MEDITERRANEAN ACTION PLAN
MED POL

UNITED NATIONS ENVIRONMENT PROGRAMME

NATIONAL MONITORING PROGRAMME OF YUGOSLAVIA
Report for 1983-1986

MAP Technical Reports Series No. 23

UNEP
Athens, 1988

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This volume is the twenty-third issue of the Mediterranean Action Plan Technical Series.

This Series will collect and disseminate selected scientific reports obtained through the implementation of the various MAP components: Pollution Monitoring and Research Programme (MED POL), Blue Plan, Priority Actions Programme, Specially Protected Areas and Regional Oil Combating Centre.

GENERAL INTRODUCTION

The United Nations Environment Programme (UNEP) convened an Intergovernmental Meeting on the Protection of the Mediterranean (Barcelona, 28 January - 4 February 1975), which was attended by representatives of 16 States bordering on the Mediterranean Sea. The meeting discussed the various measures necessary for the prevention and control of pollution of the Mediterranean Sea, and concluded by adopting an Action Plan consisting of three substantive components:

- Integrated planning of the development and management of the resources of the Mediterranean Basin (management component);

- Co-ordinated programme for research, monitoring and exchange of information and assessment of the state of pollution and of protection measures (assessment component);

- Framework convention and related protocols with their technical annexes for the protection of the Mediterranean environment (legal component).

All components of the Action Plan are interdependent and provide a framework for comprehensive action to promote both the protection and the continued development of the Mediterranean ecoregion. No component is an end in itself. The Action Plan is intended to assist the Mediterranean Governments in formulating their national policies related to the continuous development and protection of the Mediterranean area and to improve their ability to identify various options for alternative patterns of development and to make choices and appropriate allocations of resources.

MED POL - Phase I (1976-1980)

The Co-ordinated Mediterranean Research and Monitoring Programme (MED POL) was approved as the assessment (scientific/technical) component of the Action Plan.

The general objectives of its pilot phase (MED POL - Phase I), which evolved through a series of expert and intergovernmental meetings, were:

- to formulate and carry out a co-ordinated pollution monitoring and research programme taking into account the goals of the Mediterranean Action Plan and the capabilities of the Mediterranean research centres to participate in it;

- to assist national research centres in developing their capabilities to participate in the programme;

- to analyze the sources, amounts, levels, pathways, trends and effects of pollutants relevant to the Mediterranean Sea;

- to provide the scientific/technical information needed by the Governments of the Mediterranean States and the EEC for the negotiation and implementation of the Convention for the Protection of the Mediterranean Sea against Pollution and its related protocols.

- to build up consistent time-series of data on the sources, pathways, levels and effects of pollutants in the Mediterranean Sea and thus to contribute to the scientific knowledge of the Mediterranean Sea.

MED POL - Phase I initially consisted of seven pilot projects (MED POL I - VII), which were later expanded by six additional pilot projects (MED POL VIII - XIII), some of which remained in a conceptual stage only.

MED POL - Phase I was implemented in the period from 1975 to 1980. The large number of national research centres designated by their Governments to participate in MED POL (83 research centres from 15 Mediterranean States and the EEC), the diversity of the programme and its geographic coverage, the impressive number of Mediterranean scientists and technicians (about 200) and the number of co-operating agencies and supporting organizations involved in it, qualifies MED POL as certainly one of the largest and most complex co-operative scientific programmes with a specific and well-defined aim ever undertaken in the Mediterranean basin.

The overall co-ordination and guidance for MED POL - Phase I was provided by UNEP, acting as the secretariat of the Mediterranean Action Plan (MAP). Co-operating specialized United Nations Agencies (ECE, UNIDO, FAO, UNESCO, WHO, WMO, IAEA, IOC) were responsible for the technical implementation and day-to-day co-ordination of the work of national research centres participating in the pilot projects.

MED POL - Phase II (1981 - 1990)

The Intergovernmental Review Meeting of Mediterranean Coastal States and First Meeting of the Contracting Parties to the Convention for the Protection of the Mediterranean Sea against Pollution, and its related protocols (Geneva, 5-10 February 1979), having examined the status of MED POL - Phase I, recommended that during the 1979-80 biennium a Long-term pollution monitoring and research programme be formulated.

Based on the recommendations made at various expert and intergovernmental meetings, a draft Long-term (1981 - 1990) Programme for Pollution Monitoring and Research in the Mediterranean (MED POL - Phase II) was formulated by the Secretariat of the Barcelona Convention (UNEP), in co-operation with the United Nations Agencies which were responsible for the technical implementation of MED POL - Phase I, and it was formally approved by the Second Meeting of the Contracting Parties of the Mediterranean Sea against pollution and its related protocols and Intergovernmental Review Meeting of Mediterranean Coastal States of the Action Plan held in Cannes, 2-7 March 1981.

The general long-term objectives of MED POL - Phase II were to further the goals of the Barcelona Convention by assisting the Parties to prevent, abate and combat pollution of the Mediterranean Sea Area and to protect and enhance the marine environment of the Area. The specific objectives were designed to provide, on a continuous basis, the Parties to the Barcelona Convention and its related protocols with:

- information required for the implementation of the Convention and the protocols;

- indicators and evaluation of the effectiveness of the pollution prevention measures taken under the Convention and the protocols;

- scientific information which may lead to eventual revisions and amendments of the relevant provisions of the Convention and the protocols and to the formulation of additional protocols;

- information which could be used in formulating environmentally sound national, bilateral and multilateral management decisions essential for the continuous socio-economic development of the Mediterranean region on a sustainable basis;

- periodic assessment of the state of pollution of the Mediterranean Sea.

The monitoring of, and research on, pollutants affecting the Mediterranean marine environment reflect primarily the immediate and long-term requirements of the Barcelona Convention and its protocols, but also take into account those factors needed for the understanding of the relationship between the socio-economic development of the region and the pollution of the Mediterranean Sea.

For this purpose, monitoring was organized on several levels:

- monitoring of sources of pollution providing information on the type and amount of pollutants released directly into the environment;

- monitoring of nearshore areas, including estuaries, under the direct influence of pollutants from identifiable primary (outfalls, discharge and coastal dumping points) or secondary (rivers) sources;

- monitoring of offshore areas (reference areas) providing information on the general trends in the level of pollution in the Mediterranean;

- monitoring of the transport of pollutants to the Mediterranean through the atmosphere, providing additional information on the pollution load reaching the Mediterranean Sea.

Monitoring of the Mediterranean pollution in the framework of MED POL started in 1983 through the implementation of National Monitoring Programmes and at present 14 Mediterranean countries (Algeria, Cyprus, Egypt, France, Greece, Israel, Lebanon, Libya, Malta, Monaco, Morocco, Spain, Syria and Yugoslavia) have on-going programmes and are submitting data.

As in MED POL - Phase I, the overall co-ordination and guidance for MED POL - Phase II is provided by UNEP as the secretariat of the Mediterranean Action Plan (MAP). Co-operating specialized United Nations Agencies (FAO, UNESCO, WHO, WMO, IAEA, IOC) are responsible for the technical implementation and day-to-day co-ordination of the work of national centres participating in monitoring and research.

This twenty-third volume of the MAP Technical Reports Series is the report on the first four years of implementation (1983-1986) of the Yugoslav Monitoring Programme. Twelve institutions participated in the programme and the co-ordinator of the activities in Yugoslavia has been the Committee for Building, Housing, Public Works and Environmental Protection of the Socialist Republic of Croatia. The report is based on Annual National Reports for the years 1983 to 1986 and was prepared by Mr. D. Degobbis, Dr. M. Picer, Dr. L. Sipos and Dr. S. Sobot.

C O N T E N T S

NATIONAL MONITORING PROGRAMME OF YUGOSLAVIA

Report for 1983-1986

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1. INTRODUCTION

1.1. Historical background of pollution research in the Adriatic Sea

The Adriatic Sea is an elongated basin (139,000 km^2) of the northern Mediterranean, extending for 800 km into the heartland of the European continent and bordered by Italy, Yugoslavia, Albania and Greece. On its southern side the Adriatic sea is connected to the Mediterranean Sea through the relatively narrow (70 km) Otranto Strait, with a sill depth of about 800 m. The renewal of the Adriatic water has been estimated in the range of 5 to 10 years (Zore-Armanda and Pucher-Petkovic, 1976; Mosetti, 1983), which is about ten times shorter than the whole Mediterranean water renewal (70-100 years; Lacombe and Richet,1982; Ovchinnikov, 1983). Morphologically, the Adriatic Sea can be divided into three parts. The northern shallow part (max.depth 75 m) extends southward to a line joining Ancona (Italy) with the Pag island (Yugoslavia). The central part with the Jabuka Trench (max. depth 270 m) is separated by the Palagruza Sill (130 m) from the deepest southern part (max. depth 1270 m).

The shallow northern Adriatic receives considerable freshwater discharge mainly from the Po River, one of the major rivers in the Mediterranean area, and from other minor streams (total flow up to 3000 $m^3\ s^{-1}$ Cavazzoni Galaverni, 1972). A 15 million resident population lives in the Po river watershed, on seven million hectars of land, half of which is very intensively cultivated. The region has an industrial organic load (expressed in BOD_5) equivalent to 40 million inhabitants (Anon.,1977). In addition, significant quantities of wastewaters are discharged directly into the sea from the coastal regions, which are densely populated and with well developed industrial and marine activities. Finally, the tourist population increases significantly during the summer period, raising the basic level of the organic load.

Due to its particular geological, hydrological and biological characteristics, the Adriatic Sea has been the object of scientific interest since the 16th century. (Zavodnik, 1983). However, oceanographic measurements and biological sampling, covering the entire open area, or at least larger coastal regions, started at the beginning of this century, before the First World War. Several seasonal cruises were organized by the Italian-Austrian Permanent International Commission for Research of the Adriatic Sea between 1911 and 1914. The Yugoslav Academy of Sciences and Arts of Zagreb (Croatia) sponsored a series of cruises in the Kvarner Region (northeastern Adriatic Sea) in 1913-1914. In the period between the two World Wars marine research was mostly localized in coastal areas. After the Second World War, during the international geophysical year (1955), extended cruises were again carried out in the open Adriatic by Italian and Yugoslav research vessels. Beginning with the sixties research in the open sea and coastal regions was gradually intensified by both Italian and Yugoslav oceanographic institutions. In addition American (Atlantis I), Soviet (Akademik Kowalevski and Akademik Vavilov), and French (Calypso) research vessels also visited the Adriatic. A detailed historical review of marine 3 fundamental research activities, with lists of institutions and research vessels, was given by Zavodnik (1983).

During the seventies more attention was paid to pollution research in response to the increased pollutant load, due to the intensive development of agriculture, industry, marine traffic, port activities and tourism in the area.

However to date pollution distribution and processes for the open Adriatic Sea are not yet sufficiently well documented. Heavy metals and chlorinated hydrocarbons were determined in water, plankton, benthic organisms, fishes and sediments during cruises of the Yugoslav Navy research vessel "Andrija Mohorovicic" in 1973 and 1976-78 at about 30 stations covering the entire Adriatic Sea (Stirn et al., 1974; Paul and Meishner, 1976; Kosta et al., 1978, Stegnar et al., 1979). Additional analyses of heavy metals, DDT and PBCs were performed on northern Adriatic pelagic and benthic fishes (Gilmartin and Revelante, 1975; Revelante and Gilmartin, 1975). The existing data show that up to the mid-seventies no critical contamination of the Adriatic ecosystem as a whole was reached, although locally increased levels were found, particularly for mercury. A study of the Hg, Pb and Cd content of five Adriatic organisms, representing various levels of the food chain (mussels, shrimps, mullets, anchovies and tuna), carried out from 1976 to 1979, showed higher concentrations in specimens collected in the northernmost part vis-à-vis the central Adriatic area (Viviani et al., 1983).

The lack of systematic knowledge of pollution trends in the open Adriatic Sea and the increase of coastal pollution levels in both countries led the Italian and Yugoslav Governments to constitute the Joint Italian-Yugoslav Committee for the Protection of the Adriatic Sea and Coastal Regions from Pollution. In 1979, the Committee approved a joint multidisciplinary research programme with the aim to establish an essential reference for coastal studies and to identify particular problems and areas where interventions were primarily needed (Accerboni and Jeftic, 1980). Relevant to this was the agreement that data obtained and discussed by scientists participating in the joint programme would be officially recognized by the Governments of the two countries. In order to achieve the proposed aims, a monitoring programme was designed including the measurement of 75 parameters which characterize the physical, chemical, sedimentological and biological aspects of pollution processes, on a grid of 42 main stations covering the Adriatic international waters. To evaluate fully the collected data, methodology intercalibration exercises, development of data bank services and elaboration of mathematical models were also included. To date eight cruises have been conducted in the northern Adriatic on 21 stations, and four cruises in the central Adriatic on 8 stations. CTD profiling was also carried out at additional 35 stations. The preliminary results do not seem to reflect high or critical pollution levels, even in the open northern Adriatic Sea (Degobbis et al., 1987). The continuation of systematic monitoring, a better knowledge of the diffusion processes and the development of well calibrated circulation and ecological models are therefore essential, not only in order to evaluate the actual pollution levels and trends, but also to define the strategies of intervention and, subsequently, to verify the effectiveness of the technical measures applied.

In contrast to the open waters, pollution effects are clearly evident in coastal regions, particularly in the northwestern Adriatic (e.g. the Venice Lagoon, Avanzi et al., 1980, the Po River delta, Bartoletti et al., 1985, the Emilia Romagna coastal zone, Chiaudani et al., 1980). Even along the deeper, much less urbanized, Yugoslav Adriatic coast, the harbour areas of almost all urban centres are more or less subjected to a progressive degradation as shown, for instance, by changes in the benthic community structure (Zavodnik, 1977).

At several points along the Istrian, Rijeka region and Dalmatian coasts, heavy metals were analyzed in sediments and the mussel Mytilus galloprovincialis (Raspor, 1985). The most polluted region is the Kastela Bay (Split region), particularly with mercury (Vukadin et al., 1982, Stegnar et al., 1983, Mikac et al., 1983). In contrast, for other areas also highly urbanized (Rijeka, Zadar, Sibenik, Dubrovnik) significantly lower concentrations were reported. Minimum levels were found in mussels from the Lim Channel mariculture facilities (Martincic et al., 1984) and the Rabac (eastern Istria) coastal region (Valkovic, 1980).

Several chemical groups of organic pollutants (hydrocarbons, chlorinated hydrocarbons, phenols, detergents, total surfactants, methyl mercury) were also investigated along the Yugoslav coast (Picer M. 1985). However, non specific analytical techniques were often applied and the interpretation of the results is difficult. Thus, more coordinated efforts are needed in order to draw conclusions about the degree of pollution of the eastern Adriatic by these pollutants (Picer M. 1985).

A systematic and complex study of the state and influence of pollution on the basic chemical and biological processes of the Rijeka Bay (500 km^2, 60 m deep) ecosystem was undertaken from 1976 to 1980 (Jeftic, 1981, 1982). Coordinated studies on currents, water exchange rate estimations, toxicological experiments with oil products, as well as the elaboration of thermal pollution and ecological mathematical models were essential to achieve the proposed aims. The research also provided a baseline to evaluate the efficiency of future sewage and industrial wastewater disposal systems through long submarine outfalls. The population living in the region is about 200000, with a tourist load of four million nights. Several industries (refineries, a cokery, power plants, shipyards, petrochemical plants, an oil terminal, a paper-mill factory) are distributed along the northern coast of the bay.

During 20 seasonal cruises in the Rijeka Bay, meteorological parameters as well as basic physical, chemical and biological parameters in the water and sediment were measured at about 30 stations distributed in the region, including the Bakar Bay. Specific pollution parameters (hydrocarbons, chlorinated hydrocarbons, total surfactants, anionic detergents, benzopyrene monooxygenase induction, complexation capacity, heavy metals) were measured in water, sediment and organism samples collected at the oceanographic stations and along the shore. Increased concentrations of total surfactants and anionic detergents were observed only in a narrow northern coastal zone (Cosovic and Zutic, 1981). Increased chlorinated hydrocarbons were observed in mussels and sediments near pollution sources from the Rijeka and Bakar industrial zones (Picer M. et al., 1981). A similar distribution was also observed for other pollutants (Jeftic, 1982). However, the ecosystem of that

region was qualified as a whole to have a high self-purification capacity for pollutants. Research has also shown that wastes from an oil refinery should not produce significant toxic and genetic effects on the ecosystem of the region (Rijavec et al.,1981).

In the same period, a similar ecological study, with the same parameters and methodology used in the Rijeka Bay,was also performed in the coastal area (4 km width) of the western Istrian peninsula during 10 seasonal cruises at 28 stations (Jeftic and Degobbis, 1978; Jeftic and Smodlaka, 1978; Jeftic and Lucu, 1979; Ozretic, 1981). The results, concerning the degree of pollution, led to conclusions similar to those for the Rijeka Bay. Persistent pollutants were only detected in sediment and organism samples collected in proximity of the Umag, Porec, Rovinj and Pula harbours, as well as in the Mirna River estuary. However, the region presented a higher eutrophication degree with respect to the Rijeka Bay, due to the influence of the open northern Adriatic waters (Smodlaka, 1985).

Several other, more specific, studies were performed in the past 10 years along the Yugoslav coast in order to acquire basic oceanographic and pollution data on sites in which wastewaters are disposed, or are planned for future disposal,(e.g. Piran, Rabac, Zadar, Split and Dubrovnik coastal areas, and Sibenik, Kastela and Maloston bays), or on those proposed for tourist exploitation (e.g. Kvarner Islands, several Dalmatian centres), mariculture activities (the Lim Channel, Rasa, Budava and Klimno bays), and also for the building of a nuclear power plant (the Vir Island, Zadar Region). Unfortunately, most of the collected data are not yet published.

The Government of Yugoslavia signed in 1976, and ratified in 1977, the Convention for the Protection of the Mediterranean Sea against Pollution (Barcelona Convention). The Mediterranean Action Plan (MAP) is an action plan for the implementation of the Barcelona Convention, which was adopted by the Mediterranean governments.

One of the four basic components of MAP is the Long-term programme for Pollution Monitoring and Research in the Mediterranean Sea (MED POL), which has been implemented in two phases. As part of the the Yugoslav MED POL activities, Yugoslav National Monitoring Programme is implemented since 1983.

1.2. Overview of the MED POL activities in Yugoslavia

In the implementation of the MED POL - PHASE I, designed as the precursor of a future long-term programme, five research centres from Yugoslavia were involved in the following seven pilot projects:

- MED POL I: Baseline Studies and Monitoring of Oil and Petroleum Hydrocarbons in Marine Waters;

- MED POL II: Baseline Studies and Monitoring of Metals, particularly Mercury and Cadmium, in Marine Organisms;

- MED POL III: Baseline Studies and Monitoring of DDT, PCBs and other Chlorinated Hydrocarbons in Marine Organisms;

- MED POL IV: Research on the Effects of Pollutants on Marine Organisms and their Populations;

- MED POL V: Research on the Effects of Pollutants on Marine Communities and Ecosystems;

- MED POL VI: Problems of Coastal Transport of Pollutants;

- MED POL VII: Coastal Water Quality Control.

The following Yugoslav institutions participated in the above mentioned pilot projects of the MED POL - PHASE I:

- Center for Marine Research Rovinj- Zagreb, "Rudjer Boskovic" Institute, Zagreb (MED POL I, II, III, IV, V, VI and VII);

- Marine Biological Station, Portoroz, Institute of Biology, University of Ljubljana (MED POL II, III, V and VII);

- Institute of Oceanography and Fisheries, Split (MED POL II, III, IV, V, VI and VII);

- Laboratory for Trace Element Analysis, Department of Physics and Mathematics, Faculty of Industrial Pedagogy, University of Rijeka, Rijeka (MED POL II);

- Biological Institute, Dubrovnik (MED POL III, IV and V).

The activities in the framework of the MED POL pilot projects started in 1975 and ended in 1980. During this period most of the institutions carried out specific activities depending on their research orientation and available instrumentation. They carried out with no major difficulties the research and monitoring measurements planned in the second phase of the MED POL programme.

Twelve Yugoslav institutions are involved in the realization of the MED POL-PHASE II activities, consisting of research and monitoring programmes.

The following research projects are carried out by Yugoslav institutions in the period 1983-1986:

- Activity A: Development and testing of sampling and analytical techniques for monitoring of marine pollutants;

- Activity C: Formulation of the Scientific rationale for Mediterranean environmental quality criteria;

- Activity D: Epidemiological studies related to environmental quality criteria;

- Activity F: Research on oceanographic processes;

- Activity G: Research on toxicity, persistence, bioaccumulation, carcinogenicity and mutagenicity;

- Activity H: Eutrophication and concomitant plankton blooms;

- Activity I: Pollution-induced ecosystem modifications;

- Activity K: Biogeochemical cycles of specific pollutants;

- Activity L: Pollutant-transfer processes;

- Jellyfish Project.

The following Yugoslav institutions participated in the above mentioned research projects of the MED POL - PHASE II:

- Marine Biological Station, Piran, Institute of Biology, "Edvard Kardelj" University, Ljubljana (Activity F, G, H and Jellyfish Project);

- "Jozef Stefan" Institute, "Edvard Kardelj" University, Ljubljana (Activity D);

- Center for Marine Research Rovinj, "Rudjer Boskovic" Institute, Zagreb (Activity G, I, K and Jellyfish Project);

- Department for communicable diseases, Pula (Jellyfish Project);

- Center for Marine Research Zagreb, "Rudjer Boskovic" Institute, Zagreb (Activity A, C, F, G, H, K, L and Jellyfish Project);

- Department of Physics, "Rudjer Boskovic" Institute, Zagreb (Activity A);

- Institute of Public Health of SR Croatia, Zagreb (Activity D);

- Institute for Oceanography and Fisheries, Split (Activity C, F, G, H, K and Jellyfish Project);

- Biological Institute, Dubrovnik, Institute for Oceanography and Fisheries, Split (Activity I and Jellyfish Project);

- University "Veljko Vlahovic", Titograd (Activity K);

- Federal Hydrometeorological Institute, Beograd (Activity L);

- Institute of Chemistry, University of Beograd, Beograd (Activity G).

The designing and discussions on the Yugoslav National Programme of the Monitoring of Pollution in the Adriatic Sea started in 1982, while its realization commenced at the beginning of 1983.

During the first year of the programme only four institutions one from Slovenia and three from Croatia participated in the monitoring. The following year five other institutions joined the programme, so that in 1985 and 1986 twelve institutions, two from Slovenia, eight from Croatia and two from Montenegro worked in the programme. In this way, pollution was monitored almost in all important areas of the Yugoslav Adriatic coast.

In the following chapters the organization of the programme (participating institutions, methodology, geographic coverage, measurement schedules) will be described in detail, and the results obtained in the period 1983 - 1986 will be discussed thoroughly. Finally, extensive concluding remarks and recommendations for future work will also be given.

2. ORGANIZATION OF YUGOSLAV NATIONAL MONITORING PROGRAMME

2.1. Participating institutions

The following institutions participate in the present programme:

- Marine Biological Station, Piran, Institute of Biology, "Edvard Kardelj" University, Ljubljana (MBS-P);
- Centre for Marine Research Rovinj, "Rudjer Boskovic" Institute, Zagreb (CMR-R);
- Institute of Public Health, Pula (IPH-P);
- Institute of Public Health, Rijeka (IPH-R);
- Faculty of Civil Engineering Sciences, University of Zagreb (FCES-Z);
- Centre for Marine Research Zagreb, "Rudjer Boskovic" Institute, Zagreb (CMR-Z);
- Institute of Public Health, Split (IPH-S);
- Institute for Oceanography and Fisheries, Split (IOF-S);
- Biological Institute, Dubrovnik, Institute for Oceanography and Fisheries, Split (BI-D);
- Institute for Marine Biology, Kotor (IMB-K);
- Institute for Subtropical Cultures and Environment Protection, Bar (ISCEP-B).

Collaborating institutions:

- "Jozef Stefan" Institute, Ljubljana (JSI-Lj);
- Hydrographic Institute of the Yugoslav Navy, Split (HI-S)
- Kernforschungsanlage, Julich, FRG (KFA-J)

The participants to this programme are scientific and applied research organizations with a long tradition in this type of work.

Information about the participating institutions and their main research activities is given in ANNEX I.

2.2. Parameters and methods

2.2.1. List of parameters measured

For effluents, the following parameters were included:

Priority parameters

- total mercury (Hg)
- total cadmium (Cd)
- high molecular weight halogenated hydrocarbons (HM)
- petroleum hydrocarbons (PH)

Other parameters

- biochemical oxygen demand (BOD_5)
- chemical oxygen demand (COD)
- total suspended solids (TSS)
- total phosphorus (P)
- total nitrogen (N)
- faecal coliforms (FC)
- detergents (anionic) (DET)
- phenols (index) (PHE)
- total lead (Pb)
- total chromium (Cr)
- total zinc (Zn)

In coastal zones, parameters in water, suspended matter, sediments and biota were determined as follows:

Estuarine water (E)

- faecal coliforms (FC)
- total mercury (Hg)
- basic oceanographic and meteorological observations (BO&M)
- high molecular weight halogenated hydrocarbons (HH)
- total cadmium (Cd)

- total phosphorus (P)
- total nitrogen (N)
- biochemical oxygen demand (BOD_5)
- chemical oxygen demand (COD)

- Coastal water (C)
  - basic oceanographic and meteorological observations (BO&M)
  - oil slick observations (OS)
  - faecal coliforms (FC)
  - petroleum hydrocarbons dissolved (PH)
- Suspended matter (SM)
  - total mercury (Hg)
  - total cadmium (Cd)
- Sediments (SD)
  - total mercury (Hg)
  - high molecular weight halogenated hydrocarbons (HH)
  - petroleum hydrocarbons (PH)
- Biota
  - total mercury (Hg)
  - total cadmium (Cd)
  - high molecular weight halogenated hydrocarbons (HH)
  - petroleum hydrocarbons (PH)
  - faecal coliforms (edible bivalves only) (FC)

2.2.2. Sampling and analytical methods

Generally for all the above mentioned parameters, standard sampling and analytical procedures proposed by UNEP (published in UNEP's series of Reference Methods for Marine Pollution Studies) were used. However, in cases where there were no methods recommended by UNEP, or if there was a shortage of recommended equipment in some institutions, standard, well-known procedures were adopted. Moreower, some institutions also used their own recently developed sampling and analytical procedures.

A detailed description of sampling and analytical procedures used in this monitoring programme is given in ANNEX II.

To improve the reliability and accuracy of the data obtained, participating institutions took part in standardization and intercalibration exercises organized at national and international level.

In this way the sampling and analytical procedures to determine the following group of parameters were standardized: basic parameters of effluents (national level), heavy metals (IAEA), chlorinated hydrocarbons (IAEA), petroleum hydrocarbons (IOC) and microorganisms (WHO).

2.3. Investigated areas and sampling stations

The pollution monitoring programme of the Adriatic Sea has been subdivided into:

1. Pollution sources monitoring with the aim to obtain information relative to the type and quantity of pollutants entering sea water from coastal sources.

2. Coastal waters monitoring, including estuaries which are under direct influence of pollutants (sewage outfalls) or indirect by rivers.

3. Reference areas monitoring, areas not under direct influence of pollutants from the mainland.

Pollution sources monitoring and coastal waters monitoring were carried out in the following areas:

- Slovenian coastal area (from Koper to Savudrija),

- Rovinj area (from the Lim channel to the Red Island),

- Pula area (from Peroj to the Rasa Bay).

- Rijeka area (from Moscenica to Crikvenica),

- Sibenik area (from Skradin to Zlarin),

- Split area (from Vranjic to Stobrec),

- Dubrovnik area (from Orebic to Cavtat),

- Montenegrin coastal area (from Herceg Novi to Ulcinj).

Reference areas were monitored at:

- The Rovinj-Po river profile,

- Kornati area,

- The island Vis area,

- Coastal area of Montenegro.

In Fig. 2.3.1 the positions of the investigated areas in the Adriatic and along the Yugoslav coast are indicated by arrows.

Figs. 2.3.2 - 2.3.15 show each investigated area in detail along with the sampling stations.

In the next chapter, each area will be briefly described geographically. In addition, a description of the station locations will also be given. The abbreviated name of the institutions in charge of monitoring activities is added in parentheses to the section titles.

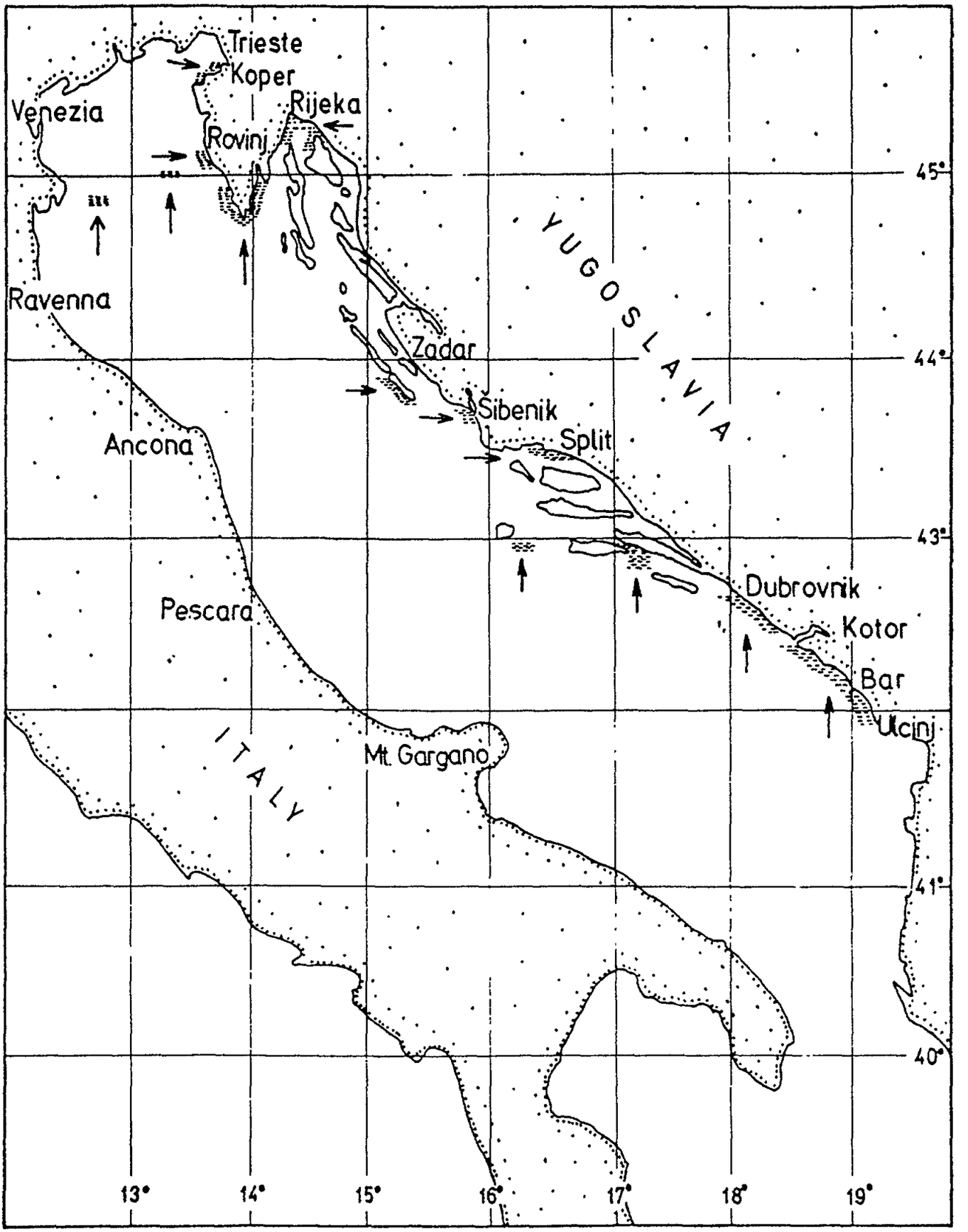


Fig. 2.3.1 The Adriatic coast - investigated areas

2.3.1. Slovenian coastal area (MRTC-P)

Monitoring was carried out along the Slovenian coast which includes the coastal sea from the Cape of Debeli Rtic to the Cape of Savudrija. It is a part of the Gulf of Trieste which is the most distant region of the marginal Adriatic sea.

In the greatest part of the coast in which the Bay of Koper and the Bay of Piran are located the flysch topography prevails, with the exception of the limestone Savudrian coast. To the east of the Koper and Piran bays there are the flat-bottomed valleys of the river Rizana and the river Dragonja.

The karst topography, which is extensively developed on the Istrian peninsula, continues farther under water and represents a deeper geological basis for the entire region. The Adriatic Sea reaches here a depth of about 20 m. Locally, depths up to 38 m are reached due to the buried karst relief.

The general circulation in the Gulf of Trieste can be conceived as a main gyre driven by the boundary conditions, i.e., by the flow coming from the Adriatic across the Grado-Savudrija line, modulated on a daily period by the local wind field. Semidiurnal tidal currents are ineffective as regards the water renewal in the Gulf. The ENE bora wind, which blows in Trieste, with a frequency of 21% and with a mean velocity of 6 m s^{-1}, is therefore the main agent for the renewal of the surface waters in this area.

The region is heavily populated (about 50000 inhabitants) and during the summer it is visited by a large number of tourists. However sewage is efficiently disposed into the sea by a long submarine outfall.

The Monitoring of Sources of Pollution was carried out at the following stations (Fig.2.3.2):

Pa, Pb, Ia, Ka, Kb - outlets of domestic sewage of the towns Piran, Izola and Kopar, respectively;

DE - outlet of industrial effluents discharged by the "Delamaris" fish canning industry, Izola;

RI, BA - stations in the Rizana and Badasevica streams polluted with industrial and agricultural effluents;

DN - station in the Drnica stream polluted with agricultural effluents;

DR - reference station in the relatively unpolluted Dragonja stream.

Samples from stations Pa and Kb represent wastes with primary (mechanical) treatment. All samples of industrial effluents are a mixture of fresh or brackish water and effluents.

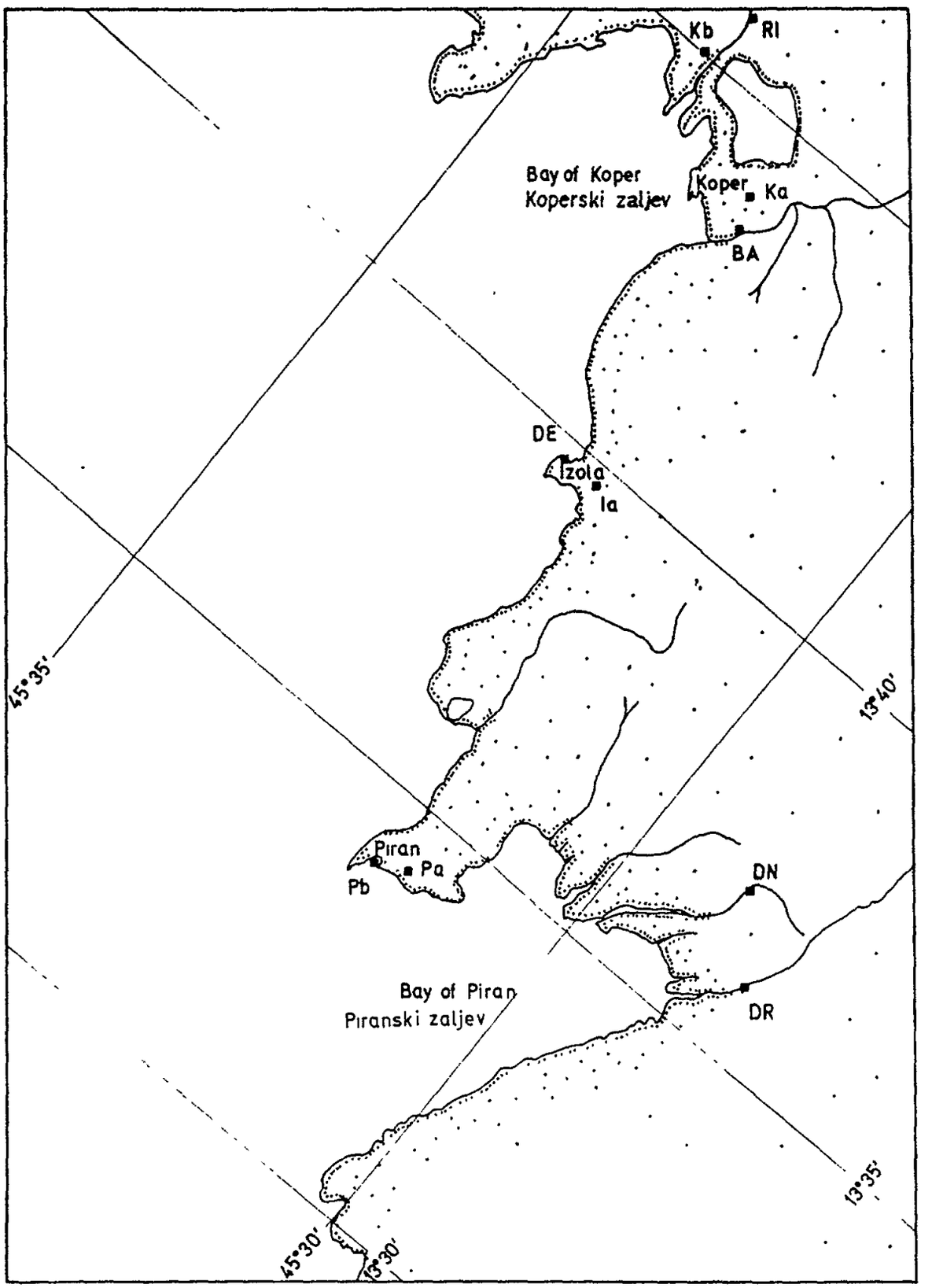


Fig. 2.3.2 Slovenian coastal area - effluent sampling stations

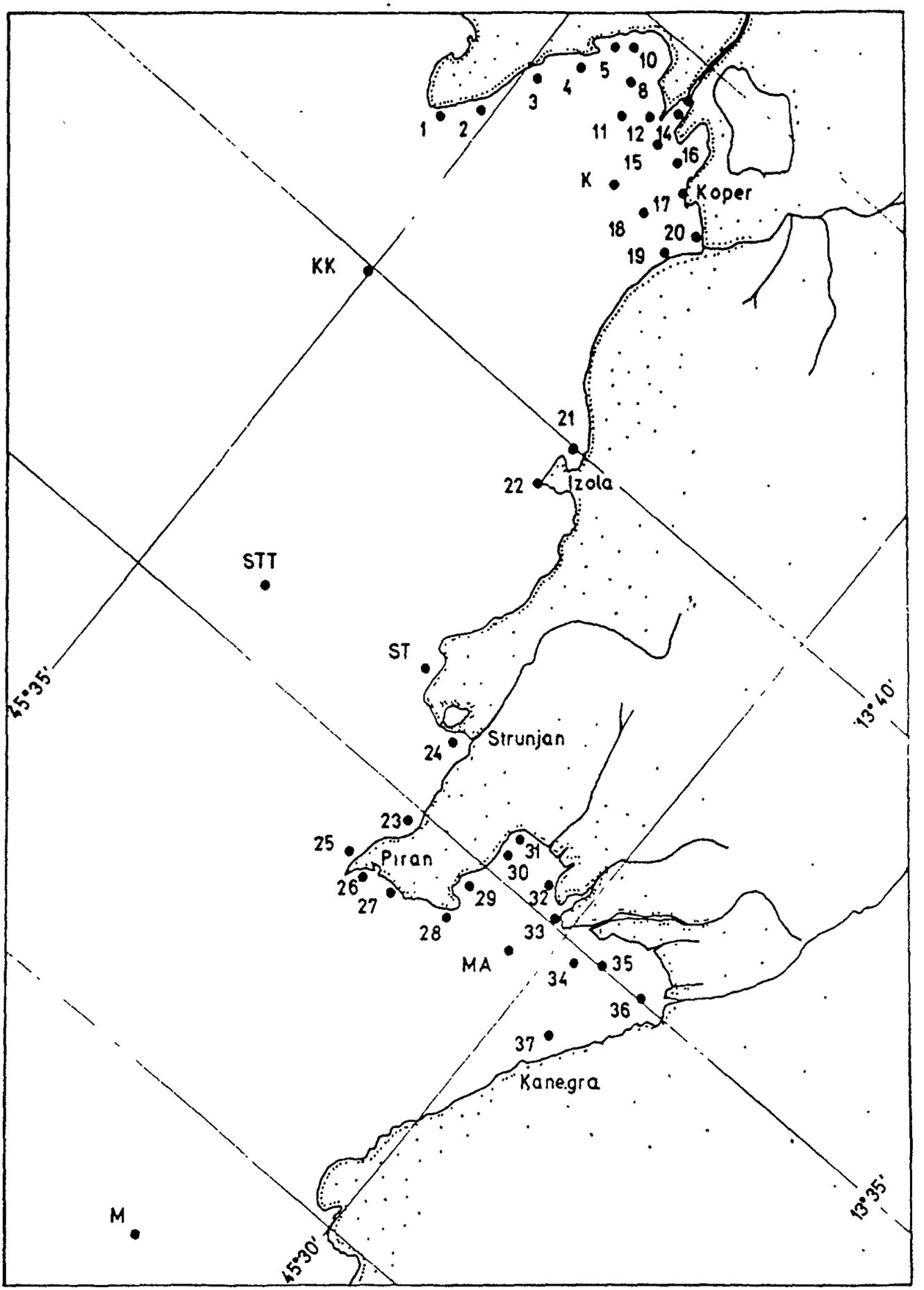


Fig. 2.3.3
Slovenian coastal area - coastal water sampling stations

The stations, at which the sampling for the programme Monitoring of Coastal Waters was carried out, are shown in Fig 2.3.3. At stations 1-37 bacteriological parameters were measured. The stations cover nearshore waters under the influence of urban agglomerations, including all public beaches and shellfish growing areas. At the stations labeled with capital letters monitoring of heavy metals in the sediments, suspended matter and in fish tissue was carried out. At stations K, ST and MA, the influence of pollution caused by human activities at the shore was monitored. At stations KK, and ST the possible influence of pollution from the open waters was monitored. Station M was chosen as a reference station.

2.3.2. Rovinj area (CMR-R)

The Rovinj coastal region is located in the central part of the western Istrian coast, north of the Pula region and south of the Porec region. The coast is rocky and relatively deep (up to 30 m a few hundred meters from the coastline), with many embayments and islands. Along the coastline the only urban centre is Rovinj, a town with a population of about 10000. However, in the summer, an additional 40000 tourists are accommodated in the town and in tourist villages and camping sites, situated a few kilometers to the north and to the south of town. The organic load is then increased several times, while sewage is disposed directly on the coastline without treatment.

