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Useful tracer parameters to investigate the environmental conditions in areas of the Venice Lagoon

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Abstract

Grain-size and redox potential distributions in sediments were used as tracers to investigate environmental conditions in a shallow water area of the Venice Lagoon subjected to summer anoxic events. Data are presented showing different environmental characteristics within the study area. The results illustrate the reliability of these tracers to acquire a preliminary knowledge of the aquatic ecosystem behavior. Even small differences in morphology and hydrodynamics are observable because of the marked influence they exert on sediment parameters.

Introduction

The Venice Lagoon is a complex and heterogeneous ecosystem, where areas with different environmental characteristics and behavior can be identified on the basis of morphology, hydrodynamics, and biogeochemical conditions. Anthropogenic activities affect various portions of the lagoon differently, depending on local water renewal and proximity to contamination sources. Anoxic events, pollutant accumulation, and the progressive impoverishment of the aquatic fauna and flora occur in the more confined shallow water areas. These areas are mainly located at the land-lagoon interface, where pollutants from the drainage basin and industrial plants are discharged, and where the tidal influence is lower than in the zones closer to the three inlets communicating with the Adriatic Sea.

Despite their rather uniform morphology, these areas are characterized by a noticeable spatial variability of environmental conditions (Zonta *et al.*, 1992; Zonta *et al.*, 1994). The study of degradation processes therefore requires a methodological approach that permits acquiring both basic knowledge of the system behavior and identification of representative sites where biogeochemical processes may be investigated in a greater detail. This task could be achieved by the measurement, in a representative set of sites in the area, of selected sediment parameters that respond on a longer time scale to physical and biogeochemical conditions in the water-sediment column. Because these parameters describe environmental conditions and are particularly informative about processes acting on the investigated ecosystem, they may be regarded as "environmental tracers". The tracers we used were the grain size of surficial sediments and redox potentials along the vertical profile. Tides are the principal driving force of water circulation in this ecosystem, and the simultaneous characterization of both the hydrodynamics and water chemistry is essential and constitutes the basis for this kind of investigation. To interpret the results, we therefore also characterized water circulation and salinity in the area influenced by freshwater input.

The study area is interested by a project that supports morphological interventions to restore the ecosystem conditions, carried out by the Consorzio Venezia Nuova on behalf of the Ministry of Public Works through its local authority (Magistrato alle Acque).

Site description

The study area (Fig. 1) is located between the City of Venice and the mainland. It has a mean water level of about 50 cm and is crossed, from the South to the North, by the S. Secondo, Campalto and Tessera tidal channels, which have a mean depth of about 2 m. These channels act as drainage collectors from the lateral shallow water zones, mainly during the final stages of the ebb-tide. In recent years they were subjected to progressive silting, particularly the Campalto channel that is closed at the mainland interface. Dredging these channels to improve water circulation is one of the planned interventions in the aforementioned project. The study area receives the fresh water discharge of the Osellino channel, that collects untreated municipal and industrial wastewaters (Bernardi *et al.*, 1986); its principal discharge point corresponds to the upper Tessera channel.

The area is often dystrophic, and intense macroalgal production may occur, particularly during summer. Anoxic conditions in the lower part of the water column are favored by a thick decomposing algal cover, which leads to undesirable environmental quality.

