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Original Scientific Paper

Sedimentological and Surface Characteristics of the Northern and Central Adriatic Sediments

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Key words: Sediment distribution, Surface properties of sediments, Adriatic Sea

Ključne riječi: Raspodjela sedimenata, površinska svojstva sedimenata, Jadransko more

Abstract

The results of this investigation reveal mutual relationship between some sedimentological and surface chemical characteristics, such as granulometric and mineral composition, specific surface area (SSA) and organic matter content, of northern and central Adriatic surface sediments.

Grain size distribution and mineral composition enabled the reconstruction of the sedimentation pattern in the northern and central Adriatic Sea. It was shown that sands are spread in the east, along the Croatian coast. Toward the west, the share of finer sediments increases, so that the western region (parallel to the Italian coast) is covered with pelites. Such a pattern is typical for the northern Adriatic and the 401-407 profile of the central Adriatic. Most of the central region is covered with pelites.

Granulometric and mineral composition are interrelated, indicating that sediments having more clay minerals (aluminosilicates) are always fine-grained, while coarser sediments contain more quartz and carbonates.

The SSA and organic matter content are dependent on the grain size and mineral composition - fine-grained clay minerals have larger SSA's and contain more organic matter attached to their surface. These organic substances influence considerably the SSA of sediments. It was noted that, after removing the organics, the SSA of sediments changed. This indicates that, effecting the SSA of sediments, organic matter effects their adsorptive ability.

1. INTRODUCTION

The sediments investigated in this work were sampled as part of a broader international and multidisciplinary research project on the environmental characteristics of the Adriatic Sea. The aim of the project was to elucidate interrelations between sedimentological and surface chemical properties of sediments in order to determine the role of particulates in the fate of pollutants in the aquatic environment.

The present work focusses on the sedimentological part in order to reconstruct the sedimentation pattern in the northern and central Adriatic Sea (the border between these two areas is the Ancona-Zadar line). The reconstruction was done on the basis of the results obtained from 33 sediment box cores sampled during

Sažetak

Istraživanja sedimenata sjevernog i srednjeg Jadrana uključila su sedimentološku i površinsku karakterizaciju uzoraka - određivanje mineralnog i granulometrijskog sastava, specifične površine i udjela organske tvari. Rezultati istraživanja pokazali su međusobnu ovisnost navedenih značajki. Pored toga, raspodjela veličina zrna i mineralni sastav omogućili su rekonstrukciju načina sedimentacije u sjevernom i srednjem Jadranu. Pokazalo se da je pijesak istaložen u istočnom dijelu, uz hrvatsku obalu, te u dvije manje zone u sjevernom dijelu područja. Idući prema zapadu povećava se udio sitnozastog materijala, koji konačno prevladava u području paralelno talijanskoj obali. Takav raspored sedimenata nalazimo u sjevernom Jadranu i duž profila 401-407 u srednjem Jadranu. U najvećem dijelu srednjeg Jadrana istaloženi su peliti.

Granulometrijski i mineralni sastav međusobno su ovisni - sedimenti s više minerala glina su uvijek sitnozastavi, dok krupnozastavi sadrže više kremenca i karbonata. O veličini zrna i mineralnom sastavu ovisi i specifična površina i udio organske tvari u sedimentu. Sitnozastavi minerali glina imaju visoke specifične površine i na njihovu je površinu vezano više organske tvari. S druge strane, organska tvar znatno mijenja specifičnu površinu sedimenata, utječući pri tome na njihove adsorpcijske sposobnosti.

the ASCOP 16 cruise of the R/V Salvatore Lo Bianco, and completed with data from the literature. The surface sediments and sedimentation in the Adriatic Sea has already been investigated by various authors (VAN STRAATEN, 1965; PIGORINI, 1968; MEISCHNER, 1973; COLANTONI et al., 1979; BRAMBATI et al., 1983; HIEKE MERLIN et al., 1989; PUŠKARIĆ, 1991; BOLDRIN et al., 1992).