Most of the urban sewage is discharged into the main harbour. Some of the sewage and wastewaters of the Mirna cannery, heavily loaded with organic material is discharged into the northern harbour (the Valdibora Bay). Sewage and wastewaters from a tobacco factory are discharged in the southern harbour (the Lone Bay), in which a marina with 200 yachts is operating. Each tourist village and camping disposes its waters through inadequate submarine outfalls, often near the beaches.

The construction of a modern system of sewage disposal through long submarine outfalls was started a few years ago. But the work proceeded slowly because of limited financial means.

The Lim Channel, located on the border between the Rovinj and Porec territories is a very narrow (less than 600 m) and relatively long (11 km) embayment of the western coast of Istria. In the first third from the entrance the depth reaches more than 30 m, decreasing gradually after that. The coastline is high (up to 100 m) and rocky and the bottom is muddy. The area is biologically very important as a fish spawning site and for specific vegetation. For these reasons it is under special protection and is reserved for mariculture. At present, about 750 tonnes of shellfish, (in a pilot farm) and about 20 tonnes of fish (sea bass) are produced. Water quality monitoring is essential for this region, for which a substantial increase in mariculture production is planned, in addition to the fact that there are restaurants in the inner part and large tourist centres at the mouth of the embayment. Furthermore, about fifteen springs discharge into the Lim Channel significant quantities of groundwater from a relatively large watershed within a very porous karstic region, which receives urban and industrial mostly untreated wastewaters, of about 15000 inhabitants.

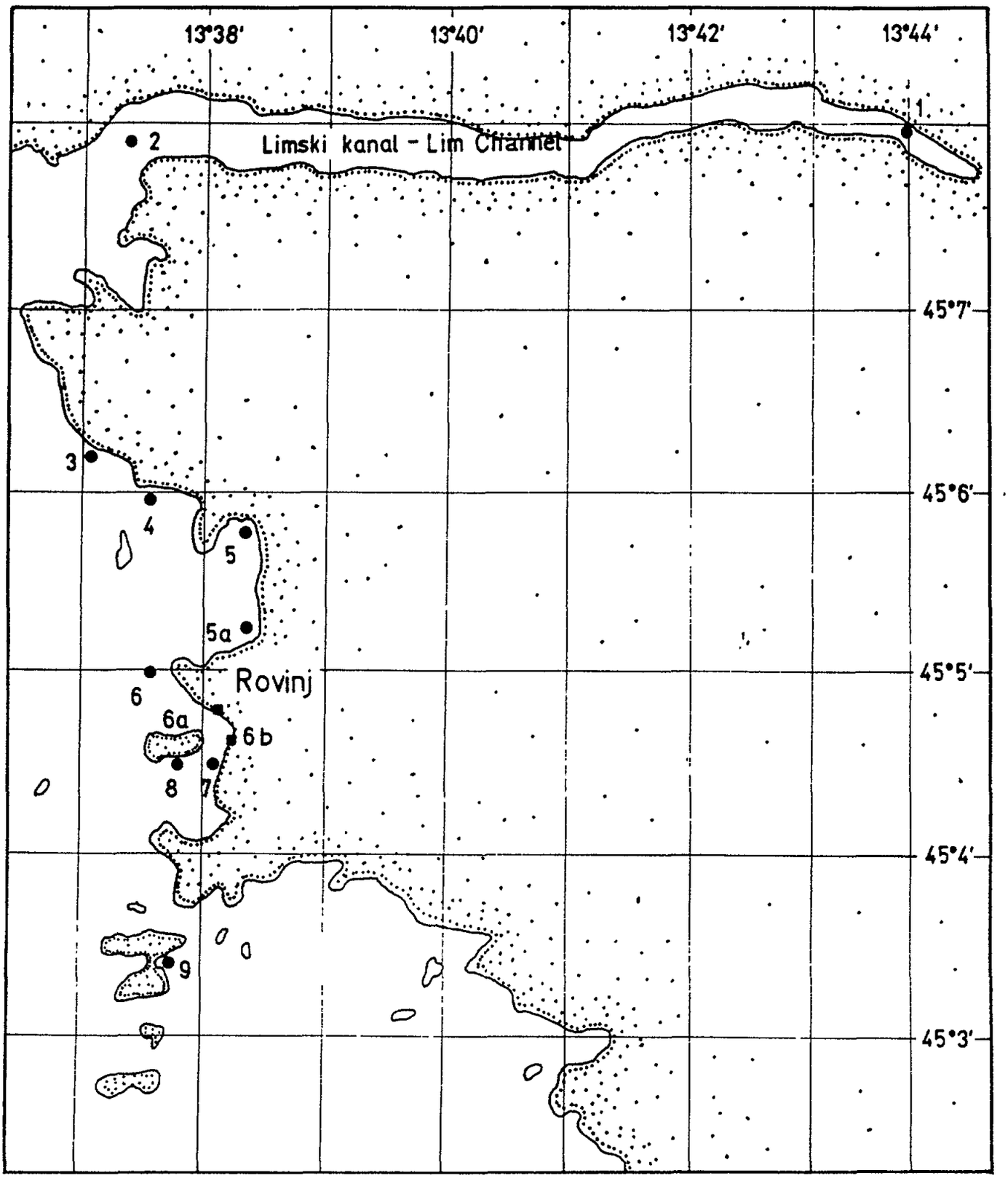


Fig. 2.3.4 Rovinj area - sampling stations

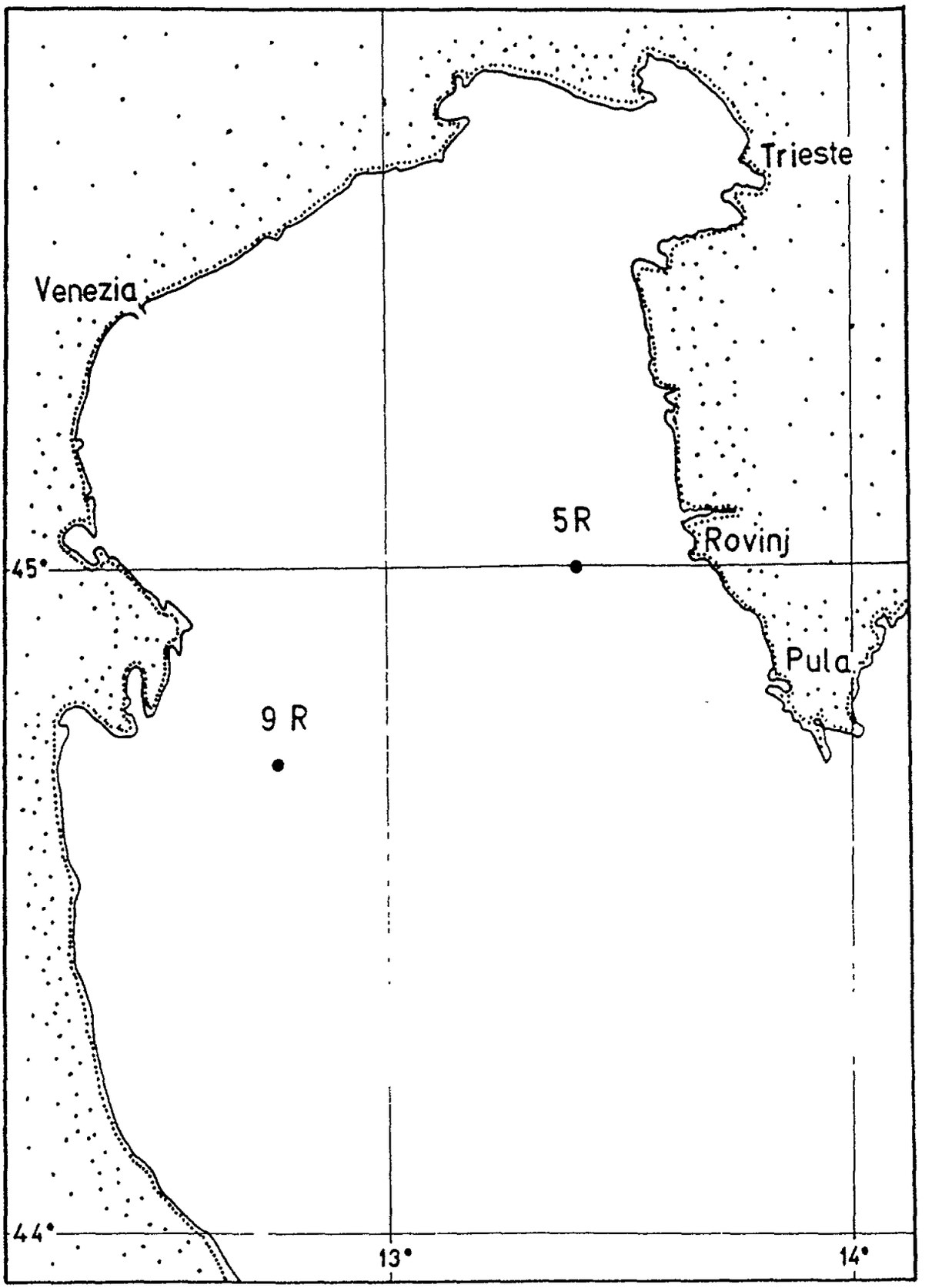


Fig. 2.3.5 Po profile - sampling stations

In the framework of the National Monitoring Programme, investigations focused on a limited coastal area surrounding the town of Rovinj and two main tourist centres to the north of the town, as well as in the Lim Channel.

The sanitary quality of the tourist centres and the Rovinj main beaches was monitored at stations 3 - 9. Additional pollutant measurements were carried out at station 5A in the northern harbour close to the discharge area of the Mirna cannery at stations 6a in the main harbour and 6b in the southern harbour, in the discharge area of the tobacco factory wastewaters (Fig. 2.3.4).

Effluents were collected from the wastewater system of the Mirna cannery (sampling point 5a - I) and of the tobacco factory (6b - II).

Measurements in the Lim Channel were performed in the inner part (station 1), in which fish and shellfish are grown and at the entrance of the embayment (station 2) to estimate the influence of the Istrian coastal waters (Fig. 2.3.4). The northern Adriatic open waters were monitored at two stations (Fig.2.3.5). During winter station 5R, 25 km off Rovinj, is under the influence of oligotrophic waters from the central Adriatic. But in the spring and summer the eutrophic influence of the fresh waters from the western part of the northern Adriatic prevails in the surface layer at this station. Station 9R, 25 km to the southeast of the Po River delta, is constantly under the influence of fresh water very rich in nutrients and pollutants.

2.3.3. Pula area (IPH-P)

The Pula area coastline is characterized by numerous natural bays, coves, gulfs, harbours, inlets and islands. The beaches consist predominantly of natural rock and gravel, while only a smaller part is sandy.

The total length of the beaches monitored amounts to 192 km, 55 of which are adequate for bathing. Thus, in this part of the Istrian peninsula tourism is quite developed.

In the town of Pula and in the large suburban areas live about 75000 residents. During the tourist season the total population is doubled and in some areas it is increased more than ten times.

Along the coast, from Peroj to Medulin, there are large tourist centres with many hotels, restaurants and other facilities, various recreational centres and campings as well as small and large tourist villages.

The western and southern parts of the coast are under the influence of pollution caused by wastewaters from industry, urban areas, tourist villages and agriculture. This area also includes the Pula harbour in which 20000 m^{-3} d^{-1} of faecal and industrial wastewaters are discharged through 14 outfalls directly on the coastline.

In the harbour, intensive dinoflagellate blooms (red tide) occur periodically. On the remainder of the western and southern coasts mostly untreated sewage from the urban and tourist areas are discharged into the sea through about twenty five outfalls of different lengths.

Pollution sources were monitored at the following sampling points (Fig.2.3.6):

I - Pula outfall effluents,

II - Medulin tourist centre outfall effluent,

SI - chemical industry outfall effluent,

RA - the Rasa River polluted by industrial effluents.

The eastern part of the Istrian coast, although not under direct influence of pollution from the urban centres, is polluted by urban, industrial and agriculture wastes carried into this region by karstic groundwaters and by the Rasa river.

The Rasa Bay is an elongated (less than 1000 m wide, 13 km long), irregular embayment with very high coasts. The depth at the entrance is about 40 m, gradually decreasing toward the end of the bay, where the waters of the Rasa River are discharged. The region also receives groundwaters through numerous springs from a watershed extending to the central Istrian region. The Blaz Bay spring has a flow rate of 0.5 m^{-3} s^{-1}. The bottom is muddy, and in a shallow narrow coastal belt, sandy or rocky. Research has shown that some sites in the bay are biologically suitable for shellfish cultivation, but the sanitary quality of the water is not always satisfactory.

Monitoring of the coastal waters pollution was carried out at the following 13 stations (Fig. 2.3.6):

Peroj and Valbandon areas, with several small and large recreational centres,

Valovine, Banjole, Premantura and 2 sites in the Medulin area in which the urban centres, recreational sites, hotels, bungalows and tourist villages are numerous,

The Gortan cove, the tourist areas around the hotels Splendid and Brioni with about 90000 inhabitants and tourists during the summer.

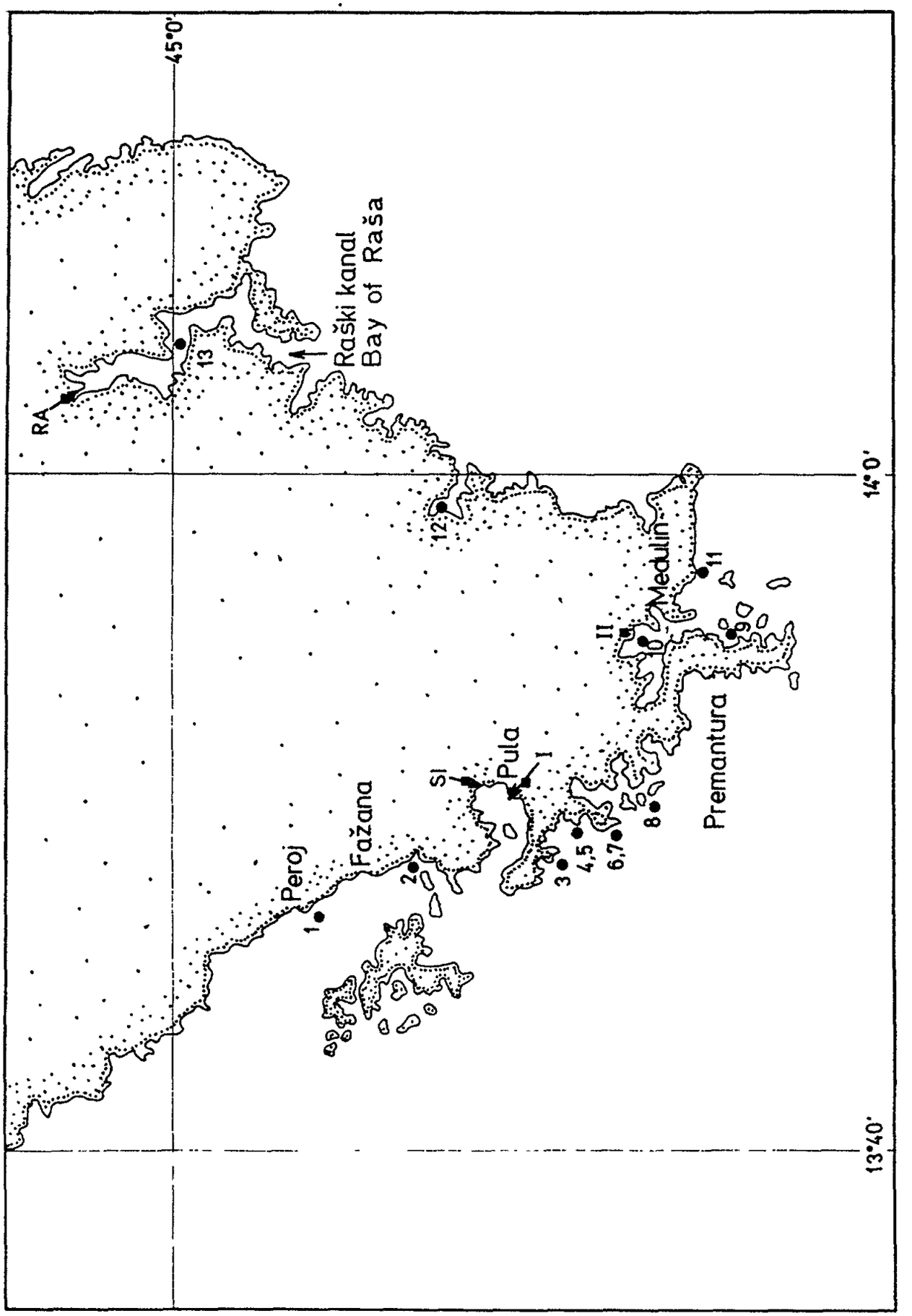


Fig. 2.3.6 Pula area - sampling stations

On the eastern side of the Istrian coast, monitoring was carried out at one station in the Budava Bay and the Rasa Channel. Mussels Mytilus galloprovincialis and sediments were also analyzed.

2.3.4. Rijeka area (FCES-Z and CMR-Z)

The Rijeka coastal region is narrow and separated from the hinterland by mountains. The coast is rocky and very steep.

The Rijeka Bay (about 450 km^2), with a depth of about 60-65 m, receives large quantities of freshwater discharged into the sea from mountain streams, coastal and submarine springs and by the Rijecina river, particularly during the rainy season. The water exchange with the oligotrophic Kvarner area is relatively fast, especially in winter. In the other seasons however vertical circulation limits the exchange in the northernmost part of the bay.

The greatest freshwater contribution occurs in the area of the Bakar Bay, as well as on the entire northern coastline from Moscenicka Draga to Bakarac.

In the Rijeka Bay area, including the city of Rijeka and other coastal towns and settlements, live about 200000 people. During the tourist season the population doubles. The wastewaters of towns and settlements enter the sea mainly untreated, directly on the coastline or through inadequate submarine outfalls.

The coast of the Liburnia riviera and the Vinodol Channel is an exclusively tourist area. On the northern coast of the Krk island, tourist and industrial facilities are both present. The major part of the Rijeka coast is occupied mostly by harbours and industries.

Among the biggest industrial plants here are oil refineries in Rijeka and Urinj, an oil terminal in Omisalj, a petrochemical complex in Omisalj, all discharging high quantities of wastewater. The port of Rijeka and a number of minor industries located in the Rijeka city area also represent significant pollution sources.

Pollution sources were monitored at the following sampling points (Fig. 2.3.7):

U-1 - Opatija outfall effluents,

U-2-5 - Rijeka outfall effluents,

U-6 - industry outfall and urban effluents mixed,

U-8-12 - Martinscica, Bakar, Kraljevica, Crikvenica and Omisalj outfall effluents,

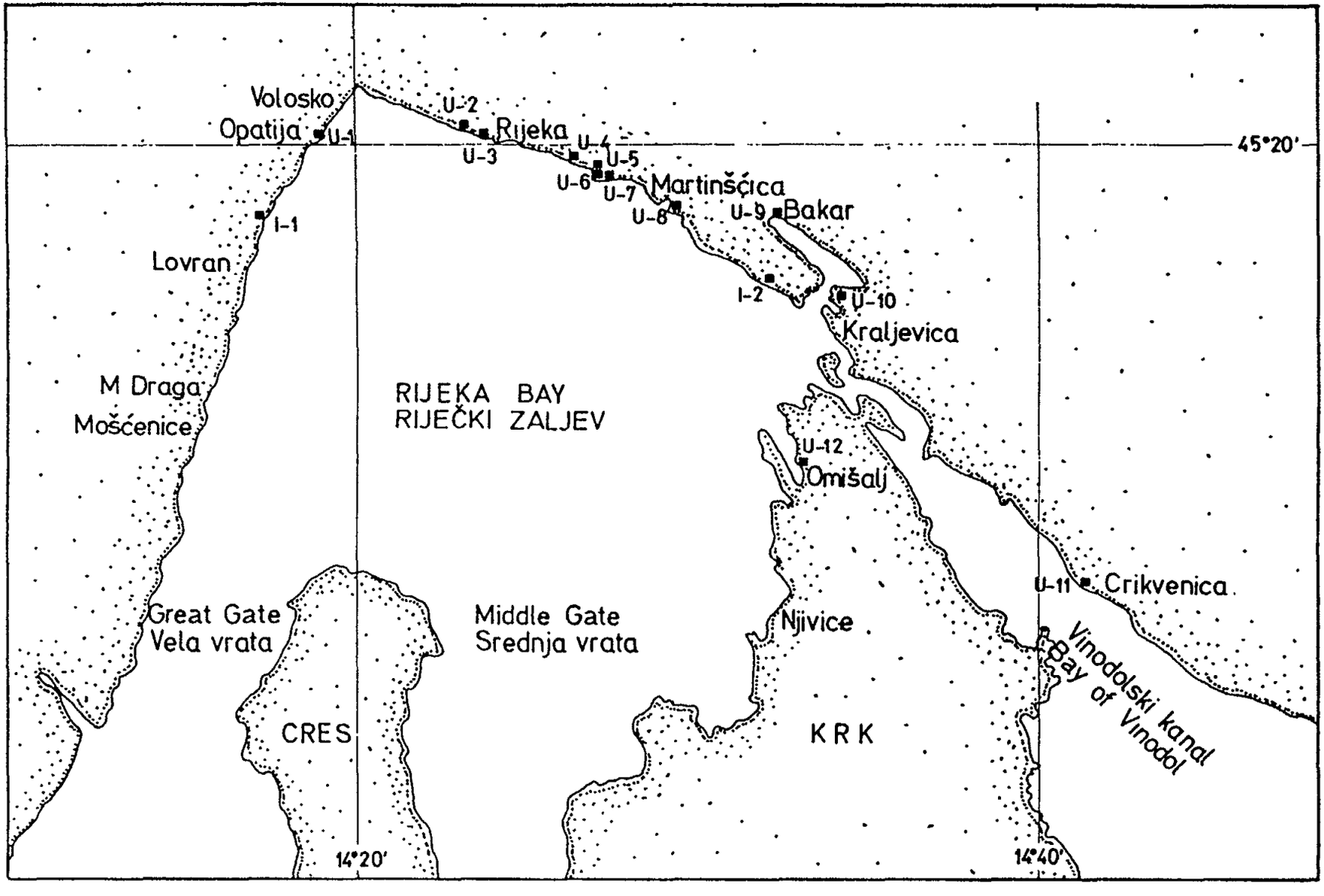


Fig. 2.3.7 Rijeka area - effluent sampling stations

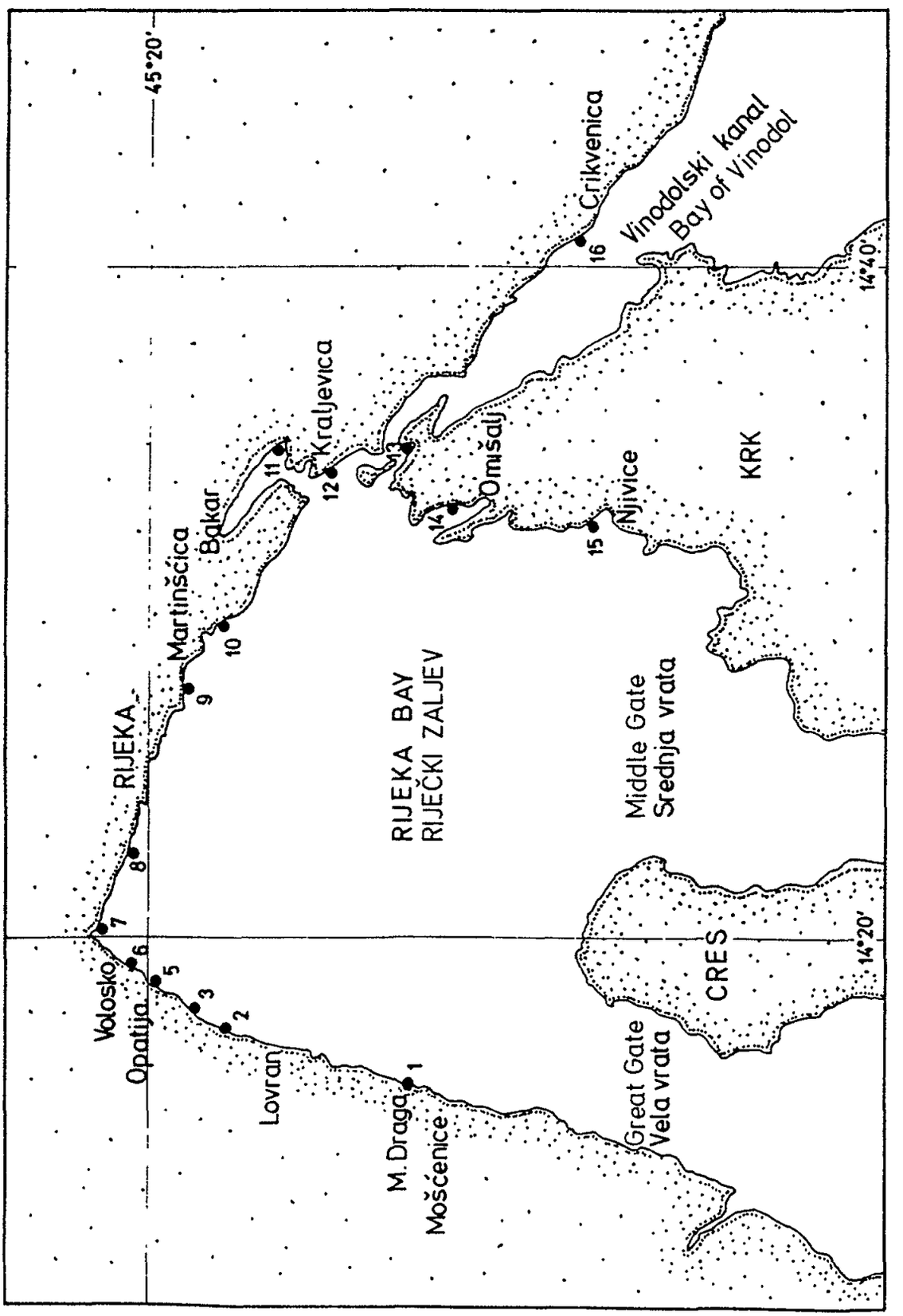


Fig. 2.3.8 Rijeka area - coastal water sampling stations

I-1 - Ika outfall effluents and fish processing plant outfall effluents, mixed,

I-2 - Urinj oil refinery effluent outfall.

The coastal sampling stations are shown in Fig.2.3.8. Stations are distributed along the Liburnia riviera (stations 1-6), the Rijeka coastal area (stations 7-22), the northern coast of Krk island (stations 13-15) and in the Vinodol Channel (station 16).

Faecal coliforms in the sea and in marine organisms were monitored at beaches of Moscenicka Draga, Lovran, Opatija, Volosko, Rijeka, Kostrena, Bakarac, Kraljevica, Omisalj to Njivice, as well as those of Crikvenica in the Vinodol Channel.

2.3.5. Sibenik area (CMR-Z)

The watershed of the 72.5 km long karstic Krka River and its estuary accounts for about 2100 km^2. The estuary is 25 km long and of complex morphology, with several channels, Lake Prokljan and Sibenik Bay. In the region the population is 53000 people, most of whom (72%) are concentrated in the lower part of the estuary in the city of Sibenik. The latter is an industrial centre with metal working (iron alloys, aluminium production) and shipping activity,including transport of phosphate ores. Tourism (about a million per year) and mariculture are also developed. The Skradin marina (upper estuary) capacity is about 100 yachts. In contrast, agriculture and forestry activities are negligible.

The region of the Kornati Island National Park is not under direct anthropogenic influence and may be used as reference to evaluate the water quality of the Sibenik coastal area and the Krka River estuary.

Due to the importance of this area, which has two national parks, mariculture and tourist activities, but also several industries and no wastewater treatment plants, the need for pollution control has been fully recognized.

Pollution sources were monitored at sampling point S-1 in the light metal and food processing plant effluent outfall (Fig. 2.3.9).

In the monitoring of coastal waters the following stations were included (Fig. 2.3.9): 6 stations in the estuary (E-1, E-2, E-3, E-4, E-4A and E-5), two coastal stations (C-1, C-2) in front of the entrance to the estuary and one (C-3) near the beach of the Solaris tourist complex. Microbiological pollution was measured at three locations on larger beaches located in the vicinity of the stations at which other parameters were determined.

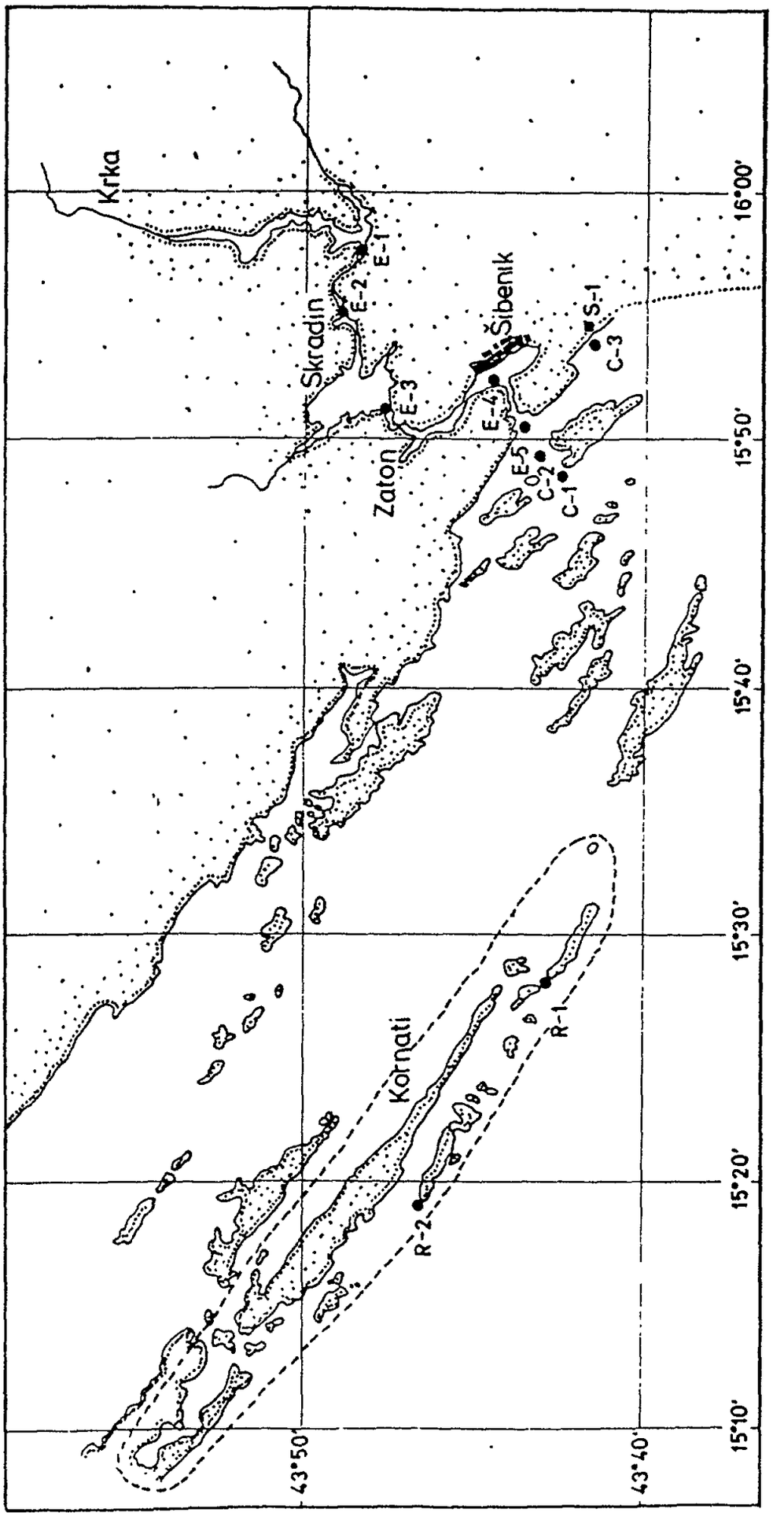


Fig. 2.3.9 Krka estuary and the Kornati Archipelago - sampling stations

In order to measure the effects of pollution in the estuarine area, stations R-1 and R-2 within the Kornati Island National Park, (Fig. 2.3.9),which is not under direct influence of pollution, were selected as reference stations.

During seasonal cruises, chosen in the characteristic periods with respect to the Krka river flow rate, meteorological conditions and biological activities, measurements of the basic hydrographic, chemical and biological parameters, nutrients, organic matter and pollution parameters (heavy metals, petroleum and chlorinated hydrocarbons, detergents and faecal coliforms) in the water, organisms and sediments were carried out.

2.3.6. Split area (IOF-S and IPH-S)

In the Split urban area live about 250000 inhabitants. By size it is the second largest city on the Yugoslav Adriatic coast. The Split area and the region of the southern Adriatic make a unique geographical area with common Mediterranean characteristics with respect to climate, landscape, culture and economy.

The whole coastal region is bound by the mountain massif which separates the city of Split from its hinterland. To the south of the city there are the Dalmatian islands. The Ciovo Island is close to the Bay of Kastela. The inner islands of Drvenik, Solta and Brac are located to the south and border the Split and Brac Channels.

Close to the geographical centre of the Split region a promontory with the Marjan hill covered with a pine forest rises from the sea. At the foot of the Marjan hill, in an easterly direction, lies the historical centre of the city. In front of it there is the city harbour for passenger and cargo ships. On the other side of the promontory, within the Bay of Kastela, there is a new commercial and industrial port, cement plants, chemical plants, shipyards and other factories. To the north of the Marjan hill there is the well-developed, wide Kastela plain. In several places in the coastal region extending from the city of Split to Stobrec there are sheer rocks rising from the flat land.

Pollution sources were monitored (IPH-S) at 7 stations of the Split sewage system through which urban and industrial effluents are discharged (Fig.2.3.10).

In the Split coastal area, investigations were carried out in the coastal sea region, from the easternmost part of the Bay of Kastela (the Vranjic basin) to Stobrec, where the estuary of the river Zrnovica is situated. Nutrients, heavy metals, PH and HH were monitored to identify possible effects of industrial (station 1) and urban wastewaters (station 5) as well as of freshwater in the estuarine area. On the city beaches, in addition to the basic hydrographic parameters, the sanitary quality of the seawater was followed up as well (stations 2-4, 6-10 ; Fig. 2.3.11).

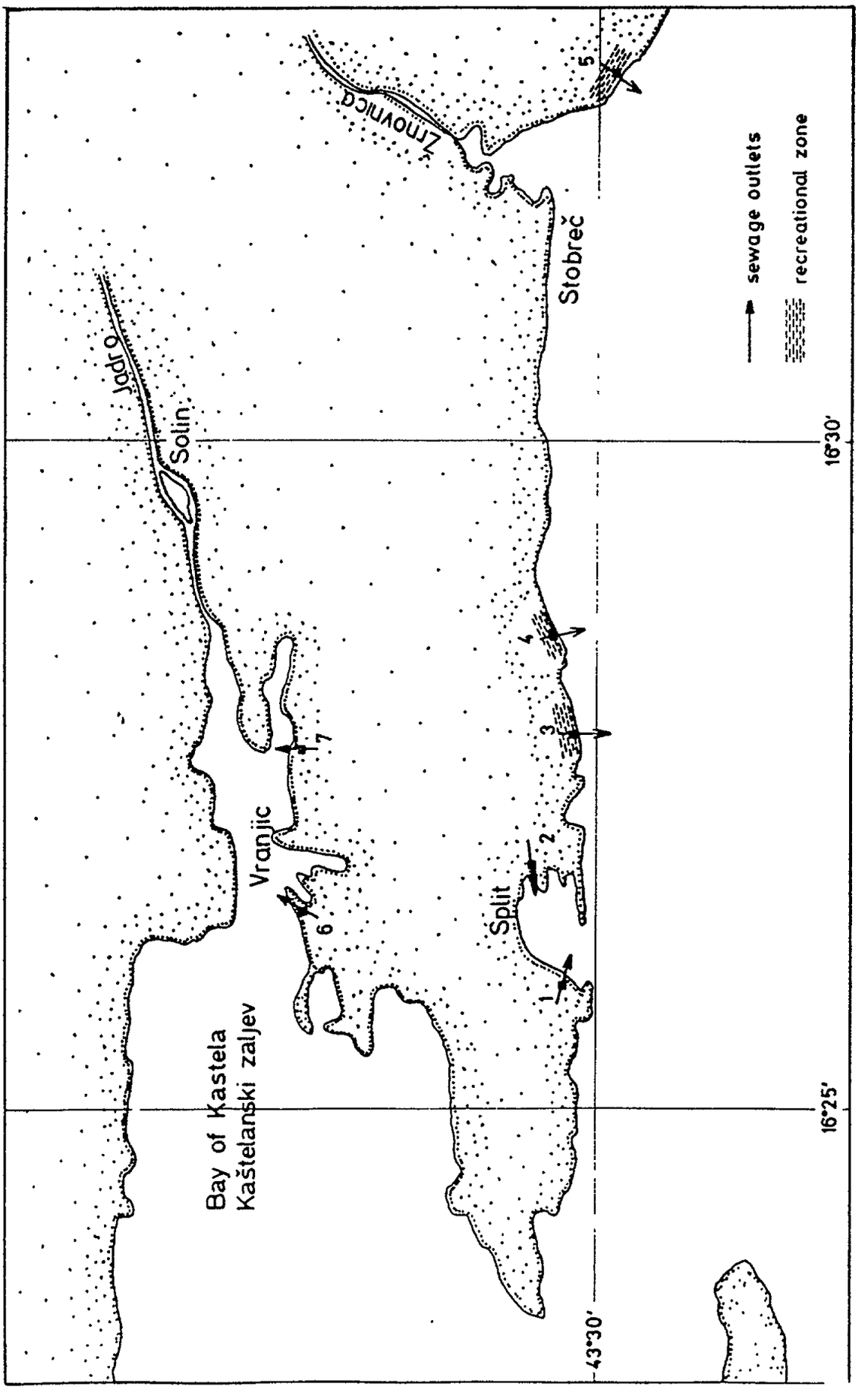


Fig. 2.3.10 Split area - effluent sampling stations

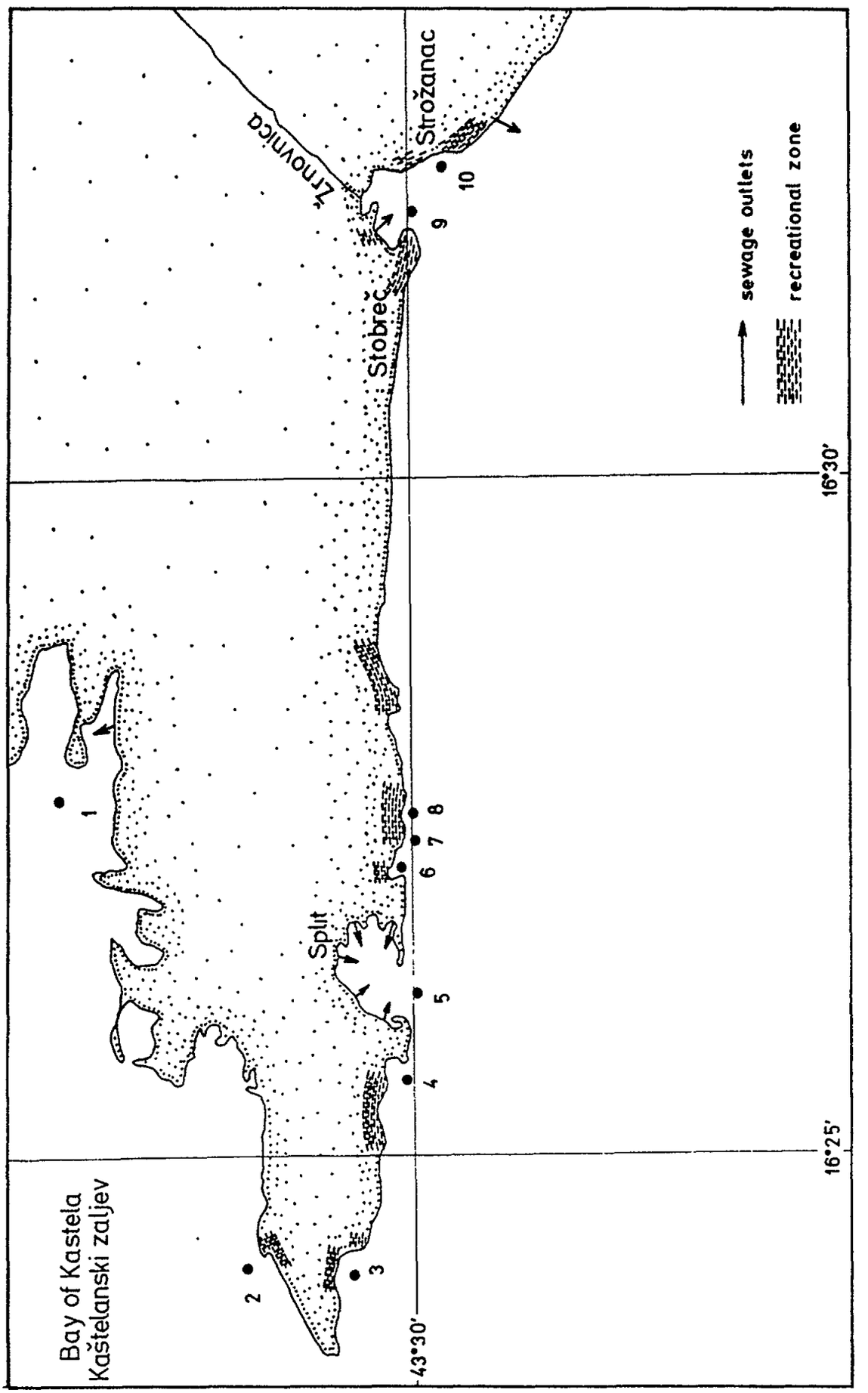


Fig. 2.3.11 Split area - coastal water sampling stations

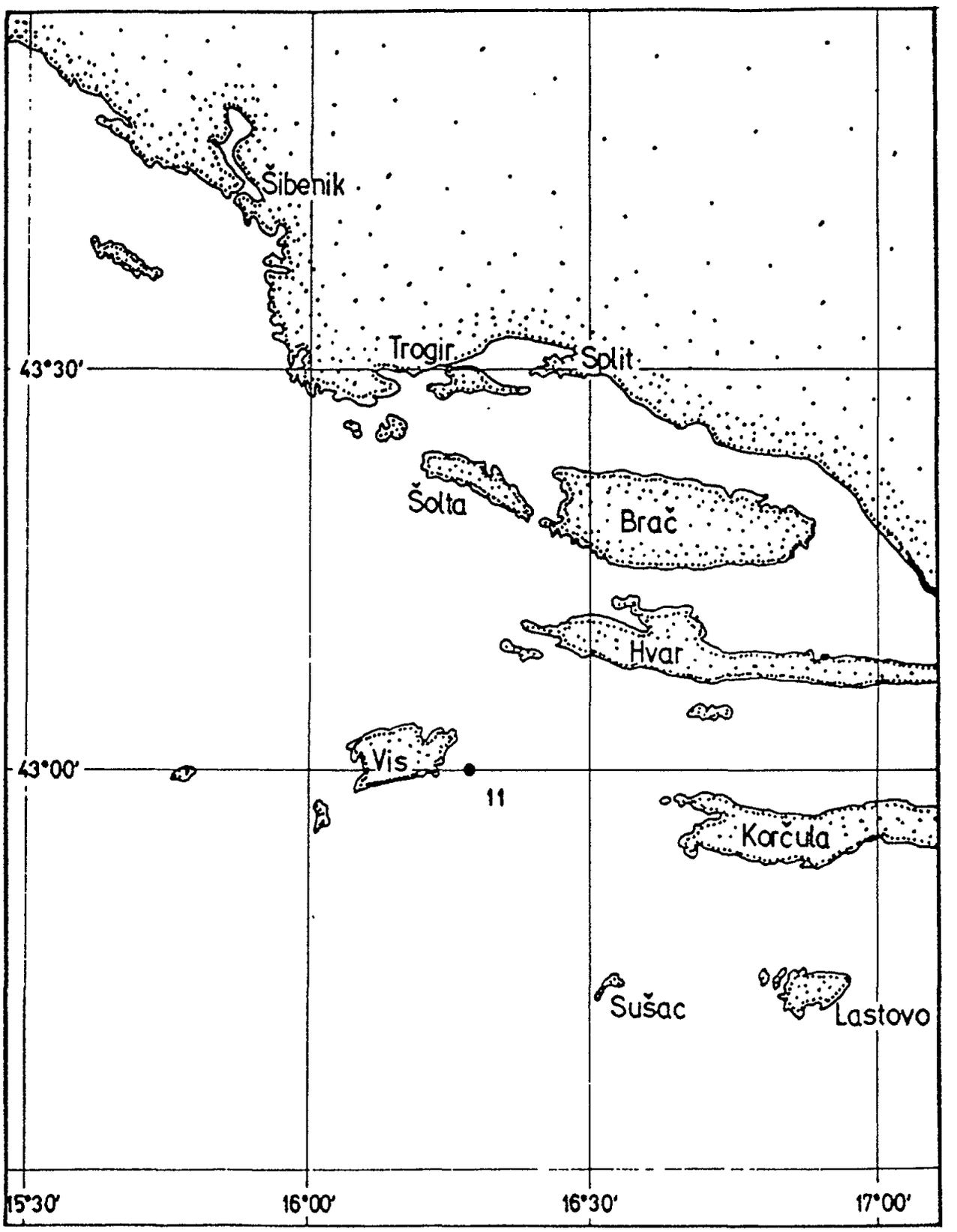


Fig. 2.3.12 Vis island area - reference station

The location of the stations at which mussels (Mytilus galloprovincialis) were collected for the *DDT, TDE, DDE,* dieldrine and PCB investigations is somewhat different. Namely, sampling station 1a was located in the industrial zone, close to station 1, while station 3a was situated on the opposite side of the Bay of Kastela, on the island of Ciovo, where there are no significant sources of pollution.

