplinary study of the MBM2 sediments pointed out a succession in which six cycles are recognized. The first five are clearly of continental origin, even if at 54.00 mbsl a marine influx is evident. Only the VI cycle was deposited in marine environment. The combination of sedimentary analyses of MBM2 deposits with the faunal analyses and the 14C absolute age of the correlated MBM1* sediments indicate the fitting of the six sedimentary cycles within the first three Oxygen Isotopic stages. The sedimentary cycles related to the Oxygen Isotopic stages suggest a variable hydraulic regime, probably determined by climatic modifications which occurred during the last Glacial time (II and III isotopic stage) in the palaeo-plain corresponding to the present Venice lagoon.

The concentration/depth profile of dissolved ammonia, phosphate ions and gases are related to the occurrence of a relatively high organic content in the sediment core. The presence of maxima in their concentrations may be considered to be the product of early diagenetic reactions during the decomposition of organic material.

Carbon dioxide to methane ratio shows a constant value below 20 mbsl, suggesting methanogenic conditions, while above that level only carbon dioxide was detected. This may indicate that the biogenic methane diffusing upward in the sediment column into the sulphate-rich marine sediments is effectively oxidized by the sulphate ions. A sulphate gradient inversely related to that of ammonia in the transition zone between marine to fresh water interval helps to confirm the oxidation. These findings support that diffusive transport of methane from marine sediments to the atmosphere is to be considered minimal.

The concentration/depth profile of nitrate appears peculiar, with a greater variability with respect to other anions. This emphasizes the idea of consideration of climatic variation when evaluating biogeochemical sedimentary succession cycles.

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