Sedimentation characteristics of microtidal semi-enclosed marginal seas have a prominent influence on the fate of pollutants, since this depends on the surface properties of particulates. These properties are, to some extent, represented by specific surface area (SSA), which can be an indicator of the surface reactivity of particulates (JURAČIĆ et al., 1986; BOLDRIN et al., 1989; BIŠĆAN et al., 1991). Moreover, systematic investigations of SSA on native and organic-free sam-

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ples indicate surface processes such as adsorption, adhesion and flocculation which occur in the aquatic environment (EISMA et al., 1983; GIBBS, 1983; MARTIN et al., 1986; BIŠČAN et al., 1991).

The dependence of SSA on grain size, mineral composition and organic matter content has been reported in the literature. MAYER & ROSSI (1982), RABITTI et al. (1983), HOROWITZ & ELRICK (1987) and VDOVIĆ et al. (1991), found higher SSA's for fine-grained particles. The results reported on the SSA of different minerals are rather diverse, but in spite of that, it is generally agreed that clay minerals show high SSA's, whereas quartz and carbonates show considerably lower SSA's (MEYERS & QUINN, 1973; MADSEN, 1977; DAVIS, 1982; ESTES & VILKER, 1989; MURRAY & QUIRK, 1990).

The effect of organic matter on the SSA is evident, but its role in effecting the adsorption ability of sediments is still uncertain (JEDNAČAK-BIŠČAN & JURAČIĆ, 1987; BIŠČAN et al., 1991; GARNIER et al., 1991).

2. EXPERIMENTAL

2.1. SAMPLING AND SAMPLE PREPARATION

Sediment samples were taken at 33 stations located in the northern and central Adriatic Sea (Fig. 1) during the cruise of the R/V Salvatore Lo Bianco, in the period from June 17th to June 30th, 1990. The sediments were collected by box corer. After sampling, the sediments were sliced, frozen at -18°C and kept until further use. For our investigations, surface sediments (0-3 cm) and 12- to 15-cm-deep sediment samples were used. Before the analyses, the samples were thawed at room temperature and dried at 100°C . Dried samples were divided in two portions - one was used for grain size analysis, and the other was ground for 10 minutes in an agate mortar for all other analyses.

2.2 ANALYSES

2.2.1. Grain size analysis

Samples were granulometrically characterized by wet sieving, using ASTM standard sieves for fractions $>32\ \mu\text{m}$, and by a Coulter Counter (Model TA II) for fractions $<32\ \mu\text{m}$.

2.2.2. Mineral composition analysis

Qualitative identification of major minerals was made using a Phillips 1050 PW X-ray diffractometer. The amounts of carbonates were determined by the gasvolumetric method (JOBSTRAIBIZER, 1970).

2.2.3. Organic matter content

The content of organic matter was determined by weighing the sample before and after H_2O_2 treatment

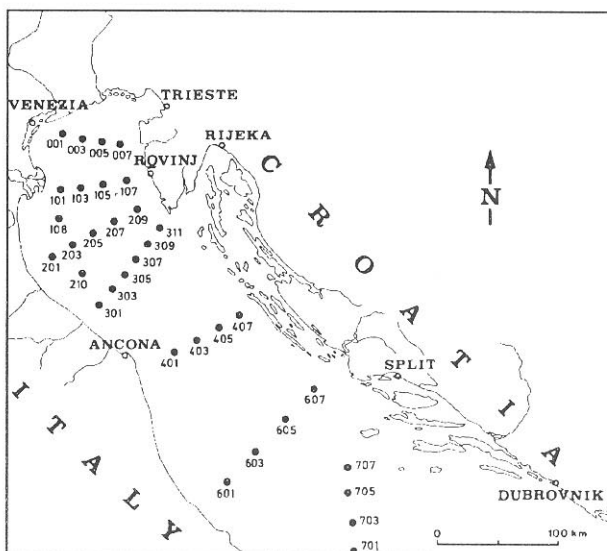


Fig. 1. Sediment sampling stations in the northern and central Adriatic Sea.

Sl. 1. Postaje uzorkovanja u sjevernom i srednjem Jadranu.

and heating at 450°C for 6 hours. The weight loss was attributed to organic matter oxidation and combustion.

2.2.4. Specific surface area measurements

The specific surface area of native and organic-free samples was determined by single-point nitrogen adsorption, using a Micromeritics FlowSorb II 2300 instrument. Prior to measurement, native samples were degassed in an N_2/He stream for 30 min at 100°C , and organic-free samples for 30 min at 200°C .