As a reference area for all parameters an open sea station, close to the Island of Vis, was chosen (station 11; Fig. 2.3.12).

2.3.7. Dubrovnik area (BI-D)

The Dubrovnik area covers the Mali Ston Bay, the Peljesac Channel and the area of the city of Dubrovnik with 30000 inhabitants.

The continental area near the coast is made of a highly permeable limestone mass, which has specific hydrogeological characteristics and causes intensive drainage towards the sea through shallow holes and submarine springs during the rainy periods. The transport of allochthonous inorganic and organic materials is especially intensive in the Malostow Bay area.

The fate of pollutants in the coastal area is strongly influenced by seawater currents. In addition, due to specific meteorological and hydrographic conditions in the eastern Adriatic, the strong north and south winds influence the exchange of water between the open sea and neritic regions especially in winter.

During monitoring samples were taken in three areas (at 5 stations): in the Malostow Bay, the Peljesac Channel, near the city of Dubrovnik and Cavtat (Fig. 2.3.13). Station 1 at Bistrina, an inlet of the Malostow Bay, is an important oyster and mussel farming place in the southern Adriatic. In the period of strong west winds, it may be influenced by the Neretva River waters. The highly productive lowland in the area of the Neretva river estuary abounds in fruit trees, vegetables and flowers. Some industry is located upstream from the Neretva river. In the Malostow Bay area a stronger influence of underground freshwater is noticed, especially in winter and spring. In this area surrounded by a dense vegetation cover, there are only a few minor settlements. Station 2 (Orebic) is influenced by a strong current which comes from the south and brings clean oligotrophic eastern Mediterranean and south Adriatic water towards the middle and north Adriatic regions. Station 3 is situated on the eastern coast of the island of Daksa in the vicinity of the harbour of Dubrovnik. The harbour itself and a small ship-repairing yard, in which motor boat servicing and paint work are carried out, are possible sources of heavy metal and chlorinated hydrocarbons pollution. Stations 4 and 5 are located in the vicinity of several tourist centres, but are strongly influenced by the open sea waters.

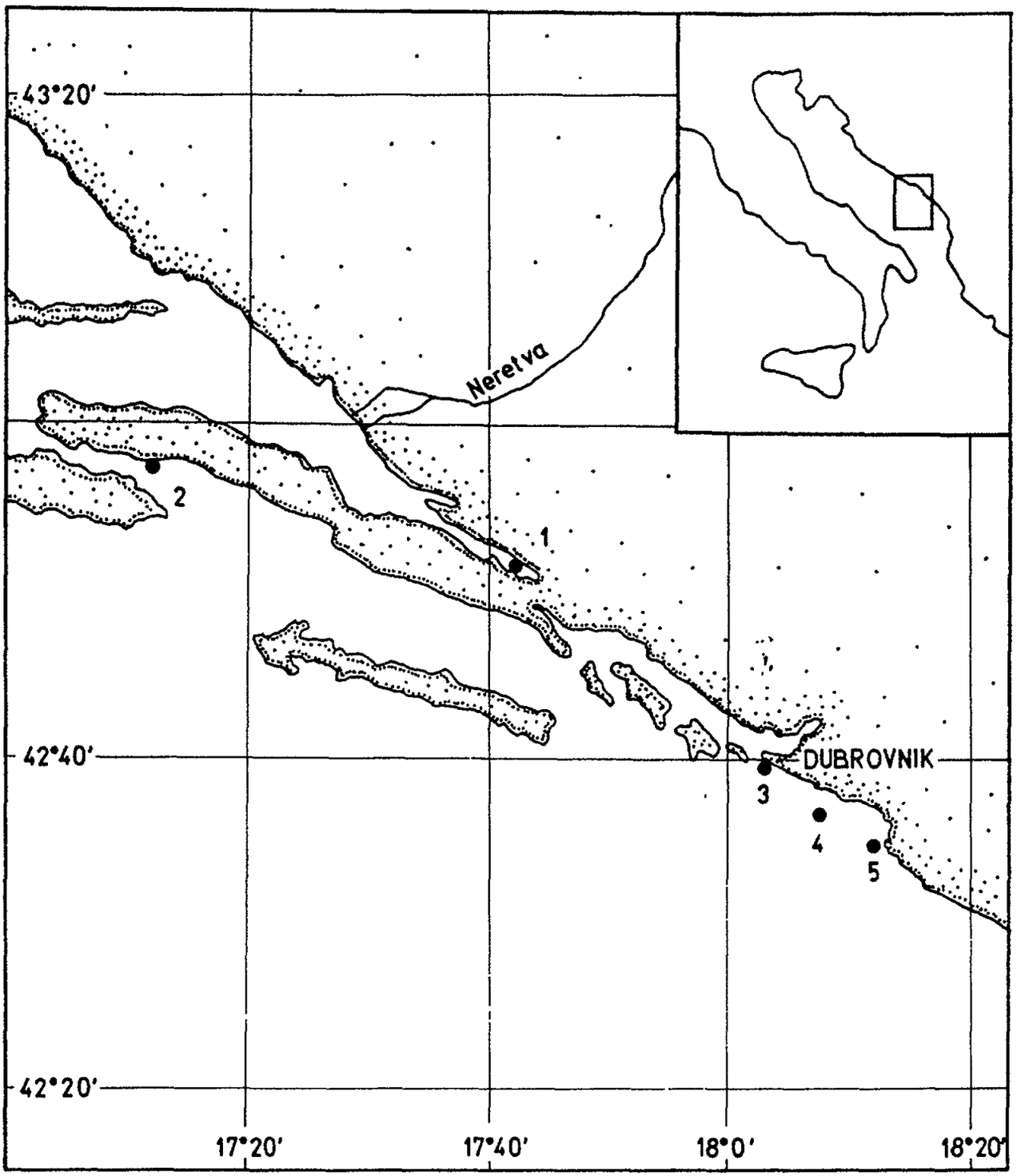


Fig. 2.3.13 Dubrovnik area - sampling stations

2.3.8. Montenegrin coastal area (IMB-K and ISCEP-B)

The Montenegrin littoral is a narrow zone located in the area between the town Herceg Novi and the Bojana river, sharply separated from the hinterland by the Orjen, Lovcen and Rumija mountains. Its width is only 10 km in the region of Gulf of Kotor and Ulcinj while at Budva it is even less than 2 km.

In the vicinity of the coast, limestone hills alternate with Quaternary sedimentation regions in which shallow and gentle marine embayments were formed with sandy and gravel beaches. In contrast, in the northernmost part of the region the irregularly elongated Kotor Bay cuts deeply into the coast.

Due to the recent intensive economic development, the coastal region is almost completely urbanized. At present the resident population stands at 120000, the number doubling in summer during the tourist season.

In the waters of the Kotor Bay (Fig. 2.3.14) measurements were performed off Igalo (station 1) in the entrance zone of the bay, in which open waters mix with the bay waters, off Bijela (station 2) near a shipyard, off Orahovac (station 3) near mariculture facilities (shellfish) and off Kotor (station 4), in which the influence of sewage and industrial wastewaters (detergents, metal and rubber products) is evident. Station 1, located in front of the entrance to the bay, represents a reference station for open waters.

In the region of Budva (station 5) and near the Sv. Stefan Island (station 6; Fig. 2.3.14) the influence of land is minimal.

In the Bar region (Fig. 2.3.15) station 8 is located in front of the Rikavac Stream mouth (loaded with hospital and food industry wastewaters), station BA is within and station 7 outside the city harbour. Reference station II is located 3 km off Budva.

In the southernmost part of the region (Fig. 2.3.15) station 9 is located on the main sandy beach, which is influenced by discharges from a hotel complex and agriculture water drainage, station UL is in the Ulcinj harbour and station 10 in front of the Bojana River mouth. This river is connected to the Skadar Lake, which is loaded with wastewaters from a large agroindustrial complex.

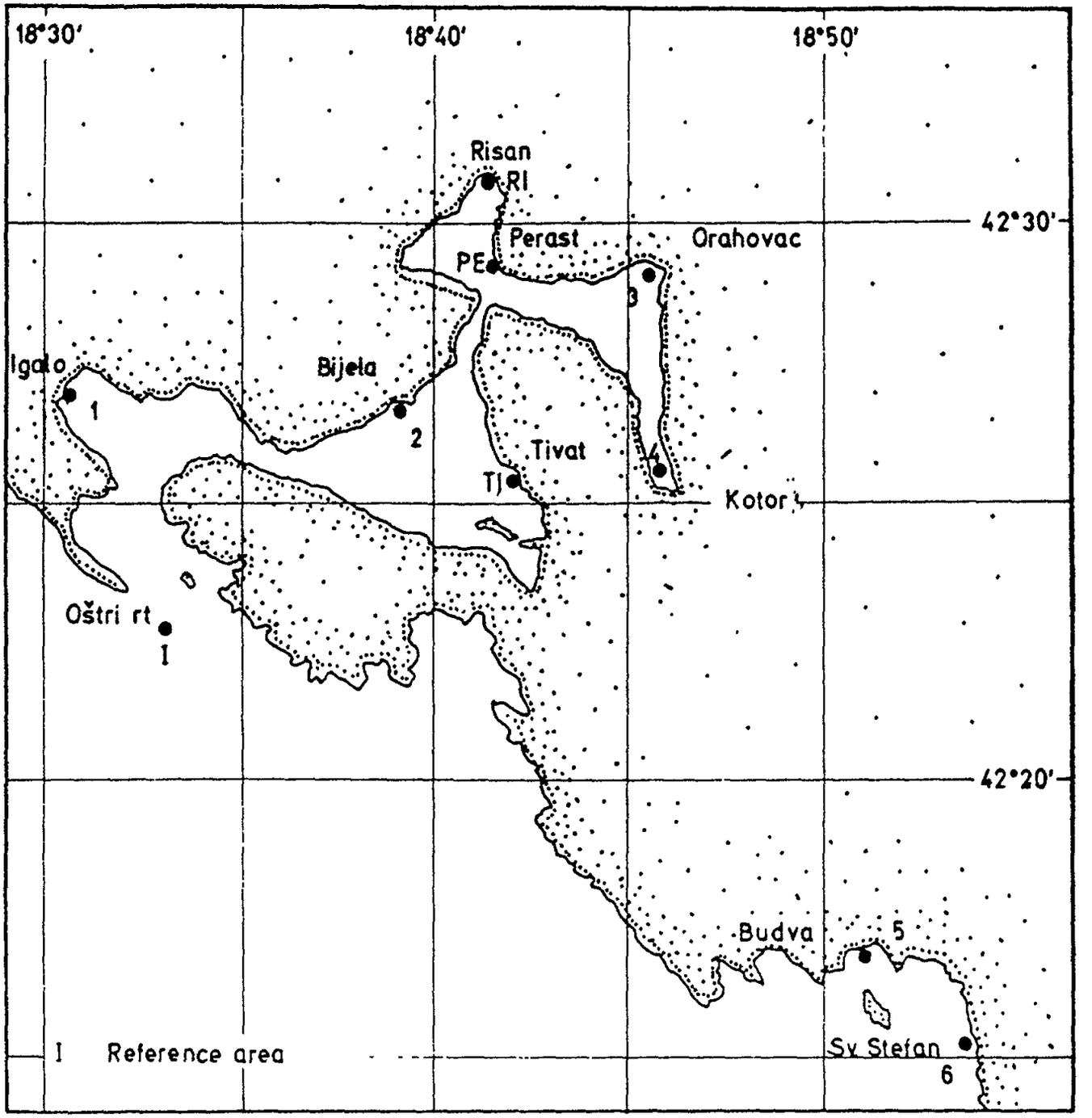


Fig. 2.3.14 Gulf of Kotor area - sampling stations

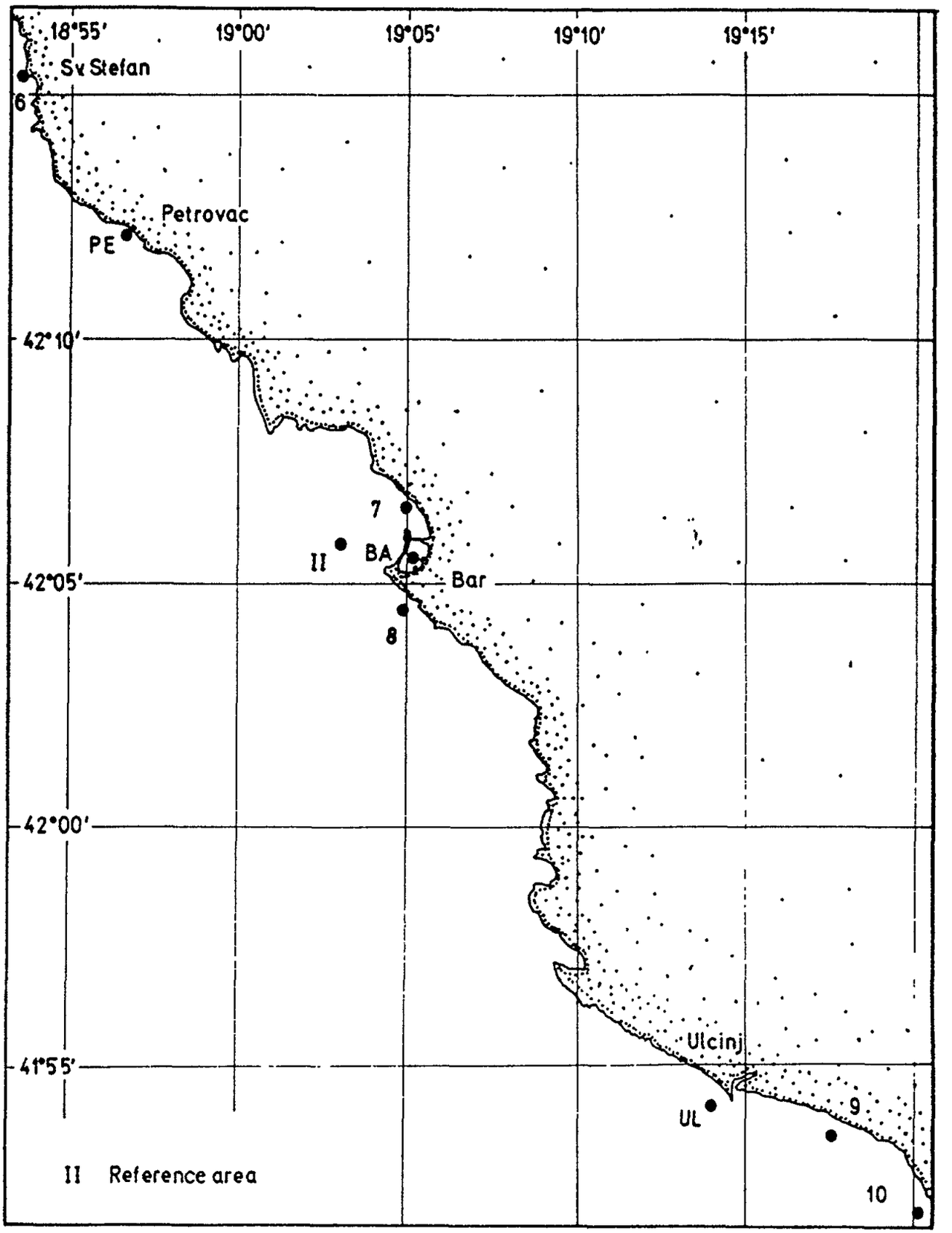


Fig. 2.3.15 Montenegrin coastal area - sampling stations

2.4. Measurement frequency

Effluents

Biochemical (BOD_5) and chemical (COD) oxygen demands, total suspended solids (TSS), total nitrogen and total phosphorus were determined in the effluents of the Slovenian coastal area twice a year and seasonally in the Pula, Rijeka and Split areas. In the wastewaters from the Pula, Rijeka and Split regions pH, ammonia, nitrite and nitrate were also determined.

Heavy metals in effluents were monitored in the Sibenik and Slovenian coastal areas twice a year and seasonally in the Pula, Rijeka and Split areas.

Detergents were determined in the Slovenian coastal area twice a year in Pula, Rijeka and Split areas seasonally and sporadically in the Sibenik and Montenegrin areas.

Phenols were measured seasonally in the Pula, Rijeka and Split areas.

In the Rijeka, Sibenik and Split areas petroleum hydrocarbons were monitored seasonally and sporadically in the Montenegrin coastal area.

Chlorinated hydrocarbons were monitored three times in only one year in the Rijeka area.

Faecal coliforms were determined seasonally on the Slovenian coast and in the Rovinj, Pula, Rijeka and Split areas.

Sea water

Total nitrogen and total phosphorus were monitored monthly in the inner part of the Lim Channel (station 1, 15 m, station 2, 32 m). These parameters were also measured seasonally in the open northern Adriatic, (station 5, 37 m, station 9, 32 m). Total phosphorus was determined seasonally at the Krka River mouth (station E1) and its estuary (station E2-E5, E9, 8-42 m), in the Sibenik coastal region in front of the estuary entrance (station C1 and C2, 20-32 m), at the Solaris hotel beach (C3) and in the Kornati Island region (R1 and R2, 20-30m).

Nutrients (ammonia, nitrite, nitrate, reactive phosphorus) and basic oceanographic parameters were determined seasonally in the regions described above, as well as at three stations in the Split region (S2, the Vranjic Bay, 22 m, S5, the Split harbour, 10 m, S9 the Zrnovica River estuary, 12 m) and at the reference station near the Island of Vis (S11, 100 m).

Total phosphorus, ammonia and Kjeldahl nitrogen were determined seasonally in samples collected at one point on the shore in the Budava and Rasa Bays.

Heavy metals in estuarine and seawater samples were analyzed seasonally in the Sibenik area, twice a year in the Dubrovnik area and once a year in the Montenegrin coastal area.

Oil slicks and other floating material were monitored sixteen times a year in the Rijeka area. In the Sibenik and Split areas dispersed/dissolved petroleum hydrocarbons were monitored seasonally.

Phenols and detergents were analyzed sporadically in the Sibenik and Montenegrin areas.

Faecal coliforms were determined biweekly from June to September and monthly in February, May, October and December on the Slovenian and Montenegrin coasts, in the Rovinj, Pula, Rijeka and Split areas and sporadically in the Sibenik area.

Sediments

Heavy metals in sediment samples were measured twice a year in the Slovenian coastal area, the Rovinj area and Split area, once or twice in the Pula area, from one to four times in the Sibenik area and once a year in the Montenegrin coastal area.

Chlorinated hydrocarbons were determined once a year in the Pula, Sibenik, Dubrovnik and Montenegrin areas. Petroleum hydrocarbons were analyzed with the same frequency in the Sibenik and Split areas.

Marine organisms

Heavy metals in marine organisms were measured twice a year in the Rovinj, Dubrovnik and Split areas, seasonally at the Rijeka and Slovenian coastal areas, from one to three times in the Sibenik area and once in the Montenegrin coastal area.

Chlorinated hydrocarbons were determined seasonally in mussels from the Rovinj, Pula, Sibenik, Split and Dubrovnik areas and sporadically in the Montenegrin coastal area. In the net plankton from the open northern Adriatic this parameter was monitored seasonally.

Petroleum hydrocarbons were measured sporadically in mussels from the Sibenik area.

Faecal coliforms in mussels were determined seasonally on the Slovenian coast and in the Rovinj, Pula and Split areas and once in the Rijeka area.

In Tables 2.4.1 - 2.4.4 the total number of samples collected and each parameter determined in the investigated areas are summarized.

Table 2.4.1

Number of data of basic parameters and total nitrogen and phosphorus in the investigated areas in the period 1983-1986.

Type of samples	Parameters	Number of samples in areas: I	II	III	IV	V	VI	VII	VIII	Total
EFFLUENTS										
	BOD	62	42	48	137	-	84	-	-	373
	COD	39	-	39	149	-	84	-	-	311
	TSS	61	42	48	148	-	84	-	-	383
	TN	62	18	48	84	-	84	-	-	296
	TP	62	30	48	84	-	84	-	-	308
COASTAL WATER	Basic param.	-	330 (240)	-	-	355	128	-	-	1053
	Nutrients	-	258 (200)	-	-	347	128	-	-	933
	TN	-	236 (200)	24	-	-	-	-	-	460
	TP	-	258 (200)	24	-	347	-	-	-	1289

Areas: I-Slovenian coast; II-Rovinj; III-Pula; IV-Rijeka; V-Sibenik; VI-Split; VII-Dubrovnik; VIII-Montenegrin coast; ()-Open northern Adriatic.

Table 2.4.2

Number of data of heavy metal concentrations in the investigated areas in the period 1983-1986.

Type of samples	Metals	Number of samples in areas: I	II	III	IV	V	VI	VII	VIII	Total
EFFLUENT										
	Hg	51	18	46	154	-	84	-	-	353
	Cd	51	22	46	88	11	80	-	-	298
	Pb	-	-	30	38	11	79	-	-	158
	Cr	-	-	-	-	-	83	-	-	83
	Zn	-	-	-	86	7	56	-	-	149
	Cu	-	-	14	-	7	-	-	-	21
SUSPENDED MATTER										
	Hg	95	-	-	-	-	-	-	-	95
	Cd	91	-	-	-	-	-	-	-	91
SEAWATER										
	Hg	-	-	-	-	52	-	25	5	82
	Cd	-	-	-	-	122	-	25	12	159
	Pb	-	-	-	-	95	-	32	12	139
	Zn	-	-	-	-	93	-	31	12	137
	Cu	-	-	-	-	96	-	30	12	138
SEDIMENTS										
	Hg	34	17	5	-	48	22	-	9	135
	Cd	-	-	5	-	58	20	-	17	100
MARINE ORGANISMS										
	Hg	53	45	26	8	79	33	55	-	299
	Cd	46	43	23	8	77	33	55	-	285

Areas: I-Slovenian coast; II-Rovinj; III-Pula; IV-Rijeka; V-Sibenik; VI-Split; VII-Dubrovnik; VIII-Montenegrin coast.

Table 2.4.3

Number of data of organic pollutants in the investigated areas in the period 1983-1986.

Samples and pollutants	Number of samples in areas:								
	I	II	III	IV	V	VI	VII	VIII	Total
EFFLUENTS									
DDTtotal	-	-	-	12	-	-	-	-	12
PCB	-	-	-	12	-	-	-	-	12
PH (as oil)	-	-	-	42	14	84	-	1	141
PH (as chrysene)	-	-	-	12	15	-	-	1	28
Phenols	-	-	48	138	-	84	-	6	276
Anionic detergents	59	-	48	158	10	84	-	6	365
SEAWATER									
PH (as oil)	-	-	-	-	64	12	-	2	78
PH (as chrysene)	-	-	-	-	59	41	-	2	102
Oil slick and other Floating materials	-	-	-	352	-	-	-	-	352
Phenols	-	-	-	-	-	-	-	30	30
Detergents	-	-	-	-	-	11	-	31	42
SEDIMENTS									
DDTtotal	-	16	5	-	14	-	3	17	55
PCB	-	16	5	-	14	-	3	17	55
PH (as oil)	-	-	-	-	15	4	-	-	19
PH (as chrysene)	-	-	-	-	15	12	-	-	27

TABLE 2.4.3 (cont'd)

Samples and pollutants	Number of samples in areas:								
	I	II	III	IV	V	VI	VII	VIII	Total
MUSSELS									
DDTtotal	-	30	24	8	14	19	11	2	108
PCB	-	30	24	8	14	19	11	2	108
PH (as oil)	-	-	-	-	5	-	-	-	5
PH (as chrysene)	-	-	-	-	5	-	-	-	5
ZOOPLANKTON									
DDTtotal and PCB	-	12	-	-	-	-	-	-	12
Total	59	104	154	742	258	370	28	117	1832

Areas: I-Slovenian coast; II-Rovinj; III-Pula; IV-Rijeka; V-Sibenik; VI-Split; VII-Dubrovnik; VIII-Montenegrin coast.

Table 2.4.4

Number of microbial pollution data in the investigated areas in the period 1983-1986.

Type of samples	Number of samples in areas: I	II	III	IV	V	VI	VII	VIII	Total
EFFLUENT	71	31	48	163	-	56	-	-	369
SEAWATER	1373	404	429	528	108	420	-	140	3402
MARINE ORG.	30	70	29	7	-	44	-	-	180

Areas: I-Slovenian coast; II-Rovinj; III-Pula; IV-Rijeka; V-Sibenik; VI-Split; VII-Dubrovnik; VII-Montenegrin coast.

3. RESULTS AND DISCUSSION

3.1. Basic parameters, nitrogen and phosphorus

The wastewaters of almost all urban centres on the Yugoslav Adriatic coast are inadequately disposed of in the sea, often with evident consequences on the trophic characteristics of the receiving waters. Research performed within the framework of the project "Jadran III" (Anon., 1976) in the period 1972-1974 led to the conclusion that eutrophication rose to critical levels only in a few restricted harbour areas and that the natural bioecological system of the Adriatic Sea as a whole is not disturbed. However recently, more frequent nonseasonal phytoplankton blooms were observed in the northern Adriatic Sea (Smodlaka, 1985). Extreme eutrophication events, which led to a marked decrease in oxygen concentration of bottom layers and caused minimum values during the summer, occurred in 1977 over the whole region (Degobbis et al., 1979) and in 1983 in the Gulf of Trieste (Faganeli et al., 1985).

The northwestern Adriatic coast is under direct influence of a heavy nutrient load carried by rivers which receive wastewaters from large, highly urbanized, intensively cultivated and industrialized watersheds as well as sewage discharged directly into the sea from numerous urban and tourist centres on the coast. As a consequence, intensive algal blooms, anoxia of bottom layers, fish and shellfish kills have often been observed in summer during the past ten years in the Emilia-Romagna coastal region (Montanari et al., 1984) and in the Venice Lagoon (Degobbis et al., 1986).

Other examples of serious alteration of the ecological equilibrium, with fish and shellfish kills, are the Pula harbour red tide, which has recently been occurring regularly in summer (Maretic et al., 1978) and the red tide in the Vranjic Bay (Split region) in 1980 (Marasovic and Vukadin, 1982).

Although it was recognized several years ago that long submarine outfalls represent an optimal technique for wastewater disposal along the relatively deep Yugoslav coast (Price, 1980), such a system was built only in a few centres. A 3450 m-long outfall with a 120 m long diffuser at a depth of 20 m in the sea was proven effective in disposing urban wastewaters from the towns Piran, Portoroz and from Lucija (in northwestern Istria), as well as the surrounding tourist facilities (Avcin et al., 1979; Malej, 1980), without significantly affecting the nutrient content of the discharge area (Faganeli, 1982). The Rabac (eastern Istria) 250 m-long outfall, without diffuser, but discharging sewage at a depth of 45 m effectively serves 10000 persons in summer, preserving high water quality on the beaches and in the coastal region (Fuks and Degobbis, 1983).

For these reasons it is essential to consider more fully the eutrophication problem, particularly in the areas, such as for example the Lim Channel or the Krka River estuary, that have unique natural characteristics, but at the same time are designed for economic exploitation, often with conflicting activities. Relevant to this is the monitoring of the northern Adriatic open waters, which can periodically have a significant impact on the western Istrian coastal area.

Since 1983 a monitoring programme of effluent and coastal water quality has been conducted in several regions of the Yugoslav Adriatic coast in the framework of the UNEP Long-term Programme for Pollution Monitoring and Research in the Mediterranean Sea (MED POL - Phase II). In this programme measurements of basic oceanographic parameters, nutrients, total phosphorus and total nitrogen concentrations were also included. The results obtained to date are presented and discussed in the light of other relevant data available for the regions studied.

3.1.1. Basic chemical characteristics, total nitrogen and total phosphorus in rivers, karstic groundwaters and wastewaters

River waters and groundwaters

In the Adriatic Sea, particularly on the Yugoslav side, reliable concentration data series of nitrogen and phosphorus compounds are available only for a few rivers. The Po river, one of the major rivers in the Mediterranean, has been monitored in the past fifteen years and a significant increase of the nitrogen and phosphorus loads was registered in its waters (Table 3.1.1). Similar trends were also observed in the Adige River and in the groundwaters discharged into the Lim Channel (Table 3.1.1). Other rivers and groundwater watersheds were not investigated systematically and only scarse concentration data exist.

However, the data available(Table 3.1.1) clearly indicate that significant differences in the concentration levels exist among different watersheds. The most polluted streams are found in the Emilia Romagna region, some of them with concentrations orders of magnitude higher than in the Po river. The lowest values were generally measured in the karstic watershed on the Yugoslav Adriatic coast: nitrogen contents were several times, and phosphorus contents an order of magnitude lower than in the Po river waters.

Some of the data reported in Table 3.1.1 were obtained indirectly by extrapolation of the concentration values measured in the discharge area to salinity zero (the Lim Channel, the Rjecina River, Rijeka, Bakar and Sibenik bays freshwaters). This method is satisfactory for samples with minimal biological activities (Chiaudani et al., 1983). A few analyses of freshwater samples taken from a spring in the inner part of the Lim Channel gave similar results to those obtained with the indirect method (Table 3.1.1).

Table 3.1.1

Mean flow rate and concentration of nitrogen and phosphorus compounds in some Adriatic rivers and streams and in karstic groundwaters.

River[a]	Flow rate[b] ($m^3 s^{-1}$)	Concentration (mmol m^{-3})[c]					
		NH_4	NO_2	NO_3	TN	TDP	TP
I t a l y							
1) Po, 1968-72	1585	17		68	1.6		
2) Po, 1978-79	1585	20	3.3	102	2.4	2.7	7.5
3) Po, 1981-84	1585	21		147	4.6		9.9
4) Adige, 1968-72	212	4.5	0.7	49	1.4		
5) Adige, 1978-79	212	9.5	1.1	68	1.7	1.9	5.7
6) Isonzo (Soca)	204	1.4	0.3	58	0.3		
7) Po di Goro		43	3.6	53.5	3.3		7.4
8) Po di Volano	4.5	83	7.1	46	4.5		7.7
9) Reno	59.1	99	14	43	17		32
10) Destra Reno		125	18	34	31		47.5
11) Lamone	8.8	34	19	48	23		40
12) Candiano		95	14	36	5.0		10
13) Montone & Ronca	20.5						
Montone		157	21	44	26		42
Ronca		43	12	34	13		26
14) Bevano	2.0	18	2.1	31	17.5		30
15) Savio	10.8	30	21	51	9.0		20
16) Cupa	0.2	364	47	443	121		160
17) Tagliata		86	0.7	7.5	16		28
18) Rubicone	2.05	64	25	75	129		145
19) Uso	1.5	107	137	195	10.5		13
20) Marecchia	9.1	36	4.3	22	2.3		6.0
21) Marano	0.2	18	7.9	90	3.2		4.2
22) Melo		573	5.7	61	87.5		108
23) Conca	2.1	14		32	1.0		3.0
24) Ventena	0.2	998	28	71	90		108
25) Tavollo		1819	12	118	241		264
26) Metauro	20	4.9	1.0	28	0.2		
27) Arzilla		5.7	2.1	59	0.8		

Table 3.1.1 Cont'd

River[a]	Flow rate[b] (m^3 s^{-1})	Concentration (mmol m^{-3})[c] NH_4	NO_2	NO_3	TN	TDP	TP
Yugoslavia							
28) Rizana River	0.05	4.5	0.3	26		0.5	1.0
29) Rizana River	0.05				106		6.6
30) Dragonja	0.01	3.5	0.1	51		0.6	0.9
31) Dragonja	0.01				105		4.0
32) Drnica	-				120		6.5
33) Badasevica	-				290		11
34) Groundwater into Limski kanal 1969-86	-		0.2	53		0.5	0.7
35) Groundwater into Limski kanal 1980-86	3	0.3	106	0.8	1.2		
36) Groundwater into Limski kanal 1985	-	0.7	0.4	130		0.9	1.25
37) Rasa					77		3.3
38) Groundwater into Bakar Bay	-	7	0.3	39		0.3	
39) Freshwater into Rijeka Bay	70	7	0.4	35		0.5	
40) Rijecina	15	4	0.2	31		1.1	
41) Rijecina	15				556		24.9
42) Krka	49	1.1	0.25	18		0.10	0.24
43) Freshwater into Sibenik Bay	-			19	0.68		1.4

[a]Measurement frequency: 1) Biweekly from June 1968 to June 1972, ammonia estimate includes a fraction of aminoacids (Marchetti et al., 1985); 2) and 4) Approx. weekly from May 1978 to Nov. 1979 (Provini et al., 1980); Monthly during 1981-84 (Marchetti et al., 1985); 5) Biweekly from June 1968 to June 1972 (Fossato, 1971, 1973); 6) Monthly from June 1976 to Dec. 1977 (Bregant and Catalano, 1978); 7) - 25) Monthly during 1977 (Anon., 1978); 26) and 27) Monthly during 1967-69 (Olmo and Poli Molinas, 1980); 28) and 30) Monthly from Feb. 1978 to May 1979 (Faganeli and Tusnik, 1983); 29) and 31) Aug. 1983, Feb., Aug., Sept. 1984, March, Aug. 1985 (this study); 32) and 33) March, Aug. 1985 (this study); 34) Estimated by extrapolation to salinity zero from monthly data collected in 1969-75 and 35) from Oct. 1980 to December 1986 (this study); 36) Dec. 1984, Feb., Apr., Aug. 1985 (Anon.,1985); 37) May, July, Aug., Oct. 1984, May, Aug., Oct., Dec. 1985, June, Aug., Oct., Dec., 1986 (this study); 38) - 40) Estimated by extrapolation to salinity zero from data collected during 20 cruises in the period 1976-1980 (Degobbis, 1983); 41) May, July, Aug., Oct. 1984, June, July, Aug., Oct. 1985 (this study); 42) Jan., May, July, Oct. 1983, Feb., May, July, Nov. 1984, Apr., July, Nov. 1985, Feb., May, July, Nov. 1986 (this study); 43) Extrapolated to salinity zero from data collected during cruises listed in 42). [b]From Cavazzoni Galaverni (1972), Anon., (1978), Degobbis (1983),and this study. [c]NH_4 - ammonia; NO_2 - nitrite; NO_3 - nitrate; TN - total nitrogen; RP - reactive phosphorus (orthophosphate) TDP - total dissolved phosphorus; TP - total phosphorus

Sewage and industrial wastewaters

High variability was also observed for total nitrogen and phosphorus concentration and for basic chemical parameters (BOD, COD and TSS) in the sewage and industrial wastewaters monitored in the framework of the National Programme in several major Yugoslav Adriatic centres (the Slovenian coastal area, Pula, Rijeka and Split regions; Table 3.1.2).

However, the data for sewage tend to be grouped in particular areas. Relatively homogeneous data were observed for all parameters at all seven sampling points of the Split region with the lowest mean values. Similar values were also found in the Piran area. In contrast, the highest loads were measured in the Opatija sewage system. Generally the Rijeka region sewage values were higher than those in the other regions. The Izola, Kopar, Pula and Medulin levels were intermediate between the two extremes (Table 3.1.2).

The chemical characteristics of industrial wastewater varied much more than those of sewage, depending on the type of technological process and on the relative contribution of degradable organic matter. In the wastewaters of the canneries at Izola and Ika the organic load was higher than in sewage. On the contrary, the oil refinery and cement industry wastewaters gave significantly lower values than sewage (Table 3.1.2).

In the Pula, Rijeka and Split sewage, pH, ammonia, nitrite and nitrate concentrations were also measured. The pH value range was broader in the Rijeka sewage (6.6-8.3) than in the Split sewage (7.0-7.7), but the mean values were approximately the same (7.4 and 7.5 respectively). Ammonia represented the main nitrogen form both in sewage and in industrial wastewaters, generally accounting for more than half of the total nitrogen concentration (on average 74% in the Rijeka region and 67.5% in the Split area). Nitrite concentration was mostly around the detection limit of the analytical method and always below 0.3% of total nitrogen. The nitrate percentage was on average 0.4% of total nitrogen in the Split wastewaters, with a range of 0-1.6%.

At the Brajdica sampling point (U6, Rijeka city) daily variations of parameter values were studied on June 1 and June 2, 1984 (Fig.3.1.1). The parameter values varied within an order of magnitude. This also highlights the importance of selecting a suitable sampling period during the day in order to get reproducible and comparable data.

Table 3.1.2

Basic chemical parameters and total nitrogen and phosphorus in sewage and some industrial waters discharged into the sea along the Yugoslav Adriatic coast (n= number of samples; x= average value; R= range).

Locality[a]		Flow rate	BOD	COD	TSS	TN	TP
		(10^5 m^3 y^{-1})			(mg l^{-1})		
S e w a g e							
1) Piran	n		12	2	14	14	14
	x	1.5	114		106	26.7	5.7
	R		21-318	256-1070	18-596	7-79	0.8-15.5
1) Izola Kopar	n		15	4	17	18	18
	x	3.8	230	447	136	70	14.8
	R		95-472	221-815	52-338	19-247	4.4-67.7
2) Pula Medulin	n		24	15	24	24	24
	x	87	353	531	163	30	8.7
	R		79-980	200-960	18-386	1.0-74	0.06-12.1
3) Opatija Ul	n		7	8	8	7	7
	x	15	465	729	337	111	58
	R		245-660	200-1420	86-532	30-191	9.3-125
3) Rijeka Bakar Kraljevica	n		55	62	63	56	56
	x	100	292	454	199	55	23.1
	R		105-680	155-1060	51-362	4.4-114	0.6-94
3) Rijeka,U5 Mixed sewage and groundwater	n		7	8	8	7	7
	x		104	190	121	19.2	4.5
	R		21-470	24-1020	20-652	3.0-50	1.2-8.8
4) Split	n		84	84	84	84	84
	x	178	165	270	85	18.2	17.7
	R		20-46	47-920	14-453	3.9-60	0.5-23.9

Table 3.1.2 (cont'd)

Locality[a]		Flow rate	BOD	COD	TSS	TN	TP
		(10^5 m^3 y^{-1})			($mg\ l^{-1}$)		
I n d u s t r i a l w a s t e w a t e r s							
1) Izola	n		6	6	6	6	6
Cannery	x	2.2	495	1721	436	45	6.2
Delamaris	R		223-880	1246-3302	198-775	31-56	5.7-9.2
2) Pula	n		12	8	12	12	12
Cement	x	0.09	280	246	214	20.5	2.1
Siporex	R		101-670	77-808	9.5-901	5.4-43	1.5-3.1
3) Ika	n		7	8	8	7	7
Cannery	x		710	2962	929	162	40
	R		300-1660	450-14600	132-4620	68-312	18-82
3) Rijeka,U6	n		7	8	8	7	7
mixed	x		388	609	210	20	7.3
urban-ind.	R		130-1150	270-1620	125-452	6.6-182	3.0-11
waste							
3) Urinj	n		6	8	8	6	7
Oil	x	11	82	196	28	9.6	0.6
refinery	R		10-202	50-590	9-85	0.0-25	0.0-1.5

[a]Measurement frequency: 1) Feb., Aug., Sept. 1984., March, Aug. 1985 and 1986; 2) May, July, Aug., Oct. 1984, May, Aug., Oct., Dec. 1985 and 1986; 3) May, July, Aug., Oct. 1984, June, July, Aug., Oct. 1985; 4) May, July, Aug., Oct. 1984, 1985 and 1986.

