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DISTRIBUTION OF PHOSPHORUS AND ORGANIC CARBON IN SURFACE MARINE SEDIMENTS OF THE NEAR-SHORE AREA OF SPLIT

RASPODJELA FOSFORA I ORGANSKOG UGLJIKA U POVRŠINSKIM MORSKIM SEDIMENTIMA SPLITSKOG PRIOBALNOG PODRUČJA

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New analytical methods for the determination of phosphorus and organic carbon in sediments are described. It was proved that obtained data could be reproduced so that the methods are recommended as suitable for monitoring phosphorus and organic carbon in sediments.

Observed parameters were determined in three seasons, and obtained data were compared to the data from other Adriatic and world areas.

INTRODUCTION

The problem of environmental pollution has become increasingly important irrespective of whether it includes air, soil or water pollution. Pollution of natural waters poses the problem for normal life of not only organisms inhabiting these waters but also for man. The necessity to recognize the present state of the environment and monitoring and control of pollution processes calls for the development of new analytical methods.

The purpose of this study was to test the more recent analytical methods, and their suitability for monitoring phosphorus and organic carbon in marine sediments.

Being, to a certain extent, conservative parameters, phosphorus and organic carbon may be used as indicators of pollution and eutrophication processes in marine environments.

Four analytical methods for the determination of total, inorganic and reactive phosphorus, as well as for the determination of organic carbon are described. The quantity of organic phosphorus was calculated and organic matter estimated. These methods were for the first time applied to this study area.

The composition of marine sediments

The studies of sea bottom showed it to be covered by a very fine sediments almost throughout the study area. Rocky bottom was rarely encountered. Chemistry of marine sediments varies much. Therefore it is rather processes affecting their composition. A number of different components have different sources. There have been several attempts to classify these components (Arrhenius, 1963) of which the last one is actual after which the most important sediment components are of detrital, authigenic and biogenous origin.

Detrital (terrigeneous) components consit of rock fragments and minerals derived from the continents subject to subaerial weathering and supplied to the oceans by rivers, ice or wind.

The authigenic fraction includes precipitates of inorganic origin of different types, formed in the water of near-shore and offshore areas but it may be formed also after deposition of the bulk sediment, that is by diagenetic processes.

The biogenous fraction is derived from inorganic skeletal remains of marine organisms or from dispersed organic material produced by the degradation of organic tissues. This fraction may be derived from the overlying water or may be supplied from the continental areas.

In near-shore sediments these three principal components occur in all possible mutual proportions to yield a wide range of sediment types which may be distinguished from one another by their mineralogy, geochemistry or biochemistry.

The concentration of a given element in a sediment is governed by its concentration in, and relative proportions of, the various components discussed above. Many elements show tendencies to be partitioned beween two or three mineral components.

As to the topography, at least two genetically different sediment types may be distinguished: pelagic and non-pelagic. Characteristics of these two sediment types are highly different. Non-pelagic sediments are accumulated in the wide variety of environments to be found close to the continents. Here, physical, chemical and biological properties are much more variable in the coastal than they are in the open sea. Consequently, near-shore sediments are very heterogeneous and cover the entire range of sediments accumulated in the ocean at the present time. They include calcareous mud, siliceous mud, pure sands, phosphorites and ferromanganese nodules.

Sediments accumulating in near-shore areas are found in estuaries, fiords, bays, lagoons, deltas, tidal flats, continental terraces and marginal basins.

Much attention has recently been paid to near-shore sediments particularly since they are important removal sites for several elements from sea water, because the accumulation rates are very much higher than those found in the open-ocean.

Role and cycle of phosphorus in the sea

Sea water

Phosphorus occurs in the sea water in dissolved and particulate forms. Dissolved P exists in the form of ortophosphate ions which is in fact an inorganic form. Kester and Pytkoviecz (1967) showed the relationship of phosphate ions in the sea water of average salinity to be as follows: 87% of P exists as HPO_4^{-2}, 12% as PO_4^{-3} and 1% as $H_2PO_4^-$. Polyphosphate ions were not recorded in the oceanic waters. However, it is well known that they occur in estuaries and coastal waters as a result of detergent pollution (Solorzano and Strickland, 1968). Organic phosphorus or organic phosphorus compounds are assumed to originate from excretion of marine animals.

Principal pathway of inorganic phosphorus removal from the sea water is its assimilation with phytoplankton. It is further rapidly regenerated by bacterial activity that affects plankton and detritus and through other agencies such as higher animals (protozoa) (Fig. 1).

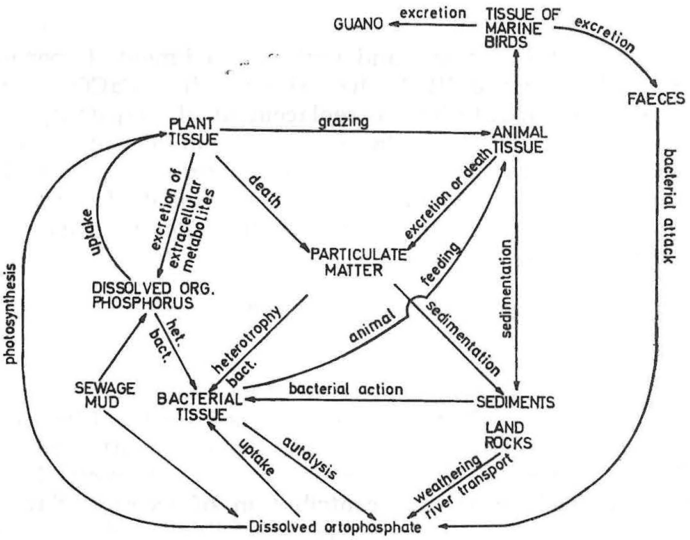


Fig. 1. The phosphorus cycle (Cooper, 1935)

It is assumed that particulate phosphorus is present as a ferrophosphate nodule which was proved by the data on the solution product which indicate that the sea water is oversaturated by this compound. Phosphate may also be adsorbed on particulate matter. Particulate organic phosphorus is that associated with live or dead organisms. They may contain a wide range of organic phosphorus compounds which are ingredients of organisms and their degradation products. Organic phosphorus is released into the solution from live phytoplankton and from dead or damaged cells as well as from animals.