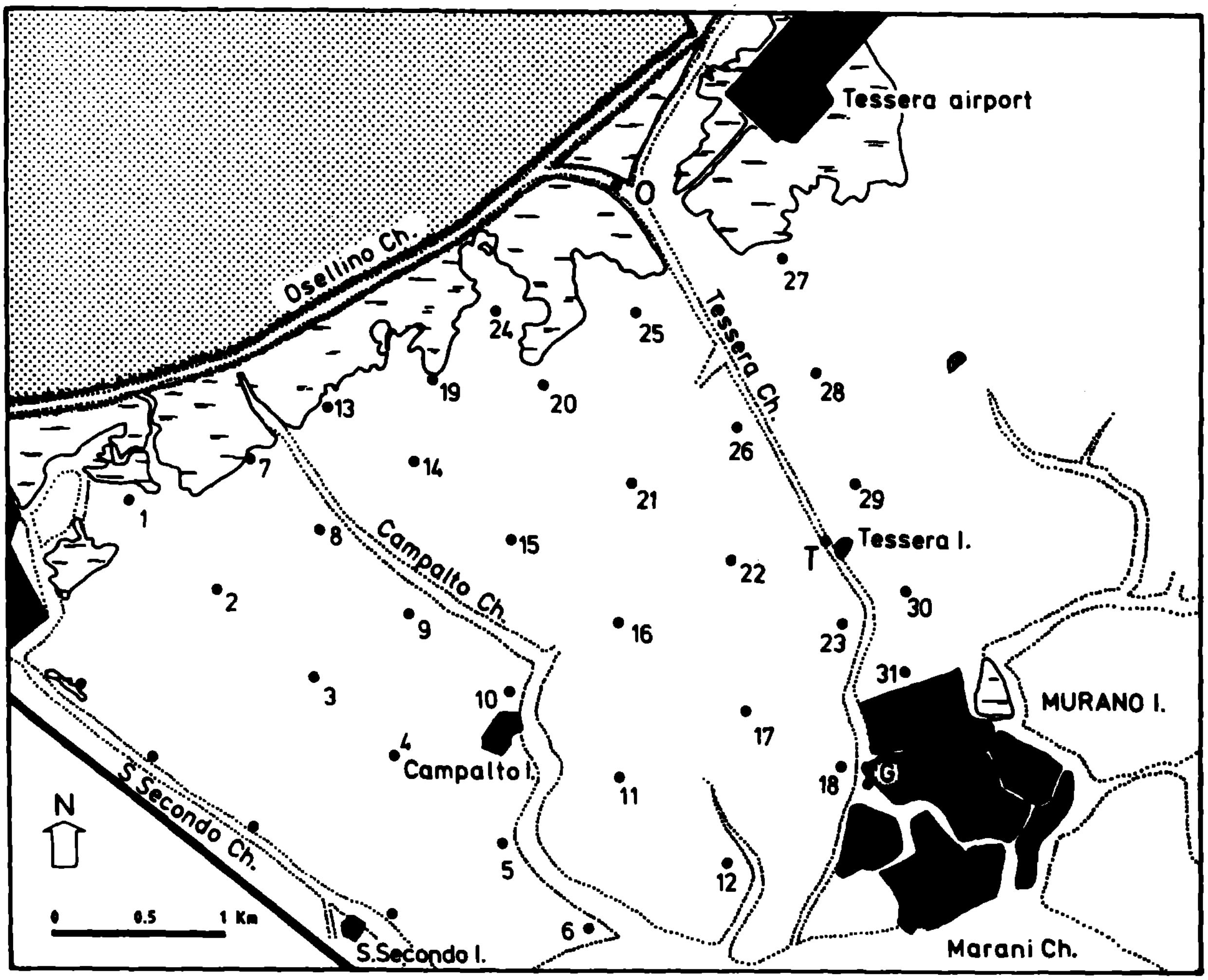

Fig. 1. Map of the investigated study area. The sampling sites and measurement stations of the November field measurements are indicated.

Methods

Field measurements were made in May and November 1991. Two self-recording current-meters (S4 InterOcean, San Diego, California) operating at 0.5 m water depth at stations O and T (Fig. 1), recorded velocity, direction and salinity at 15 minute intervals for 12 days. A tide-gauge was at station G. Occasional current measurements (by means of a Braystoke BFM 008 Mk3 current meter, Valeport Ltd., UK) were also made at various stations over different tidal phases.

The salinity field evolution in the Tessera channel and in its two lateral shallow water zones was monitored at 20 stations during a half-cycle in both spring and neap tides. Salinity values were measured at the surface and bottom layers at about 1 hour intervals using multiparameter probes (Mod. 513 D, InterOcean, USA; OTS-Sonde, Meerestechnik-Elektronik, Germany).

Grain size was determined in 5 cm-long surface sediment cores, collected at the 31 sites indicated in Figure 1. Samples were wet sieved at 125 μm to remove shell fragments and plant residues and the samples homogenized. Grain size was measured prior to and after organic matter removal, which was performed through oxidation with hot (80°C) H_2O_2 at a pH of about 8.5 with 1N NaOH (Riviere, 1977). The analysis was made in the 0.7–125 μm size range using a Microtrac particle analyzer (mod. 7995, Leeds and Northrup, USA; Plantz, 1984), that recorded volumetric percentages in 15 diameter (d) size classes corresponding to one-half phi interval on the Udden-Wentworth scale, as expressed by Krumbein (1934). This provided detailed dimensional spectra and therefore a better definition of the grain-size spatial distribution.