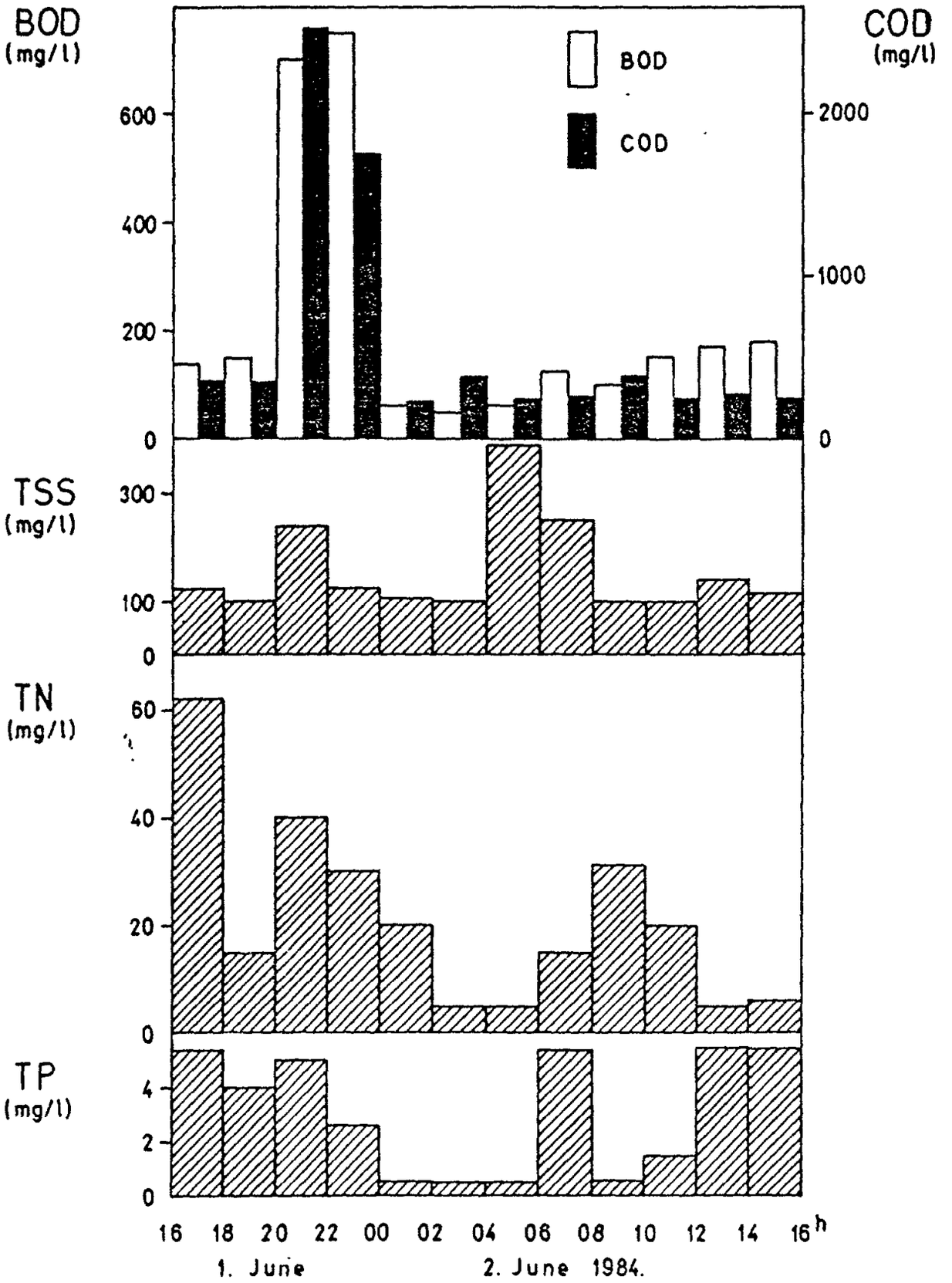


Fig. 3.1.1 Diel variations of oxygen demand (BOD, COD), total suspended solids (TSS), total nitrogen (TN) and total phosphorus (TP) in the wastewaters of sampling point U6 (Brajdica, Rijeka)

3.1.2. Nutrient loads in the Adriatic area

Calculated loads for the entire Adriatic area

Assuming average values for rivers, groundwaters, rain drainage and urban and wastewater discharge, Sekulic (1985) calculated the loads for each type of freshwater for nitrogen and phosphorus in the Adriatic area, separately for Yugoslavia and Italy (Table 3.1.3). However, other data indicate that these calculations are very crude and need a detailed re-evaluation, based on direct analytical and hydrological measurements.

Firstly, a detailed study of the freshwater discharge rate data into the Adriatic (Cavazzoni Galaverni, 1972) resulted in estimates which were at least twice as high as those used by Sekulic (1985). These estimates (143×10^6 m^3 y^{-1} from Italy and 45×10^6 m^3 y^{-1} from Yugoslavia) were related to the northern and central Adriatic area only (up to the Gargano Peninsula in Italy and to the Neretva river watershed in Yugoslavia) but account for most of the total discharge rate.

Secondly, nitrogen and phosphorus concentrations in Italian rivers are significantly higher than in the Yugoslav streams and groundwater (Table 3.1.1, Section 3.1.1). It follows that the assumption made by Sekulic (1985) according to which the freshwater concentrations are equal in both countries leads to significant errors. For instance, the total phosphorus concentration in river waters assumed by Sekulic (1985) is four times lower than the average value for the Po river, which accounts for approximately half of the total Italian freshwater discharge. If the assumption is valid that the organic nitrogen concentration in the Po River waters is of the same order of magnitude as the inorganic forms (Provini et al., 1979) then the total nitrogen concentration assumed by Sekulic for Italian rivers may be underestimated by a factor of two.

Such an evaluation is more difficult for Yugoslav freshwaters, due to a lack of sufficient data. However, from the data available, if some minor very polluted streams are excluded, it appears that the total phosphorus concentration in these freshwaters is significantly lower than the value assumed by Sekulic (1985) while the estimate for total nitrogen may be realistic.

Average values for total nitrogen and phosphorus in sewage discharged into the Yugoslav coastal region, calculated from the data collected in the framework of the UNEP MED POL programme, amount to 2900 and 480 mol m^{-3}, respectively. However, the uncertainty about these values is high, due to the limited data available. Thus, it is difficult to judge if the values assumed by Sekulic (1985) which are about 50% higher, are really overestimated.

The few data available for industrial wastewater do not allow us to draw any conclusion. It is known that nitrogen and phosphorus concentrations in such waters vary even more than in sewage, and only their detailed inventory may lead to sufficiently accurate averages. Phosphorus is particularly critical in this respect, since it was calculated that the contribution of industry to the total load was highly significant (Table 3.1.3).

Another approach, based on statistical data for population figures, consumption of detergents and fertilizers (animal and artificial), land (cultivated or not, forests), number of reared animals etc., multiplied by appropriate empirical coefficients, was used to calculate the nitrogen and phosphorus load in the Adriatic Sea from Italy (Tables 3.1.4 and 3.1.5). The loads are distributed very unevenly, since more than 80% is discharged into the most shallow northern Adriatic part (depth less than 70 m; Table 3.1.4). It is also evident that the greatest portion of the loads is anthropogenic and that total estimates are at least 50% higher than those reported by Sekulic (1985).

The above mentioned calculation method was tested with direct measurements in 15 Italian watersheds, including the Po and Adige rivers. A good agreement was found between the calculated and the measured phosphorus loads for medium and large watersheds (Garibaldi and Marchetti, 1982). In the investigated watersheds only total inorganic nitrogen was measured. However, the systematic differences observed between the calculated total nitrogen and the measured inorganic nitrogen were of the same order of magnitude as the average organic nitrogen concentration in other world rivers (Provini et al., 1979).

From the above considerations it may be concluded that the nitrogen and phosphorus loads estimated by Sekulic (1985) for Italy are underestimated and that the data of the Italian authors are more realistic. It also follows that the phosphorus load from Yugoslavia is probably overestimated, even if the freshwater flow rate is underestimated.

Many more data, preferably experimental, are needed to establish sufficiently accurate nutrient loads in the Adriatic Sea. The knowledge of these loads is also essential in order to qualify the observed impact of nutrients in the marine ecosystem and to identify their sources.

However, the existing data indicate a pressing need for monitoring eutrophication trends in the northern Adriatic Sea, particularly if the fact is taken into account that the nitrogen and phosphorus loads of the Po river waters, and probably of other Adriatic effluents, have increased significantly in the past 10 years (Marchetti et al., 1985).

Table 3.1.3

Assumed total nitrogen and phosphorus concentrations (mmol m^{-3}), average flow rate (10^6 m^{-3} y^{-1}) and calculated total loads (10^6 mol y^{-1}) in the Adriatic area (Sekulic,1985).

Source[a]	Concentration		Flow rate	Load from Yugoslavia		Flow rate	Load from Italy	
	TN	TP		TN	TP		TN	TP
Rivers	165	2.9	20000	3290	58	75000	12360	218
Rain drain	390	29	8000	3140	232	6000	2360	174
Inhabitants	3500	580	71	240	41	193	660	112
Industry	1200	65	500	610	32	1500	1820	97
Ships	3500	580	2	7	1	8	30	5
Total			28573	7290	364	82701	17230	606

[a]Rain drainage of a 7.5 km wide coastal belt; inhabitant contribution includes equivalent tourist population with a mean per capita water consumption of 120 dm^3 d^{-1}.

Table 3.1.4

Total nitrogen and phosphorus loads on the Italian Adriatic coast[a].

Load	Northern Adriatic		Central Adriatic		Southern Adriatic		Adriatic Sea	
	N	P	N	P	N	P	N	P
10^6 mol y^{-1}	20820	920	2725	100	1690	80	25235	1100
%	82.5	83.8	10.8	8.8	6.7	7.4	100	100

[a]Calculated from Provini et al. (1979), nitrogen data and Chiaudani et al. (1978), phosphorus data; northern Adriatic to Ancona, central Adriatic to the Gargano Peninsula, southern Adriatic to Otranto Strait.

Table 3.1.5

Relative contribution of various sources of nitrogen and phosphorus to the total load in the Italian Adriatic area[a].

Source[b]	Source load contribution (%)				
	Italy seas		Northern Adriatic	Central Adriatic	Southern Adriatic
	N	P	P	P	P
Urban waters					
Faecal	23.5	27.5	25.3	23.8	29.4
Detergents		33.2	30.5	28.7	35.5
Fertilizers	53.3	17.8	20.2	22.4	20.4
Animal raising	8.5	13.3	16.3	16.4	7.1
Industry	10.0	6.1	2.1	3.4	1.1
Erosion of uncultivated land	4.7	2.1	5.6	5.3	6.5

[a]From Chiaudani et al. (1978) and Provini et al. (1979).
[b]Faecal contribution was calculated from equivalent inhabitant number and unity coefficients of 160 mol y^{-1} nitrogen and 9.35 mol y^{-1} phosphorus, with the assumption that 50% of sewage reaches the sea; phosphorus from detergent polyphosphates was estimated from a coefficient of 11.3 mol y-1 per inhabitant (50% reaches the sea); 20% nitrogen and 3% phosphorus from fertilizers (animal and artificial) used in agriculture were assumed to reach the sea; 5% of the total load of the animal raising farms was assumed to reach the sea; assumed unity coefficients for nitrogen and phosphorus (mol y-1) were for horses 274 and 19, cattle 250 and 14.7, pigs 67 and 9, sheep 32 and 2.4, and chicken 0.6 and 0.1; industrial nitrogen wastewater contribution was obtained by multiplying the employer number with a unity coefficient of 715 mol y-1; phosphorus load from industrial wastewaters was taken as 10% of the urban water load; nitrogen and phosphorus contributions from erosion of uncultivated land were estimated from the surface area and unity coefficients of 143 mol ha^{-1} y^{-1} and 3.2 mol ha^{-1} y^{-1} respectively.

The nutrient loads in the Krka River estuary

The total nitrogen and total phosphorus loads in the watershed of the Krka River estuary were estimated by Lovric and Sekulic (1986) as 63 and 9.9×10^6 mol y^{-1}, respectively (Table 3.1.6). These loads were estimated from freshwater and wastewater discharge rates and the assumed nitrogen and phosphorus concentrations. Wastewaters account for 2% of the total runoff, but contribute 84% of the total loads in the region. Relevant to this is the estimate that up to 35% of the anthropogenic phosphorus load is contributed by the Sibenik port, also because of the loss of phosphate ore material during shipping operations, while the sewage of Sibenik city contributes less than 10%.

From the measured concentrations and the average flow rate of 49 m^3 s^{-1} (1545×10^6 m^3 y^{-1}) for the Krka River, Vukadin and Grzetic (1986) estimated inorganic nitrogen and phosphorus inputs into the estuary of 101 and 4.1×10^6 mol y-1, respectively. An additional 28×10^6 mol y^{-1} of inorganic nitrogen and 0.5×10^6 mol y^{-1} of inorganic phosphorus would be contributed by sewage ($4{,}5 \times 10^6$ m^{-3} y^{-1}) discharged directly into the estuary, particularly into Sibenik Bay.

Using mean concentration values measured near the Krka River mouth (station E1) and the average river flow of 49 m^3 s^{-1}, we arrive at a total inorganic nitrogen load (ammonium, nitrite, nitrate)of about 30×10^6 mol y^{-1} and at values of 0.15×10^6 mol y^{-1} for reactive phosphorus and 0.35×10^6 mol y^{-1} for total phosporus. These estimates differ considerably from those given in Table 3.1.6 estimated by Vukadin and Grzetic (1986) i.e. up to an order of magnitude for the river phosphorus load. The value for nitrogen is less than half with respect to the Vukadin and Grzetic (1986) value but it is several times higher than the estimate given by Lovric and Sekulic (1986), even if the freshwater discharge rate assumed by these authors is somewhat lower (about 16%; Table 3.1.6).

Using average concentration values for sewage, calculated from the data reported in Table 3.1.2 and the sewage discharge rate in the region used by Vukadin and Grzetic (1986) we obtain a total nitrogen load of 30×10^6 mol y^{-1} and a phosphorus load of 2.2×10^6 y^{-1}. These values would be about a third higher if calculated on the basis of the urban water discharge rate used by Lovric and Sekulic (1986) (which includes Sibenik city and other small towns and tourist centres). In that case the nitrogen value would be about 40% higher than the corresponding estimate of Lovric and Sekulic (1986). In the case of phosphorus this difference amounts to 34%. Considering that the contribution of organic nitrogen is on the average about 25% of the contribution of total nitrogen (see Section 1.2.) and that total phosphorus concentration in sewage is usually 2-4 times higher than the orthophosphate concentrations (Bond and Straub, 1974), the calculated loads agree better with the estimates of Vukadin and Grzetic (1986) than the corresponding values for river waters.

For the industrial loads, no comparison is possible with the data obtained by Lovric and Sekulic (1986).

Table 3.1.6

Average flow rate (10^6 m^{-3} y^{-1}) and calculated total nitrogen and phosphorus loads (10^6 mol y^{-1}) in the Krka River estuary region (Lovric and Sekulic, 1986; Sekulic, personal commun.).

Source	Flow rate	Load TN	Load TP
Total freshwater discharge from the watershed (estimated from precipitation)	1253	10.7	1.6
Rain drainage of the Sibenik city area	6.6	5.6	1.5
Sewage of Sibenik City (pop.38000)	2.5	9.5	0.8
Industrial wastewaters of Sibenik city	1.7	5.0	0.5
Wastewaters from the Sibenik port[a]	0.5	1.9	2.9
Industrial wastewaters from the area around Sibenik	3.4	16.8	1.6
Tourist Center Solaris	0.8	3.0	0.25
Skradin, Drnis and Knin town sewage (pop. 1000, 4000, 10000, respectively)	2.8	10.6	0.9
Total	1271	63.1	10.0

[a]840,000 t y^{-1} of phosphates are unloaded with a loss of 0.01%.

In conclusion, the load data for the Krka estuary must be improved and verified by means of more systematic and accurate direct measurements of effluent concentrations. This is particularly important because it has already been shown that, for smaller watersheds (Provini et al., 1979; Garibaldi and Marchetti, 1982), including that of the Savio River (11 m^3 s^{-1}, Emilia Romagna region, Italy; Hadrill et al., 1983) load calculations using empirical coefficients do not agree with direct measurements.

3.1.3. Oceanographic characteristics, nutrients, total nitrogen and total phosphorus in the Adriatic coastal regions of Yugoslavia

Open northern Adriatic waters

In response to the heavy nutrient load (Section 2.1.), large seasonal and spatial fluctuations (both horizontal and vertical) of nutrient concentrations, phytoplankton primary productivity and standing crop, oxygen saturation, water transparency etc. were observed in the open waters of the northern Adriatic (e.g. Smodlaka and Degobbis, 1987 and Table 3.1.7).

Long term observations in the international waters of the northern Adriatic have shown that on the average three phytoplankton blooms occur in the surface layer during a seasonal cycle (Fig.3.1.2). The late winter-early spring bloom is induced by the seasonal increase of light intensity and is mainly based on nutrients accumulated during the winter by regeneration processes and secondarily (if the region near the Po River delta is excluded) on external contributions which are minimal in that period (minimum freshwater discharge rate, Fig. 3.1.2). Afterwards, the bloom nutrients are depleted in the surface layer. At the same time, stratification processes in the water column, due to the development of a thermocline and to the influence of freshwater discharge on salinity, decrease vertical mixing between the surface and the lower layers. During late spring the second bloom occurs in the entire region, mainly in response to the increased spring river water inflow and related nutrient contribution (in Fig. 2 traced by nitrate), in conditions of marked stratification. The third, fall bloom, is generally as intense as the early spring bloom. This is not the general case either for temperate coastal areas, in which the fall bloom is secondary in respect to the spring bloom or, for instance, for the Kastela Bay, where three blooms also occur as a result of eutrophication (Pucher-Petkovic and Homen, 1979). In the northern Adriatic, a significant external nutrient contribution and a bottom layer nutrient resupply by the increased vertical mixing occur simultaneously in the fall. Smodlaka and Degobbis (1987) have proposed to monitor the anthropogenic influence on the open northern Adriatic waters by measuring the intensity changes of the second, late spring bloom, which is mainly due to external nutrient contributions.

During the past few years the value ranges for oceanographic parameters, nutrients and total phosphorus were similar to those observed during a previous long-term observation period (1965-1981; Table 3.1.7), in spite of a significant increase of nutrient concentrations in the Po River waters (Marchetti et al., 1985). Nutrient fluxes to the open northern Adriatic from coastal waters were estimated by extrapolation of the concentrations, measured at boundary stations, to salinity zero in conditions of minimal primary production (Smodlaka and Degobbis, 1987). The estimates obtained (total inorganic nitrogen 2800×10^6 mol y^{-1}, reactive phosphorus 45×10^6 mol y^{-1} were an order of magnitude lower than the total nitrogen and phosphorus loads. In fact, lagoons and coastal waters in the western part of the northern Adriatic act as a nutrient trap. For instance, in the urbanized and industrialized inner part of the Venice Lagoon very high nutrient concentrations are reduced by at least two orders of magnitude,

Table 3.1.7

Value ranges for basic oceanographic parameters, nutrients, total phosphorus and total nitrogen concentrations in the open waters of the northern Adriatic Sea in the period 1965-1981 and 1984-1986.

Parameter[a]	Layer[b]	Ranges (mmol m^{-3}) Station 5		Station 9	
		1965-81[c]	1984-86[d]	1965-81[c]	1984-86[d]
T/[a]C	s	8.1-26.6	10.1-26.8	7.2-28.1	7.7-27.4
	b	7.7-21-7	8.8-16.2	7.5-17.2	7.4-16.1
Sx10-3	s	29.8-38.5	30.6-38.5	21.6-38.1	13.1-37.9
	b	36.7-38.6	37.7-38.3	35.7-38.3	37.3-38.2
pH	s	8.05-8.50	8.1-8.6	8.04-8.72	8.1-9.2
	b	7.97-8.36	8.1-8.3	7.83-8.26	8.0-8.2
O_2%	s	93-121	96-114	90-178	88-236
	b	40-108	37-102	13-116	34-99
RP	s	0.00-0.19	0.02-0.09	0.00-0.67	0.00-0.64
	b	0.00-0.32	0.03-0.33	0.03-0.87	0.03-0.50
OP	s	0.01-0.59	0.05-0.32	0.01-1.87	0.01-1.11
	b	0.01-0.67	0.02-0.22	0.01-0.50	0.05-0.28
TP	s	0.03-0.76	0.07-0.34	0.10-2.48	0.10-1.36
	b	0.04-0.71	0.08-0.28	0.09-1.28	0.13-0.65
NH_4	s	0.0-2.8	0.1-1.8	0.1-9.1	0.1-1.2
	b	0.0-2.6	0.2-2.7	0.1-8.8	0.2-5.7
NO_2	s	0.00-0.93	0.00-0.81	0.03-2.07	0.02-1.9
	b	0.00-1.34	0.07-1.4	0.04-14.4	0.16-1.8
NO_3	s	0.0-10.4	0.1-6.4	0.1-44.5	0.1-18.1
	b	0.0-5.6	0.3-5.8	0.1-59.7	0.2-4.5
ON	s		0.9-8.8		0.9-15.9
	b		1.1-9.1		1.4-5.7
TN	s		2.6-11.4		6.0-28.9
	b		3.7-9.9		2.7-9.9

[a]RP-reactive phosphorus, OP-organic phosphorus, TP-total phosphorus, NH_4-ammonia, NO_2-nitrite, NO_3-nitrate, ON-organic nitrogen and TN-total nitrogen.
[b]-surface layer; b-bottom layer.
[c]Center for Marine Research Rovinj (CMR-R) - unpublished data.
[d]This research project.

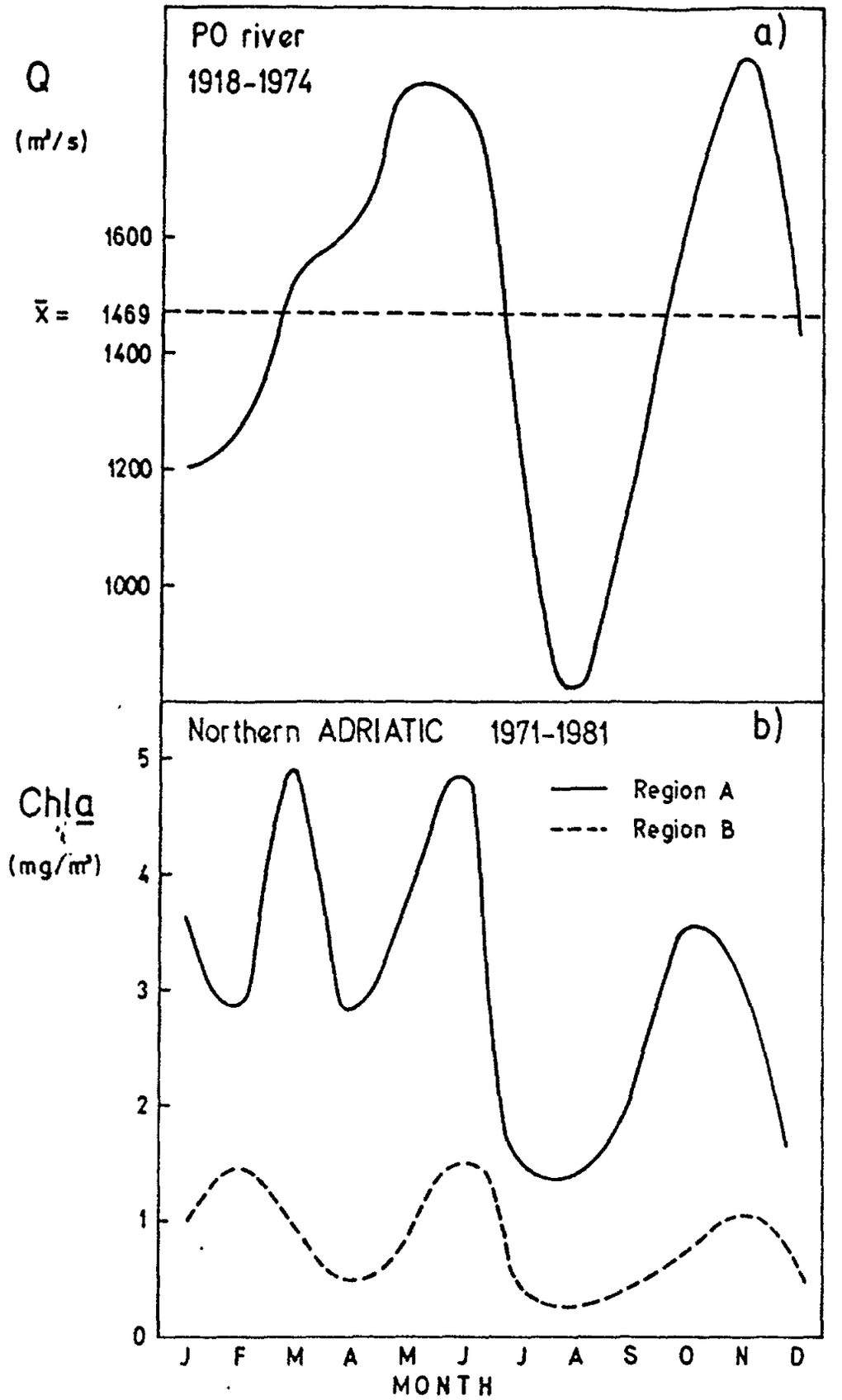


Fig. 3.1.2a,b Seasonal variations of long-term monthly means of a) the Po River flow rate at Pontelagoscuro (about 50km from the delta; Cati, 1981); b) surface chlorophyll a concentration (Chl a) in the western (A) and eastern (B) regions of the northern Adriatic Sea (Smodlaka, 1985)

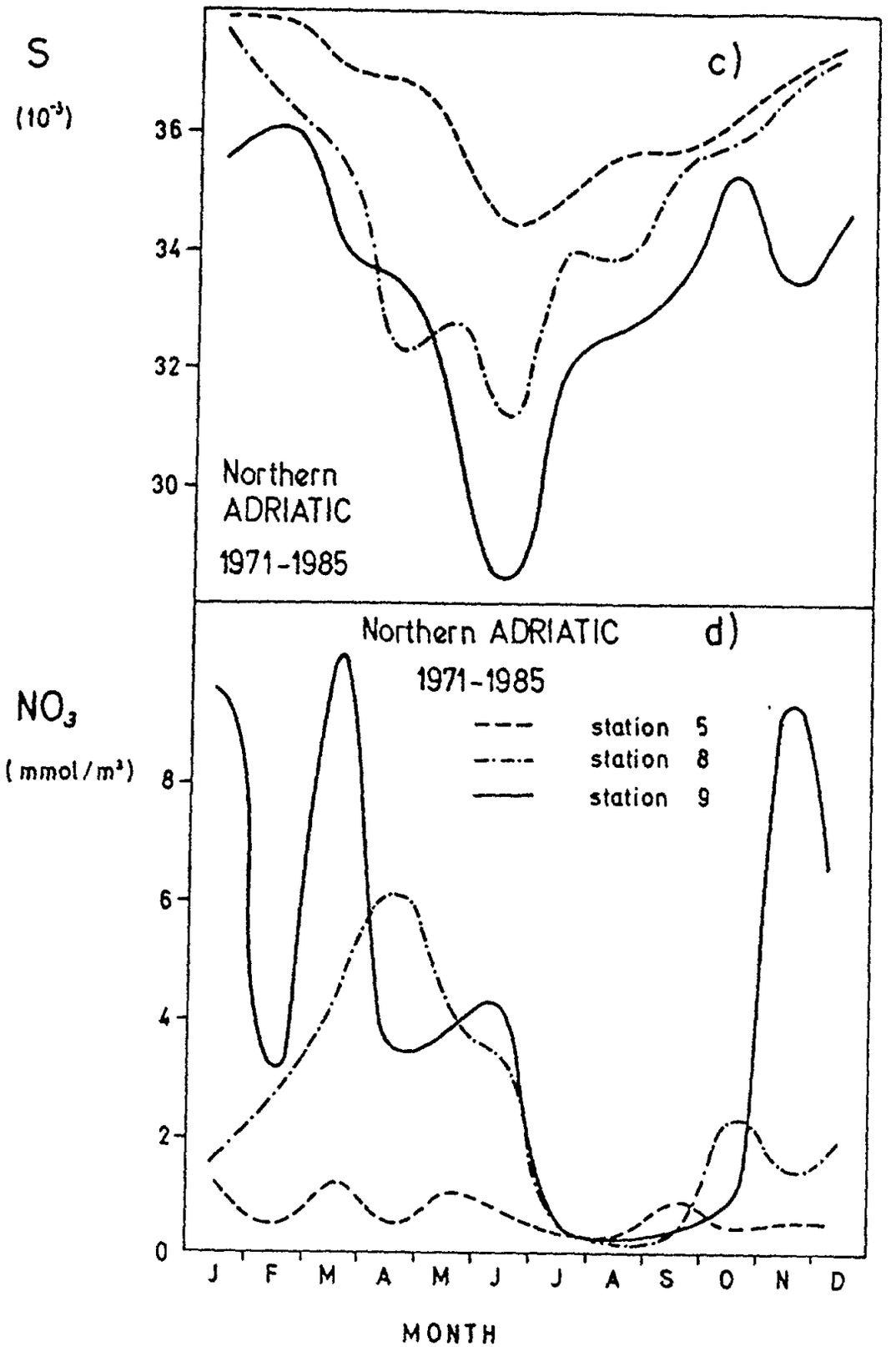


Fig. 3.1.2c,d Seasonal variations of long-term monthly means of c) salinity (S) and d) nitrate (NO_3) concentration at stations 5 (25 km off Rovinj), 8 (25 km east of the Po River delta, and 9 (25 km southeast of the Po River delta; Centre for Marine Research, Rovinj (CMR-R) unpublished results)

approximately to the open sea levels in the entrance region of the lagoon (Degobbis et al., 1986). Similar gradients were also observed along the Italian Adriatic coast, particularly in the Po River delta and Emilia Romagna regions (Chiaudani et al., 1982). In the fall and winter, when the water circulation in the region is cyclonic, the majority of freshwater is exported from the region along a 20-30 km broad coastal belt towards the south. This is reflected for instance in the very high nitrate concentration at station 9 (Fig.3.1.2d). During the spring and summer, when a cyclonic vortex is formed in the northernmost part of the region, a portion of freshwater spreads toward the western Istrian coast. Then salinity decreases and nitrate concentration increases significantly in the surface layer of the eastern stations off the Po River delta as well (e.g. stations 5 and 8, Fig.3.1.2c,d). In the lower parts of the water column a compensating current moves in the opposite direction of freshwater spreading, further enhancing the nutrient trapping effect in the western coastal regions. Furthermore, a large part of the phosphorus in the Po River waters is particulate (Provini et al., 1980), which means that it probably undergoes extensive sedimentation before being transported to the open northern Adriatic waters. In fact, it was shown that the total suspended solid load of the Po River plume decreased to almost the levels found at distances of 20 km from the delta (Nelson, 1972).

In the warm seasons a southeastern current develops in the Emilia Romagna coastal region with an arm directed toward the north in a closed circulation pattern (Malanotte Rizzoli and Bergamasco, 1983). As a consequence of the decreased water exchange, nutrients are accumulated, very intense phytoplankton blooms are induced and bottom layer anoxia occurs (Montanari et al., 1984).

The twelve year data series (1970-1981) on phytoplankton crops and primary production collected in the open northern Adriatic region did not give conclusive evidence for a recent increased biomass and primary production (Smodlaka and Revelante, 1983). Much longer and systematic data series are needed.

However, in particular meteorological and oceanographic conditions, such as those that occurred in 1977 and were characterized by an unusually high river discharge rate and a minimal water exchange rate (Accerboni et al., 1982), freshwater "flooded" the entire area (Degobbis et al. 1979). The water column was markedly stratified because of large salinity and temperature vertical differences. Assimilation processes were very intense in the upper part of the water column decreasing water transparency significantly. Regeneration processes prevailed in the bottom layer with significant oxygen consumption. These events had a strong influence on fisheries of the benthic organisms (Froglia and Gramitto, 1982). Very low oxygen concentrations were also measured in the Gulf of Trieste in September 1983, when the water column was very stable because of the unusually low frequency of the bora winds which significantly influence vertical water mixing in the region (Faganeli et al., 1985).

A synergic interaction mechanism between unusual hydrometeorological conditions, water column stratification, water exchange rate and external nutrient input causes anoxia events in the bottom layer, which seem to have been more frequent recently. This mechanism must be studied further and a systematic monitoring should be established. In a relatively open system, such as the northern Adriatic, a long-term nutrient and organic matter accumulation is not expected. During winter, increased water exchange and minimal primary production give the ecosystem a chance to reestablish its equilibrium, at least at the budget level. But the eutrophication degree of such a system, unlike that of lakes, may be defined for instance on the basis of the frequency at which intense phytoplankton blooms or bottom layer anoxia events for given oceanographic conditions are repeated at time intervals. The eventual increase in the frequency of such events may in the future seriously compromise the ecological equilibrium of the northern Adriatic region and have negative consequences for fisheries.

The Lim Channel

Value ranges of oceanographic parameters, nutrients, total nitrogen and total phosphorus concentrations, data collected in the framework of this project are compared with a previous data set and with the results for coastal waters off Rovinj (Table 3.1.8). Extreme variability of all parameters was observed in the surface layer of the Lim Channel, particularly in the inner part, but this was not the case for the lower part of the water column, in which the values were almost as low as in the coastal waters of western Istria (Table 3.1.8).

Average groundwater nitrate and orthophosphate concentrations, the main forms of nitrogen and phosphorus compounds in the freshwater discharged into the Lim Channel, were estimated by extrapolation of the measured values in the discharge area to salinity zero by means of linear regression analysis for various periods in the past fifteen years (Table 3.1.9). The estimates obtained for the period 1980-1985 were significantly higher than those for previous periods (1969-1980). This supports the hypothesis that the concentration increase is probably due to pollution within the watershed. Ammonia and organic matter added from sewage oxidize to nitrate before the freshwater reaches the sea. Very low ammonia, nitrite, organic phosphorus and organic nitrogen contents indicate that local sources (restaurants, mariculture facilities) do not contribute significantly to the Lim Channel pollution.

There are no sufficient data to evaluate fully the impact of the increased nutrient load of the Lim Channel watershed. The highest nutrient concentrations are restricted to a thin low salinity surface layer which may be dispersed relatively fast without significant impact on the primary production. In fact, the water exchange rate at the entrance of the region, which is without sills, is very fast (from several hours to a few days; Kuzmanovic, 1985). However, on a few occasions very intense phytoplankton blooms (March 1983, chlorophyll *a* concentration up to 170 mg m^{-3}, April 1984, up to 57 mg m^{-3}, CMR Rovinj, unpubl. results) were observed in the period 1978-1986 after heavy rainfalls. Generally, the chlorophyll *a* concentration is far below or, during spring and fall, around 1 mg m^{-3} and rarely reaches the maximum values of 3-4 mg m^{-3} (CMR Rovinj, unpubl. results). Unfortunately phytoplankton data are not available for the period before 1978.

Table 3.1.8

Value ranges for basic oceanographic parameters, nutrient concentrations, total phosphorus and nitrogen contents in the Lim Channel and in the coastal waters off Rovinj.

Parameter[a]	Layer	Ranges (mmol m^{-3}) Lim Channel Station 1 1978-82[c]	Lim Channel Station 1 1983-86[d]	Rovinj Station 2 1984-86[d]	Rovinj Station 3 1978-80[c]
	s	10.1-20.9	8.5-25.0	8.5-25.1	9.5-21.8
	b	10.1-18.5	9.1-23.0	8.7-18.2	9.5-21.2
$Sx10^{-3}$	s	11.3-38.1	9.5-38.2	29.1-38.3	34.2-38.0
	b	30.0-38.1	37.4-38.4	37.7-38.3	34.5-38.2
pH	s	7.9 -8.4	7.1-8.4	7.1-8.5	8.2-8.3
	b	8.2 -8.4	8.1-8.4	8.0-8.4	8.1-8.3
O_2 %	s	85-108	80-137	81-119	94-113
	b	54-110	64-102	53-108	77-113
RP	s	0.03-0.51	0.00-1.01	0.00-0.16	0.02-0.13
	b	0.03-0.11	0.02-0.26	0.02-0.55	0.01-0.15
OP	s		0.05-1.35	0.01-0.15	0.03-0.29
	b		0.03-0.20	0.00-0.29	0.02-0.21
TP	s		0.09-2.19	0.09-0.23	0.08-0.40
	b		0.05-0.43	0.04-0.73	0.08-0.32
NH_4	s	0.0-2.0	0.1-2.1	0.1-2.5	0.1-1.5
	b	0.1-2.1	0.1-2.4	0.3-3.1	0.0-1.3
NO_2	s	0.03-0.70	0.05-1.8	0.03-1.2	0.02-0.75
	b	0.00-0.74	0.04-1.8	0.03-1.4	0.16-0.75
NO_3	s	0.5 -56.8	1.0-78.1	0.8-38.4	0.3-1.7
	b	0.7-2.5	0.2-20.8	0.4-6.7	0.1-2.4
ON	s		0.2-26.5	0.7-8.0	
	b		0.3-7.7	0.1-8.3	
TN	s		2.7-98.7	2.6-43.6	
	b		2.1-17.9	2.2-9.5	

[a]RP-reactive phosphorus, OP-organic phosphorus, TP-total phosphorus, NH_4-ammonia, NO_2-nitrite, NO_3-nitrate, ON-organic nitrogen and TN-total nitrogen.
[b]s-surface layer; b-bottom layer
[c]Centre for Marine Research Rovinj - (CMR-R) unpublished data.
[d]This project.

Table 3.1.9

Correlation coefficients and statistical significance [a] of linear relationships between salinity and reactive phosphorus (RP) and nitrate (NO^3) concentrations at station 1, and estimated mean concentrations in the freshwaters discharged into the Lim Channel (mmol m^{-3}).

Time period	RP = aS + b				NO_3= aS + b			
	n	r	p	c(RP)	n	r	p	c(NO_3)
I-XII 1986					7	-0.958	0.001	94
XII/84-XII/85					9	-0.966	0.001	92
XI/82-XII/84	17	-0.850	0.001	0.9	22	-0.882	0.001	103
X/80-V/82	13	-0.925	0.001	0.8	16	-0.908	0.001	124
XII/78-II/80	17	-0.982	0.001	0.3	17	-0.882	0.001	48
X/73-XII/75	24	-0.718	0.001	0.5	16	-0.728	0.005	46
IV/71-VI/73	22	-0.730	0.001	0.5	7	0.949	0.005	66
IV/69-IV/71	13	-0.798	0.005	0.5				

[a]The statistical significance of the correlations is expressed by the probability level p at which the calculated correlation coefficient value is higher than the critical value given by the formula:

$$rt = \left(\frac{t^2}{t^2 + df}\right)^{1/2}$$

for a given degree of freedom n = n - 2 (Parker, 1979; p. 118).

The Budava and Rasa bays

The Budava and Rasa bays are located on the eastern Istrian coast and communicate with the relatively deep Kvarner Bay (up to 50 m). They have been earmarked as sites suitable for mariculture (Filic and Degobbis, 1979).

Very few nutrient data were collected in the framework of this project, data which were not considered representative of these bays, because of the inadequate sampling performed from the shore. Moreover, no salinity or other basic oceanographic data were provided. Literature or other available data are also limited, but adequate to describe, at least qualitatively, the oceanographic and trophic characteristics of the Budava and Rasa bays.

In the 30 m deep Budava Bay no significant freshwater discharge occurs (Babic et al., 1967), but shellfish cultivation, which started in 1982, is now in operation. The data available refer to a period immediately before mariculture started and were collected during an investigation carried out to determine whether the region was suitable for such an activity. Unfortunately the monitoring was not continued at the same stations near the mariculture facilities to detect eventual changes in the water quality.

Two cruises in March and May 1979, as well as 13 monthly cruises from March 1981 to May 1982, were performed in the inner part of the Budava Bay (depth 15-20 m). The results have shown that during the greatest part of the year the ranges of salinity (34.55-38x10^{-3}), orthophosphate (0.02-0.16 mmol m^{-3}), total phosphorus (0.07-0.37 mmol m^{-3}), ammonia (0.0-1.7 mmol m^{-3}), nitrite (0.00-0.28 mmol m^{-3}) and nitrate (0.2-8.1 mmol m^{-3}) concentrations are relatively small (CMR Rovinj, unpubl. results). Only in March 1979 (31.4x10^{-3}) and 1981 (26.6x10^{-3}) was the surface salinity significantly lower with respect to the rest of the year, with increased nitrate content (up to 10.3 mmol m^{-3}).

Seasonal measurements in the Rasa Bay (March and May 1979, August, September and October 1983 at 7 stations, depth 20-40 m) were also performed during an experiment related to mariculture. Very low surface salinity was observed in the inner part of the bay in March and May (12.4-29.8x10^{-3}) with increased nitrate concentrations (up to 32 mmol m^{-3}) and orthophosphate (up to 0.3 mmol m^{-3}). On the contrary, in summer and fall, the ranges were smaller: salinity 36.5-38.1x10^{-3}, oxygen saturation 92-116%, concentrations of orthophosphate 0.02-0.09 mmol m^{-3}, total phosphorus 0.06-0.27 mmol m^{-3}, ammonia 0.3-1.6 mmol m^{-3}, nitrite 0.02-0.11 mmol m^{-3}, nitrate 0.2-3.3 mmol m^{-3} and total nitrogen 3.0-9.6 mmol m^{-3}.

In conclusion, the Budava and Rasa Bays were not exceptionally loaded with nutrients since the concentrations were generally only somewhat higher than in the open Kvarner waters (Degobbis, 1983.). However, systematic monitoring should be improved as soon as possible in order to test whether any significant changes have occurred recently because of mariculture, and, in Rasa Bay, because of some additional activities undertaken in the meantime.

The Krka River estuary, the Sibenik coastal area and the Kornati Island region

The estuary is markedly stratified. The salinity of a relatively thin surface layer is always very low or near zero over the region, from the mouth of the Krka River to the entrance of Sibenik Bay (stations E1-E5 and E-9). But at the 6 m depth, salinity has never been below 33x10^{-3}and is usually near 38x10^{-3}. The Krka river discharge rate varies greatly from year to year, usually reaching its maximal value in the period from December to February (up to 170 m^3 s^{-1}) with a maximum of 300 m^3 s^{-1} (Sekulic and Lovric, 1986). Even in summer, when the river flow rate drops to minimum values (5-20 m^3 s^{-1}), stratification persists. Moreover, significant and variable precipitation (0.8-5.5 m^3 y^{-1}) also influences the groundwater discharge rate into the estuary (Sekulic and Lovric, 1986).

Due to these hydrographic characteristics, large nutrient concentrations and oceanographic parameter ranges occur both in the surface and in the bottom layers (Table 3.1.10). Particularly in the upper part of the estuary, significant quantities of nutrients accumulate in the bottom layer through regeneration processes, also traced by a significant decrease of dissolved oxygen saturation (down to 14%). In Sibenik Bay oxygen saturation did not decrease below 80% and the nutrient ranges were lower (Table 3.1.10).