Many algal species are able to reassimilate dissolved organic phosphorus which they excrete as well.

Observing the nutrient distribution in oceans Postma (1971) came to the conclusion that, on the average, a phosphorus atom passed twice through the assimilation and regeneration cycles before it was lost in deep water by sedimentation.

Sediments

Sediments seem to act as a reservoir of phosphorus in natural systems. Phosphate concentration in waters overlying and within sediments is buffered by solubility, adsorption and ion exchange equilibria (Stumm and Morgan, 1970). Although the nature of this control is not really understood, there seems to exist general agreement that chemical interactions of phosphate (ortophosphate) with Ca^{+2} are important. Such interactions appear to be dependent on the following:

1. The availability of Ca^{+2} ions relative to others (e.g. (Fe^{+2}, Al^{+3})
2. The pH of the interstitial environment
3. The susceptibility of clay minerals to take up phosphate (Weaver and Wampler, 1972).

Evidently, phosphate-rich solutions are capable of converting calcite to carbonate-apatite at the surface, and within a sediment. Experimental work by Stumm and Leckie (1971), has shown that $CaCO_3$ is converted to hydroxy or carbonate-apatite by the replacement of CO_3 group by PO_4. They have also shown that the precipitation of calcium phosphate at marine pH values is greatly accelerated by calcium carbonate, the surface of which acts as a nucleating agent for crystallization. The phosphate for carbonate-apatite formation is likely to originate from decomposition of organic phosphorus compounds and diatoms.

The role and cycle of organic carbon in the sea

Sea water

Two categories of organic matter in the sea may be distinguished: dissolved and particulate. They are distinguished by the filtration of sample by membrane filter of 0.45 μm diameters. Organic matter in solution that occurs in the sea is derived from four main sources: terrestrial contributions, decomposition of dead organisms, contribution of extracellular algal metabolites, mainly phytoplankton as well as zooplankton and protozoa excretion.

Humic materials are very resistant to oxidation and may contain a considerable amount of yellow substance (Gelbstoff) in the near-shore waters. In addition, a rather large quantity of organic material enters the sea via domestic and industrial effluents. Most of them are rapidly oxidized and decomposed by bacterial activity.

Skopintsev (1964) showed that 70% of particulate organic carbon in dead algal culture was oxidized to carbon dioxide after six months, while 5% was converted to stable organic compounds.

Some phytoplankton species excrete from 3 to 6% photosynthetically fixed carbon while some others may release much more, 10—25%. Release of these materials takes place both at the daylight and at night. Khailov and Burtalova (1969) reported big brown and red algae from natural sea waters to release up to 39% of their total photosynthetic production as dissolved organic compounds.

Excretion by zooplankton and marine organisms may be one of very important sources of dissolved organic matter in the sea. Compounds derived in this way are mainly nitrogen compounds (Corner and Newel, 1967) such as urea, purines, threemethylamine oxide and amino acids. Organic matter quantity is also increased through bacterial degradation of faecal pellets.

Sediments

Even though organic matter is rarely a major constituent of sediments in near-shore areas and estuaries, it may be a good indicator of environmental conditions of the area where it is deposited.

Environmental factors controlling the input of organic matter to sediments fall into four general categories: biological, physical, chemical and geological. However, attempts to use categories such as these to classify organic matter lead to difficulties because these divisions are so broad. For this reason the distinction in terms of well-defined segments of the oceanic biogeochemical cycle is more real:

1. Primary production
2. Terrestrial contributions
3. Efficiency of the recycling of organic matter in the euphotic zone
4. Depth of the water column
5. Topographical factors and
6. Redox conditions

Knowledge of alternating changes in oxic and anoxic conditions within a sediment, may be important when the composition and behaviour of organic compounds are being interpreted.

Modification of organic matter in the surface sediments is to a large degree dependent on microorganisms and the metazoan biomass.

Decomposition of organic matter

Unlike most natural inorganic systems, for which the mineral and ionic components at equilibrium are determined by a few chemical parameters such as pH and Eh, organic substances are unstable and their geochemistry is dominated by kinetically controlled processes.

During diagenesis, the less stable organic compounds are eliminated by reactions that lead to a randomizing of the ordered structures which were created by organisms. Prominent or typical among these are reactions based on the elimination of functional groups by deamination, decarboxylation and condensation, depolymerization, isomerization and oxidation and reduction. Most of these reactions are irreversible. The rates of such processes are very slow. Many of the organic groups which may show considerable modification in the initial stages of diagenesis may survive unaltered for very long periods. In addition, much of the uncertainty in the interpretation of the changes of organic substances within sediments often stems from an incomplete knowledge of the history of sedimentation. Knowledge of changes in anoxic conditions may be important when the composition and behaviour of organic compounds are being interpreted.

Modification of organic matter in the surface sediments is to a large degree dependent on microorganisms and the metazoan biomass. Principal elements which show a marked loss of organic matter during sediment burial are: C, N, P and S. Each of these elements is directly or indirectly connected with the decomposition of organic matter. Oxidized carbon is present in the interstitial water overlying sediments as CO_2 aq and H_2CO_3 aq. They are produced by the decomposition of organic matter. In cases of sulphate bacterial reduction it will be present as HCO_3^- aq.

Characteristics of the study area

The area chosen for this study comprises sediments of the Kaštela Bay and the coastal belt of the south side of the town of Split to the Stobreč cove (Fig. 2). A station situated near the Vis Island (Fig. 3) was chosen as a reference station.