3. RESULTS

Table 1 contains the results of sedimentological and surface chemical analyses of the characteristic sediment

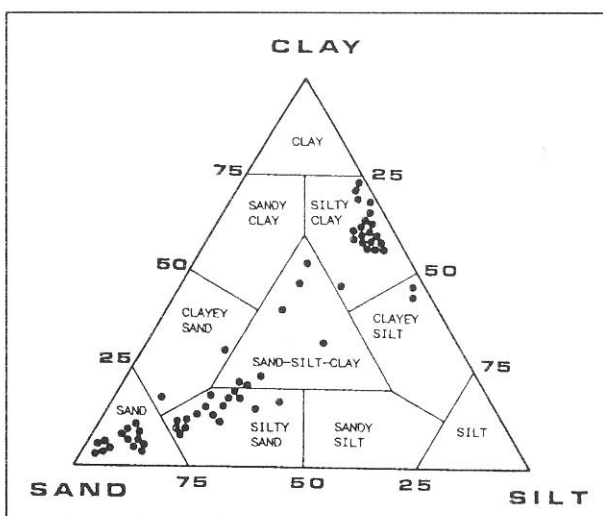


Fig. 2. Classification of investigated sediments according to SHEPARD (1954).

Sl. 2. Klasifikacija istraživanih sedimenata prema SHEPARDU (1954).

| Sediment/ station | Mz (μm) | Mineral composition* | Carbonates (%) | Organic matter(%) | SSA m^2/g | |
|--------------------------|-------------------------|----------------------------|-------------------|----------------------|---------------------------|---------|
| | | | | | native | treated |
| sand (705) | 250.0 | Ca,Mg-Ca, Ar,Q,D | 76.0 | 2.5 | 3.4 | 3.2 |
| sand (305) | 106.6 | Q,Ca,D,F,I, Ch,Ar,Mg-Ca | 32.0 | 1.6 | 1.3 | 1.7 |
| silty sand (005) | 41.2 | Q,Ca,F,D I,Ch,S,Ar | 33.0 | 4.1 | 4.3 | 3.4 |
| clayey sand (210) | 24.2 | Q,Ca,D,F, I,Ch,S,K,Ar | 25.0 | 4.5 | 7.4 | 6.7 |
| sand-silt -clay (203) | 12.1 | Q,Ca,D,F, I,Ch,S,Ar | 28.0 | 4.3 | 8.6 | 6.4 |
| clayey silt (201) | 5.2 | Q,Ca,D,F, I,Ch,S | 28.0 | 6.8 | 14.6 | 12.3 |
| silty clay (601) | 3.5 | Ca,Q,I,Ch S,D,F | 31.0 | 10.1 | 18.7 | 13.3 |

Q - quartz, Ca - calcite, D - dolomite, F - feldspars, I - illite, Ch - chlorite, S - smectite, K - kaolinite, Ar - aragonite, Mg-Ca - high-magnesian calcite

* The sequence of minerals indicated reflects their abundance in samples.

* Minerali su navedeni prema opadajućem slijedu u uzorku.

Table 1. Characteristics of main sediment types.

Tablica 1. Karakteristike glavnih tipova sedimentata.

types encountered. The results of analyses for all samples were published in the ASCOP report (JURAČIĆ & VDOVIĆ, 1992).

The investigated sediment samples vary considerably in size. Their mean grain size ranges from 2.5 - 250 μm . According to the sand-silt-clay ratio (SHEPARD, 1954) they can be classified into several types - from silty clay to pure sand (Fig. 2).

Spatial sediment distribution shows that the finest sediments are deposited along the Italian coast (south of the Po River delta) and in the central Adriatic, while sands are spread along the Croatian coast, as well as at stations 001, 007 and 705. The area between these two sedimentation regions is covered with mixtures between the two main sediment types. The data on the surface sediment distribution are presented in Fig. 3. The grain size distribution does not show any significant or systematic change with the depth (0-3 cm vs 12-15 cm).