Redox potential (E_h) profiles were measured at various sites in May and November, following a previously tested methodology (Argese *et al.*, 1992). A 4 cm-diameter and 45 cm-long core was collected at the sampling site and directly transferred into a Plexiglas cylinder with the same diameter as the core, that was sealed to avoid contact with atmospheric oxygen and loss of volatile constituents. Each cylinder had 5 stoppered pore-holes at depths corresponding to 2, 5, 10, 20 and 40 cm from the core top. Five combined Pt electrodes with a Ag|AgCl reference half-cell (201/L-SM-PT, CLR, Italy), connected to a pH-meter, were plugged into the pore-holes. Measurements were made immediately after the sampling, following the trend of E_h values until a stable reading was reached (generally about 40 minutes are required). A standard redox solution (Zobell, 1946) was used to test the system before each measurement and all the readings were converted into E_h values. No significant changes in the redox conditions during sampling and measurement are introduced by this methodology. It permits the transfer of the core while maintaining the "in situ" structure and stratification (Argese *et al.*, 1992). The standard deviation was evaluated at each depth by measuring two groups of 8 replicated samples collected at sites 4 and 8, assuming that they were representative of all the investigated sites. It was greater at upper depths (= ±10 mV at -2 cm) than at lower depths (= ±6 mV at -40 cm), because of the greater heterogeneity of the surface sediment layer.

Organic matter content was determined by weight loss on ignition at 550°C for 2 hours for aliquots of the 31 samples previously dried for 16 hours at 90°C. This analysis was performed to obtain a spatial distribution to be compared with those of grain size and redox potential.

Results and discussion

Hydrodynamics and salinity field

Tides enter the study area from the south through the Marani channel. Tidal influences are reduced towards the mainland interface; the hydrodynamics, and therefore water renewal, are more intense in the south-eastern zone. The discharge of the Osellino channel determines different conditions in the two stations O and T (Fig. 2a): the salinity values at O were, in fact, subjected to strong tidal variations, ranging from fresh water values at the end of the ebb phase, to about 26 psu late in the flood. In contrast, only small variations (between 22 and 27 psu) were recorded at station T.

The current evolution in the two stations showed a comparable trend during the flood phase, while higher velocities were measured during the ebb phase at the station O (Fig. 2b). Furthermore, flow reversal occurred early at station O in the first part

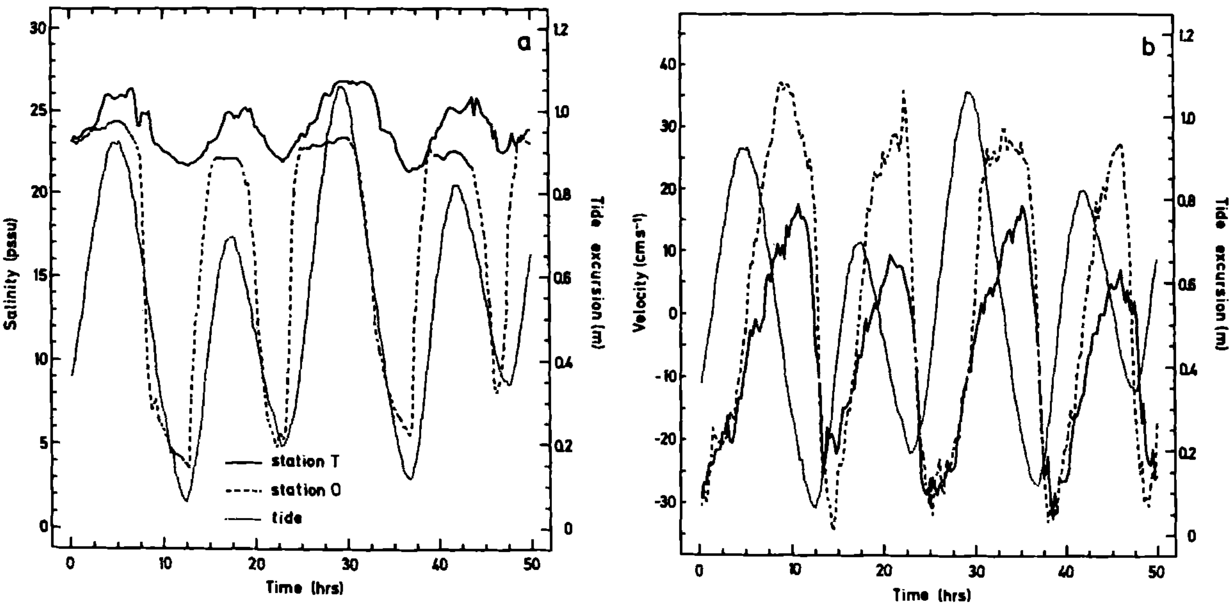

Fig. 2. Salinity trend (a) and axial component of the current velocity (b) recorded at stations O and T; tidal excursion is superimposed. The data are from the 12-day acquisition in November 1991.