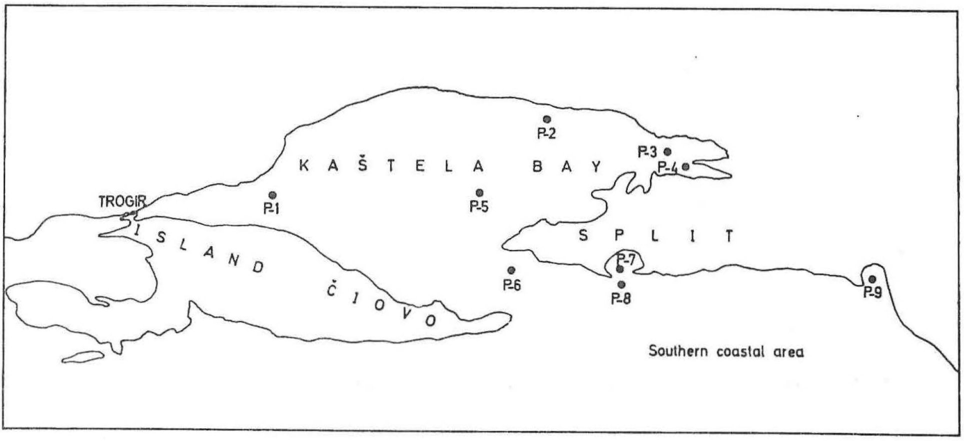


Fig. 2. Study area

The Kaštela Bay is a coastal area strongly affected by human and natural activities. Natural impacts include freshwater drainage, coastal errosion, atmospheric deposition, water exchange with the adjacent Brač Channel, while domestic and industrial (food, concrete, shipyard, PVC factory, and ironworks) effluents count among anthropogenic effects (Buljan and Zore, 1971).

The Kaštela Bay is also a highly productive area. Main annual maxima, occuring in spring and winter and characteristic of phytoplankton production, have recently a trend of decrease. Productivity and biomass show continuous increase (Pucher-Petković and Marasović, 1980).

An excessive production of a defined phytoplankton organisms causing mass fish mortality have occurred on several occasions in the north-easternmost shallow part of the bay.

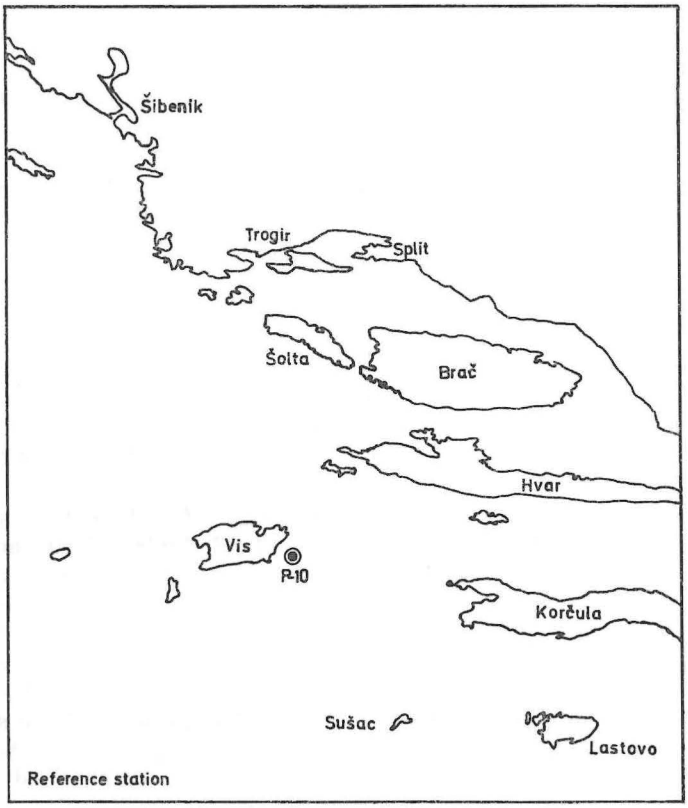


Fig. 3. Reference station

Water exchange takes place through a strait between the Marjan cape and Čiovo cape, and to a lesser extent through the opening near the town of Trogir. The Kaštela Bay water is rather rapidly exchanged.

Four facies may be distinguished in sediments of the Kaštela Bay: rocky bottoms, gravel, sand and mud.

The bathymetry of the basin reveals two markedly different parts of the bay, the westernmost and eastern parts which are shallower and deeper central part (Alfirević, 1980).

The distribution pattern of sediments shows sand in the shallower areas while the bottom of deeper areas is covered with muddy deposits of transitional type.

Southern coastal area which extends along the southern coastal area of the town of Split includes: town's port, Bačvice, Zenta, Trstenik, Žnjan and Stobreč coves.

The anthropogenic impact is best marked here, including domestic sewage effluents, which untreated enter the waters of the town port. This material is rapidly dispersed since this is an open area.

MATERIAL AND METHODS

The samples were collected from the Kaštela Bay stations (6 stations, from P-1 through P-6), town port (2 stations, P-7 and P-8), Stobreč cove (1 station, P-9) (Fig. 2). Station Stončica (P-10) was used as a reference station (Fig. 3).

The samples were collected by a »gravity corer«, (Meischner, 1974), Surface layer of 0—5 cm thickness was sampled. Each sample was wrapped in Al-foil and freezed until the analysis.

Phosphorus determination

The determination of phosphorus was carried out by spectrophotometric method (Aspila *et al.*, 1976), with the phosphomolybdenum-blue procedure. For the determination of total, inorganic, organic and reactive phosphorus four respective methods are possible. Three are experimental approaches and fourth is mathematical.

Phosphorus present in inorganic minerals of sediment was extracted by samples shaking for 16 hours in dissolved hydrochloric acid (0.1 N). Phosphorus is released as ortophosphate. Mixed reagent is added after filtration and solution with distilled water. The dye intensity of created complex of phosphomolibdenum blue compound is measured by spectrophotometry.

For the extraction of total phosphorus in sediments the sample was heated at 550°C for 2h to destroy the organic matter. Then the extraction with hydrochloric acid was performed (like in inorganic) and the sample was shaken for 16 h. With mixed agent a complex compound of phosphomolybdenum-blue is obtained the dye intensity of which is determined by spectrophotometry.

Phosphorus adsorbed to sediment surface is the stage of the so called rective phosphorus. The sample was treated with the artificial sea water and shaken for 2 h for phosphorus extraction. Phosphorus concentration was determined by spectrophotometry with mixed reagents.

Calibration curves are constructed from known concentrations of KH_2PO_4 solution and respective extinction values read on spectrophotometer.

After our experimental conditions (size of test-tubes, volume of extract, sample quantity, apparatus sensitivity) sensitivity threshold was 0.001.

Described methods are not liable to the influence of silica or acidity. They are sufficiently reliable, results could be reproduced so that they are suitable for the monitoring of inorganic, organic and total phosphorus in sediments.