X-ray diffraction analyses were made on the surface samples taken at the following stations: 001, 005, 101, 107, 108, 201, 203, 209, 210, 301, 303, 305, 311, 401, 407, 601, 605, 607, 701, 705 and 707. The results revealed the presence of quartz, calcite, dolomite, feldspars, illite, chlorite and smectite in all samples. Kaolinite occurred sporadically, while biogenic aragonite and high-magnesian calcite are found in sandy sediments. The sediment sample from station 705 is an exception to all other sediments because it is composed mainly of carbonates (calcite, high-magnesian calcite, aragonite and dolomite) and smaller amounts of quartz. The majority of the carbonates in this sediment sample

are the shell and skeletal fragments.

The gas-volumetrically determined concentrations of carbonates vary from 17 - 76 % and confirm the mineral distribution revealed by X-ray diffraction analysis. One can observe the general trend of westward diminution of carbonate share, especially at the profiles 300, 400 and 600.

The SSA was measured for native and organic-free samples. The results range from 1-26 m^2/g . Low values

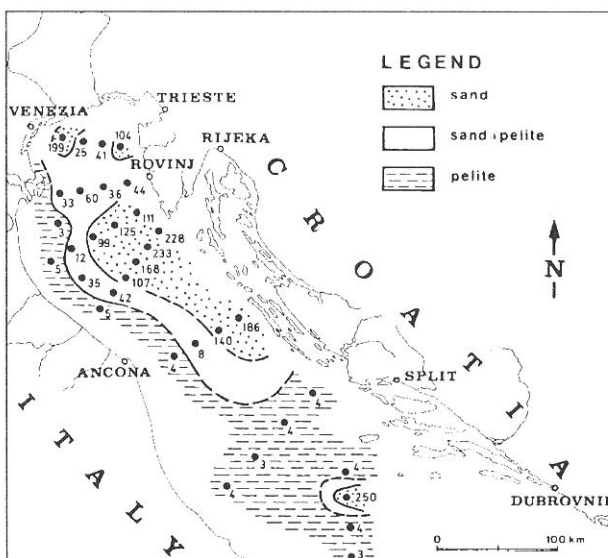


Fig. 3. The distribution of mean grain sizes and sediment types in the northern and central Adriatic Sea (surface samples 0 - 3 cm).

Sl. 3. Raspored tipova sedimentata s pripadajućim prosječnim veličinama zrna u sjevernom i srednjem Jadranu (površinski uzorci 0 - 3 cm).

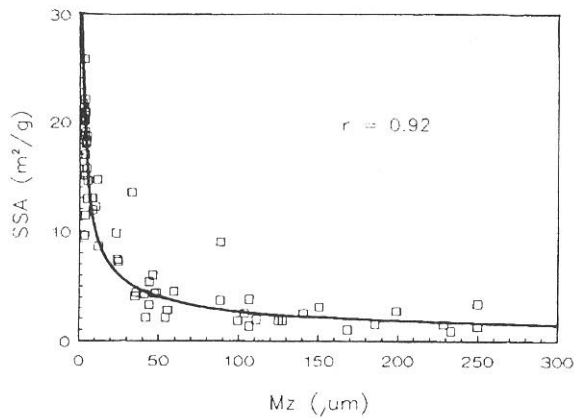


Fig. 4. The dependence of the SSA of the native samples on their mean grain size (Total of 62 samples).

Sl. 4. Ovisnost specifične površine nativnih uzoraka o prosječnoj veličini zrna (Ukupno 62 uzorka).

of SSA are measured for sands, while fine-grained clays show high SSA (Fig. 4).

Organic matter content in the samples ranges from 0.8-12%, being higher in fine-grained sediments and lower in sands.

Organic matter attached to the surface of particulates changes the SSA (JEDNAČAK-BIŠČAN & JURACIĆ, 1987; BIŠČAN et al. 1991). In the case of northern and central Adriatic sediments, this change is evident in the increase or decrease of the SSA. After removing the organic matter, the SSA decreased for 65% of the samples, increased for 30% of the samples and remained the same for 5% of the samples. A greater change in the SSA was observed for the samples with a higher content of organic matter (Fig. 5).