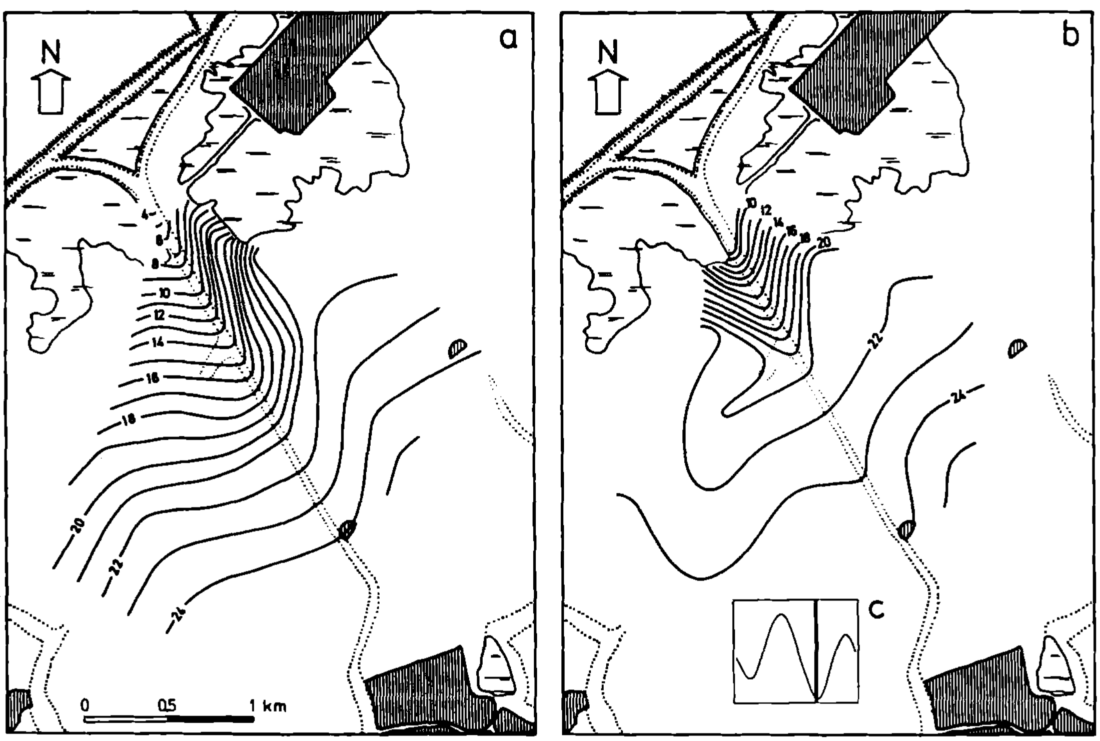

Fig. 3. The salinity field at the end of the ebb phase in spring tide conditions. Contour maps were drawn from data simultaneously recorded in the surface (a) and bottom (b) layers. The measurement interval is indicated on the tidal excursion curve (c).

of the ebb phase, and the current velocity rapidly increased, reaching values greater, or even opposite, to those observed at the same time at the station T. This behavior corresponds to a diversion of part of the water mass, that is swept westward from the channel to the shallow waters. It is also consistent with the observed evolution of the salinity field in the nearby shallow water zone and with the results of the current spot measurements. As evidenced by the asymmetric pattern of isohalines in the surface layer during the ebb phase (Fig. 3a), the outflowing water from the Osellino channel more directly influences the western shallow water zone, producing lower salinity values. The situation depicted in Fig. 3a is well established from the second half of the ebb phase, and is more marked during spring than during neap tide conditions. The presence of a small dead-end branch (Fig. 3b) of the Tessera channel extending into the shallow water zone, also favors the intrusion of less saline water late in the ebb, resulting in a reduction of salinity values in the bottom layer in the zone corresponding to the site 21. The observed reduction is less pronounced during neap than spring tides.