Since the role of phosphorus, either deposited or original in sediments, is that of being the principal factor reflecting the ageing or eutrophication of natural systems particular attention is given to the form it is found in sediments as well as to the further degradation of phosphorus compounds.

The method applied for the determination of inorganic phosphate, by which the phosphate is released by extraction of non-ignited dry sediment with hydrochloric acid with shaking for 16 hrs, renders possible a very good determination of inorganic phosphorus, even of the most inert forms.

Organic phosphorus was calculated from the difference between the total and inorganic phosphorus quantities.

Ability of the method to be reproduced determined after the coefficient of variations (Aspila *et al.*, 1976) was 2.6% for the total phosphorus, 2.5% for inorganic phosphorus, while after Giordani and Astorri (1985) these values were 1.6% for the total phosphorus, 0.6% for inorganic and 3.0% for reactive phosphorus.

All the described methods are characterized by the fact that they were derived from the methods earlier used for waste and sea waters.

Determination of organic carbon

Quantity of organic carbon in sediments of the study area was determined by the oxidation procedure with chromium acid, Walkey and Black (1934) modified by Jackson (1958).

Elementary carbon present as graphite and carbon in sediment is eliminated by this method. In oxidation procedure these elements remain inoxidized. Since the carbon bound to organic matter makes up 58% of the total organic matter in sediment, organic carbon content may be converted to organic matter content by multiplying it by the factor 1.72 (Walkey and Black, 1934). Carbon is oxidized with chromium acid and then the inoxidized bichromate is reduced in ferro solution.

Sensitivity treshold of this method for our conditions was 0.075 mg carbon. Reproducibility of the method expressed by standard deviation was lower than 0.25% (Gaudette *et al.*, 1974).

A comparison of Walkey-Black titration method with the »LECO combustion« method (Gaudette *et al.*, 1974) gave a very good agreement of organic carbon values. Since a very expensive equipment is needed for LECO method (LECO carrier analyzer) the authors would recommend the titration method for routine sediment analyses.

RESULTS

Sediment samples collected from the study area were analysed by the above described methods. Analyses for the total, inorganic and reactive phosphorus were carried out while organic phosphorus was calculated from the difference between the total and inorganic phosphorus.

Phosphorus concentrations in sediments are determined indirectly by means of light absorption, that is by monochromatic light absorbed by the sample.

To obtain the relation between absorption and phosphorus concentration in the sample, calibration curves are constructed by standard solution. We used the standard solution of dihydrogenophosphate.

The quantity of organic matter was calculated from the results of the analyses obtained from the analysis of organic carbon.

At least triple analysis of each parameter was performed. In samples in which the agreement between results was not satisfactory the analysis was repeated up to five times.

The results are given in tables, and seasonal distribution of each individual parameter graphically presented in figures. Histograms of all the parameters of the study area stations are given in the end (mean values) (Fig. 4).

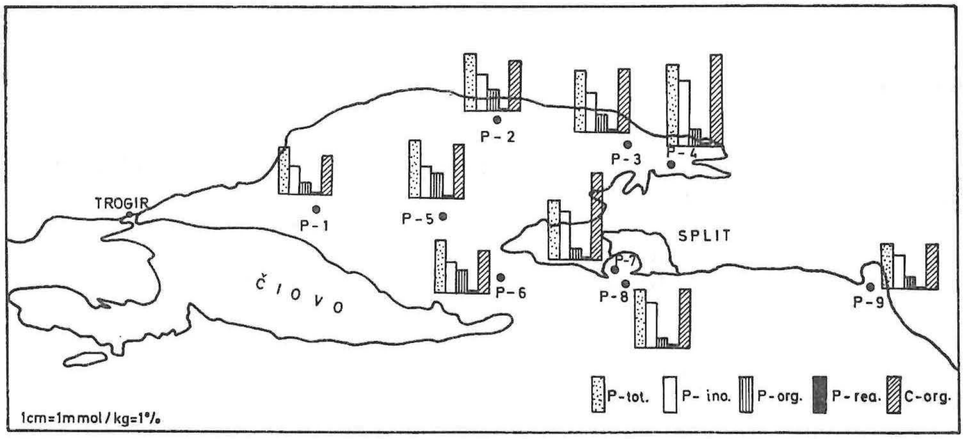


Fig. 4. Histogram of distribution of total, inorganic, organic and reactive phosphorus (expressed in mmol/kg dry weight) and organic carbon (°/o) in surface sediments of the Split near-shore area (annual mean values)

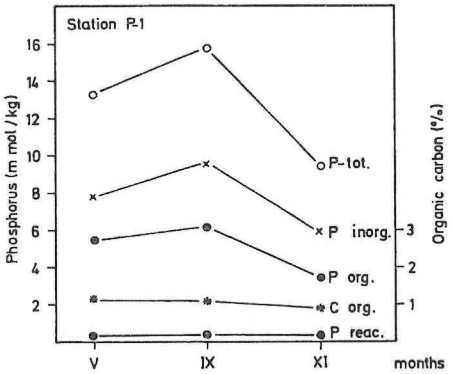


Fig. 5. Graphically presented distribution of phosphorus and organic carbon at station P-1