4. DISCUSSION

4.1. SEDIMENTATION IN THE NORTHERN AND CENTRAL ADRIATIC

The shallow continental shelf of the northern Adriatic is supplied with lithogenic particles mainly by the Po River. The Po carries siliceous material from igneous and metamorphic rocks, and to a lesser extent, detrital carbonates from the central and western parts of the Alps and from the central Apennines. Other sources of material are the rivers of the northern Italian coast (Adige, Brenta, Piave, Tagliamento, Isonzo), which carry more detrital carbonates from the eastern Alps. The sedimentation of this material is limited to a zone facing the region of Venice (PIGORINI, 1968; BRAMBATI et al., 1983; VENIALE, 1976). Erosion of the red soil (terra rossa), the formation of biogenic carbonates and the biogenic destruction of calcareous shells provide the material which has settled along the Istrian coast (MEISCHNER, 1973). Biogenic carbonates are produced throughout the area, but are important as a sediment constituent only in areas where the input of terrigenous matter is negligible.

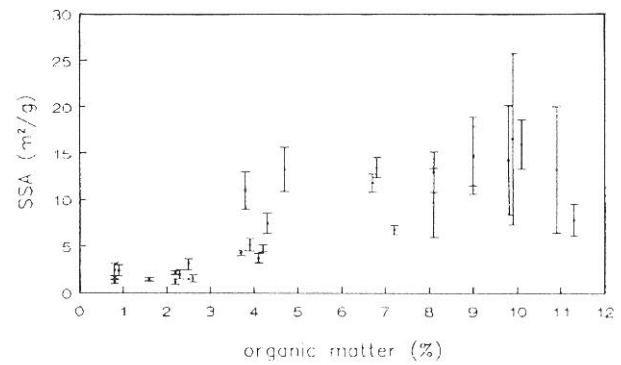


Fig. 5. The change of SSA depending on the organic matter content (vertical bar indicates absolute change of SSA for each sample; only surface samples considered).

Sl. 5. Promjena specifične površine s količinom organske tvari (okomicom je označena apsolutna promjena specifične površine za svaki uzorak; u obzir su uzeti samo površinski uzorci).

The lithogenic material carried mostly by the Po River consists of variously sized particles. The larger particles drop out immediately when the river water meets the denser marine water in the delta zone. Due to the longshore current and wave transport, a narrow littoral belt of coarser and finer sand above the wave base is formed, spreading along the western and northwestern Adriatic coast. The pelitic material continues northeastward until the Adriatic drift current prevails and changes its direction to the south. Because of that, the pelitic material has settled in a belt below the wave base parallel to the Italian coast (COLANTONI, 1979; TOMADIN, 1981; BOLDRIN et al., 1988).

In the offshore direction, where minor quantities of fine-grained material settle, pelites are mixed with older sands by means of bioturbation and resuspension, resulting in sediments characterized by a wide range of grain size - from clayey silt to silty sand (PIGORINI, 1968; BRAMBATI et al., 1983; HIEKE MERLIN et al., 1989).

The remaining part of the northern Adriatic shelf is covered with relict sands deposited as shore sands during the Holocene transgression. These sands cover sediments deposited by the Pleistocene Po, Adige, Brenta, Piave and Tagliamento. During that period the recent continental shelf of the northern Adriatic was a fluvio-lacustrine plain with swamps and bogs where peat soils were formed (the peat was found in the sample taken at the station 005 at the sediment depth of 30 cm). This area of relict sands is now under prevalently non-depositional conditions due to the lack of any significant input of lithogenic material. This deficiency of clastic material is a consequence of the karstic character of the eastern Adriatic shore. There are no large rivers draining these terrains, and the small quantities of material that eastern Adriatic rivers carry (Mirma, Raša, Rječina, Zrmanja, Krka) are deposited in their estuaries (VAN STRAATEN, 1965; TOMADIN, 1981; BRAMBATI et al., 1983; JURACIĆ & PROHIĆ, 1991; SONDI et al., in press).

The central Adriatic is a shelf edge covered mostly by mud. The source of the material is partly the Po River and partly the Apennine hinterland. In this part the sedimentary supply is both longitudinal and lateral, and the distribution of the material is governed by marine agents (VAN STRAATEN, 1965; PIGORINI, 1968; VENIALE, 1976).