If we compare the measured nutrient concentrations at the Krka mouth (station E1) with the surface phosphorus concentrations in the low salinity layer of the entire estuary we obtain a clear trend. A gradual enrichment of phosphorus compounds occurs as we move towards the open sea. This is particularly pronounced in the Sibenik Bay, in which the reactive phosphorus concentrations extrapolated to salinity zero are often several times higher than those at the mouth of the Krka River (Table 3.1.1), particularly in summer when the river flow rate is minimal. Interestingly, in summer, the inorganic nitrogen concentration was reduced almost to zero, indicating that it may be a primary limiting nutrient for phytoplankton primary production. The relatively significant enrichment of phosphorus with respect to nitrogen in the Sibenik Bay is probably due mainly to losses incurred during phosphate ore manipulation.

At the river mouth, significant seasonal nutrient variations characterized by minimal values during the warmer seasons were also noticed (Table 3.1.11).

Only a few chlorophyll a concentration values are available for the estuary (April, September and November 1985, May and November 1986). Maximum values were observed at the surface of the Sibenik Bay (up to 7 mg m^{-3}), while in the upper estuary values were lower and always below 4 mg m^{-3} (CMR Rovinj, unpubl. results). However, records of phytoplankton number and species composition indicate that the primary production has increased in the past 10 years (Marasovic, 1986). Moreover, dinoflagellate number percentage during blooms, previously dominated by diatoms, increased significantly in recent years. In the summers of 1983, 1984 and 1985, a new dinoflagellate species for this area, Prorocentrum minimum, accounted alone for about 15-30% of the total number of phytoplankton cells.

The coastal area stations C1 and C2, even if located in front of the entrance to the estuary, are mainly under the influence of oligotrophic open waters, thus high concentrations were rarely measured there. In contrast, at the nearshore station C3 the parameter values varied more widely than in the remainder of the coastal area and even the estuarine area (salinity 30.8-38x10^{-3}, oxygen saturation 103-123%, concentrations of reactive phosphorus 0.0-0.9 mmol m^{-3}, total phosphorus up to 2.9 mmol m^{-3}, ammonia up to 15 mmol m^{-3}, nitrite up to 1.2 mmol m^{-3}, and nitrate up to 32 mmol m^{-3}).

Maximal concentration values in the Kornati Island region were an order of magnitude lower than in the estuarine and polluted coastal areas and were typical for the open oligotrophic central Adriatic waters (Degobbis, 1983).

Table 3.1.10

Value ranges for basic oceanographic parameters, nutrient concentrations and total phosphorus contents in the Krka River Estuary, Sibenik coastal area and Kornati Island region (1983-1986).

Parameter[a]	Layer[b]	Ranges			
		Krka River Estuary Station E2,E3,E9	Sibenik area Station E4,E4A,E5	Coastal area Station C1,C2	Kornati Island area Station R1,R2
T/C°	s	5.4-23.6	7.1-24.0	10.4-23.0	13.3-22.1
	b	12.6-22.6	12.7-20.3	13.1-20.2	13.1-20.3
$Sx10^{-3}$	s	0.0-24.3	3.5-32.7	21.7-38.5	35.3-38.6
	b	34.6-38.4	36.4-38.4	33.3-38.5	37.0-38.6
pH	s	7.5-8.4	8.2-8.4	8.2-8.3	8.25-8.3
	b	7.9-8.4	8.2-8.4	8.2-8.3	8.2-8.3
O_2%	s	94-144	82-157	88-127	98-127
	b	14-141	79-128	91-129	93-138
RP	s	0.02-0.27	0.04-1.48	0.00-0.29	0.00-0.07
	b	0.04-0.45	0.02-0.40	0.00-0.26	0.00-0.03
TP	s	0.05-0.87	0.16-2.26	0.06-0.35	0.05-0.21
	b	0.13-0.75	0.03-0.70	0.00-0.42	0.06-0.23
NH_4	s	0.4-3.9	0.2-2.9	0.1-2.6	0.0-0.8
	b	0.1-10.4	0.0-3.0	0.1-1.7	0.0-0.7
NO_2	s	0.03-0.45	0.00-0.50	0.00-0.23	0.00-0.21
	b	0.00-1.12	0.00-1.00	0.00-0.15	0.00-0.35
NO_3	s	0.8-46.2	0.0-59.2	0.0-13.9	0.0-1.1
	b	0.0-6.2	0.0-6.0	0.0-0.5	0.0-0.7

[a]RP-reactive phosphorus, TP-total phosphorus, NH_4-ammonia, NO_2-nitrite, NO_3-nitrate (mmol m^{-3}).

[b]s-surface layer; b-bottom layer.

The Split coastal area

Seasonal nutrient measurements were performed in the Vranjic Bay (western Kastela Bay), in which mainly wastewaters are discharged, in front of the Split harbour influenced by sewage, in the estuary of the Zrnovica River and at a reference station near the Vis Island which is mainly under the influence of oligotrophic open central Adriatic waters. The value ranges of the parameters (Table 3.1.12) show increased concentrations, sometimes relatively high, particularly of reactive phosphorus, in the Split harbour and estuarine regions with respect to the reference station. However the dissolved oxygen saturation was always very high, indicating effective water mixing which minimizes the nutrient impact.

A "red tide" event occurred in the Vranjic area during September 1980 in conditions of minimal water exchange rate with the rest of Kastela Bay, with fish and shellfish kills due to oxygen depletion in the bottom layer (Marasovic and Vukadin, 1982). The densest blooms (up to 18×10^6 cells per liter) occurred in the sewage outfall discharge zone of the Vranjic Bay and were composed mainly of Gonyaulax polyedra Stein and in minor fractions of other dinoflagellates. Leaching of soil material excavated to build a marina may also have played a role in inducing the bloom.

Table 3.1.11

Nitrate and reactive phosphorus concentrations in the waters of the Krka River mouth and in the freshwater discharged into the Sibenik Bay, estimated by extrapolation to salinity zero.

Date	Concentrations (mmol m^{-3})[a]					
	Krka River mouth Station E1		Sibenik Bay Stations Station E4		Station E5	
	RP	NO_3	RP	NO_3	RP	NO_3
January 1983			0.17	20	0.14	15
February 1984	0.11	27	0.12	22	0.29	23
February 1986	0.26	45	0.39	57	0.47	47
April 1985	0.05	22	0.15	21	0.32	31
May 1983	0.16	13	0.29	4	0.17	3.5
May 1984	0.03	18	0.53	12	1.4	99
May 1986	0.36		1.0	9	1.1	13
July 1983	0.03	10	0.07	5	0.17	1
July 1984	0.02	7.9	0.18	7	0.54	0.3
July 1985	0.06	7.7	0.80	3	1.80	2
July 1986	0.11	11	1.7	1	1.2	2
October 1983	0.03	8.9	0.51	7	0.67	5
November 1984	0.00	25	0.58	22	0.80	32
November 1985	0.08	16	1.3	30	1.2	34
November 1986	0.10	17			1.4	18

[a]RP - reactive phosphorus; NO_3- nitrate.

Table 3.1.12

Value ranges for basic oceanographic parameters, nutrient concentrations and total phosphorus contents in the Split coastal area (1984-1986).

Parameter[a]	Layer[b]	Ranges Vranjic Area Station 1	Split harbour Station 5	Zrnovica Estuary Station 9	Vis Island area Station 11
T/C°	s	11.4-24.2	11.0-23.6	10.4-22.6	13.4-23.9
	b	11.5-19.3	13.2-18.2	12.4-20.3	13.5-14.9
$Sx10^{-3}$	s	29.0-36.8	30.9-37.7	32.8-37.7	37.1-38.6
	b	36.9-38.1	32.2-38.0	35.5-37.9	38.3-38.9
pH	s	7.7-8.4	8.1-8.4	8.1-8.3	8.18-8.24
	b	8.1-8.4	8.1-8.3	8.1-8.3	8.17-8.21
O_2%	s	88-138	94-120	100-125	100-107
	b	80-101	92-111	100-117	91-97
RP	s	0.04-0.14	0.06-0.52	0.05-0.53	0.03-0.07
	b	0.05-0.06	0.06-0.14	0.06-0.07	0.05-0.08
NH_4	s	0.8-2.3	0.4-3.0	1.1-3.9	0.4-2.0
	b	0.5-1.7	0.7-2.8	0.6-3.9	0.4-1.7
NO_2	s	0.03-0.22	0.05-0.57	0.05-0.38	0.03-0.09
	b	0.04-0.10	0.06-0.18	0.06-0.11	0.03-0.12
NO_3	s	0.8-2.1	0.7-1.8	0.5-1.3	0.3-0.8
	b	0.7-0.9	0.7-0.9	0.6-0.8	0.3-1.1

[a]RP-reactive phosphorus, NH_4-ammonia, NO_2-nitrite, NO_3-nitrate.

[b]s-surface layer; b-bottom layer.

Comparison of the investigated areas

The results obtained in the framework of the Monitoring Programme and other available data are summarized in Figs. 3.1.3 and 3.1.4 where ranges of relevant parameters in the investigated areas are compared, separately for surface and bottom layers. While in some regions (e.g. the Lim Channel, the northern Adriatic) the available data sets are very large (almost 20 year data series), in others the results are restricted to seasonal measurements in the past three or four years. However ranges are indicative for a preliminary estimate, at least qualitative, of the eutrophication degree in the investigated regions.

The marked differences between the surface nutrient concentration ranges among the various regions were related to salinity fluctuations (Fig.3.1.3). This indicates significant freshwater nutrient contributions in the northern Adriatic, the Lim Channel and the Krka River estuary with respect to the other regions. Fluctuations were more marked for nitrate, a chemical species among nutrients which is present in large concentrations in freshwater of the Yugoslav watersheds (Table 3.1.1). In contrast, very high phosphorus contents were measured in the Sibenik Bay, without a corresponding increase in nitrogen species concentrations. This is probably due to pollution from phosphate ore manipulation.

However the nutrient impact, traced by oxygen content variations, was very different in various regions. In the northern Adriatic, very intensive phytoplankton blooms occur in the western parts of the region, evidenced by extremely high oxygen concentrations (up to 236% of the saturation value) in the surface layer (Fig.3.1.3). However in the eastern northern Adriatic and in Yugoslav coastal regions values above 120% were exceptional (up to 137% in the inner Lim Channel and 157% in Sibenik Bay).

A serious consequence of the nutrient impact may be a severe oxygen depletion (below 50% saturation) in the bottom layer, owing to decomposition of sedimented organic matter produced during blooms in the surface layer. Benthic macrofauna and fish kills, including commercial species, usually occur during these events. Low oxygen values often occurred in the western part of the northern Adriatic at the end of the summer and the beginning of the fall as a result of the short-term marked water stability and minimal horizontal advection. However in particular oceanographic conditions, highly reduced oxygen values may occur at a larger scale in the entire northern Adriatic and persist for several months (e.g. in 1977, Degobbis et al., 1979). In the northern part of the Krka River estuary, even if relatively shallow, bottom oxygen was significantly reduced in the fall and winter, the values being mostly above 50% of saturation. Only once (in November of 1984, at a 6 m depth) was a minimal value (14%) reported (not included in Fig. 3.1.4). The nutrient concentrations in the Krka River are lower than for instance in the freshwater discharged in the Lim Channel, while the bottom oxygen ranges were similar. It is of interest to point out that in the lower, much deeper estuary region (the Sibenik Bay), in spite of more intensive primary production processes, the bottom oxygen concentrations were higher (80% of saturation value) than in the upper estuarine area. The latter is probably more closed to water circulation and highly stratified, and thus more sensitive to an increase of the nutrient load.

In the Budava and Rasa bays, as well as in the Sibenik and Split coastal area, and, particularly, at the reference stations (the Kornati and Vis Island) the fluctuations of parameters were minimal, both at the surface and at the bottom layer. Relevant to this is the fact that oxygen content values of these regions (for the Budava Bay no sufficient oxygen data were available) varied in limited ranges around the saturation value.

Exceptionally low salinity values (21.7×10^{-3} at the surface and 33.3×10^{-3} at the bottom, 10 m; not included in Fig. 3.1.3) were measured in May 1983 in the Sibenik coastal region, in front of the Krka estuary entrance. However, no significantly higher nutrient concentrations with respect to the other measurement periods were observed. Sometimes an increased reactive phosphorus concentration (up to 0.5 mmol m^{-3}) was measured at the entrance of the Split harbour and in the Zrnovica Estuary. But at the same time the inorganic nitrogen concentration was not increased. On the contrary in the Vranjic Bay, the reactive phosphorus values were always below 0.1 mmol m^{-3}. In the Rasa Bay, only a few nitrate concentration values (corresponding to salinity minima) were high, while the remainder of about 50 values were all below 3 mmol m^{-3}.

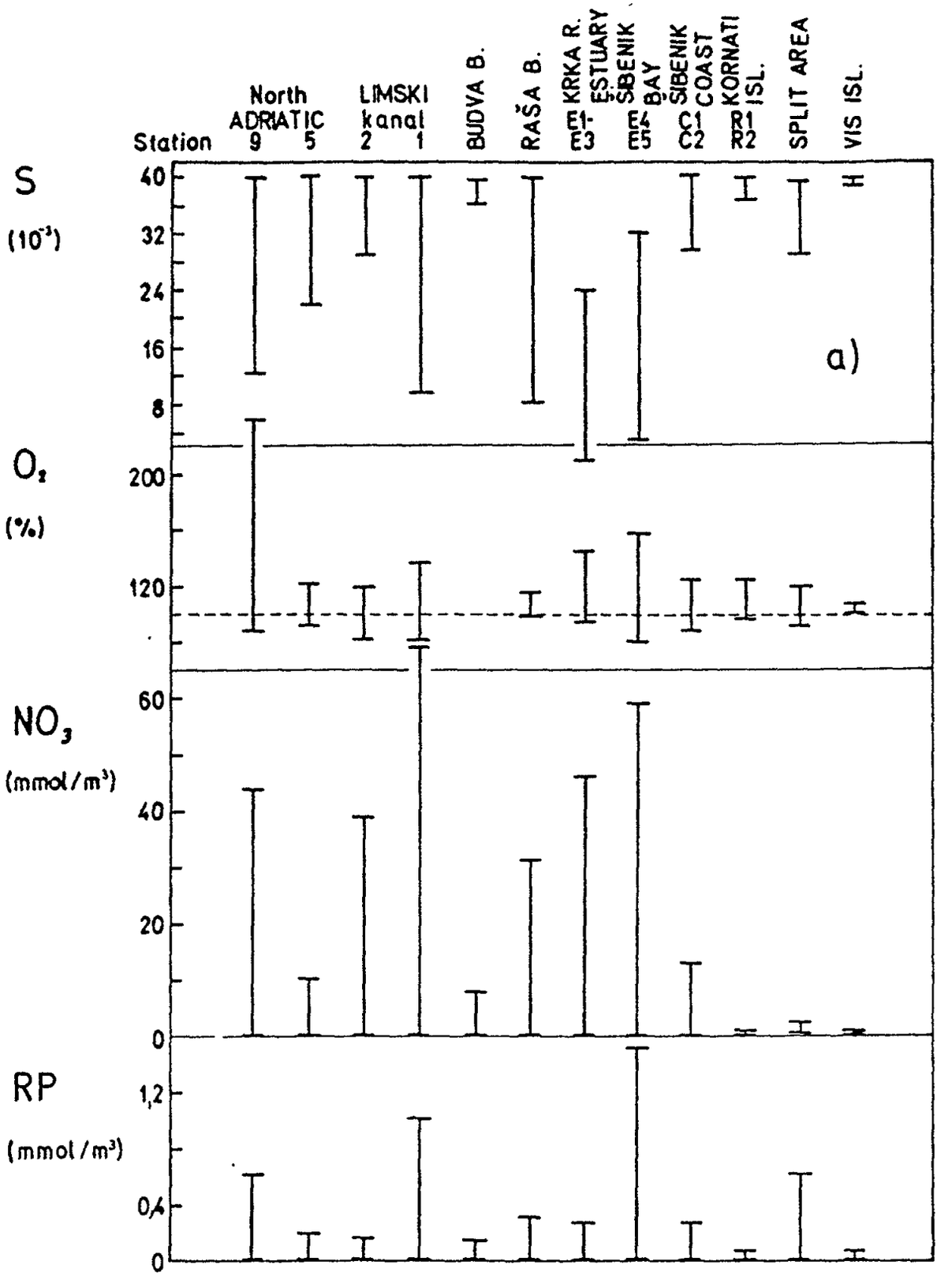


Fig. 3.1.3 Value ranges of salinity (S), oxygen saturation (O_2%), nitrate (NO_3) and reactive phosphorus (RP) concentrations in the surface layer of the monitored coastal areas in the framework of the Yugoslav National Monitoring Programme

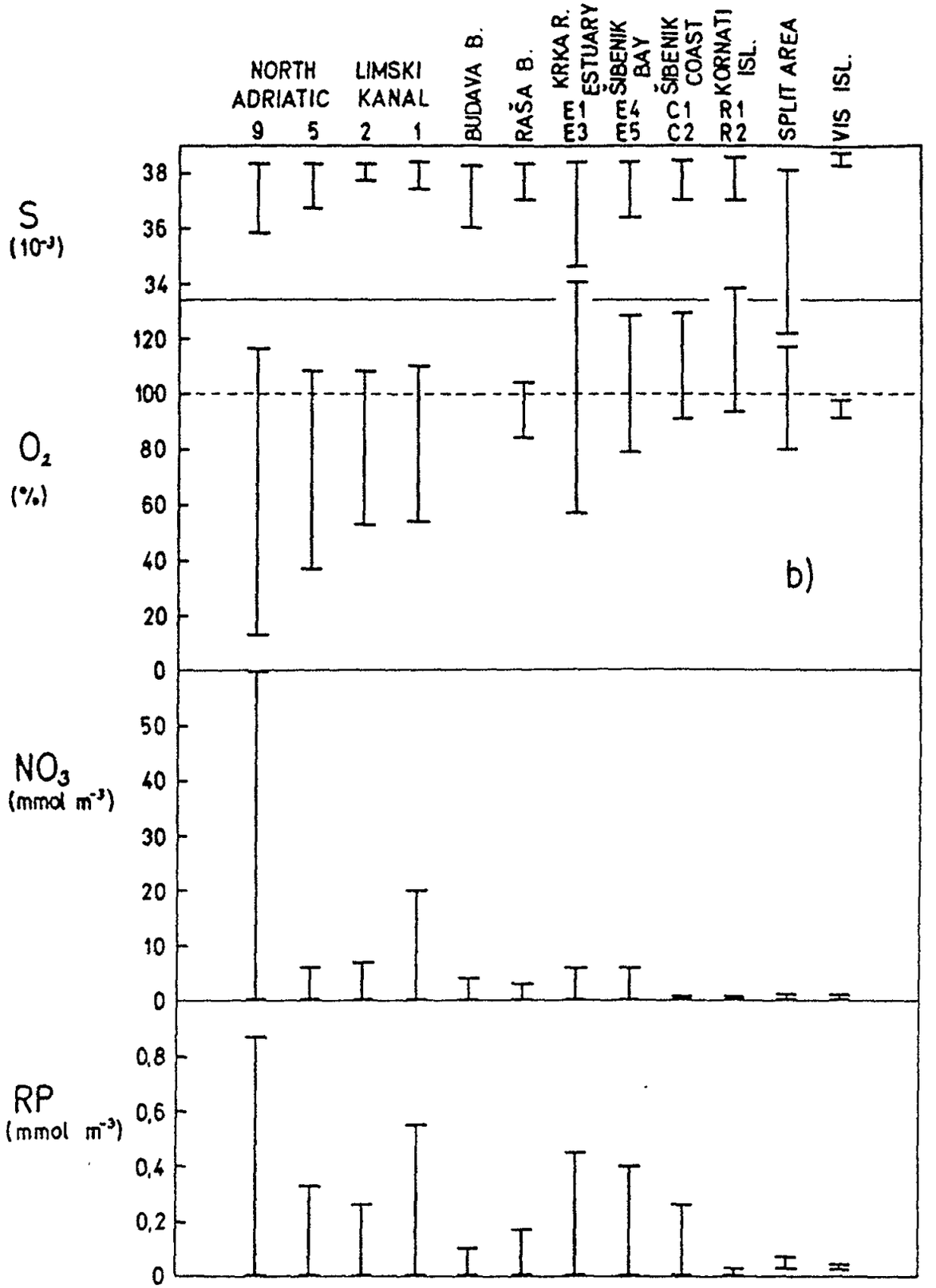


Fig. 3.1.4 Value ranges of salinity (S), oxygen saturation (O_2%), nitrate (NO_3) and reactive phosphorus (RP) concentrations in the bottom layer of the monitored coastal areas in the framework of the Yugoslav National Monitoring Programme

3.2. Heavy metals

Heavy metals in effluents

Heavy metals in wastewaters have been monitored since 1984 in the Slovenian coastal area (MBS-P), Rovinj area (CMR-R), Pula area (IPH-P), Rijeka area (FCES-Z), Sibenik area (CMR-Z) and Split area (IPH-S).

A review of the results of analysis of heavy metals in effluents in the investigated areas is presented in Table 3.2.1.

It can be generally concluded that there is no significant difference between the concentrations of heavy metals in urban (U) and industrial (I) wastewaters in the same area. However, significant differences in the concentrations of effluents in certain heavy metals could be noticed between areas as well as in the same area but different years of investigation.

The differences in the concentrations of Zn are evidently the greatest. The highest average concentration of Zn in the Slovenian area was 15500 ug l^{-1}, while an average of 12 ug l^{-1} Zn was reported for effluents in the Sibenik area. Concentration differences of one order of magnitude have been registered for Cd and Pb in different areas. The above mentioned extreme concentration differences are probably due to some methodological problems in sampling and analyzing.

Heavy metals in estuarine and sea waters

One of the basic problems in determining heavy metals in seawater is avoiding pollution of the samples during sampling, storage and analysis. The example of determining the concentrations of mercury in seawater samples in the Sibenik area (CMR-Z) shows the importance of choosing the most adequate sampling technique (Table 3.2.2).

The heavy metal content of seawater was monitored in the Sibenik, Dubrovnik and Montenegrin areas. Because of the great importance of physico-chemical processes that occur in the mixing zone of the surface and bottom waters of the Krka estuary (the Sibenik area), special attention was paid to defining the distribution and fate of heavy metals influenced by these processes. Therefore, ionic and total concentrations of certain heavy metals were monitored at various depths and salinities, starting from the Krka estuary, along the Sibenik coastal region, down to the reference stations in the Kornati Archipelago.

Examples of heavy metal distribution at station E-3 according to depth, salinity and complexing capacity are given for Zn, Cd, Pb and Cu as well as for Hg in Figures 3.2.1 and 3.2.2, respectively. The measurements date from 1985.

Table 3.2.1

Review of the results of heavy metal analysis (ug l^{-1}) in effluents of different areas.

YEAR	S[a]	Hg			Cd			Pb			Cr			Zn			Cu		
		n[b]	GM[c]	GSD[d]	n	GM	GSD	n	GM	GSD	n	GM	GSD	n	GM	GSD	n	GM	GSD
Slovenian coastal area																			
1984	U[e]	10	0.36	2.5	10	1.07	1.5	10	5.13	1.7		-		10	3550	1.6		-	
	I[f]	4	0.51	2.1	4	1.26	4.3	4	8.13	2.3		-		4	5130	2.3		-	
	R[g]	2	0.16	2.1	2	0.51	2.0	2	3.39	1.3		-		2	1230	3.2		-	
1985	U	10	0.54	2.6	10	4.26	3.5	8	8.51	1.7		-		10	15500	1.2		-	
	I	6	0.17	1.3	6	3.63	5.0	6	6.91	1.1	2	18.2	2.0	6	12300	1.1		-	
	R	2	0.21	1.6	2	0.61	1.0	2	6.76	1.1	2	25.1	1.2	2	11000	1.0		-	
1986	U	8	0.33	1.4	8	0.66	1.5	8	10.2	1.4		-		8	3540	1.4		-	
	I	7	0.17	1.2	7	0.36	1.2	7	4.16	1.4	6	9.33	1.9	7	2040	1.4		-	
	R	2	0.12	1	2	0.30	1.1	2	3.98	1.0	2	16.6	1.3	1	940	1.3		-	
Rovinj area																			
1984	I	11	0.092	1.9	12	0.04	1.7		-			-			-			-	
	II	7	0.083	2.1	10	0.85	2.7		-			-			-			-	
Pula area																			
1984	U	8	0.38	5.5	8	0.30	1.4		-			-			-			-	
	I	8	0.15	1.8	8	0.54	1.9		-			-			-			-	
1985	U	7	0.13	2.0	7	<1		7	<1			-			-		7	28.8	11
	I	7	0.25	11	7	<1		7	<1			-			-		7	389	2
1986	U	8	0.13	1.8	8	1		8	2.57	6.2		-			-			-	
	I	8	0.10	1.1	8	1		8	1.73	4.9		-			-			-	

Table 3.2.1 (cont'd)

YEAR	S[a]	Hg			Cd			Pb			Cr			Zn			Cu		
		n[b]	GM[c]	GSD[d]	n	GM	GSD	n	GM	GSD	n	GM	GSD	n	GM	GSD	n	GM	GSD
Rijeka area																			
1984	U	40	0.50	2.0	32	3.09	2.4	34	20.0	7.6		-		31	234	3.8		-	
	I	5	0.53	1.7	4	3.38	2.1	4	12.0	2.5		-		3	288	3.7		-	
1985	U	47	0.98	2.3	45	0.19	3.4		-			-		45	302	4.0		-	
	I	8	1.58	2.6	7	0.11	3.6		-			-		7	151	2.3		-	
1986	U	47	0.33	2.6		-			-			-				-		-	
	I	7	0.38	3.2		-			-			-				-		-	
Sibenik area																			
1984	I		-		3	0.04	2.5	3	2.76	3.6		-		3	25.0	2.6	3	39.1	8.9
1985	I		-		4	0.08	4.0	4	3.47	2.6		-			-		4	3.9	2.6
1986	I		-		4	0.10	15.1	4	2.34	3.5		-		4	12.0	5.1		-	
Split area																			
1984	U	28	1.08	3.2	28	2.75	2.5	28	38.3	2.7	28	3.62	2.6	28	182	2.0		-	
1985	U	28	0.89	2.6	25	6.03	1.6	24	66.1	1.9	28	25.7	3.9	28	-			-	
1986	U	28	3.38	1.8	27	8.51	2.4	27	43.6	2.4	27	7.76	2.0	110		2.3		-	

a) S: Type of samples (U-urban, I-industrial); b) n: Number of samples; c) GM: Geometric mean ($10^{\bar{X}}$(logX)); d) GSD: Geometric standard deviation (10^{σ}(log X)); e) U: Urban wastewater; f) I: Industrial wastewater; g) R: Unpolluted river.

Table 3.2.2

Effect of sampling manner on the measured concentration of Hg in sea water at station C-1 (Sibenik area), 08 September 1984.

	Hg concentration (ug l^{-1})		
Depth (m)	Manual pumping (PVC tube)	Diver (bottle)	Teflon sampler
0	1.1065	0.0015	0.0016* 0.0023
10	1.0395	0.0014	0.00087* 0.00098
21	0.5990	0.0012	0.00063* 0.00079

* independent samplings.

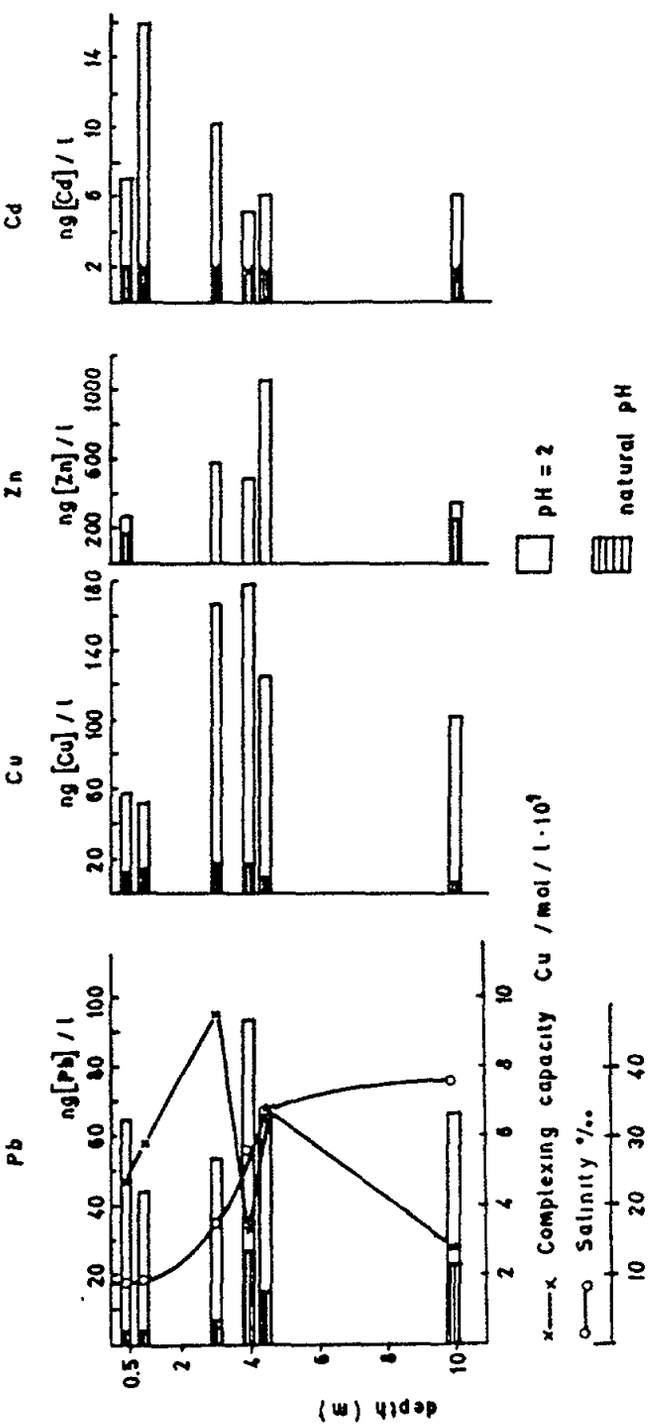


Fig. 3.2.1

Metal (Zn, Cd, Pb, Cu) distribution at station E-3 (the Sibenik area) according to depth, salinity and complexing capacity

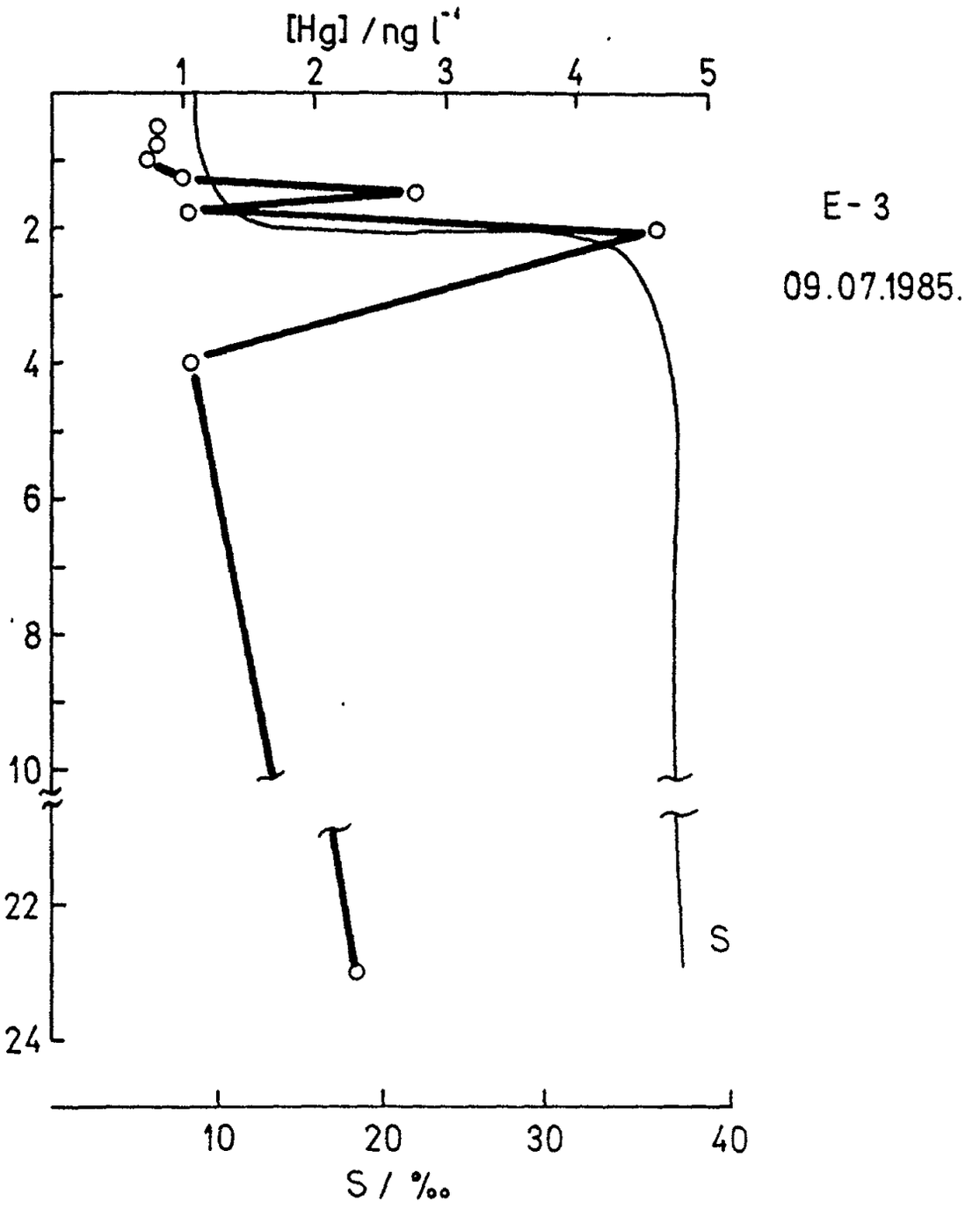


Fig. 3.2.2 Hg distribution at station E-3 (the Sibenik area) according to depth and salinity

In the mixing zone all metal concentrations were the highest, except for Cd. From the complexing capacity it is clear that in this area terrigenous dissolved organic matter was being dumped. One possible explanation of the metal concentration maxima noted in the salinity and complexing capacity discontinuity could be that they result from competition between sea water macrocomponents and complexed heavy metals with organic matter, resulting in the release of heavy metals. Another explanation could be that higher concentrations were the result of suspended matter concentration in the mixing zone.

At stations E-4 and E-5 this phenomenon shifted towards the surface and therefore the highest metal concentrations were recorded in the surface layer (above 6 m).

In addition, some seasonal variations of heavy metal concentrations are also evident, as shown for Cd in the surface water layer of the Sibenik area (Fig. 3.2.3).

However due to numerous factors which could potentially influence the data obtained, monitoring on a long time scale with a higher sampling frequency would be necessary for final evaluation of these results.

To obtain a general overview of the concentration levels of heavy metals (Hg, Cd, Zn, Pb, Cu) in the Sibenik area the geometric mean concentrations and standard deviations were calculated, separately for estuary, coastal and reference sampling stations for the period 1984-1986. The results are presented in Table 3.2.3.

Evidently, the mean concentrations of Hg, Pb and Zn were the highest (3.61, 237 and 1060 ng l^{-1}, respectively) in 1984 and of Cd (48 ng l^{-1}) in 1986, indicating the need for of more detailed future investigations.

In Table 3.2.4 the results of heavy metal determinations of the Sibenik, Dubrovnik and Montenegrin coastal areas are summarized.

The interpretation of the extremely high mean concentrations of Zn (3810 ng l^{-1}) in the Montenegrin coastal area (1985) and the increased concentrations of Cd in the Dubrovnik (34.8 ng l-1) and Sibenik (42.2 ng l^{-1}) areas, in 1985 and 1986 respectively, requires future examination.

Table 3.2.5 presents dissolved metal concentrations obtained for the Adriatic coastal waters. The Table also shows recent results for concentrations of the same heavy metals in some open seas, coastal seas and estuaries in the world.

Evidently, the range of the average dissolved Cd concentrations in the Adriatic coastal waters (8.3-42.2 ng l^{-1}, Table 3.2.4) is slightly higher than the reported concentration range of Cd for the open western Mediterranean (4-17 ng l^{-1}, Table 3.2.5, Boyle et al., 1984; Laumond et al., 1983; Kremling and Peterson, 1981) and lower than that for oceans (10-70 ng l^{-1}, Table 3.2.5, Forstner and Wittman, 1983). Moreover, the average concentration range of Hg of the Yugoslav Adriatic coastal waters (1.3-7.0 ng l^{-1}, Table 3.2.4) fits well within the concentration range of Hg (0.2 -20 ng l^{-1}), recently reported by May and Stoeppler, 1983 for various investigated areas (Table 3.2.5).

Table 3.2.3

Review of mean total heavy metal concentrations in water samples (pH 2) from the Krka Estuary and Kornati Archipelago in the 1984-1986 period.

Type of samples[a]	Hg ng l^{-1}			Cd ng l^{-1}			Pb ng l^{-1}			Zn ug l^{-1}			Cu ng l^{-1}		
	n	GM	GSD	n	GM	GSD	n	GM	GSD	n	GM	GSD	n	GM	GSD
1984															
E	9	3.61	1.40	17	10.8	2.56	34	110	2.40	34	1.00	1.79	35	133	3.57
C	6	0.95	1.44	8	11.4	2.54	12	106	2.11	12	1.06	1.86	12	122	2.91
R				7	14.9	2.44	8	237	2.30	8	1.00	1.78	8	176	2.91
1985															
E	9[b]	2.51	1.61	34	8.4	2.59	34	55.6	2.04	32	358	2.01	34	108	2.34
C	3[b]	2.26	2.02	8	8.2	2.14	8	62.5	1.33	8	446	1.58	7	148	1.90
R	2	0.55	1.14	2	2.6	3.96	2	65.	31.93	2	491	1.62	2	101	4.66
1986															
E	36	1.33	2.21	36	41.7	2.00	-	-	-	-	-	-	-	-	-
C	12	1.12	1.80	12	48.0	1.88	-	-	-	-	-	-	-	-	-
R	6	0.33	1.34	6	26.1	2.14	-	-	-	-	-	-	-	-	-

For n, GM, GSD, see Table 5.2.1

a) E: Estuary water; C: Coastal water; R: Reference station.

b) Number of average values.

Table 3.2.4

Review of mean heavy metal concentrations in sea water samples from different areas (ug l^{-1}).

Area	Hg			Cd			Pb			Zn			Cu		
	n	GM	GSD	n	GM	GSD	n	GM	GSD	n	GM	GSD	n	GM	GSD
1984															
Sibenik	21	2.1	2.1	31	11.7	2.5	53	118	2.5	53	1020	1.8	54	568	3.7
Dubrovnik	5	7.0	1.5	12	9.0	3.3	14	59.6	3.7	13	614	1.9	12	52	3.7
1985															
Sibenik	11	2.1	1.8	42	8.3	2.5	42	53.8	2.0	40	374	1.9	42	115	2.3
Dubrovnik	10	1.4	1.8	5	34.8	1.4	10	34.0	1.6	10	254	1.5	10	158	2.1
Montenegrin coast	5	2.0	1.6	12	10		12	140	3.0	12	3810	2.4	12	357	1.6
1986															
Sibenik	50	1.3	2.1	49	42.2	2.0	-	-	-	-	-	-	-	-	-
Dubrovnik	10	4.8	1.8	8	27.8	2.3	8	23.7	2.0	8	361	1.7	8	52.9	2.6

For n, GM, GSD, see Table 3.2.1.

Table 3.2.5

Heavy metal determination data in seawater (ug l^{-1}).