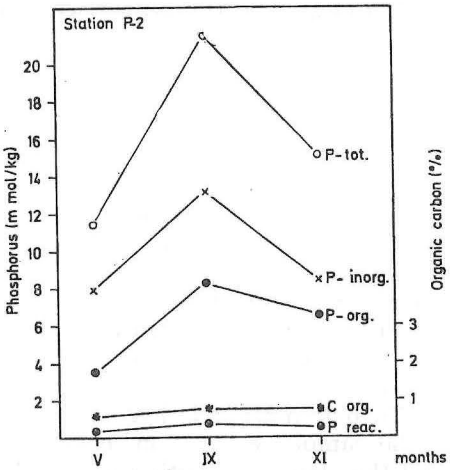
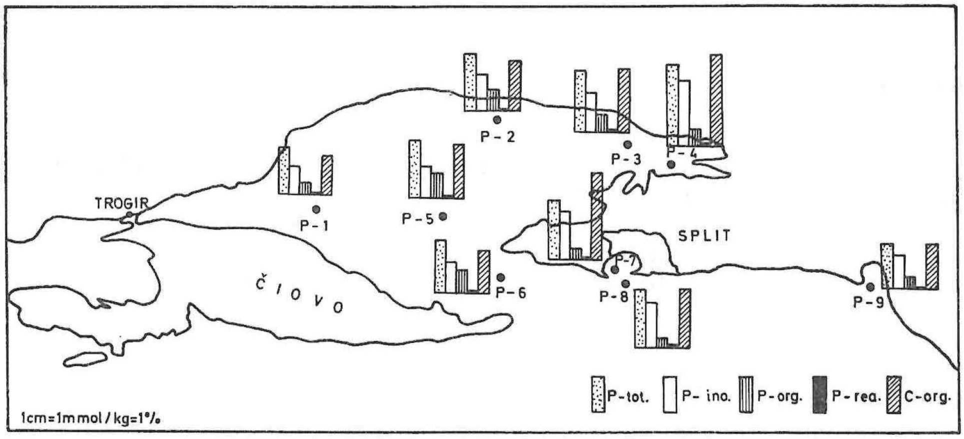


Fig. 6. Graphically presented distribution of phosphorus and organic carbon at station P-2

At least triple analysis of each parameter was performed. In samples in which the agreement between results was not satisfactory the analysis was repeated up to five times.

The results are given in tables, and seasonal distribution of each individual parameter graphically presented in figures. Histograms of all the parameters of the study area stations are given in the end (mean values) (Fig. 4).



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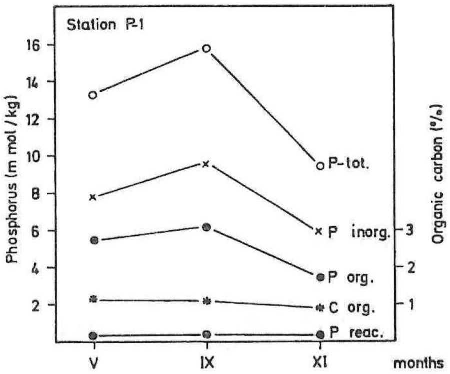

Fig. 5. Graphically presented distribution of phosphorus and organic carbon at station P-1

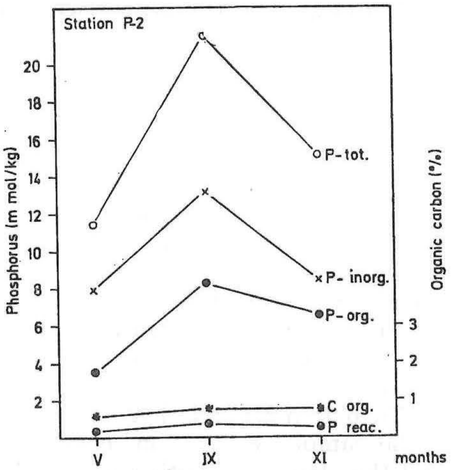

Fig. 6. Graphically presented distribution of phosphorus and organic carbon at station P-2

The following concentrations of phosphorus in the sediments of the Kaštela Bay and southern near-shore area of the town of Split were obtained.

Maximum values of all phosphorus forms were recorded from station P-1 in summer while the values recorded in autumn were lower than the spring ones. Reactive phosphorus showed no seasonal differences. Organic matter quantities were constant in spring and summer with a slight decrease in autumn (Fig. 5).

All phosphorus forms increased at station P-2 in summer and decreased in autumn. Its seasonal variations are more alike those at station P-5. Organic matter quantities were increased in summer to remain constant in autumn (Fig. 6).

The total phosphorus levels were considerably increased at station P-3 in summer (from 13.6 to 19.1) to remain at the same level in autumn. Inorganic phosphours was constant all year round while organic phosphorus showed a considerable increase in summer (from 1.1 in May to 7.7 in September) and a slight decrease in autumn. Reactive phosphorus showed the same tendency. Organic matter quantities were slightly higher here than at stations P-5, P-1 and P-2 in May, while they were considerably higher in summer and autumn (3.2 and 3.4% respectively) (Fig. 7).

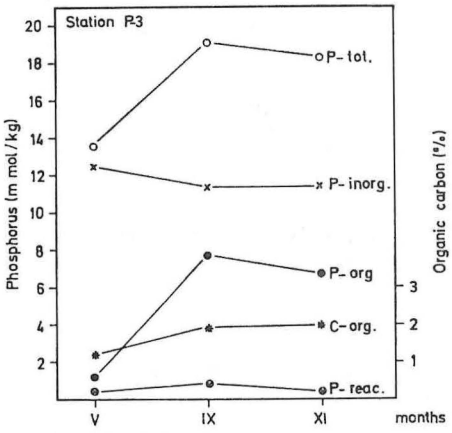

Fig. 7. Graphically presented distribution of phosphorus and organic carbon at station P-3

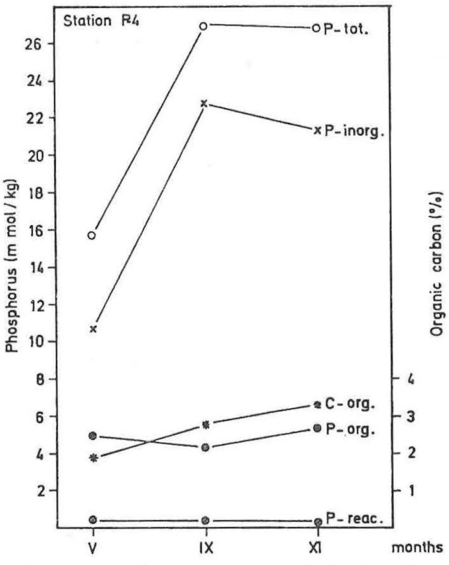

Fig. 8. Graphically presented distribution of phosphorus and organic carbon at station P-4

All the observed parameters, that is all the phosphorus forms and organic matter, were considerably higher at station P-4 than at other stations (Fig 8). A tendency of increase of the total and inorganic phosphorus was established in summer and decrease in autumn, like at other stations, with the difference in absolute values between individual parameters.

Mean organic phosphorus and reactive phosphorus values were constant all year round. However, absolute values of organic matter were considerably higher here than at other stations (3.25% at station P-4 and 2.3% at other stations). In summer these values amounted to 4.8% and in autumn to as high as 5.6% (Fig. 8).