Grain Size

The spatial distribution of grain size in the surface sediment is useful to characterize water transport in these shallow areas, because the current speed is often too low to be accurately measured by direct current-meter measurements. The deposition of larger amounts of silt and clay occurs in zones of lower flow competence. Furthermore, because of their adsorption capacity (Rashid, 1985), fine particles and organic matter are frequently associated together, providing a transport vehicle for contaminants (Rashid, 1985; Salomon and Förstner, 1984). Mineral-organic aggregations begin in the water column and continue in the sediment, where biochemical transformations generally give rise to stable aggregates with various sizes, shapes and densities (Carson *et al.*, 1988). The resulting coarsened spectrum more reflects the effects of diagenetic processes, than the size distribution of inorganic material transported in the overlying water column.

The presence of particle aggregates in the range 8 to 40 μm was observed by SEM analysis of sediment specimens from sites 8 and 22. They are constituted by finer clay particles appearing bounded together by organic matter films. Organic matter removal produced a shift in the dimensional spectrum towards the finer diameters in all samples because of the disruption of these aggregates. Generally, the higher the percentage of finer particles in the sample, the greater was the shift. Therefore, the organic-free spectrum furnishes a clearer differentiation among sampling sites that emphasizes the existence of two different zones in the study area. Figure 4 reports, as an example, the spatial distribution of particle percentage in the clay range ($d<3.9$ μm) after the removal of organic matter. Sites south-east of the line α (6, 12, 17, 18, 23, 30, 31) have a lower fine particle content than the rest of the study area. As evidenced by the histogram of Figure 5, the higher hydrodynamics in this zone determines a greater presence of coarse silt and fine sand. Sites of the north-western zone show small variations in the percentage of clay particles; however the highest values were found in the more distal portion of the study area (sites 1, 7 and 13), where the more quiescent hydrodynamics promotes their deposition.

The only exception to these patterns was observed at site 21: the grain size in the corresponding zone is characterized by a fine-sand content quite similar to the nearby sites, but its clay percentage is comparable to that observed in the south-eastern zone. These differences account for the higher percentages observed in the coarse to fine silt dimensional interval and are attributable to the flushing effects created by the water input from the dead-end branch referred to earlier. These features emphasize how minor diversification in morphology and hydrodynamics produces noticeable differences in sediment characteristics in this study area.

Figure 4 also depicts the distribution of the organic matter, which further emphasizes the difference between the two zones discriminated by the line α. Values in the distal zone (sites 1 and 7) are 2- to 3-times higher than in sites of the south-eastern zone.

Significant statistical correlations exist between organic matter content and percentage of finer particle in selected size ranges, that confirms their strong association. Figure 6 shows the regressions that produced the highest correlation coefficient (r; significance level $p<10^{-4}$) for the sediment collected in the