Area	Cd	Cu	Pb	Zn	Reference
Eastern coast of England	0.46	2.9	1.3		Taylor, 1979
North Sea	0.025-0.200	0.2-1.0			Jones and Jefferies, 1983
Southern Bight	0.02-0.12	0.2-1.2		0.3-12	Duinker and Nolting, 1982
Western Atlantic	0.023	0.26		0.16	Bruland and Franks, 1981
Coast of Belgium and the Nederlands	0.012-0.077	0.34-1.91	0.041-0.857		Balls, 1985
Humber Estuary	0.026-0.600	0.32-3.3	0.010-0.055		Balls, 1985
Western Frisian Islands (North Sea)	0.017-0.040		0.038-0.078		Mart, 1984
Italian estuaries	0.004-0.029	0.11-0.95	0.025-0.950		Breder, et al., 1980

Table 3.2.5 (cont'd)

Area	Cd	Cu	Pb	Zn	Reference
Ligurian coast	0.002-1.4	0.010-7.4			Baffi, et al., 1983
Bay, Greece		1.7-1.9	2.3-2.9	4-13	Scoullos and Dassenakis, 1983
Ocean basic concentrations	0.01-0.07	0.1-0.3	0.005-0.015	0.01-0.6	Forstner and Wittmann, 1983
Sibenik coastal waters	0.001-0.030	0.034-0.412	0.040-0.104	0.210-0.900	*
Dubrovnik coastal area	0.022-0.056	0.058-0.420	0.011-0.063	0.210-0.900	*
Western Mediterranean coastal waters	0.004	0.11			Boyle, et al., 1984
	0.005-0.010	0.06-0.13	0.025-0.075		Laumond, et al., 1983
	0.017±0.007	0.21±0.07		0.40±0.16	Kremling and Peterson, 1981
	0.008	0.090	0.030-0.040		Laumond, et al., 1984

	Hg ng l^{-1} seawater	Reference
Magra Estuary	1.8-13.5	May and Stoeppler, 1983
La Spezia Bay	1.4-20	May and Stoeppler, 1983
Open Ligurian Sea	1.3-7.2	May and Stoeppler, 1983

Table 3.2.5 (cont'd)

Area	Hg ng nl^{-1} seawater	Reference
North Sea coastal waters	4.6-15.2	May and Stoeppler, 1983
Baltic Sea coastal waters	0.4-3.7	May and Stoeppler, 1983
Open Baltic Sea	0.2-2.2	May and Stoeppler, 1983
Northwestern Pacific coastal waters	0.2-1.0	Bloom and Crecelius, 1983
Northern Tyrrhenian Sea	1.7-12.2	Seritti, et al., 1982
Sibenik coastal waters	1.1-4.6	Anonymous, 1987
Kornati Archipelago	0.5-0.6	Anonymous, 1987
Dubrovnik coastal waters	0.5-3	Anonymous, 1987
Adriatic Sea	10-210	Kosta, et al., 1978
Southwestern Mediterranean	16-30	Fukai and Huynh-Ngoc, 1976
Western Ligurian Sea	17-30	Fukai and Huynh-Ngoc, 1976
Tyrrhenian Sea	20-30	Fukai and Huynh-Ngoc, 1976

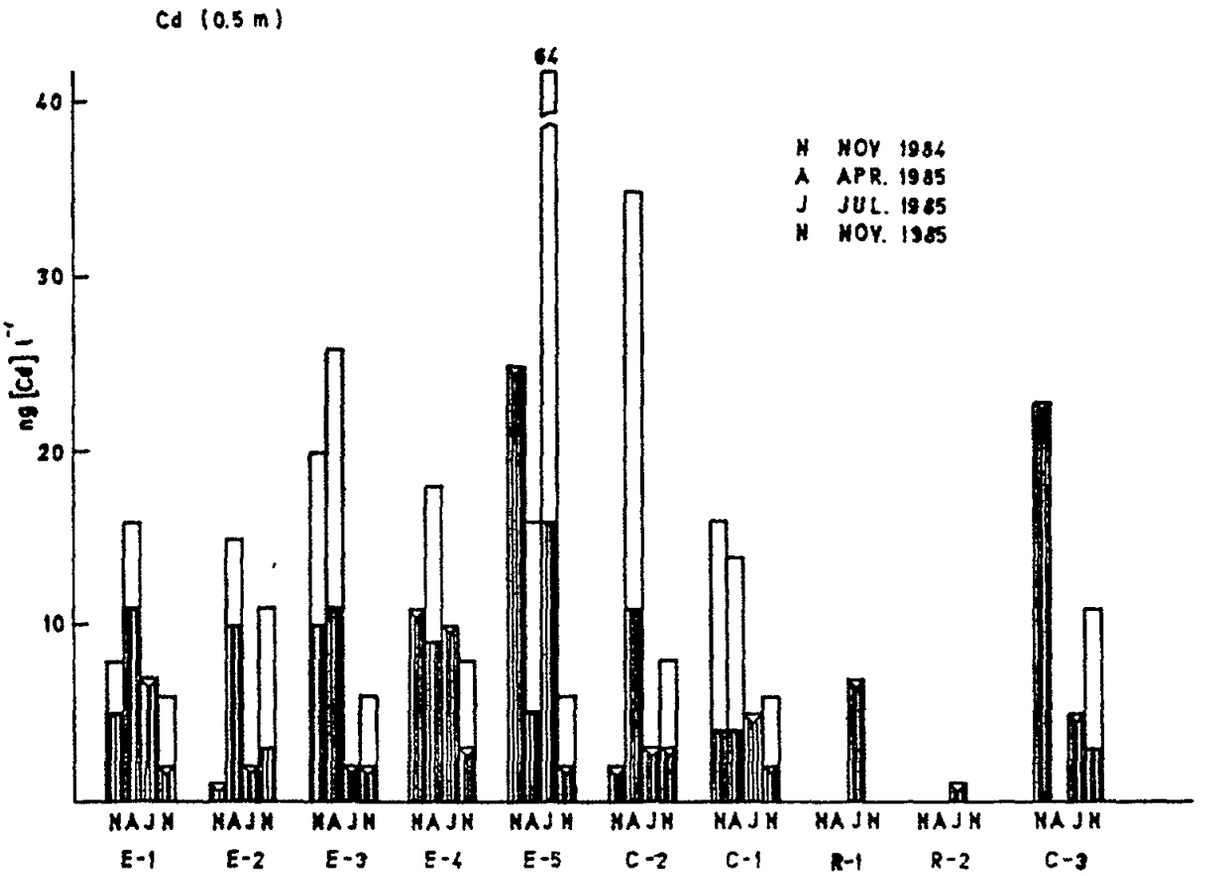


Fig. 3.2.3 Cd periodical concentration distribution in the surface water layer in the Sibenik area

Thus, despite the fact that the coastal and estuarine Adriatic waters are under the impact of urban, industrial and recreational centres, their water Cd and Hg contents indicate no significant pollution if compared with the above mentioned areas.

Heavy metals in suspended particles

Cd and Hg in suspended particles were measured in the period 1983-1986 in the Slovenian coastal area only.

An overview of the results obtained is presented in Table 3.2.6. The data obtained in 1985 are generally much higher than those obtained in 1986.

The majority of the data from 1986 are in fairly good agreement with Cd concentration values ranging from 0.4 to 2.5 mg kg^{-1} DW in suspended matter of the Duinkerque and Schuldt (Gillanin et al., 1979) as well as the Elbe river estuaries (Ahlt, 1983).

Apart from some extremely high values of Hg concentrations found in 1985 in suspended particles of the Slovenian coastal area, expressed in ng l^{-1}, the values correspond with those found in northern Tyrrhenian coastal waters (1.5-8.0 ng l^{-1}, Ferrara et al., 1986), an area which is influenced by Hg of anthropogenic origin.

The well defined Hg concentration maxima in suspended particles, found in May 1985 at all stations of the Slovenian coastal area and indicating a seasonal change of Hg concentrations, could not be justified on the basis of the investigations carried out in 1986.

Heavy metals in biological material

The Hg and Cd content of Mytilus galloprovincialis was monitored in all investigated areas. Furthermore, in some areas other heavy metals (Zn, Pb, Cu) and marine organisms were also monitored. An overview of the results obtained since 1983 is presented in Table 3.2.7. A graphic representation of the mean Hg and Cd concentrations in mussels along the Yugoslav Adriatic coast is given in Fig. 3.2.4.

On the basis of the geometric mean concentrations of Hg and Cd in mussels (Mytilus galloprovincialis), one can generally conclude that in all investigated areas, except the Split area, no significant concentration change can be observed.

In the Split area however, in the period 1983-1986, a decrease of the average concentration of Hg from 532 to 35.3 ug kg^{-1} WW and of Cd from 114 to 27.6 ug kg^{-1} WW was noticed. The Hg concentration decrease is especially evident at station 1, which is directly influenced by the effluents of the chloralkali plant "Jugovinil" and is probably due to the positive effects of the sewage treatment plant. A certain decrease of Cd contamination of mussels is also evident (Fig. 3.2.5).

Table 3.2.6

Review of heavy metal concentrations in suspended matter in the Slovenian coastal area.

Metal	Year of sampling	Concentration range ng l^{-1}	No of samples	GM ng l^{-1}	GSD	GM mg kg^{-1} DW	GSD
Hg	1983	9.9-12.3	2	11.0	1.2		
	1985	<1-273	45	13.2	4.1	7.69	5.2
	1986	2-14	48	6.3	1.7	1.61	1.7
Cd	1983	2.1-3.2	2	2.6	1.4		
	1985	<0.1-61	52	6.55	5.9	2.91	4.7
	1986	<0.7-28	37	4.42	3.0	1.23	3.5

For GM and GSD see Table 3.2.1

Table 3.2.7

Review of heavy metal concentrations in marine organisms in different areas.

Year	Hg (ug kg^{-1} WW)				Cd (ug kg^{-1} WW)			
	n	range	GM	GSD	n	range	GM	GSD
Slovenian coastal area								
Mytilus galloprovincialis								
1983	4	18-51	25.1	1.6	4	120-216	164	1.3
1984	8	24-40	30.5	1.2	4	170-304	218	1.3
1985	7	19-32	27.7	1.2	8	222-434	266	1.3
1986	16	18-32	25.0	1.2	16	180-295	228	1.2
Pagellus erythrinus								
1983	2	420-618	509	1.3	-	-	-	-
1984	5	338-1413	782	1.8	5	3.3-5.1	4.4	1.2
1985	7	390-827	437	1.6	7	1.9-5.5	2.8	1.6
1986	4	47-410	134	2.7	4	20.7-3.4	1.5	2.0
Rovinj area								
Mytilus galloprovincialis								
1983	8	17-28	20.1	1.2	8	60-240	135	1.6
1984	10	6-28	15.8	1.8	10	50-240	109	1.8
1985	11	9-60	24.8	2.0	9	10-230	78.7	3.4
1986	10	11-44	21.4	1.5	10	41-219	90.0	1.5
Zooplankton								
1985	6	3-9	5.1	1.6	6	62-180	97.0	1.4

Table 3.2.7 (cont'd)

Year	Hg (ug kg^{-1} WW)				Cd (ug kg^{-1} WW)			
	n	range	GM	GSD	n	range	GM	GSD
Mytilus galloprovincialis								
Pula area								
1984	10	6-86	32.0	2.6	7	175-230	190	1.1
1985	8	1-133	33.8	4.5	8	98-208	135	1.3
1986	8	13-36	28.3	1.5	8	131-242	193	1.3
Rijeka area								
1986	8	11-31	20.7	1.4	8	84-210	131	1.4
Sibenik area								
1983	7	6-77	36.2	2.3	7	100-338	152	1.7
1984	27	11-458	42.5	2.7	27	85-310	152	1.5
1985	19	2-64	22.1	2.1	17	80-373	126	1.5
1986	26	20-49	31.2	1.3	26	69-447	140	1.5
Split area								
1983	4	300-730	532	1.5	4	75-280	114	1.8
1984	8	20-240	149	2.3	8	10-140	64.9	2.3
1985	12	10-93	39.6	2.6	12	40-240	87.3	1.6
1986	9	12-84	35.3	2.1	9	5-85	27.6	2.8

Table 3.2.7 (cont'd)

Year	Hg (ug kg^{-1} WW)				Cd (ug kg^{-1} WW)			
	n	range	GM	GSD	n	range	GM	GSD
Dubrovnik area								
Mytilus galloprovincialis								
1984	6	14-28	19.5	1.3	6	116-213	162	1.2
1985	15	16-45	23.0	1.6	15	110-248	168	1.3
1986	12	18-55	28.6	1.4	12	158-810	259	1.5
Ostrea edulis								
1984	2	17-22	19-4	1.2	2	457-672	554	1.3
1985	3	22-47	36.6	1.5	3	525-1140	766	1.5
1986	2	31-55	41.3	1.5	2	690-810	748	1.1
Plankton (mg kg^{-1} DW)								
1984	5	20-70	33.0	1.6	5	276-683	395	1.5
1985	10	10-36	13.5	1.8	10	95-1460	383	2.6
1986	9	9.5-93.9	38.1	2.4	9	747-3570	1750	1.7

For n, GM and GSD see Table 3.2.1

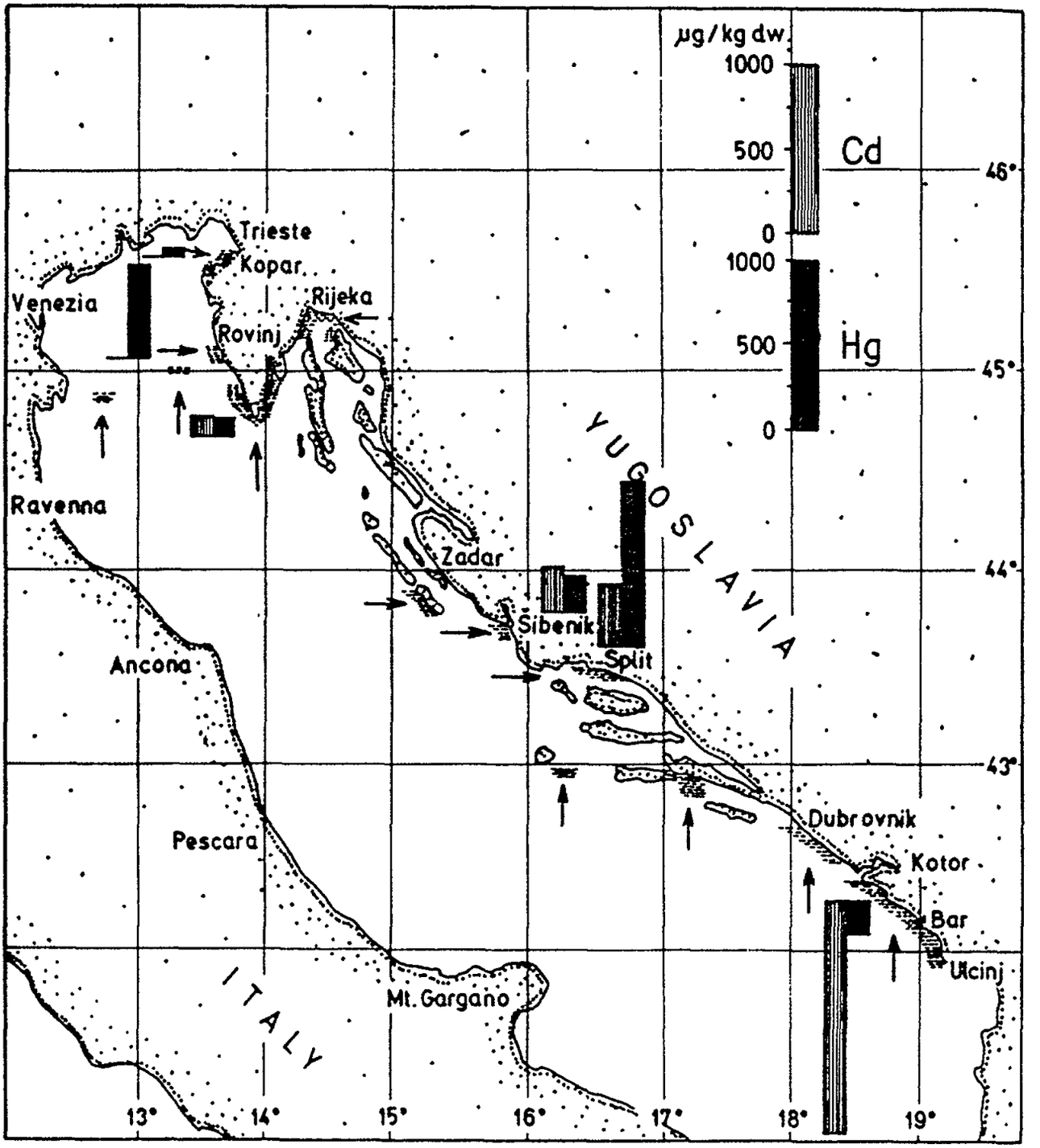


Fig. 3.2.4 An overview of Hg and Cd content of mussels (Mytilus Galloprovincialis) in various investigated areas

Except for the Split area, the average concentrations of Hg in Mytilus galloprovincialis are relatively uniform with values generally between 20 and 40 ug kg^{-1} WW. The mean Cd concentrations in Mytilus galloprovincialis differ more significantly. The average of the geometric mean concentrations of Cd is the highest (216 ug kg^{-1} WW) in the Slovenian coastal area and the lowest (65 ug kg^{-1} WW) in the Split area.

Heavy metals in sediments

A review of Hg and Cd content of sediments in the investigated areas is presented in Table 3.2.8. The highest concentrations of Hg were registered in the Rovinj and Split areas. A graphic representation of Hg and Cd content of sediments in the investigated areas is presented in Fig. 3.2.6.

Results for mercury concentrations in sediments of the Slovenian coastal area, obtained in 1986, confirmed previously reported results from the years 1983, 1984 and 1985. The samples from the offshore stations (KK and STT) revealed a significantly higher content of mercury than the samples from the corresponding inshore stations (K and ST). The mean value of the mercury content ratio between offshore and inshore stations (KK/K and STT/ST) was 2.5. These results confirm the assumption that the highly polluted North Italian rivers represent an important part of the pollution impact on the Gulf of Trieste.

However for the final interpretation of the data, the granular structure, influenced by sedimentological processes and the distribution of heavy metals in conjunction with granular size must also be studied. In other words, it is possible that the difference in the granular structure of the sediments and the fact that the small particles with relatively large specific surfaces capable of adsorbing large amounts of heavy metal create to a certain extent the differences in heavy metal content in sediments of the offshore and inshore stations.

Furthermore, it must be noted that the Soca river, with its effluent carrying waters from the mercury mining district of Idrija in Yugoslavia, contributes a substantial part of the mercury load mentioned above.

The results from the inshore stations (K, ST and MA) show that the rather heavily industrialized Koper basin, represents the most polluted inshore area with respect to heavy metals, while the lowest pollution has been found in the basin of Piran, the recreational tourist area.

In the Rovinj area the concentration of Hg in sediments ranged from 100 to 4380 ug kg^{-1} DW. The highest concentration of Hg (Fig. 3.2.7) of non identified origin has been found at station 6a (the main harbour) and station 6b (a tobacco factory). These data are of the same order of magnitude as those reported for the Split area.

Table 3.2.8

Review of heavy metal concentrations in sediments of different areas in the 1983-1986 period.

	Hg (ug kg^{-1} DW)				Cd (ug kg^{-1} DW)			
Year	n	range	GM	GSD	n	range	GM	GSD
Slovenian coastal area								
1983	5	9.6-66.4	31.7	2.1				
1984	5	23.9-155	64.4	2.0				
1985	12	24-463	58.7	2.5				
1986	12	258-270	72.8	2.0				
Rovinj area								
1983		110-4380						
1984	5	150-2330	526	3.7				
R	1		34					
1985	5	100-3270	449	4.3				
1986	5	100-3240	745	6.0				
R	1		160	1.2				
Pula area								
1984	2	132-202	163	1.35	2	260-270	265	1.0
1985	2	122-138	129	1.10	2	51-221	106	2.8
1986	1	-	76	-	1	-	75	-
Sibenik area								
1983	-	-	-	-	8	42-1145	227.32	2.9
1983 R	-	-	-	-	2	94-136	113.07	1.3
1984	32	5.4-667	88.90	4.1	32	97-765	263.40	1.9
1984 R	6	10-15.5	12.35	1.2	6	71-218	132.67	1.5
1985	8	170-973	409.26	1.8	8	361-3103	830.90	2.3
1985 R	2	237-422	316.25	1.5	2	189-308	241.27	1.4
Split area								
1983	4	120-2290	598	4.7	4	110-1950	513	3.9
1984	2	1680-4800	2839	2.1	2	200-1480	483	2.8
1984 R	1	-	122	-	-	-	-	-
1985	9	90-2430	461	4.0	9	182-540	313	1.3
1985 R	2	50-122	78	1.9	2	-	100	1
1986	3	380-3860	1207	3.2	3	120-400	238	1.9
1986 R	1	-	40	-	-	-	60	-
Montenegrin area								
1985	9	113-328	146	1.4	10	490-2880	1538	2.0
	-	-	-	-	7	910-1530	1236	1.4

For n, GM and GSD see Table 3.2.1.

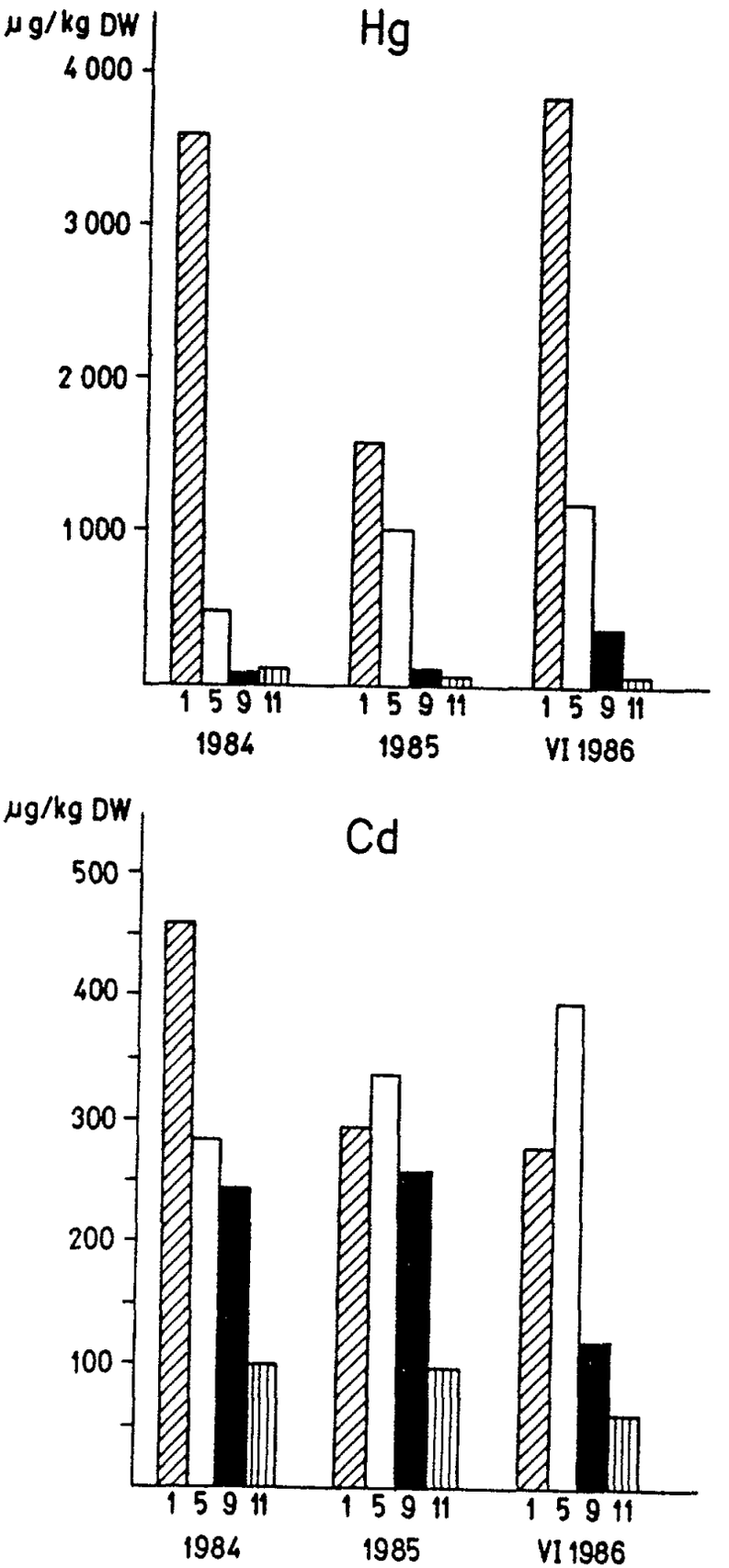


Fig. 3.2.5 Hg and Cd content of Mytilus Galloprovincialis at stations 1, 5 and 9 of the Split area in the 1984-1986 period

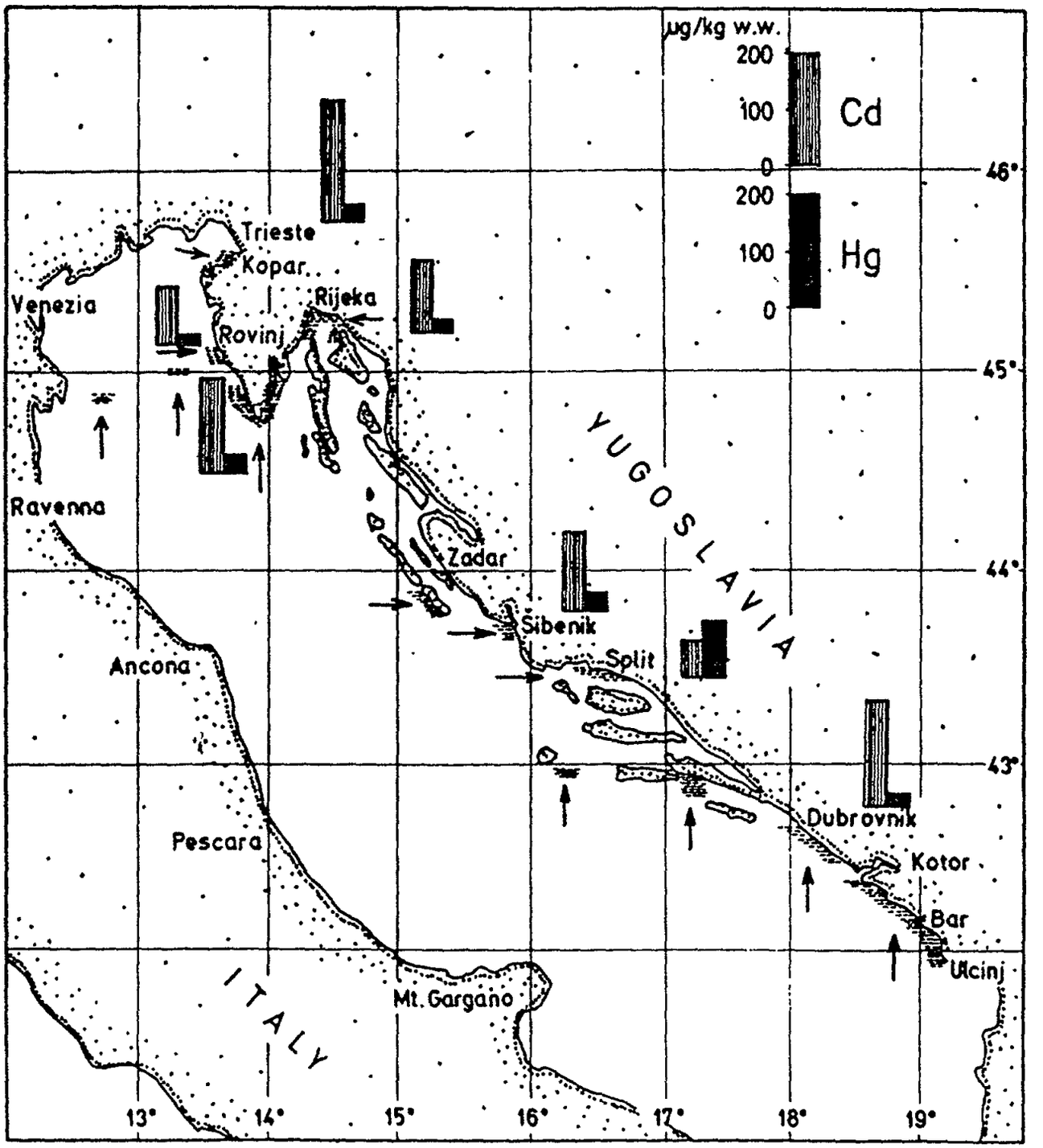


Fig. 3.2.6 An overview of Hg and Cd content of sediments in various investigated areas

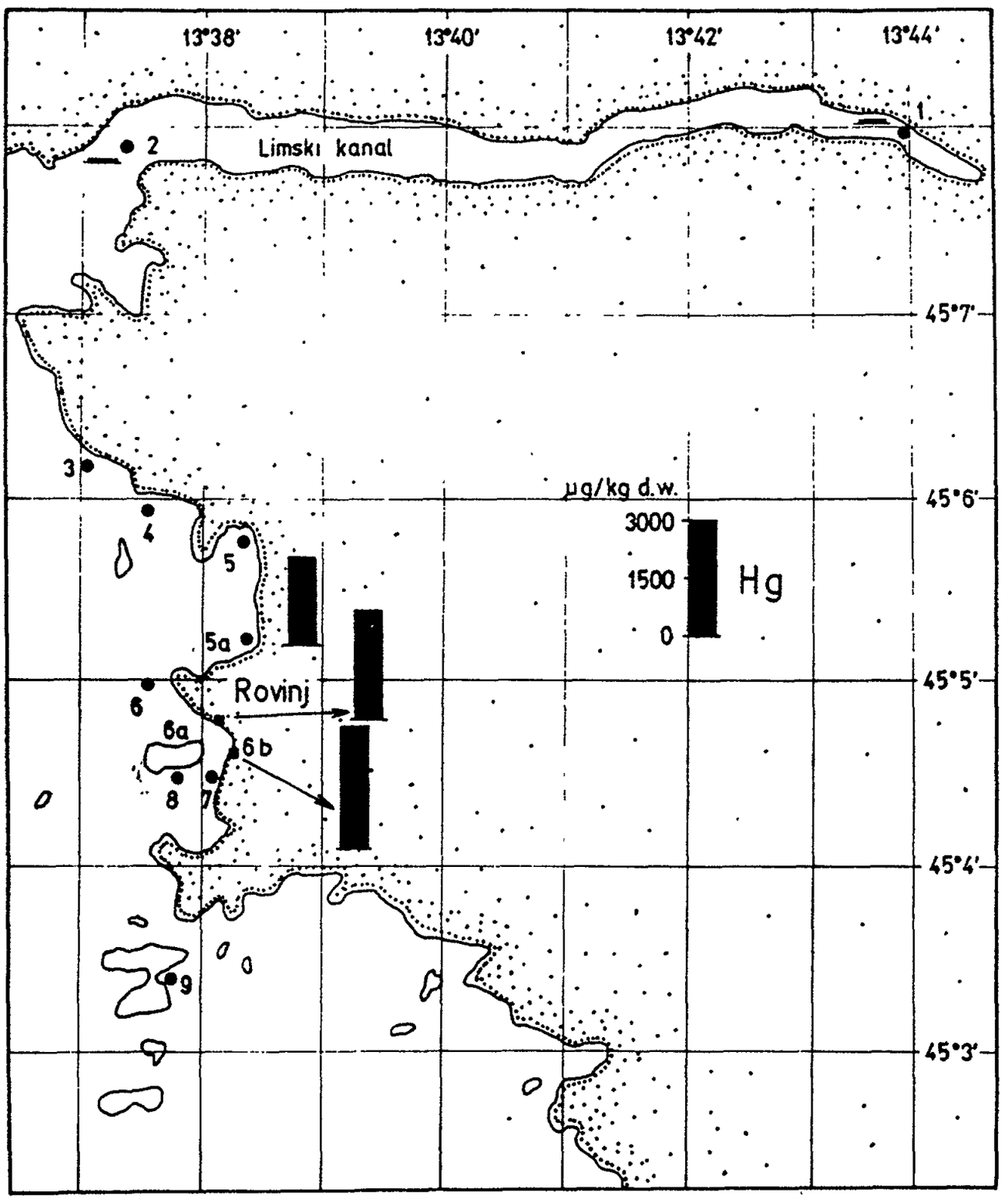


Fig. 3.2.7 Hg content of sediments in the Rovinj area

The Hg concentrations reported from the Pula area are relatively low (122-202 ug kg^{-1} DW) and uniform. However, concerning the extremely low concentrations reported for Pb and Cu,the analytical techniques used have to be verified before final conclusions can be drawn.

In 1983, different grain sizes of sediment samples of the Sibenik area were analyzed for Pb, Cd, Cu and Zn. The results of measurements show that the heavy metal content of various grain sizes was different. Generally, the smallest grain sizes investigated (75-(20-25) um) contained the largest amounts of heavy metals.

In 1984, only the total heavy metal content of the sediments was measured. The average metal concentrations obtained are presented in Table 3.2.9. The highest concentrations of the investigated metals were measured at the estuarine stations E-2, E-3, E-4 and E-5 as well as at the coastal station C-3.

In 1985 and 1986, the heavy metal content of sediments with grain size of only $<$75 um was determined. The data obtained are presented in Table 3.2.10. The concentrations measured in 1985 were generally maximal at station C-3, but at the other sampling stations, except for some extreme values (Zn at station E-1 and E-4, Cd at stations E-4 and C-1), the data obtained were generally uniform with no significant differences between estuarine, coastal and reference stations. In 1986 however the maximal concentrations of Hg and Cd were measured at the estuarine stations E-4 and E-2, respectively.

The data obtained can neither be directly compared with the previous results nor with the results of the other investigated areas. This indicates an urgent need for the standardization of analytical procedures.

The results of Hg and Cd determinations in sediments (fractions $<$250um) of the Split coastal area indicate a significant Hg and Cd contamination (maximum values 4800 and 1950 ug kg^{-1} DW, respectively) in the coastal area in comparison with reference station 11 (maximum values 422 and 218 ug kg^{-1} DW, respectively).

Contrary to the heavy metal content of mussels, no significant change of Hg and Cd concentrations in sediments of the Split area could be noticed during the period of investigation 1983-1986 (Fig 3.2.8).

Table 3.2.9

The average metal concentration in sediments of the Sibenik aquatorium (mg kg^{-1} and Hg ug kg^{-1}) at various locations in 1984.

Location	Zn	Cd	Pb	Cu	Hg
E-1	30.6	0.48	3.4	8.6	6.1
E-2	61.0	0.61	29.4	25.3	300.0
E-3	100.9	0.50	31.8	21.2	268.0
E-4	105.0	0.31	26.7	14.4	243.0
E-5	69.6	0.51	22.4	30.0	143.0
C-2	11.3	0.13	8.6	4.9	49.0
C-1	9.0	0.13	7.0	3.6	24.0
R-1	6.1	0.16	6.1	3.3	11.0
R-2	8.2	0.12	6.9	4.3	12.5
C-3	86.9	0.37	43.23	64.5	155.3

Table 3.2.10

Heavy metal concentrations in sediments (grain size 75 um) of the Sibenik aquatorium in 1985 and 1986. All concentrations are expressed in mg kg^{-1} DW except for Hg which is expressed in ug kg^{-1} DW.

Station	Hg		Cd		Zn	Pb	Cu
	1985	1986	1985	1986	1985	1985	1985
E-1	170	-	0.448	0.752	105.2	16.1	6.01
E-2	352	500	0.705	0.990	155.6	36.5	28.41
E-3	318	413	0.368	0.540	97.6	43.1	14.89
E-4	682	1875	1.553	0.250	250.6	95.8	41.00
E-5	613	754	0.361	0.540	99.9	49.5	20.31
C-2	410	711	0.529	0.500	48.6	61.2	12.99
C-1	248	886	3.103	0.340	90.4	69.7	15.48
R-1	422	-	0.308	-	47.2	35.2	10.40
R-2	237	-	0.189	-	47.9	28.7	18.27
C-3	973	967	2.124	0.710	352.7	164.2	84.51

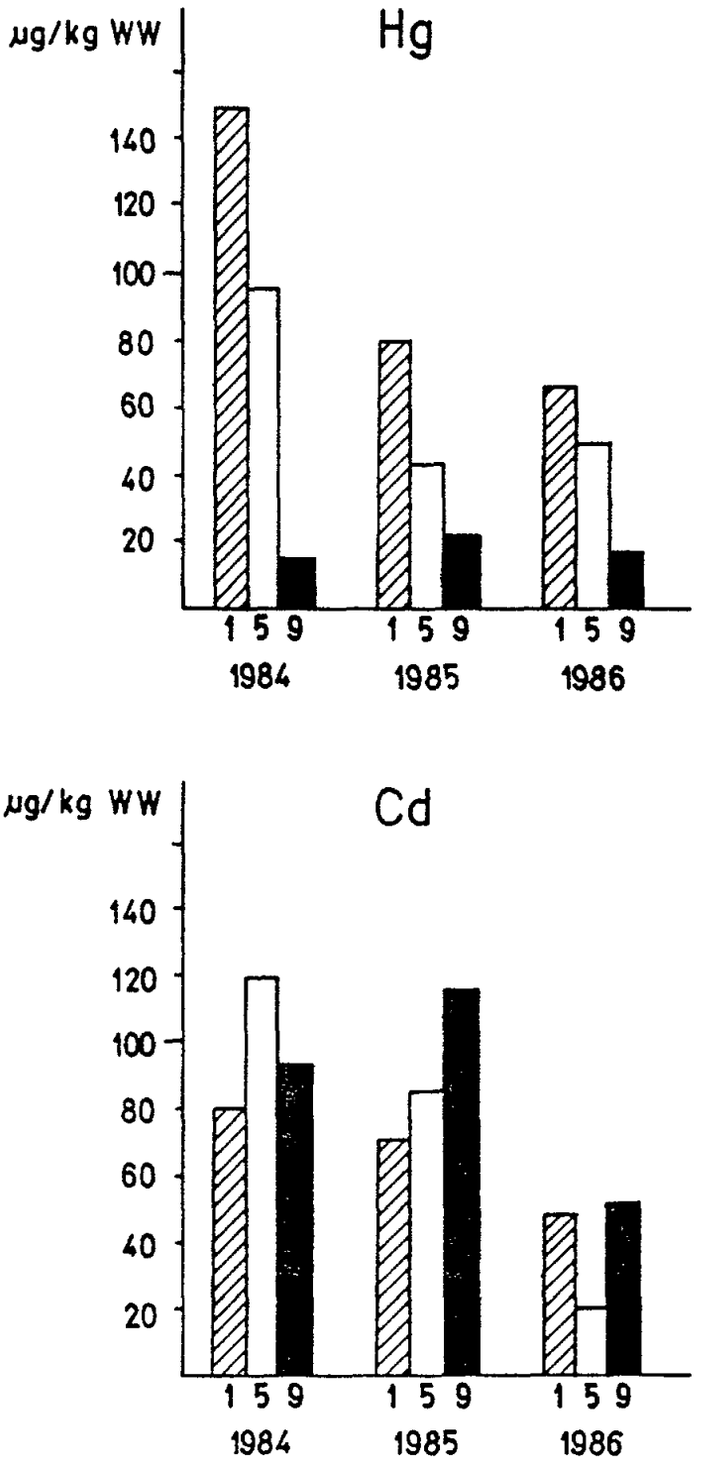


Fig. 3.2.8 Hg and Cd content of sediments at stations 1, 5, 9 and 11 of the Split area in the 1984-1985 period

3.3. Organic pollutants

3.3.1. Chlorinated hydrocarbons

It is well documented that synthetic halogenated residues are widespread throughout the oceanic system. The Adriatic Sea, as a semienclosed water body, is of special interest and there are some baseline studies to measure the existing levels of these contaminants in various components of the ecosystem and to gauge the magnitude of possible future pollution by these and similar chemicals.

Chlorinated hydrocarbons in effluents

Although many baseline studies have been conducted on the Adriatic and Mediterranean ecosystems, no data on chlorinated hydrocarbon concentrations in wastewaters entering the Adriatic and even other Mediterranean areas are found in the literature. Table 3.3.1 shows some data on concentrations of chlorinated insecticides and PCBs in various wastewaters from around the world and compares them with the data obtained in the framework of the Yugoslav Monitoring Programme. It can be seen that the ranges of concentrations are extremely high: from "non detected" (varying and depending on the analytical methodology: in the Yugoslav Monitoring Programme for instance, sensitivity was about of 0.001 ug l^{-1} DDTs) to values reaching 130,000 ug l^{-1} for DDT, (Portman, 1979). As observed, the concentrations of chlorinated hydrocarbons in wastewaters from the city of Rijeka show that the latter belong to the group of less polluted wastewaters. Table 3.3.2 shows that DDTs in the wastewaters investigated are equally distributed between the particulate and dissolved phases. However only 20% of the PCBs present were in the dissolved phase. In the petroleum refinery wastewaters investigated, DDTs were not found and the concentrations of PCBs were significantly lower than in the mixed (urban) wastewaters of the city of Rijeka. The PCB/DDT ratio for the wastewaters monitored has a value of 12 for the particulate phase and 3.7 for the dissolved phase. However for total wastewater samples this ratio amounts to about 9. The results show that the inflow of PCBs through the Rijeka wastewaters entering Rijeka Bay is significantly higher than that of DDT and its analogues.

It has to be pointed out that there are many ECD peaks in the "pesticide" fraction of the investigated eluates obtained after the purification and separation steps of the extracted lipophilic materials from wastewater samples. However the peaks could not be ascribed to DDTs. It is recommended that in the future identification of these substances be carried out, since, owing to their chromatographic characteristics, it is very probable that they are highly lipophilic and potentially dangerous to the marine environment.

Table 3.3.1

Chlorinated hydrocarbons in wastewaters and sewage sludge (ug l^{-1}).

Location and year	Compound(s)	Average	Minimum	Maximum	References
Great Britain, sewage effluents	DDT	36		130	Holden and Marsden 1966,
	Dieldrin	200		300	
Great Britain, sewage effluents	DDT	130.9(21)		800	Lowden, et al., 1969
	BHC	92.5(21)		390	
	Dieldrin	145.0(21)		1900	
Canada, Southern Ontario raw sewage (5 cities)	PCB	2.0(8)	0.6	4.4	Lawrence and Tosine 1977,
Hamilton (raw sewage)	PCB	10.8(38)	1.5	27.3	
Sewage	DDT		36,000	130,000	
	Dieldrin		100,000	300,000	
Sewage sludge	PCB (ug kg^{-1} wet weight)		40	5,000	Portman, 1979
Sewage sludge	DDT (ug kg^{-1} wet weight)		10,000	500,000	
	Dieldrin (ug kg^{-1} wet weight)		1,000	2,500,000	

Table 3.3.1 (cont'd)

Location and year	Compound(s)	Average	Minimum	Maximum	References
Los Angeles County tertiary treatment system (1978)					
Influent	BHC	0.056	0.025	0.080	
Influent	Dieldrin	0.010	0.005	0.030	
Effluent	BHC	0.044	0.005	0.080	Baird, et al., 1979
"	Dieldrin	0.009	0.005		
"	DDTtotal		Not detected		
Tokyo treatment plants (four plants)	PCB		Not detected		Terada Kazuya, 1980
Great Britain Sewage effluent	BHC	0.193(5)	0.02	0.32	Anonymous, 1984
	Dieldrin	0.170(5)	0.12	0.21	
Ispra standard sewage sludge	PCB	2600(4)	1150	4900	Tarradellas, et al., 1985
Aluminium smelt wastewater from sedimentation basin	Decachlorobi-phenyl	54			Vogelgesang, 1986
	Hexachloro-benzene	470			
Rijeka town waste-waters, 1986	DDTtotal	0.008(12)	ND	0.027	Anonymous, 1987
	PCB	0.069(12)	ND	0.223	

ND = Not detected (under sensitivity limit).
Number of samples in brackets

Table 3.3.2

Chlorinated hydrocarbons in various samples from the Adriatic Sea.

Investigated area	Investigation period	Samples	Concentrations	DDTtotal Average	DDTtotal Range	PCB Average	PCB Range	PCB/DDTtotal
Rovinj (reference stations)	1984-86	Sediment	ug kg^{-1} DW	27.6(6)	19.4 39.4	21.3(6)	16.1 28.5	0.77
"	1983-86	Net zooplankton	ug kg^{-1} WW	<0.1(14)		<0.1(14)		
Rijeka area	1986	Urban waste (particulate)	ng l^{-1}	7.8(6)	1.6 15.9	95.8(6)	29.9 194	12.28
"	"	Urban waste (dissolved)	"	6.0(6)	2.3 11.0	22.3(6)	7.0 43.2	3.71
"	"	Urban waste (total)	"	10.5(9)	1.6 26.9	90.7(9)	12.4 223	8.63
"	"	Industr.waste (oil refinery)	"	<0.4(3)		2.6(3)	<1 4.1	
"	"	Mussels	ug kg^{-1} WW	0.9(8)	0.3 1.8	13.1(8)	1.9 27.8	14.55
Sibenik area (reference stations)	1984	Sediment	ug kg^{-1} DW	<0.5(1)		<0.6(1)		
"	1984-85	Mussels	ug kg^{-1} WW	1.8(3)	<1.2 4.2	1.5(3)	<1 3.4	0.83

Number of samples in brackets.

Chlorinated hydrocarbons in sediments

A comparison of the concentrations of chlorinated hydrocarbons in sediment samples obtained from various areas of the Mediterranean Sea and of the concentrations of these pollutants in sediments analyzed during the Yugoslav Monitoring Programme is presented in Table 3.3.3. As can be seen, the average of the DDT and PCB concentrations in sediments analyzed for the Yugoslav Monitoring Programme is higher than that obtained for the whole Adriatic Sea for which all available published results have been taken into account. Comparing the averages of DDT concentrations in sediments of the whole Adriatic with the averages of concentrations in the other areas of the Mediterranean it can be seen that in six areas (II, III, VI, VIII, IX and X) these concentrations are higher. For PCBs the concentrations are higher in five areas (I, II, IV, VI and VIII). The comparison of the average concentrations obtained during the Yugoslav Monitoring Programme shows that for DDTs there are only two areas (VIII and X) that have higher average concentrations and four areas (II, IV, VIII and X) that have higher averages for PCBs.