All four phosphorus forms (total, inorganic, organic and reactive) showed a slight increase at station P-5 in summer-autumn while organic matter remained constant all year round (Fig. 9).

The station P-6 is at the entrance to the Kaštela Bay so that the variations of various phosphorus forms showed a tendency different from that at the stations inside the bay. Total phosphorus remained almost constant all year round. Inorganic phosphorus quantities slightly decreased in the spring-autumn (Fig. 10).

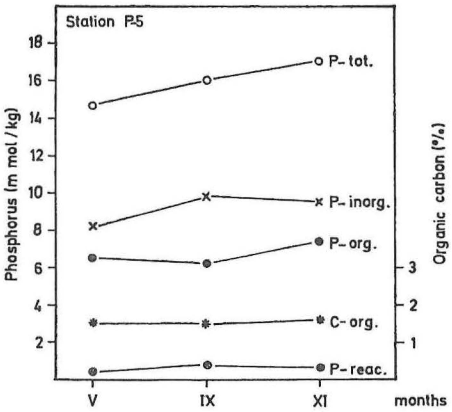

Fig. 9. Graphically presented distribution of phosphorus and organic carbon at station P-5

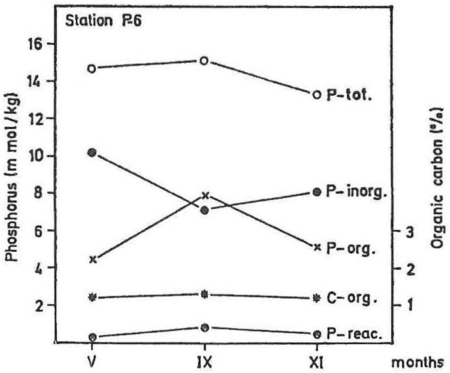

Fig. 10. Graphically presented distribution of phosphorus and organic carbon at station P-6

Organic phosphorus was lower at this station in May, reaching maximum in summer and decreasing in autumn. The same behaviour pattern was observed for reactive phosphorus. Organic matter levels were almost constant all year round (Fig. 10).

In addition, going towards the southern part of the Split peninsula, quantities of all phosphorus forms and organic matter were still high. So, at station P-7, which is in the town port, all phosphorus forms had rather high concentrations constant all year round (Table 1).

The same situation was recorded from station P-8 in front of the town port. Organic matter values were constant all year round (Table 1).

Table 1. Phosphorus (mmol/kg) and organic carbon (%) at station P-8

	May	September	Mean
P-tot	15.8	13.5	14.6
P-inor.	13.0	11.7	12.3
P-org.	2.8	1.8	2.3
P-reac.	0.53	0.46	0.50
C-org.	1.7	1.6	1.65
O. M.	2.9	2.8	2.85

Station P-9 in the estuary of the Žrnovnica River east of the town port, showed lower total phosphorus quantities than the stations of the Kaštela Bay. However the values did not differ much. (In the Kaštela Bay the mean values ranged from 13—15 and at station P-9 they were 12 mmol/kg). Quantities of inorganic and organic phosphorus ranged also within the normal limits and were constant all year round.

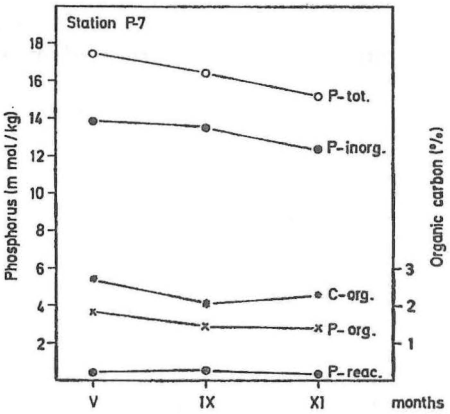

Fig. 11. Graphically presented distribution of phosphorus and organic carbon at station P-7

Reactive phosphorus values were slightly lower. Since, however, it was sampled only in May no definite conclusions could be drawn. As to the organic matter, this station showed considerable differences from the values recorded from the Kaštela Bay. The mean value was 1.8% at this station and 2.4% in the Kaštela Bay (Table 2).

Table 2. Phosphorus (mmol/kg) and organic carbon (%) at station P-9

	May	November	Mean
P-tot.	12.7	12.1	12.4
P-inorg.	9.6	8.8	9.2
P-reac.	0.29	—	0.28
P-org.	3.2	3.3	3.25
C-org.	1.0	1.1	1.65
O.M.	1.75	1.9	1.8

DISCUSSION

Phosphorus

When the data from each of the studied stations are compared to those from the reference station P-10, it may be concluded that the concentration of total and inorganic phosphorus are slightly lower at station P-10; in relation to stations P-4 and P-7 these concentrations are considerably lower while the values at station P-9 are almost equal to those at station P-10.

It is of particular interest that inorganic phosphorus values at station P-10 exceed those at stations P-7 and P-8 in the town port, which are probably due to the higher quantities of particulate organic matter.

Reactive phosphorus shows marked differences in values between the station P-10 and other stations. Its concentration is almost for an order of magnitude lower at the reference station than at other stations. The only exception is the station P-9 where the values recorded were almost the same as at the station P-10. Organic matter levels at the station P-10 differred much from those at other stations being lower for an order of magnitude (Table 3).

Table 3. Phosphorus (mmol/kg) and organic carbon (%) at station P-10

	September
P-tot.	12.3
P-inorg.	8.2
P-org.	4.1
P-reac.	0.09
C-org.	0.35
O.M.	0.6

To show clearly the relationship between total phosphorus and organic carbon the histogram of their values at studied station was made. This relationship was similar at stations P-1, P-6, P-2 and P-9, and at the group of stations P-3, P-4, P-7 and P-8, while at station P-5, which is in the middle of the bay, the relationship between these two parameters represents the mean between the relationships obtained for these two groups of stations (Fig. 12).