There is only one sandy sediment in the central Adriatic (the station 705). This rather coarse-grained sample (mean grain size is 250 μm) consisting of a large portion of carbonate shells belongs to an elongated area of sand deposits which are spread in the southern part of the Adriatic. These sediments are presumed to be a product of the displacement of sublittoral materials (PIGORINI, 1968).

4.2. THE RELATION BETWEEN SEDIMENTARY AND SURFACE CHARACTERISTICS OF ADRIATIC SEDIMENTS

In all analyzed samples it was observed that the grain size diminished as the SSA increased (Fig. 4). The largest SSA's were measured for the samples with mean grain size less than 10 μm . The share of clay fraction in these samples was 45 - 70 %. A good correlation between mean grain size and SSA was also found by HOROWITZ & ELRICK (1986), while MAYER & ROSSI (1982), RABITTI et al. (1983), HIEKE MERLIN et al. (1989), and VDOVIĆ et al. (1991) found a linear correlation between SSA and percentage of clay fraction.

The grain size of sediments in natural samples is interrelated with the mineral composition. The X-ray diffraction data showed a presence of clay minerals in all samples, but their content was larger in fine-grained sediments than in sands. On the other hand, sand contained more quartz and carbonates. A larger amount of clay minerals in fine-grained Adriatic sediments was also found by BOLDRIN et al. (1989) and HIEKE MERLIN et al. (1989). MAYER & ROSSI (1982) gave a detailed description of mineral distribution in fractions of different sizes. They observed irregular clay mineral plates in clay fraction; weathered quartz and feldspar grains and mica plates in silt fraction; and round quartz grains, micas and feldspars in sand. Since it was shown that fine-grained sediments have large SSA's and larger amounts of clay minerals, it is obvious that clay minerals are those which mostly contribute to the SSA of sediments. The literature data on this subject are rather diverse: 30 - 270 m^2/g for montmorillonite, 10 - 50 m^2/g for kaolinite, 0.7 - 12.5 m^2/g for calcite, 0.25 - 5 m^2/g for quartz (MEYERS & QUINN, 1973; MADSEN, 1977; JURAČIĆ, 1979; DAVIS, 1982; ESTES & VILKER, 1982; HOROWITZ, 1985; MURRAY & QUIRK, 1990). But generally, it is evident that quartz and calcite have considerably lower SSA's than clay minerals.

Organic matter was found in large concentrations in the investigated samples (up to 12%). Its content was

higher in pelitic sediments spread near the Italian coast, not only because of the higher content of clay minerals, but also because of the high nutrient supply by the Po River. Namely, the organic matter distribution and its content in sediments depend on its primary production in surface waters as well as its sedimentation environment. The latter includes a low-energy area of sedimentation and an abundance of clay minerals, since organic matter has a physico-chemical affinity for clay minerals (BARGAGLI & BALDI, 1983; HUC, 1988). Moreover, the often encountered hypoxia and anoxia in the bottom water of the northern Adriatic (PUŠKARIĆ, 1991; DEGOBBIS, in press) contribute to the preservation of the organic matter in the surface sediments.

A change of the SSA (either decrease or increase) after removing the organic part was observed in almost all samples. The greatest change occurred in the samples with a high content of clay fraction and a high SSA (Fig. 5).

Whether the effect of organic matter on SSA is diminution or enlargement depends on the composition and structure of the organic matter and environmental conditions (salinity, pH, temperature) (MARTIN et al., 1986; JEDNAČAK-BIŠĆAN & JURAČIĆ, 1987; BIŠĆAN et al., 1991).

4.3. POSSIBLE IMPLICATIONS OF THE SEDIMENTATION PATTERN TO THE FATE OF POLLUTANTS

Combining the results of sedimentological research with the surface characteristics of sedimenting particles, one can conclude that the fate of pollutants will be different in the area with recent sedimentation from that in the area where relict sediments are still on the seabottom surface. Most of the riverborne pollutants will be scavenged and accumulated in the area where suspended matter settles. In the case of the Adriatic, this area is a wide belt of recent pelitic sediments that spreads parallel to the Italian coast in the northern part and the entire central part of the Adriatic Sea.

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