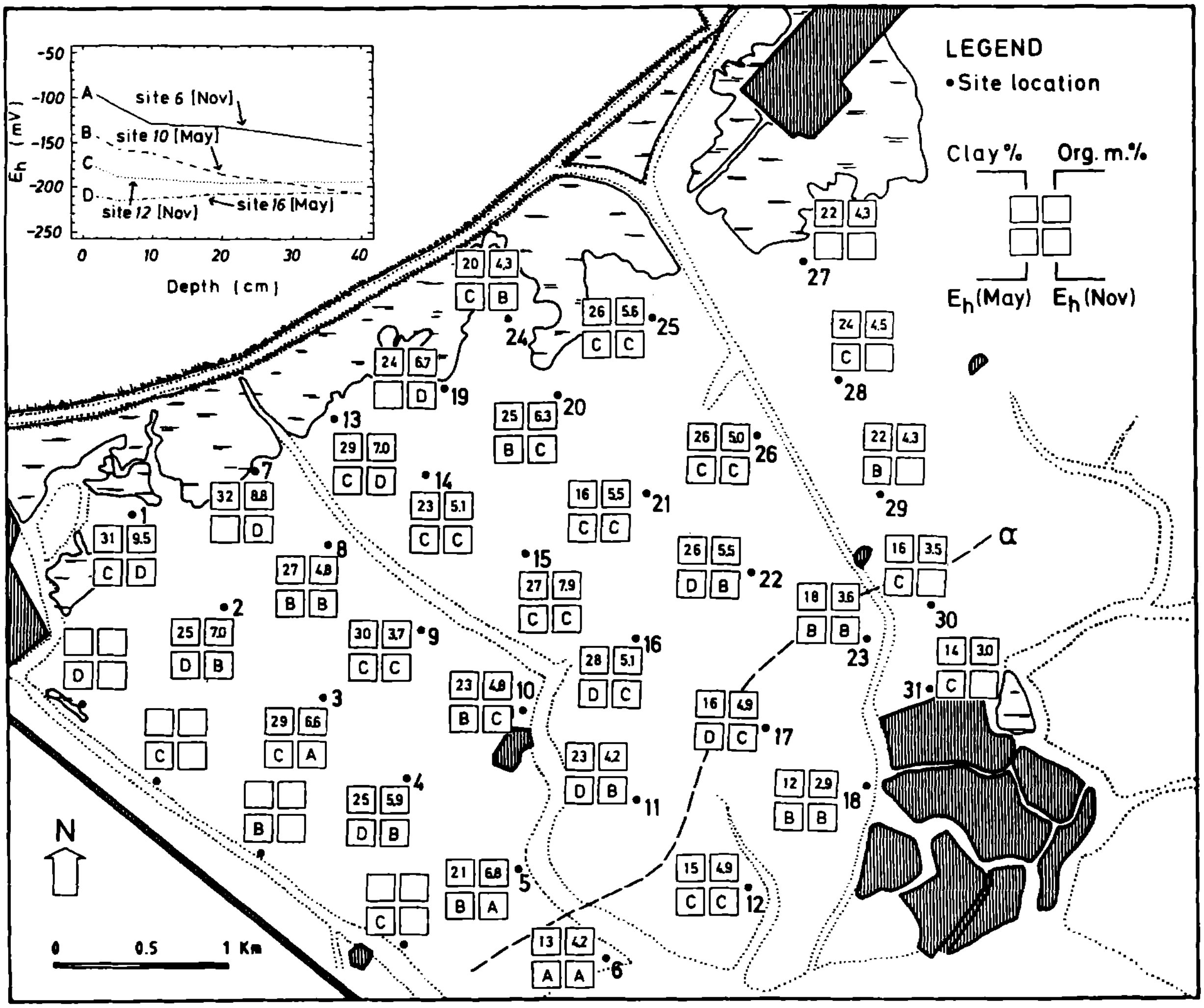

Fig. 4. The spatial distributions in the study area of the clay particle (d<3.9 μm) percentage after the organic matter removal, organic matter content, and redox conditions in both the field measurements. The E_h trends in the four sites chosen as seed points are in the top-left corner.

field and after organic matter removal. In the first case, r=0.76 and was obtained with the 3.9<d<16 μm dimensional range, emphasizing the presence in the sediment of mineral-organic aggregates, particularly in the fine-silt class. In the second case, r=0.75, corresponding to the 1.4<d<5.5 μm dimensional range, confirming that the aggregates are principally constituted by clay particles.

Redox profiles

Because of the large variety of redox reactions occurring in the sediment and the numerous chemical species involved, the redox potential (E_h) readings are generally characteristic of the sediment as a whole, and do not provide quantitative information on specific redox equilibria. However, redox values at different depths in the sediment are a consequence of diagenetic reactions that are responsible for organic matter degradation. In the upper sediment layer, this process implies the consumption of dissolved oxygen in pore waters. In deeper layers it can proceed further by utilizing other electron acceptor species (*e.g.*, NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}), thus following a sequence of bacterially mediated reactions that are accompanied by progressively decreasing redox values (Stumm, 1967). These condi-

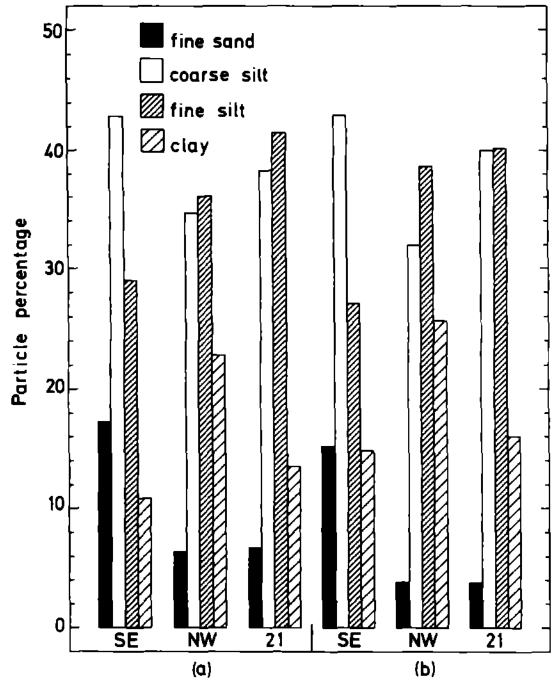

Fig. 5. Histograms of particle percentage in the four principal size classes for site 21 and the average distribution in north-western and south-eastern zones of the study area. Samples (a) prior and (b) after the organic matter removal. Fine sand = $62<d<125$ μm; coarse silt = $16<d<62$ μm; fine silt = $3.9<d<16$ μm; clay = $d<3.9$ μm.