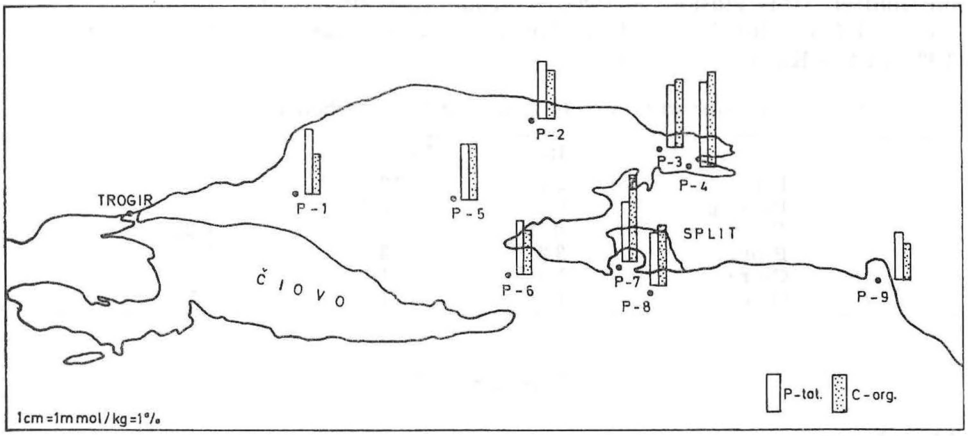

Fig. 12. Histogram of distribution of total phosphorus and organic carbon in study area (expressed in mmol/kg and % dry weight of sediments)

A general conclusion may be drawn that the phosphorus from surface sediments is liable to changes dependently on seasons. It reaches maxima in summer, which may be accounted for by the intensified organic matter production in the water column in spring, followed by a sedimentation process occurring somewhat later as well as to the small depth of the water column. This is also the time of water column stratification so that the accumulation process is more pronounced than the dilution process.

The obtained results show all phosphorus forms to increase slightly at station P-5 by seasons. This station is in the central part of the Kaštela Bay, so that its position may, to a certain extent, explain the recorded situation, that is, this station is relatively far offshore if compared to the stations P-2, P-3, P-4, and P-6 (Fig. 12).

Concentrations of total and inorganic phosphorus were on the average higher on clayey and muddy sediments at stations P-2, P-3, P-4 and P-5 than on sandy bottoms at P-1 and P-6.

Reactive phosphorus distribution resembles that of the above two forms. its concentrations being higher in muddy sediments. This is in agreement with the fact that muddy sediments do not readily release phosphorus.

Station P-4 is distinguished from other stations by the quantities of total and inorganic phosphorus. It may be assumed that phosphorites, small black nodules containing large quantities of organic matter, are produced at this station. They were found during the analysis of the material. This is supported by the fact that larger quantities of organic matter were recorded there.

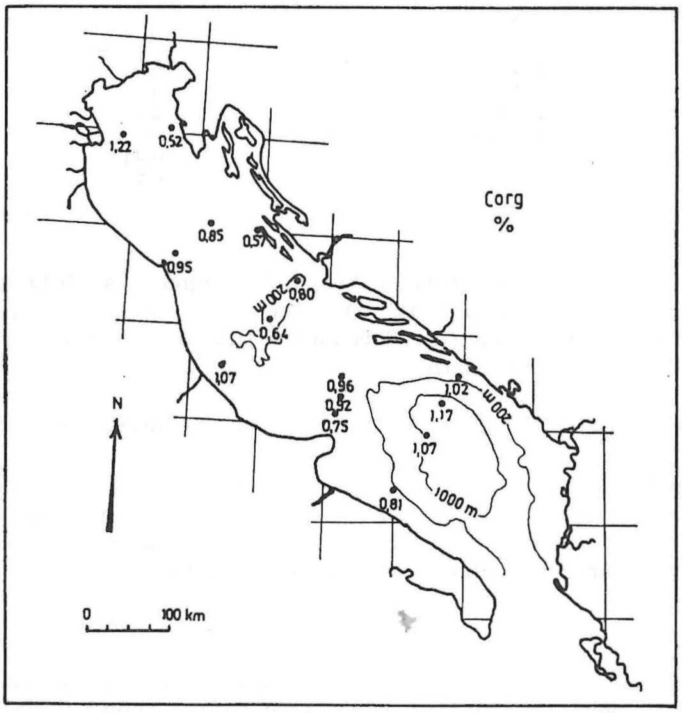

Fig. 13. Distribution of organic carbon in surface sediments of the Adriatic Sea (March, 1973) (Štirn *et al.*, 1974).

After recent approaches the phosphorites are considered to be the mineral fluorpartite, within which structure the anion oxides are replaced by phosphate anions.

Increased quantities of organic matter may be derived from greater land runoff (what is the case at this station) and limited circulation and consequently accumulation.

The concentrations of total, inorganic and organic phosphorus are approximatively the same at stations P-9 and P-10 while they differ considerably with respect to reactive phosphorus concentrations and percentage of organic matter (the values were not plotted since samples were not collected in all seasons).

A possibility to explain this is to assume that these two stations contain oxidized sediment with ferro III oxides and hydroxides, which have the property to bind firmly ortophosphate deccelerating thus its release into the water column. This assumption should be proved by iron analyses.

The inorganic and reactive phosphorus distribution by seasons is given by Angeloni *et al.*, (1978) for the area of Italian coast Emilia Romagna. A comparison between the Split near-shore area and the area of Emiglia Romagna is given in Table 4.

Table 4. Phosphorus (mmol/kg) and organic carbon (%) in the a) Split near-shore area b) Emilia Romagna (Angeloni *et al.*, 1978)

	a	b
P-tot.	16.6	18.9
P-inorg.	12.4	15.5
P-org.	4.1	2.4
P-reac.	0.41	0.2
C-org.	1.8	0.44
O.M.	3.1	0,75

It can be seen that the area of Emilia Romagna is slightly more loaded by total and inorganic phosphorus, while the area of Split is more loaded by organic and reactive phosphorus. This means that the Split area receives larger quantities of organic matter (which the organic phosphorus is derived from), and that the sediment is of such a constitution that it contains more reactive phosphorus which is a direct threat for the increase of phosphorus in the water column.

The fact that larger quantities of organic matter were recorded from this area (3.1% in relation to 0.75%) confirms the assumption that higher quantities of organic matter are accumulating in sediments with respect to the higher quantities of organic phosphorus which they contain.