Figure 3.3.1 presents the levels and the trends of DDTtotal in sediments from the coastal and estuarine stations obtained in the framework of the Yugoslav Monitoring Programme. Especially interesting are the extremely high concentrations of DDTs and their rapid decrease in the Dubrovnik area. For PCBs, these levels are presented in Fig. 3.3.2. It should be mentioned that at the beginning of the monitoring programme extremely high DDT concentrations were observed in the Dubrovnik area, decreasing rapidly afterwards. Fluctuations in the levels of PCBs are also significant in the Sibenik and Montenegrin coastal areas; however these variations may be explained as a consequence of changes in the number and location of the sampling stations.

In order to investigate the nature of chlorinated hydrocarbon pollution, the PCB/DDT ratio is very useful (Picer M. et al.,1978a). Figure 3.3.3 presents the PCB/DDT total ratios obtained for sediments from the investigated area in the course of the monitoring programme. As can be seen, for the Rovinj and Dubrovnik areas these ratios are relatively constant and slightly above the value of 1. In the Sibenik and Montenegrin areas, the ratio is significantly higher than 1 and its fluctuation could be attributed to the changes in the number and location of the sampling stations. A very high increase of this ratio in the Pula area might be explained by the changes in the methodology adopted in order to calculate the amounts of PCBs and DDTs through the use of gas chromatograms (Picer M., 1983).

The levels of chlorinated hydrocarbons in sediments collected at reference stations are presented in Table 3.3.2. A comparison of the levels of DDTs and PCBs obtained at reference stations and those recorded at coastal stations in the Rovinj area did not show any significant differences in concentrations. On the contrary, in the Sibenik area the chlorinated hydrocarbon levels in sediments collected at the reference station were under the sensitivity limit, i.e. much lower than in the estuarine and coastal areas.

Table 3.3.3

Chlorinated hydrocarbons in sediments from the Mediterranean sea (ug kg^{-1} dry weight).

Area*	Pollutant	Average	Minimum	Maximum	References
I	DDTtotal	2.7	0.4	11.0	Cousteau, 1979, Elder et al.,1976,
	BHCtotal	0.3	0.2	0.3	Villeneuve and Burns, 1983
	PCB	34.6	0.3	323	
II	DDTtotal	8.2	0.4	200	Arnoux et al., 1981a, Arnoux et al.,
	BHCtotal	225	0.1	1880	1981b, Arnoux et al., 1981c, Badia and
	PCB	85.5	0.2	15850	Garcia, 1979, Burns, et al., 1985
	Hexacloro-benzene	5.6	ND	32	Cousteau, 1979, Chabert and Vicente, 1981, Marchand et al., 1985, Monod and Arnoux, 1979, Burns and Villeneuve, 1985. Marchand, 1983.
III	DDTtotal	11.0	1.2	40.0	Cousteau, 1979, Elder, et al., 1976,
	BHCtotal	1.6	0.9	2.1	Villeneuve and Burns, 1983.
	PCB	7.4	0.1	14	
IV	DDTtotal	4.3	0.2	27	Amico et al., 1982, Baldi, et al., 1983
	BHCtotal	1.8	0.1	27	Cousteau, 1979, Elder et al., 1976,
	PCB	102	0.6	3200	Monod and Arnoux, 1979, Pucetti and Leoni, 1980, Villeneuve and Burns, 1983.
VI	DDTtotal	10.3	0.1	35.5	Amico, et al., 1982, Cousteau, 1979,
	BHCtotal	0.7	0.1	2.6	Villeneuve, et al.,1981
	PCB	38.1	0.8	347	Villeneuve and Burns, 1983.
VII	DDTtotal	0.2	0.1	0.4	Cousteau, 1979, Villeneuve and Burns,
	BHCtotal	1.1	0.2	2.2	1983.
	PCB	0.8	0.1	1.1	

Table 3.3.3 (cont'd)

Area*	Pollutant	Average	Minimum	Maximum	References
VIII	DDTtotal	128	0.3	1893	Cousteau 1979, Dexter and Pavlou 1973,
	BHCtotal	0.6	0.4	0.8	Villeneuve et al., 1981, Villeneuve
	PCB	155	0.6	775	and Burns 1983.
IX	DDTtotal	12.0	0.4	29.0	Balkas et al., 1979, Bastyrk et al.,
	BHCtotal	0.2	0.2	0.3	1980, Cousteau 1979, Villeneuve et
	PCB	1.5	ND	3.0	al., 1981, Villeneuve and Burns 1983.
X	DDTtotal	390	1	780	Cousteau 1979, Villeneuve and Burns 1983,
	BHCtotal	0.7	-	-	Villeneuve et al., 1981.
	PCB	2.2	0.6	5.1	
	DDTtotal	6.8	ND	47.8	Cousteau 1979, Fossato 1983,
The	BHCtotal	1.1	0.1	4.6	Picer M. and N. Picer 1982,
Adriatic	PCB	24.1	ND	332	Picer et al., 1985,
Sea	Hexachloro-benzene	7.2	-	-	Picer M. and N. Picer 1987, Picer N. and M. Picer 1979, Picer et al., 1981,
	Dieldrin	0.1	ND	0.7	Picer N. et al., 1985, Vilicic et al., 1979.
	DDTtotal	20.8	ND	114	Anonymous, 1987.
	PCB	45.5	ND	132	

ND = Not detected (under sensitivity limit); No data available
* = See Fig. 3.3.4

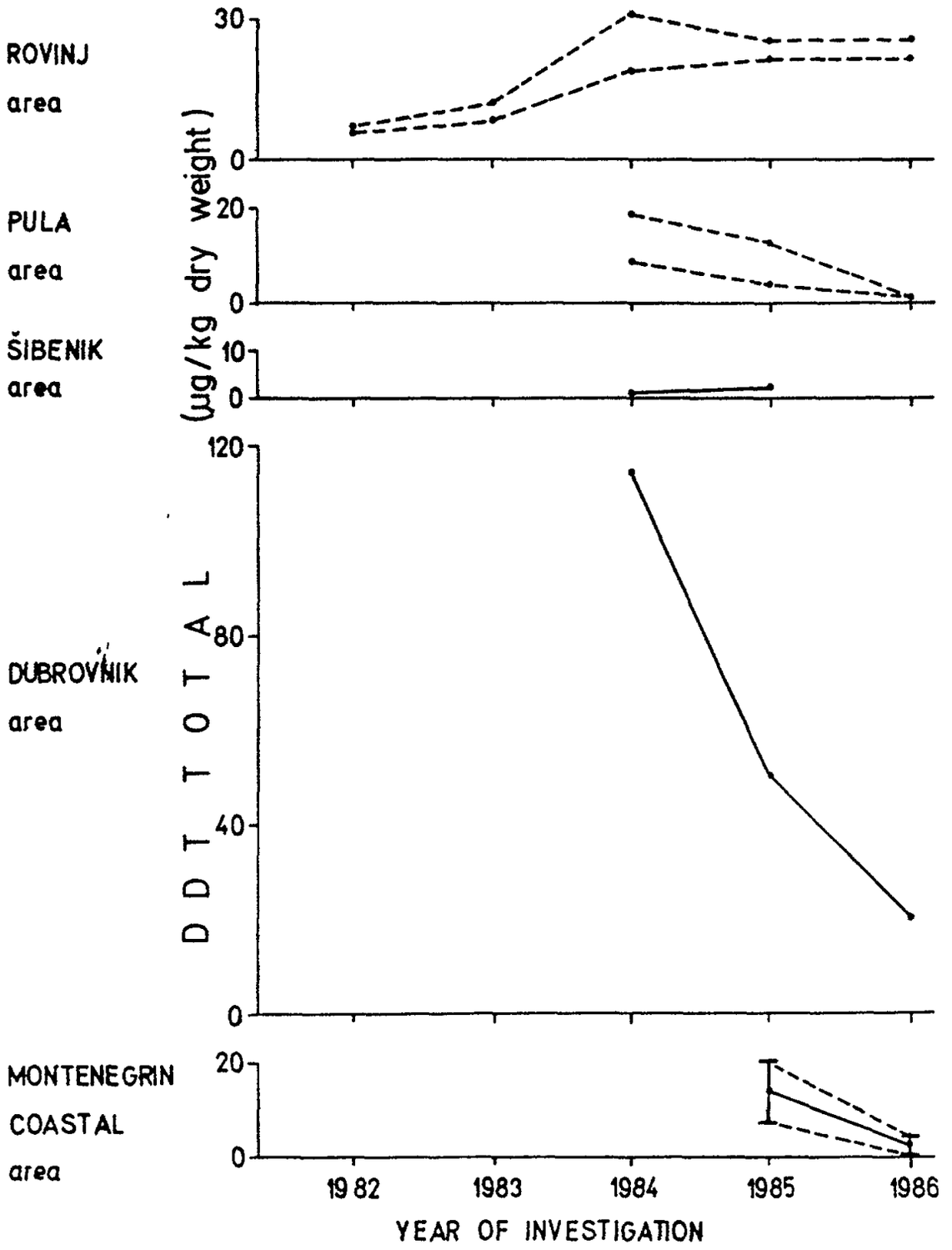


Fig. 3.3.1 DDTtotal in sediments from coastal and estuarine stations

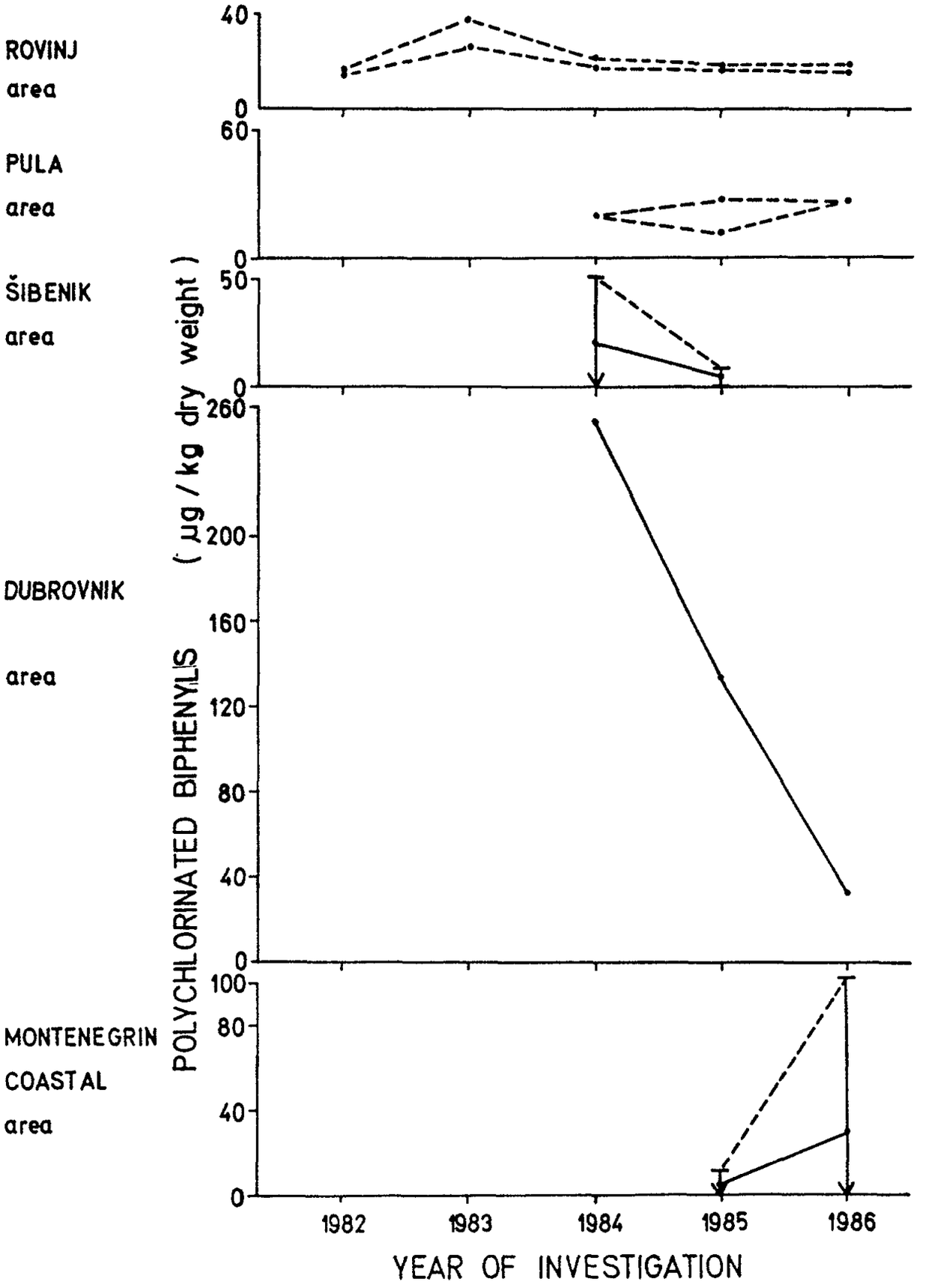


Fig. 3.3.2 PCB in sediments from coastal and estuarine stations

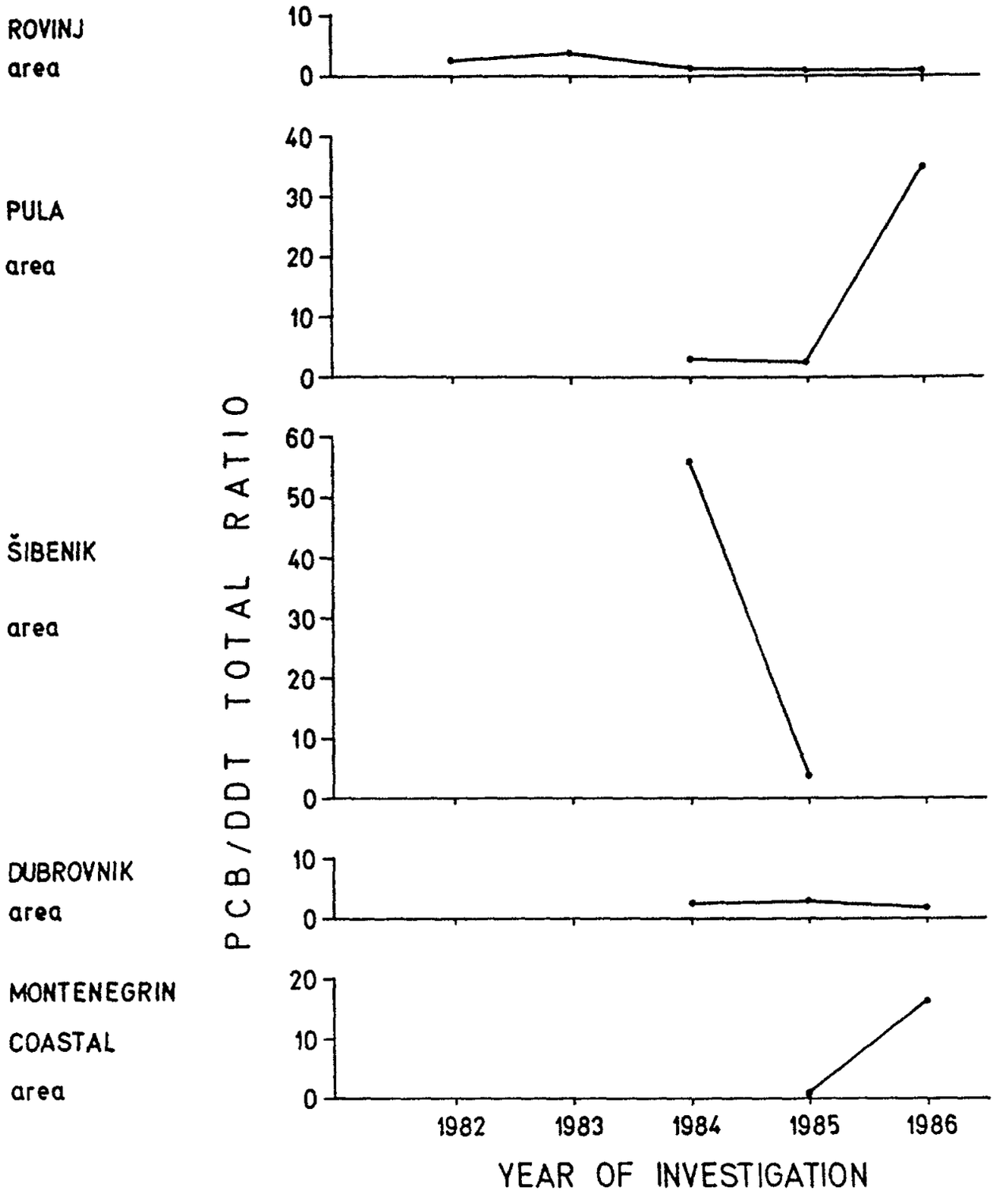


Fig. 3.3.3 PCB/DDTtotal ratios in sediments from coastal and estuarine stations

Chlorinated hydrocarbons in organisms

In baseline studies on chlorinated hydrocarbon pollution in the Mediterranean Sea, pollutants are measured in various marine species, from plants to various planktonic organisms, from fish to birds and mammals. However mussels, because they are very popular and good indicator organisms, have been analyzed more frequently than other species (Picer, M., 1986a). Fig. 3.3.4 presents the summarized data of such baseline studies on chlorinated hydrocarbon pollution of mussels from the Mediterranean Sea. The data are published in the literature and are available in other ways too. The levels of DDTs and PCBs in mussels obtained during the Yugoslav Monitoring Programme are compared with those obtained for the other areas of the Mediterranean and given in Table 3.3.4. When comparing the most recent data on these levels obtained for each area with the data obtained during the Yugoslav Monitoring Programme, it can be noticed that for DDTs and PCBs the levels recorded during the Yugoslav Monitoring Programme are much lower. Furthermore, as regards the mussel data obtained from the analysis of samples collected from the Adriatic Sea in the period between 1976 and 1980, the Yugoslav monitoring data are lower for DDTs by about 50% and even more (about four times) for PCBs. Fig. 3.3.5 presents the concentration levels (averages as arithmetic means with standard deviations) for DDTs in mussels collected from six areas in the Yugoslav coastal waters during the 1982-86 period. Except for the Sibenik and Split areas, where DDT concentrations are low (about 2-5 ppb on wet weight), variations in the DDT levels are relatively important. The increase in the DDT concentrations in the Rovinj area recorded in 1984 has been stabilized in the past two years. An increase in the DDT concentrations in mussels from the Pula area, observed in 1985, was followed last year by a decrease. A very high increase in the DDT concentration recorded in mussels from the Montenegrin coastal waters is probably accidental because the value was obtained from the analysis of only one sample. The samples of mussels from the Rovinj and Dubrovnik areas are in general analyzed by CMR-R; however last summer two samples from the Rovinj area and two samples from the Dubrovnik area were analyzed by CMR-Z. The results obtained, marked by an asterisk, are presented in Fig. 3.3.5 and are significantly lower than the values obtained by CMR-R.

The levels of PCBs in mussels are presented in Fig. 3.3.6. For the Rijeka area, the average concentrations are presented in Table 3.3.2. As seen, markedly lower concentrations are recorded in the Rovinj area than in the other areas. In the same way as for DDTs, the results of the mussel analysis carried out by CMR-Z on the samples originating from the Rovinj and Dubrovnik areas and collected in 1986 are also denoted by an asterisk. It can be seen that the results here are quite the opposite from those for DDTs. Namely, the results for PCBs obtained by CMR-Z give higher values than those recorded by CMR-R.

Table 3.3.4

Chlorinated hydrocarbons in mussels from the Mediterranean Sea (ug kg^{-1} fresh weight).

Area*	Period	DDTtotal		BHCtotal		P C B		References
		Average	Range	Average	Range	Average	Range	
II	1970-74	150.2(92)	10.0-900.0	29.8(18)	3.0-67.0	395.4(105)	33.1-2073	De Lappe et al., 1973, Marchand et al., 1976, Risebrough et al., 1976, Soler 1973,
II	1976-79	25.9(15)	1.5-46.0	0.90(11)	0.02-1.87	126.1(15)	10.9-233.0	Contardi et al., 1981, Contardi et al., 1979, Arnoux et al., 1981a, Bolognari et al., 1979, Ferro et al., 1979, Monod and Arnoux 1978, Risebrough et al., 1983,
II	1979-82	20.5(34)	4.6-55.4	1.84(34)	0.63-7.07	92.7(17)	9.1-327.3	Ballester et al., 1982, Marchand 1985,
IV	1978-81	34.7	9.0-57.3		2.30-4.29	96.4	20.0-172.7	Bolognari et al., 1979, Focardi et al., 1984
VI	1977-78	33.1(4)	9.0-35.6	1.80(4)	0.31-3.30	78.0(4)	42.0-100.9	Amico et al., 1979, Bolognari et al., 1979,
VIII	1975-79	23.9(96)		1.74(56)		383.4(96)		Kilikidis et al.,1981.

Table 3.3.4 (cont'd)

Area*	Period	DDT total Average	DDT total Range	BHCtotal Average	BHCtotal Range	P C B Average	P C B Range	References
T	1973	34363(7)		6160(7)				Stirn et al., 1974,
H E A D R I A T I C S E A	1973-74	98.7(67)	ND-506.9			153.9(67)	ND-390.1	Picer N. et al., 1985, Picer M. and N. Picer 1987, Bolognari et al., 1979, Dujmov et al., 1979, Fossato and Craboleda 1981, Nasci and Fossato 1982, Picer M. and N. Picer 1982, Picer M. et al., 1981, Nazansky et al., 1978, Vilicic et al., 1978, Picer N. et al., 1985, Picer M. et al., 1986b, Dujmov et al., 1985, Anonymous 1987.
	1976-80	12.9(140)	ND-301.1	1.67	0.40-3.05	82.5(77)	ND 1586	
	1983-86	8.7(108)	ND 41.0	Only	several data	21.2(107)	ND 68.0	

ND = Not detected (under sensitivity limit); Number of samples in brackets
* = See Fig. 3.3.4.

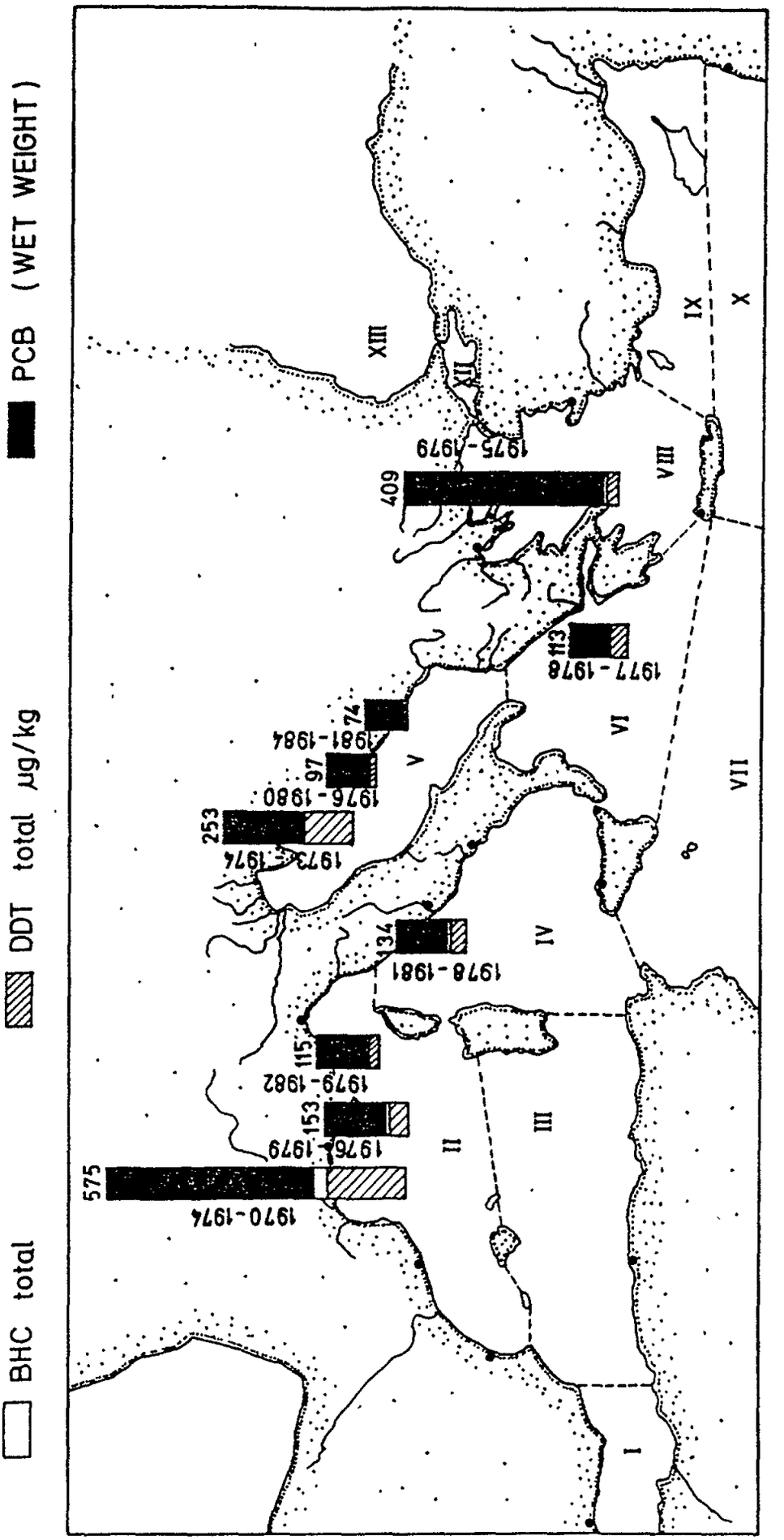


Fig. 3.3.4 DDTtotal, BHCtotal and PCB in mussels from the Mediterranean Sea

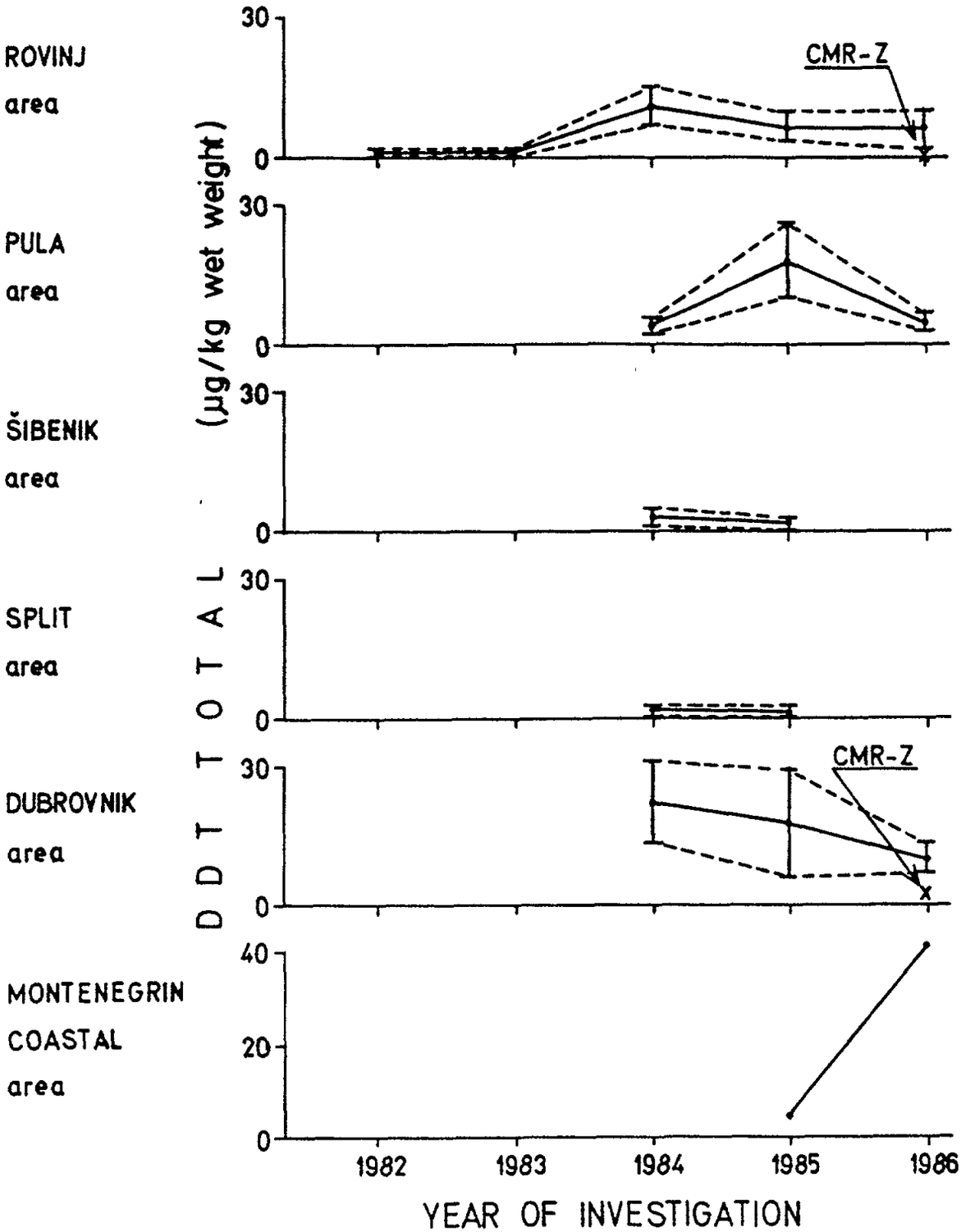


Fig. 3.3.5 DDTtotal in mussels from coastal and estuarine stations

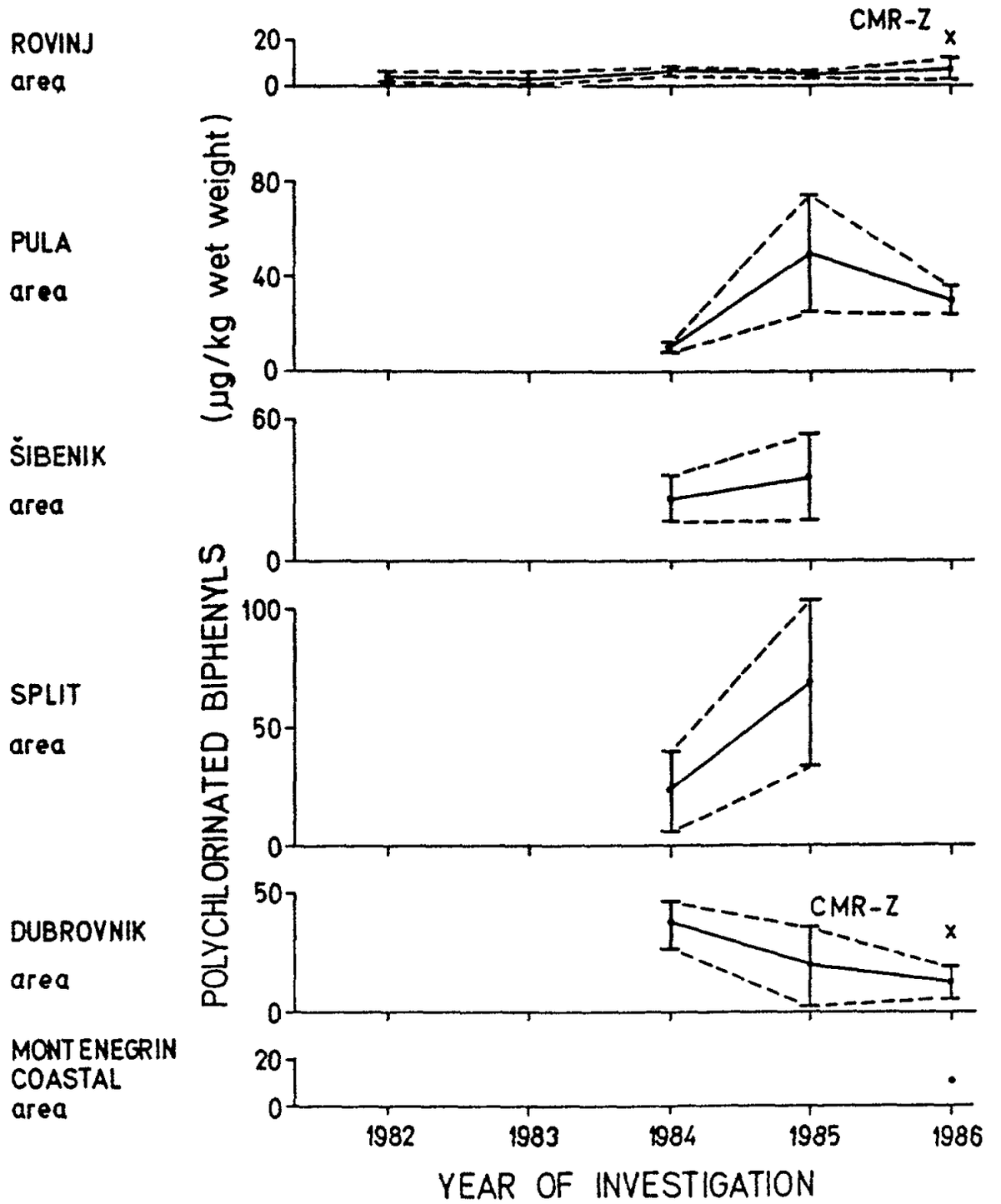


Fig. 3.3.6 PCB in mussels from coastal and estuarine stations

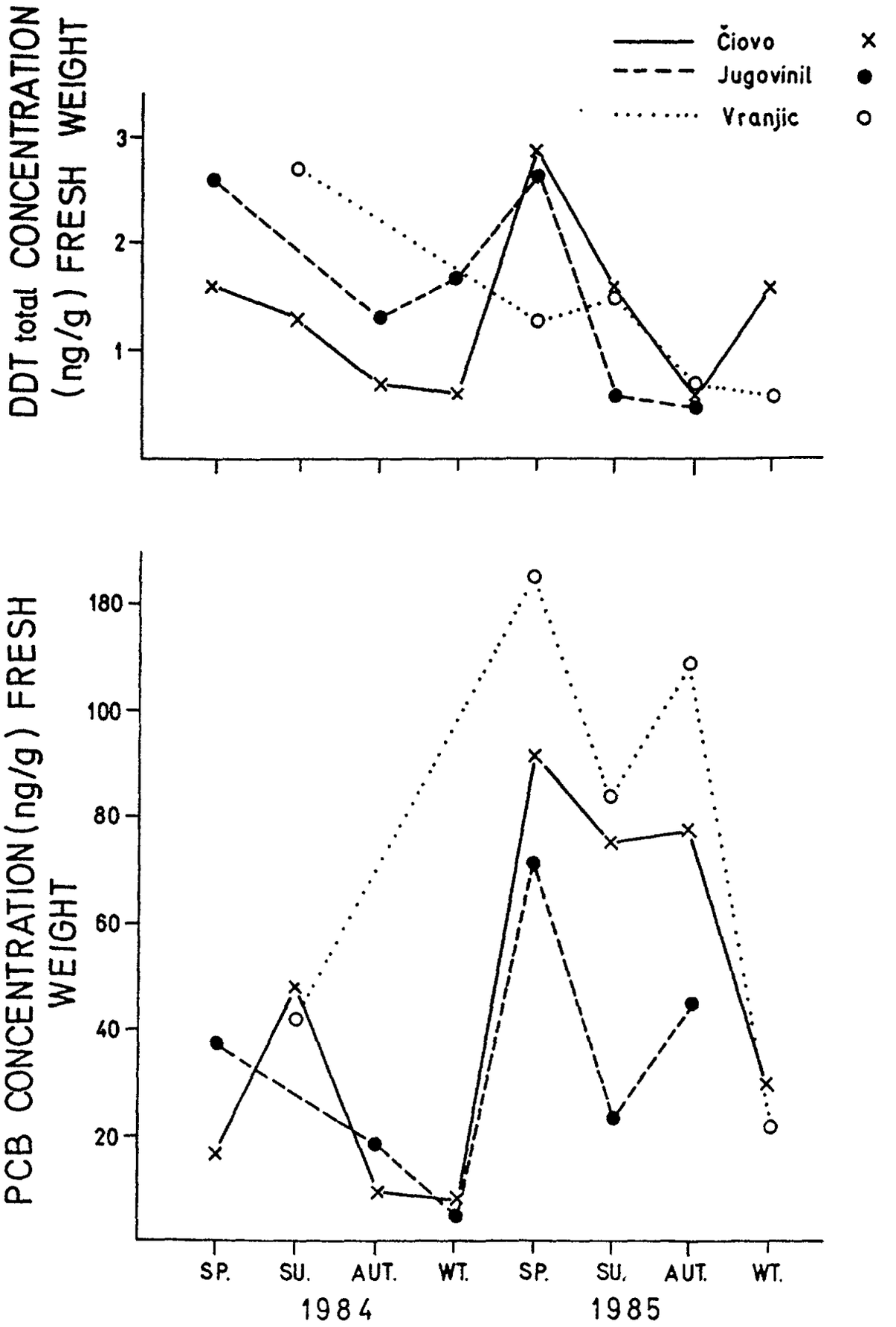


Fig. 3.3.7 DDTtotal and PCB in mussels from the Kastela Bay sampled from spring 1984 to winter 1985

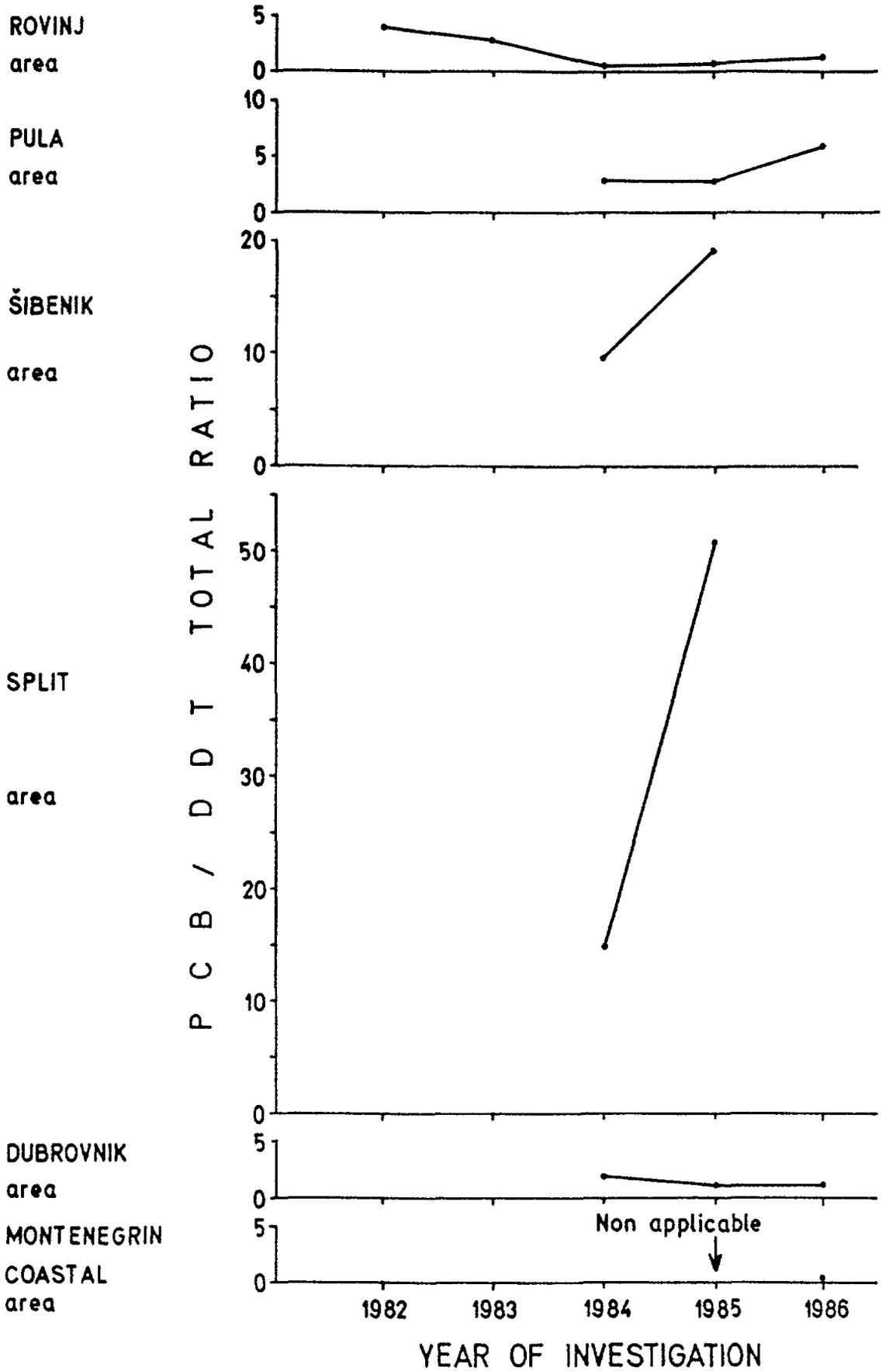


Fig. 3.3.8 PCB/DDTtotal ratios in mussels from coastal and estuarine stations

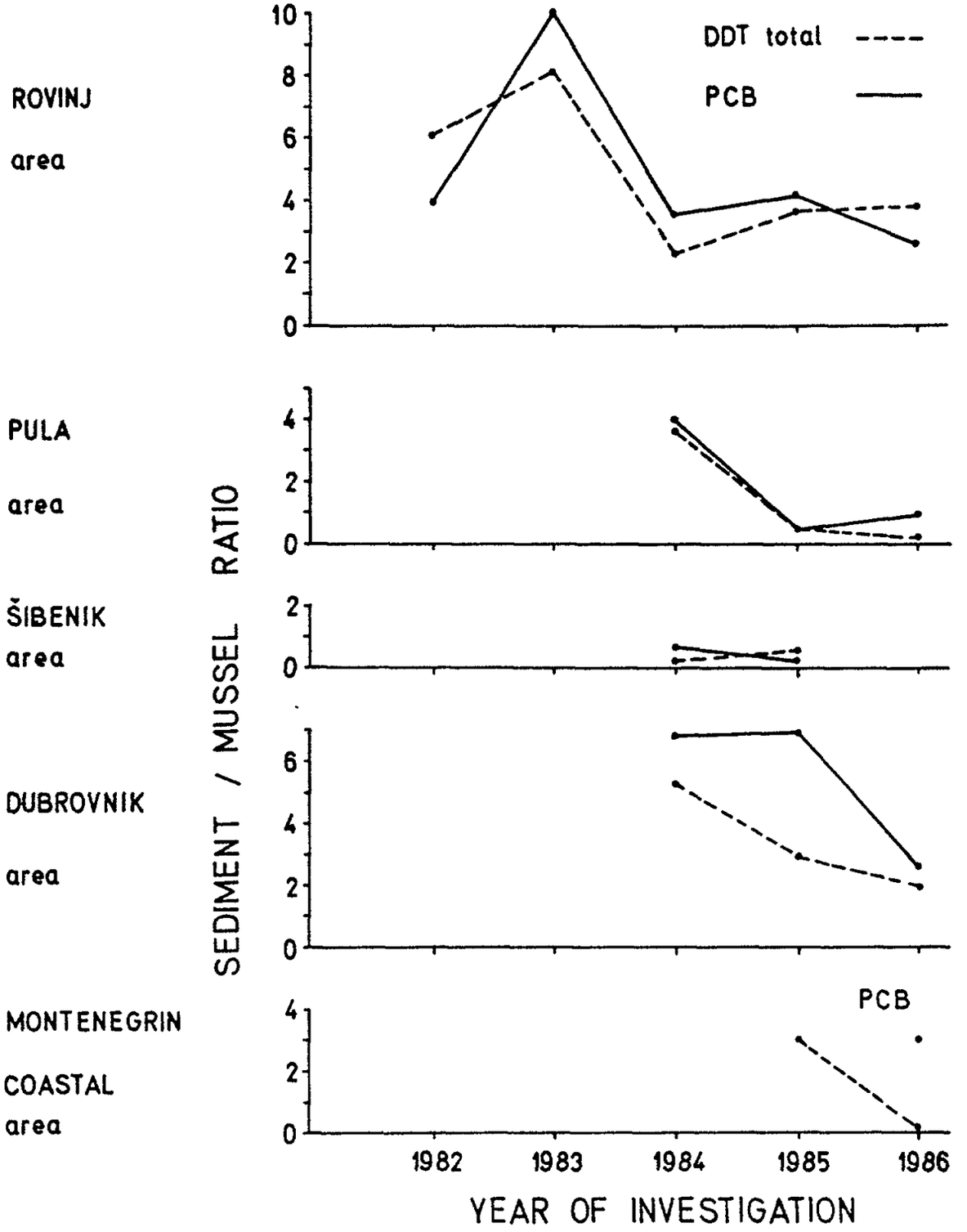


Fig. 3.3.9 PCB and DDTtotal concentration ratios among various matrices

Table 3.3.2 shows that the levels of PCBs and DDTs are relatively low and that for the reference station of the Sibenik area the values for DDTs and PCBs are similar. The averages presented show that PCB concentrations are especially high and variable in the Split area. Mussels were collected here in the Bay of Kastela at three stations. The results of the investigation are presented in Fig. 3.3.7. It can be noted that in a certain way each station is unique with respect to residue levels, variations in concentrations and in the PCB/DDT total ratios.