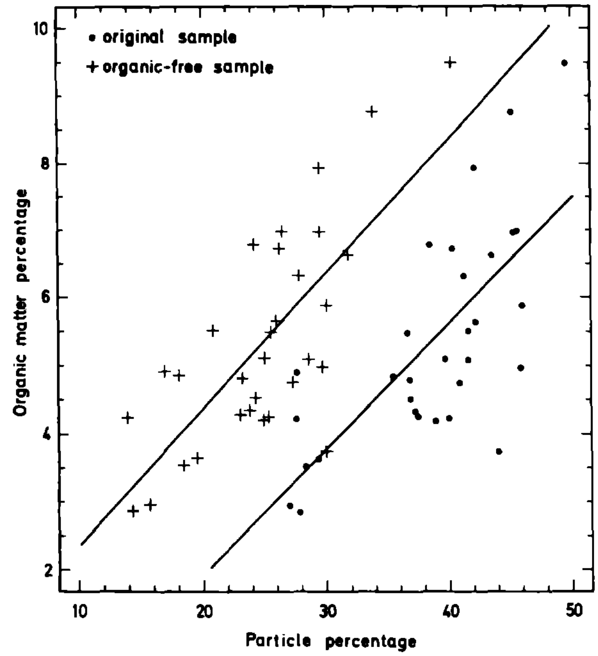

Fig. 6. Linear regression between organic matter content and particle percentage in the two dimensional ranges that produce the highest correlation coefficient, respectively, for original and organic-free samples: r = 0.76 for $3.9<d<16$ μm, r=0.75 for $1.4<d<5.5$ μm.

tions can only be modified by a flux of oxygen by direct diffusion or bioturbation.

The oxygen depletion in the water column – that typically occurs in the confined areas of the Venice Lagoon – and oxygen consumption in the sediments, determines a progressive extension of anoxic conditions towards the water interface. The E_h vertical profile measured in a set of representative sites then provides a tri-dimensional distribution of values that traces the imbalance between oxygen supply and demand in the water-sediment system (Zobell, 1946; Callamé, 1968). It therefore constitutes an index of the effects of water circulation on the environmental conditions in the study area. However, while the grain-size distribution is not subjected to variations in the short time period, the redox potential values can vary monthly. Therefore, the redox potential should be measured several times annually to account for seasonal variability.

The acquired profiles are reported in Table 1 for both the samplings. E_h values diminished with depth. At -20 cm from the water interface the sediment was strongly reduced ($E_h \approx$-200 mV) at most sites and for both the samplings. As it was previously found in other shallow water areas of the Venice Lagoon, (Argese *et al.*, 1992; Zonta *et al.*, 1990), from about this depth, we conclude that exchange processes, bioturbation, and bacterial activity do not cause significant temporal variations in redox conditions.

In contrast, different oxidation-reduction conditions were observed in the upper sediment layer (corresponding to the -2, -5, and -10 cm depths), and variations between the two samplings also occurred at most sites. This indicates that the surface sediment responds to different physico-chemical conditions in the overlying water column and to their seasonal evolution. To summarize E_h values measured in this upper sediment layer, and to discern the characteristics of their distribution, a cluster analysis with the seeded method (Anderberg, 1973) was made on data from both the samplings, thereby taking into account the seasonal variations. The analysis was initialized with 4 seeds, corre-

Table 1. E_h values measured in cores from the 31 sampling sites in the study area. n.m. = no measurements.