Organic matter

Seasonal behaviour of organic matter quantities resembles that of reactive phosphorus. Namely, the quantity of organic matter shows very little variability, it may be said to be practically constant at most of the stations. Here count the stations P-1, P-2, P-5, P-6, P-7. The differences were recorded for station P-3 where organic matter quantities are increased in summer and remain at that level throughout autumn (Fig. 7) while the station P-4 shows a constant increase in summer and continues to increase in autumn (Fig. 8).

Values were considerably higher than at reference station P-10.

The data for organic matter quantities in the Kaštela Bay in 1980, obtained by the method of oxidation with peroxide (Mikac *et al.*, 1985) compared with our data are presented in the following table.

Table 5. Organic matter quantity in surface sediments of Kaštela Bay (%) (A-our data, B-Mikac *et al.*, 1985)

	Station	P-1	P-2	P-3	P-5	P-6	P-8
A	May	2.3	1.9	2.5	2.5	2.0	2.9
	September	2.3	2.7	3.7	2.5	2.3	2.8
	November	1.3	2.7	3.4	2.7	2.1	—
B	June	8.2		7.7	6.5	5.1	
	October	4.5	7.4	10.8			8.5

Quantities of organic matter obtained by this other method were considerably higher. With respect to the fact that in the paper by Mikac *et al.*, (1985) the number of analyses by oxidation method with peroxide is too small, no conclusions on the relationship between organic matter quantities obtained by these two methods could be drawn.

Comparison of our values for organic carbon, that is organic matter, to the values from other localities (Table 6) shows latter to be higher.

Table 6. Quantity of organic carbon in some surface sediments (%) (Calvert, 1975)

Area	C-org
Split near-shore area	1.8 (mean value)
Santa Barbara Basin	3.2
Santa Catalina Basin	5.0
Gulf of California, Werstern slope	6.55
South West African shelf	22.3
Gulf of California, Guaymas Basin	2.91

Fig 12. presents the distribution of organic carbon in the Adriatic sediments obtained with the »Mohorovičić« expedition (Štirn et al., 1974). As shown by the figure organic carbon mean values were 1.22% for Emilia Romagna, ranged between 0.52 and 0.55% in the open sea, from 0.64 to 0.80 in the Jabuka Pit and slightly exceeded 1% in the South Adriatic Pit. When observing all these values together with ours, obtained for the area of Split, than it becomes quite obvious that the distribution of organic carbon in the Adriatic sediments is in agreement with the generally accepted knowledge that organic matter is accumulating for the most part in near-shore sediments and in the sediments of the pit areas.

CONCLUSIONS

The total, inorganic, organic and reactive phosphorus as well as organic carbon have been shown to be conveniently measured by new analytical methods used in this paper.

It is well known that the concentration of total phosphorus of 13.5 mmol/kg dry weight is held as the limit above which the sediment is taken to be polluted by this element, and limit of saturation by this element is 60 mmol/kg dry weight. According to this criteria the sediments of Split near-shore area are overloaded by phosphorus, since the total phosphorus values exceed 13.5.

Minimum values of total phosphorus concentrations of 9.4 mmol/kg were recorded from station P-1 in November 1985, and maximum of 27.1 mmol/kg dry weight from station P-4 in September 1985.

It is of interest that a very high concentration of this element of 12.3 mmol/kg was recorded from station P-10. This value is only slightly lower than the pollution limit (13.5 mmol/kg).

With respect to the organic matter and phosphorus quantities, sediments of this area are a combination of biogenous and detrital fractions admixed with the authigenic one.

According to Emery (1968) biogenous sediments in near-shore environments are the equilibrium sediments. This assumption is applicable to our case. This means that organic matter accumulates in sediments but at the same time a part is released, particularly under oxic conditions. This may account for the fact that no large quantities of organic matter were found, even if they were to be expected, because of the prevailing biogenous sediments due to strong anthropogenic influence in this bay.

It is well known that the accumulation rates are very rapid in shallow areas, as well as those of organic material burial, what results in the preservation of organic material in sediments. In many sediments anoxic conditions may be produced beneath surface oxidized layer.

Under oxic conditions organic matter is rapidly oxidized and utilized by aerobic bacteria and higher organisms, while under anoxic conditions it is degraded by fermentation and bacterial reduction.

In the Kaštela Bay this may be due to the water mass dynamics, that is strong bora wind effects which produce oxic conditions.

In addition, organic matter-rich environments, such as stations P-4 and P-7 may become anoxic. Maximum concentrations of organic carbon, that is organic matter, were recorded from station P-4 in November 1985, 3.3% C-org. and from station P-7 in May 1985, 2.7% C-org.

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RASPODJELA FOSFORA I ORGANSKOG UGLJIKA U POVRŠINSKIM MORSKIM SEDIMENTIMA SPLITSKOG PRIOBALNOG PODRUČJA

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KRATKI SADRŽAJ

U ovim istraživanjima obavljena su prvi put mjerenja ukupnog, anorganskog, organskog i reaktivnog fosfora kao i organskog ugljika odnosno organske tvari u površinskom sloju (0—5 cm) sedimenata splitskog priobalnog područja. Istraživanja su obavljena tokom 1985. godine u tri sezone (proljeće, ljeto, jesen).

Prvi put su primjenjene najnovije metode za određivanje ovih parametara u sedimentima. Rezultati su pokazali da su metode podesne za praćenje količine fosfora i organskog ugljika u sedimentima.

Prema našim istraživanjima ustanovljen je porast navedenih parametara u ljetnom i jesenskom razdoblju. Također je ustanovljeno da su ovi sedimenti znatno opterećeni fosforom a manje sa organskim tvarima.

Ustanovljeno je da je moguća komparabilnost naših podataka sa podacima sa zapadnog dijela Jadranske obale kao i sa drugim geografskim područjima. Uzimajući u obzir takve komparacije može se reći, da je sjevero-zapadni dio Jadrana opterećeniji ukupnim i anorganskim fosforom, dok je istočni dio opterećeniji organskim i reaktivnim fosforom, te znatno opterećeniji organskim ugljikom. To ukazuje na to da velika količina organske tvari ulazi i akumulira se u sediment.