	May 1991 – Depth (cm)					November 1991 – Depth (cm)				
Site	2	5	10	20	40	2	5	10	20	40
1	–189	–195	–200	–209	–212	–207	–213	–206	–223	–212
2	–170	–214	–227	–226	–209	–135	–163	–185	–199	–190
3	–168	–202	–208	–213	–212	–73	–119	–129	–197	–194
4	–206	–224	–225	–225	–211	–156	–169	–178	–193	–197
5	–112	–141	–185	–194	–202	–98	–109	–160	–185	–194
6	–72	–135	–159	–155	–174	–97	–110	–129	–131	–153
7	n.m.	n.m.	n.m.	n.m.	n.m.	–224	–231	–230	–236	–219
8	–154	–161	–182	–175	–195	–156	–170	–173	–181	–190
9	–170	–182	–197	–214	–221	–146	–192	–197	–201	–187
10	–143	–157	–162	–185	–207	–167	–180	–191	–203	–196
11	–197	–206	–199	–213	–201	–149	–161	–180	–197	–183
12	–162	–193	–185	–195	–201	–178	–188	–191	–195	–194
13	–171	–194	–201	–202	–226	–225	–222	–226	–236	–215
14	–198	–189	–184	–187	–198	–186	–195	–199	–203	–195
15	–178	–191	–201	–205	–204	–163	–182	–186	–187	–189
16	–211	–215	–213	–207	–206	–185	–167	–184	–199	–196
17	–199	–209	–200	–204	–205	–193	–200	–201	–212	–204
18	–137	–179	–162	–205	–205	–138	–148	–159	–190	–187
19	n.m.	n.m.	n.m.	n.m.	n.m.	–196	–209	–208	–215	–236
20	–122	–143	–160	–184	–214	–160	–173	–178	–198	–206
21	–152	–172	–192	–194	–205	–171	–189	–184	–196	–192
22	–204	–210	–215	–209	–213	–144	–166	–183	–209	–208
23	–160	–166	–168	–179	–187	–148	–142	–165	–189	–192
24	–153	–175	–184	–200	–196	–166	–170	–181	–192	–181
25	–175	–190	–198	–206	–191	–172	–182	–189	–194	–193
26	–177	–198	–200	–203	–197	–159	–183	–178	–197	–193
27	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
28	–172	–188	–204	–207	–200	n.m.	n.m.	n.m.	n.m.	n.m.
29	–163	–166	–175	–220	–205	n.m.	n.m.	n.m.	n.m.	n.m.
30	–181	–184	–188	–217	–209	n.m.	n.m.	n.m.	n.m.	n.m.
31	–183	–186	–187	–192	–195	n.m.	n.m.	n.m.	n.m.	n.m.

sponding to the E_h values at the first three depths in 4 sites showing different degree of reduction (labeled with A, B, C, D). Seeds and the obtained classification are represented in Figure 4. Seeds were chosen to be representative of the whole variation range at each depths and for both the samplings, and are distinct even if the ±10 mV standard deviation is taken into account.

The redox spatial distribution demonstrates the effects of water circulation in the study area. The zone characterized by a more intense water circulation (sites 5 and 6) showed less reduced sediment conditions. The better conditions observed in November in the two zones corresponding to sites 2, 3, 4, and 11, 16, 17, 22, are the result of the increased oxygen supply to the sediment during the fall period. By contrast, in the same sampling period, the more confined zone close to the mainland (sites 1 and 13), where the influence of the tide on the local oxygen balance is attenuated, showed more reduced conditions than in May. Strongly negative values were, in fact, measured at -2 cm ($E_h \approx$ -215 mV). Similar values were also observed in other sites of this zone (7 and 19). This result was the consequence of summer anoxic events that caused more reduced conditions in the majority of study sites than observed in May. It should also be considered that the sediment responds to seasonal variations of physico-chemical characteristics of the surface water with a delay that is mainly dependent on its permeability. Therefore, the oxygen availability after the summer period could not have been yet impacted the sediments at the time of the second sampling.

Finally, the behavior of the central zone of the study area (sites 8, 9, 14, 15, 21, 25, 26), where redox conditions resulted apparently unchanged between the two samplings, may be ascribed to the combined effect of this delay and summer anoxic events.

Conclusions

Small morphological and hydrodynamical differences in the study area of the Venice Lagoon subdivide it into two zones distinguished by differences in the spatial distributions of finer particles and organic matter. In the south-eastern zone, where water circulation is more intense, sediments have a coarser particle content and lower amounts of organic matter. Larger amounts of finer particles and organic matter were found in the rest of the study area, particularly in the more distal zone.

The tri-dimensional distribution of redox values supports these findings, and shows the strongest negative values in this last zone, even in the surface sediment layer. Favorable conditions for environmental degradation are established by the preferential deposition of finer particles and organic matter. Because they are efficient sinks for pollutants, this result involves a potential risk for accumulation and progressive transfer of toxic species to the biota.

The measured sediment parameters could be regarded as good tracers to acquire a preliminary description of the behavior of this shallow water system, and the methodology is suitable for studying similar aquatic ecosystems elsewhere. Sites where lower hydrodynamics and oxygen depletion create unbalanced conditions are demonstrated and may be chosen to develop detailed studies on biogeochemical and degradation phenomena like pollutant accumulation and eutrophication. These tracers may be also considered as a useful tool to plan interventions to restore environmental quality and to control the short and long term responses of the system.

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