The PCB/DDT total ratios for all the investigated areas and for the entire period of investigation are presented in Fig. 3.3.8. For the Pula, Sibenik and Split areas the PCB/DDT ratios are significantly above the value of 1. However for the Rovinj, Dubrovnik and Montenegrin areas they are close to the value of 1 or even below it. The variations in the PCB/DDT ratio of the Sibenik area could be attributed to changing sampling stations. However, a very high increase in this ratio in the Split area was obtained for the mussels collected from the same stations in 1984 and 1985.

In order to observe the relationship between the concentrations of chlorinated hydrocarbons in sediments and mussels, Figure 3.3.9 presents the DDT and PCB concentration ratios for sediments and mussels in each investigated area. As noted above, these ratios are below the value of 1 for the Sibenik and Pula areas (1985-86) as well as for the Montenegrin coastal waters (1986). In the Dubrovnik and Rovinj areas, at the beginning of the monitoring, this ratio was markedly above the value of 1 but has recently stabilized at low levels (about 3), which is still higher than in the other areas.

The chlorinated hydrocarbons were also monitored in net zooplankton samples obtained from the reference stations in the Rovinj area. However, Table 3.3.2 shows that up to now and with the methodology used, the investigated pollutants were not detected in the levels of 0.1 ppb on a wet weight basis.

3.3.2. Phenols

It is well known that "volatile phenols", as a group of organic pollutants, belong mainly to industrial pollutants (Picer, M., 1984). However, they are also found in domestic wastes, as shown in Table 3.3.5. Data in Fig. 3.3.10 indicate that they also appear in typical domestic wastewaters (the Lav collector from the Split area). From the above mentioned Table and Figure, it is evident that in wastewaters the concentration ranges of these pollutants are very high even in a relatively small area, because they greatly depend on the nature of wastewaters.

Table 3.3.5

Phenols in wastewater (mg l^{-1})

Waste	Phenolics	Method of Analysis	Levels	References
Paper mill (raw waste)	Phenols	?	10-2000	Nebel et al., 1976,
Wood preserving plant (Settling point)	o-cresol m-cresol	GC-MS GC-MS	1.4 2.5	Webb 1973,
Petroleum refinery (8-hr lagoon effluent)	o-cresol phenol	GC-MS GC-MS	0.12 0.2	Webb 1973,
Petroleum refinery (Final effluent)	phenol o-cresol	GLC GLC	3016 5842	Baird et al., 1976,
Integrated oil refinery (Raw effluent)	phenol	?	120	Volesky et al., 1974,
Petrochemicals (5-day lagoon effluent)	phenol	GC-MC	0.06	Webb 1973,
Coke plant waste	total phenol	?	410-2400	Rubin and McMichael 1975,
Non-industrial watersheds (Forest litter)	phenolics	4-AAP	0.003-0.020	Hoak 1957,
Raw domestic sewage	phenolics	?	0.070-0.100	Nebel et al., 1976,
Raw Pittsburgh sewage	total phenolics	4-AAP	0.072	Hoak 1957,
Wastewaters from Yugoslav Adriatic towns	phenols	4-AAP	ND-16.5	Anonymous 1987.

Table 3.3.6

Phenols in various water samples from the Adriatic Sea (ug l^{-1}).

Investigated area	Investigated period	Samples	Average	Minimum	Maximum
Pula area	1984-86	Industrial wastewater	132(12)	13	360
Pula area	1984-86	Domestic wastewater	27(12)	2	59
Rijeka area	1984-86	Industrial wastewater	1400(14)	23	16500
Split area	1984-86	Domestic wastewater	11(24)	<1	43
Montenegrin coastal area	1985-86	Coastal and estuarine seawater	14(30)	<1	42

Number of samples in brackets.

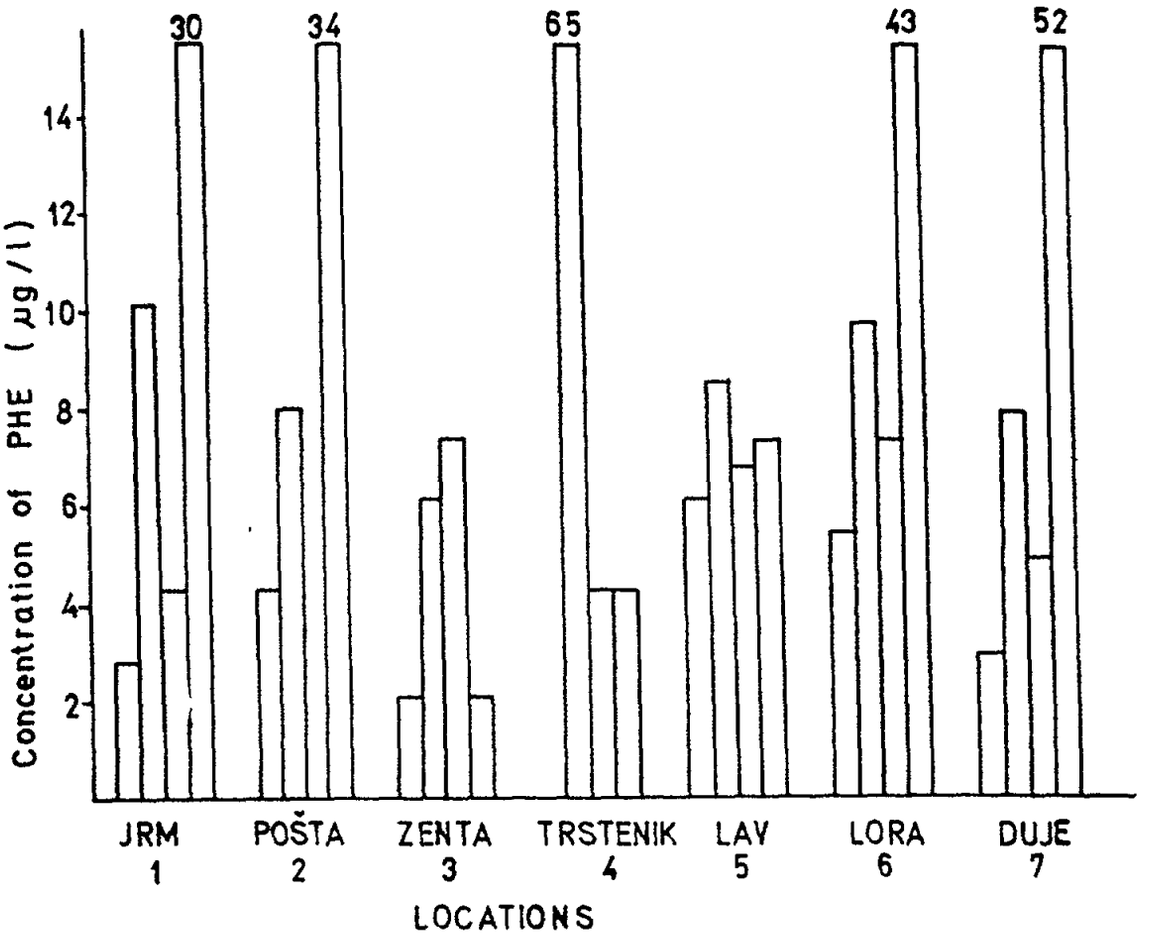


Fig. 3.3.10 Phenols in wastewaters from the Split area in 1985

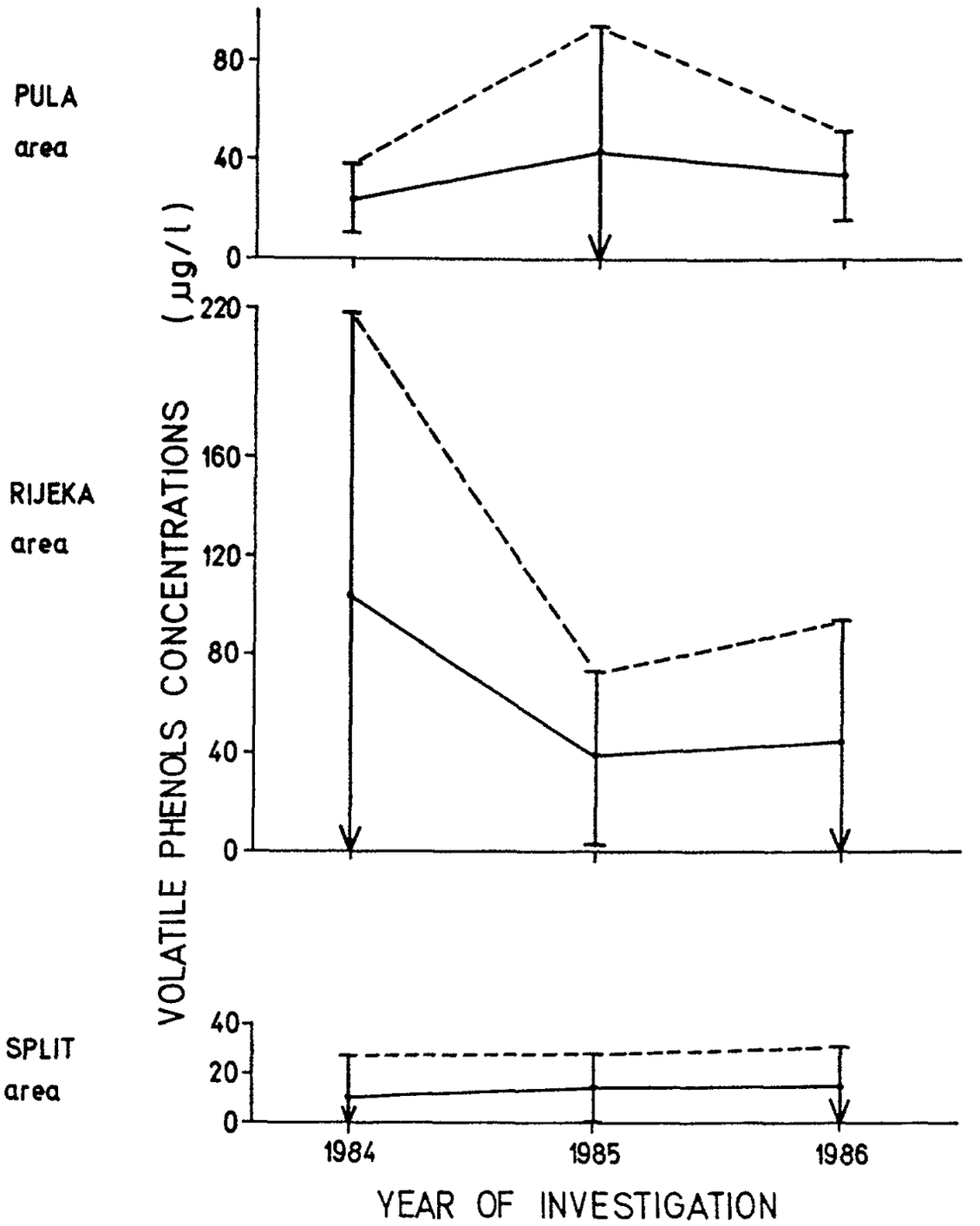


Fig. 3.3.11 Phenols in wastewaters from the investigated areas

Figure 3.3.11 compares the averages and the standard deviations of volatile phenols in urban wastewaters from areas investigated in the framework of the Yugoslav Monitoring Programme. The highest levels and fluctuations in results are observed in the Rijeka area. These very high fluctuations were particularly noticeable during the first year of the monitoring, but afterwards they were also observed in both the Rijeka and the Pula area as well. On the basis of the data shown in Fig. 3.3.11 it can be concluded that the levels and fluctuations of results are lowest in the urban waters of the Split area. Table 3.3.6 shows the averages and the ranges of phenol concentrations in industrial wastewaters and domestic wastewaters for the three areas investigated. As was expected, the highest results and the greatest fluctuations are obtained for the Rijeka area wastewaters. Domestic wastewaters show the lowest values, in the ranges described in the literature for other domestic wastewaters around the world. The phenol concentrations in wastewaters of the Pula and Rijeka areas did not show a statistically significant difference in the results obtained for the three-year investigation period, because of very high fluctuations in the concentrations of urban, industrial and even domestic wastewaters. An exception was some of the results related to the phenol concentrations in wastewaters from the city of Rijeka. If we take into account some very high levels (above 100 ppm) obtained in 1984, it is obvious that the arithmetic means for phenol concentrations recorded in 1985 are significantly lower (about 50 times). However in 1986, the levels were similar to those of 1985. It could be recommended that in the future a thorough investigation of phenols from the Rijeka area be conducted by using a more specific method.

Volatile phenols in seawater were monitored in the Montenegrin coastal area (Table 3.3.6) and a range of 1 - 42 ug l^{-1} with an average of 14 ug l^{-1} was observed. Because of previous objections regarding the 4-aminoantipyrine method for phenol determination in seawater (Picer, M., 1984; Picer, M., 1985), the results given should be used with caution.

3.3.3. Anionic detergents

Anionic detergents in domestic wastewaters are one of the most frequent groups of organic pollutants (Picer, M., 1983). Therefore, their relatively stable level of concentration in wastewater collectors of urban areas could be expected, vis-à-vis other organic pollutants. However, Figure 3.3.12 shows large fluctuations in pollutant concentrations in the Split wastewaters sampled in 1985. Namely total concentrations ranged from 1700 ug l^{-1} in the Duje wastewater outlet to 15368 ug l^{-1} in the Zenta outlet. Table 3.3.7 compares data on some concentrations of anionic detergents in industrial and urban wastewaters from various studies around the world and in Yugoslavia with the data on concentrations from wastewaters of the Yugoslav Adriatic cities obtained during the Yugoslav Monitoring Programme. The total range is very wide (from 20 to 16300 ug l^{-1}), but the average of all the samples is about three times lower than the average for domestic wastewaters in the U.S.A. Even some effluents (Haifa, Israel) from a wastewater treatment plant show concentrations of anionic detergents that are higher than the average for the anionic detergent concentrations in all wastewater samples collected during the Yugoslav Monitoring Programme. This is quite interesting, since most wastewaters from the Yugoslav Adriatic towns either enter the sea without any treatment or receive only mechanical treatment.

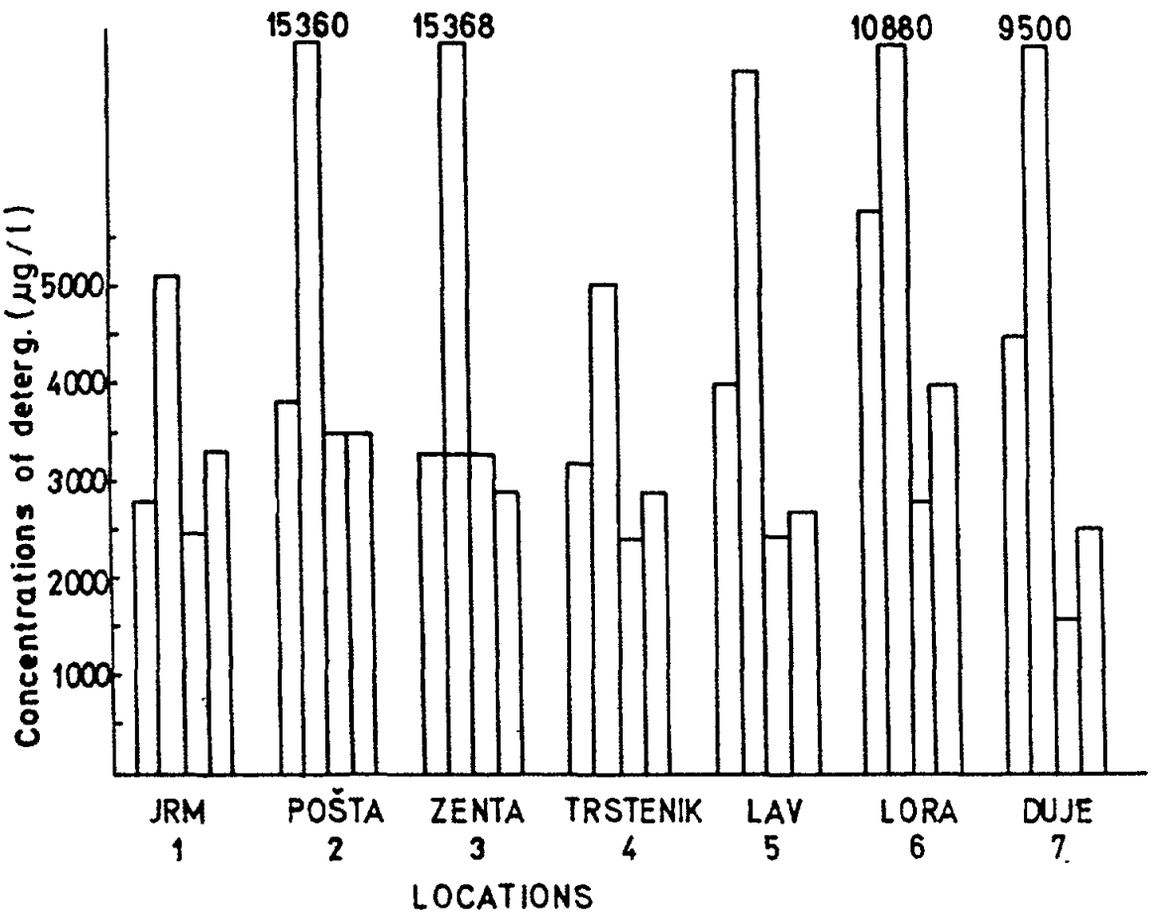


Fig. 3.3.12 Anionic detergents in wastewaters from the Split area in 1985

Table 3.3.7

Anionic detergents in wastewaters (ug l^{-1}).

Location and year	Compound(s)	Average	Range	References
Sewage from individual home, USA	Detergent	6,200(154)		Watson et al.,1967,
Effluents after primary and secondary treatment,UK	Manoxol OT	580(3)	750-2,500	Eden and Truesdale 1967,
Raw wastewater, South Nevada, USA	MBAS	7,000		Culp and Culp 1971,
Primary effluent Windhoek, South Africa	ABS	16,200		Stander and van Vuuren 1970,
Nassau County, N.Y. USA, 1965 Raw water nonfiltered	Detergent	770		Stevens and Peters 1966,
Tertiary effluent nonfiltered	Detergent	<20		
Haifa, Israel, waste-water treatmant plant Oxidation pond	Anionic detergents	8,500		Manka and Rebhun 1982,
Lime clarifier	"	6,500		
Textile factories, Yugoslavia, 1980	Anionic detergents (TBS)	6,200	70-14,280	Vojvodic et al., 1981.

Table 3.3.7 (cont'd)

Location and year	Compound(s)	Average	Range	References
Plastic industry Yugoslavia, 1979-80	Anionic detergents NaLS	36,720(17)	95-246,000	Vojvodic et al., 1981,
Laundry effluent Yugoslavia	Anionic detergents		112,000-70,000	Kozarac et al., 1976,
Yugoslav Adriatic towns, wastewaters 1984-86	Anionic detergents	2,100(325)	20-16,300	Anonymous 1987.

Number of samples in brackets.

The levels and trends of anionic detergent concentrations for urban wastewaters from the Slovenian coastal area, and the areas of Pula, Rijeka and Split are shown in Fig. 3.3.13. The lowest fluctuations in concentrations are found in the Slovenian coastal area wastewaters. For other urban wastes, fluctuations in concentrations are much higher; however, from the period of investigation alone, it is not possible to define any trend.

In Fig. 3.3.14 the averages of detergent concentrations in domestic and urban wastewaters for each sampling date during the monitoring period are presented.

To find out to what extent the tourist high season (summer months) influenced detergent concentrations in wastewaters, the ratios between concentrations of detergents recorded in summer months and those obtained in the other months were calculated for every year and area. The ratios obtained are presented in Table 3.3.8. The ratios were calculated for all samples together and separately for domestic or urban (mixed) wastewater samples, when data for domestic wastewater samples were not available. As seen from the obtained ratios, it is not possible to ascertain positively any significant influence of the tourist season on the increase of detergent concentrations in wastewater samples, because in 11 cases the ratios obtained were higher than 1, but in 13, they were below this value.

Table 3.3.9 gives the averages and the ranges of anionic detergent concentrations in industrial and domestic wastewaters, as well as for some river waters entering the Adriatic Sea. It can be seen that the highest average concentrations were obtained in the Split domestic wastewaters (3430 ug l^{-1}) and the lowest (1527 ug l^{-1}) in the Pula industrial wastewaters. The concentrations of anionic detergents in rivers entering the Adriatic were measured in the Slovenian and Montenegrin areas with similar concentration averages and ranges (63 ug l^{-1} and 45 ug l^{-1}, respectively). When observing such large fluctuations in detergent concentrations in the investigated wastewaters, it is very difficult to determine detergent concentration trends in the effluents of the areas monitored. This means that in order to obtain less variable averages, sampling frequency should be increased. Furthermore, it would also be necessary to investigate other pollution sources of detergents (for example shipyards, harbours, detergents used against oil slicks etc.). On the basis of such investigations an estimate of the inflow of anionic detergents into the Yugoslav coastal waters could be established and would prove very useful.

During 1985 and 1986 detergents were monitored in the Montenegrin coastal waters (Table 3.3.9). In comparison with the averages and the ranges of anionic detergent concentrations for the Sibenik coastal and estuarine area, the concentrations in the Montenegrin coastal waters were much higher, but similar to those found in other areas of the Mediterranean Sea (Table 3.3.10). Lower detergent levels in the Sibenik area may probably be explained if we take into account the fact that the extraction and analysis methods used were different from those used in other Mediterranean institutions.

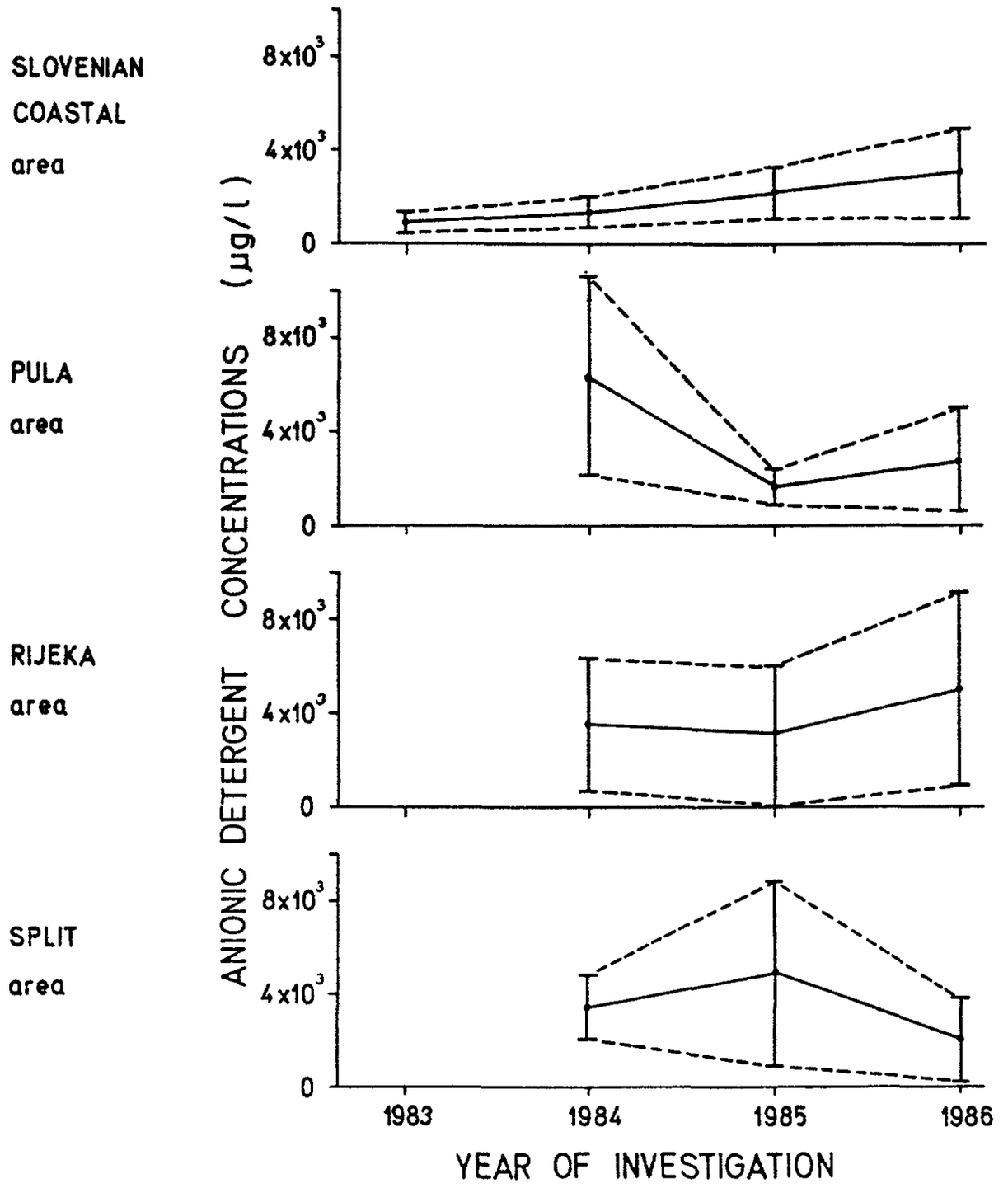
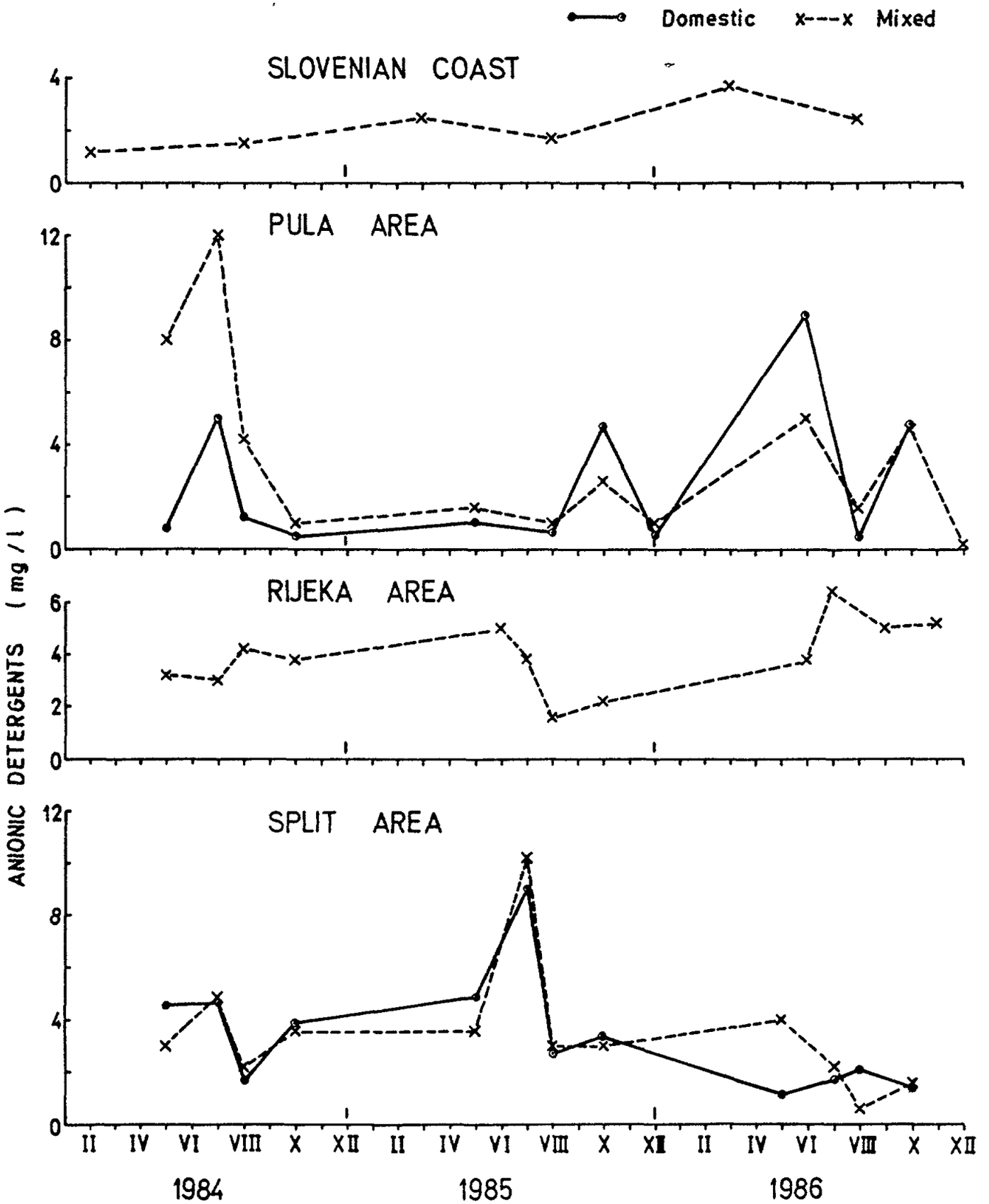


Fig. 3.3.13 Anionic detergents in wastewaters from the investigated areas



3.3.14 Averages of detergent concentrations in domestic and urban wastewaters for collection cruises during the monitoring period

Table 3.3.8

Ratios of summer and nonsummer concentrations of detergents in wastewaters from the investigated areas.

Area		Year: 1984	1985	1986
Slovenian coastal area	All samples	1.43	0.70	0.84
	Urban wastewaters	1.39	0.75	0.69
Pula area	All samples	1.67	0.47	1.20
	Domestic wastewaters	4.46	0.34	1.96
Rijeka area	All samples	0.99	0.93	1.40
	Urban wastewaters	1.02	0.77	1.30
Split area	All samples	0.94	1.82	0.68
	Domestic wastewaters	0.75	1.41	1.53

Table 3.3.9

Anionic detergents in various water samples from the Adriatic Sea (ug l^{-1}).

Investigated area	Investigated period	Samples	Average	Minimum	Maximum
Slovenian coastal area	1984-86	Source (rivers)	63(20)	5	226
Pula area	1984-86	Industrial wastewaters	1,527(12)	140	3,600
Pula area	1984-86	Domestic wastewaters	2,440(12)	70	9,000
Rijeka area	1984-86	Industrial wastewaters	2,200(20)	23	16,500
Sibenik area	1984-86	Industrial wastewaters	56	19	85
Sibenik area	1984	Coastal and estuarine waters	4(9)	2	14
Split area	1984-86	Domestic wastewaters	3,430(24)	168	10,900
Montenegrin coastal area	1986	Source (river)	43(4)	22	65
Montenegrin coastal area	1985-86	Coastal and estuarine waters	45(31)	<10	122

Number of samples in brackets.

Table 3.3.10

Anionic detergents in seawater from the Mediterranean Sea (ug l^{-1}).

Area*	Location and year	Average	Min.	Max.	References
II	French coastal waters, 1979-80	Sensitivity limit 10 ugl^{-1}	15% (positive samples)	42%	Boisson et al., 1981,
II	North Italian coastal waters	54			Blundo et al., 1985,
II	North Italian coastal waters	58(10)	9	170	De Renzi et al., 1979,
XIII	Rumanian coastal waters, 1978-79	140(84)	70	350	Serbanescu et al., 1981,
The Adriatic Sea	Gulf of Trieste	60(55)	ND	230	Majori et al.,1981,
	Rijeka Bay, 1974-78	8(35)	2	29	Cosovic and Zutic 1981,
	Estuarine and coastal waters 1983-86	21(42)	2	122	Anonymous 1987.

Number of samples in brackets.
* See Fig. 3.3.4

3.3.4. Petroleum hydrocarbons

Petroleum hydrocarbons in effluents

Petroleum hydrocarbon concentrations in wastewaters fluctuate greatly, as Table 3.3.11 shows. The Table also gives data on concentrations of these pollutants in various wastewaters around the world. It has to be stressed that these very wide concentration fluctuations are not only the result of real concentration variations, but also the consequence of different analytical methodologies applied in the analysis of these pollutants. For this reason, in addition to defining which part of oil or hydrocarbons is to be analyzed, it is also necessary to state the methodology used.

During the Yugoslav Monitoring Programme, IR spectrophotometry was used for the analysis of most wastewater samples. Some of the samples from the Rijeka and Sibenik areas were analyzed in 1986 and 1984-85 respectively, by using UV spectrofluorometry, while the samples from the Split area were analyzed in 1984-85 by UV spectrophotometry. Therefore Table 3.3.12 gives, in addition to the specification of areas and the year of investigation, the methods of analysis and the standards for the concentration evaluated as well. A comparison of the averages of petroleum hydrocarbon concentrations in industrial wastewaters from the Rijeka area obtained through the IR and UV fluorescence methods does not show any significant differences. A difference in the averages has been observed only for urban (mixed) wastewaters, but statistically it is not significant (765 and 293 ug l^{-1}). The advantage of UV spectrofluorometry is that it provides additional data on the nature of petroleum hydrocarbons in wastewaters and concentration estimates of the polyaromatic fraction of the hydrocarbons determined. The results presented show that the polyaromatic fraction in industrial wastewaters (expressed as chrysene equivalents) amounts to about 13% of all hydrocarbons. In urban wastewaters the polyaromatic fraction is about 16% (which is 23% more) of total hydrocarbons. In the Sibenik area the concentration and the percentage of the polyaromatic fraction in a wastewater collector were even higher than in industrial and urban wastewaters of the Rijeka area.

Figure 3.3.15 presents the averages of petroleum hydrocarbon concentrations in total industrial, domestic and urban wastewaters for every sampling cruise during the monitoring period.

To find out the influence of the tourist high season (summer months) on the concentrations of petroleum hydrocarbons in wastewaters for every area and year, the ratios between the concentrations obtained in summer months and those obtained in the other months were calculated. The ratios obtained are presented in Table 3.3.13. Ratios are calculated for all samples together and also separately for urban (mixed) and domestic wastewaters. As seen, it is not possible to ascertain that the high tourist season has a significant influence on the petroleum hydrocarbon concentrations in wastewaters, because in 8 cases the ratios are higher than 1 but in six cases are lower than 1. However, the effect was obvious only for the Split area in 1986.

Table 3.3.11

Petroleum and polyaromatic hydrocarbons in wastewaters (ug l^{-1}).

Location and Year	Method of Analysis	Compound(s)	Average	Minimum	Maximum	References
North Providence secondary wastewater treatment plants (3 cities) effluents, USA	GC	Hydrocarbons	7,000(9)	<500	16,200	Farrington and Quinn 1973,
Domestic wastewater		Aromatic hydrocarbons	1,300			Hunter and Jenkelekian 1965,
Domestic wastewater		Aliphatic hydrocarbons	4,000			
Petroleum refining industry :12 refineries		Oil total	57,000			McKinney 1967,
Sewage sludge (Germany)	GC	Benzo(a)pyrene	1,700		DW	Grimmer et al., 1978
		Polyaromatics	26,820		DW	
Southern California municipal wastewaters (5-effluents); 1979						
Unfiltered samples	TLC grav.	Total hydrocarb.	60,700(27)	5100	397,000	
Filtered "	"	"	3,650(25)	1200	17,600	Egenhouse and
	GC-MS	Polyaromatics		13	1,250	Kaplan 1982,
Gdansk sewage, Poland	GC	Polyaromatics		30,800	161,640	Grzybowski et al., 1983,
Oil refining industry Louisiana oil refinery	IR analyzer	Total oil	37,312	11,200	53,900	Ibievele 1986,
Influent water		Polyaromatics	607	441	837	Stubblefield
Effluent water		Polyaromatics	10			and Maki 1986,
Yugoslav Adriatic towns wastewaters	IR analysis	Total oil	1,100(113)	10	8,600	Anonymous 1987.
	UV fluoresc.	Chrysene	352(27)	3	3,310	

Number of samples in brackets

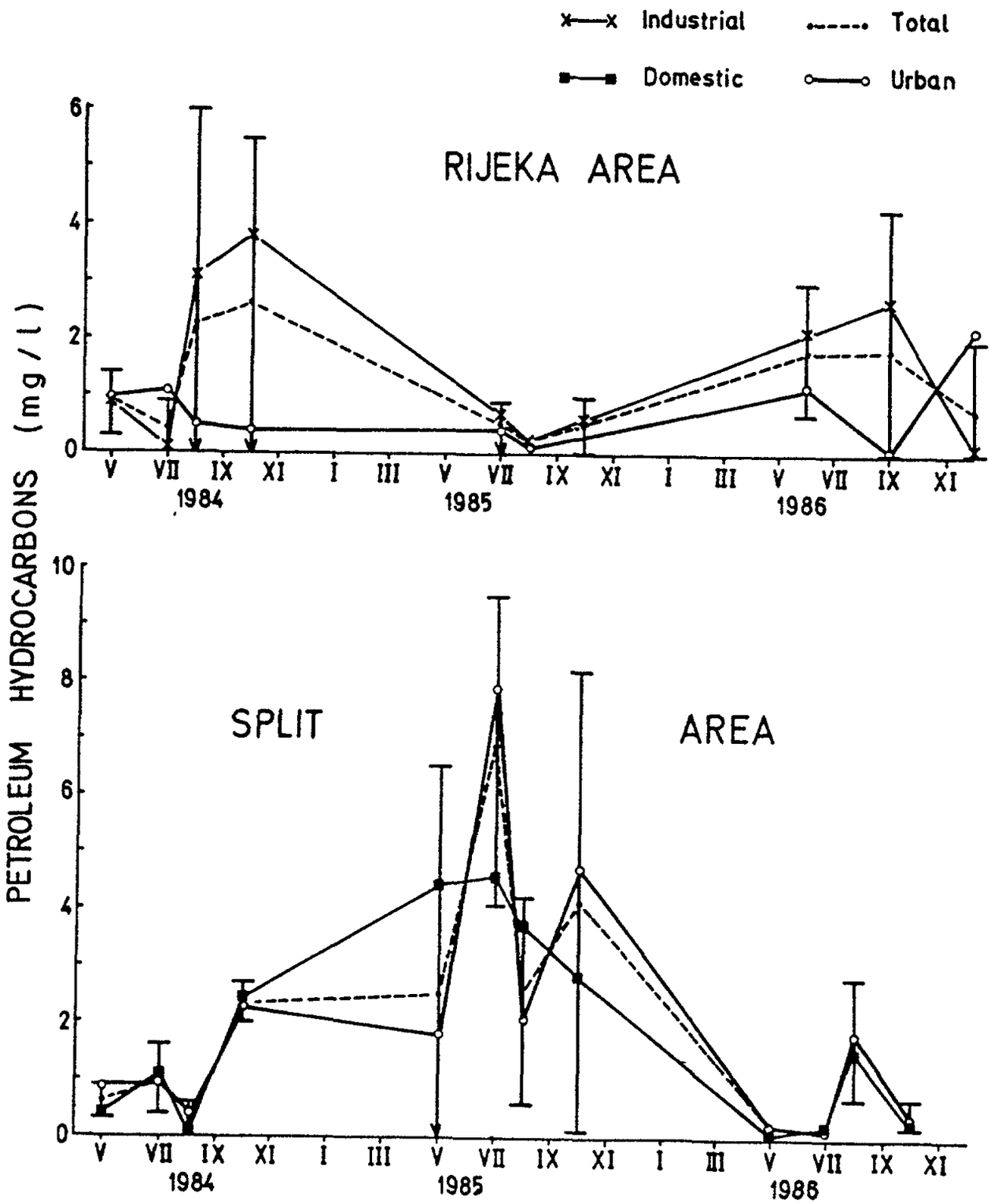


Figure 3.3.15 Averages with standard deviations of petroleum hydrocarbons concentrations in total, urban, domestic and industrial wastewaters for every collection cruise during the monitoring period

Table 3.3.12

Petroleum hydrocarbons in various samples from the Adriatic Sea.

Investigated area	Investigation period	Samples	Standard and method	Concentration	Average	Range
Rijeka area	1984-86	Industr. wastewater	IR method HC mixture	ug l^{-1}	1,350(21)	56-6,030
	1984-86	Urban wastewater	"	"	765(9)	69-2,180
Rijeka area	1986	Industr. wastewater (oil refinery)	UV-Fluoresc. Kuwait oil	ug l^{-1}	1,890(3)	360-1,106
			Chrysene	"	252(3)	82-452
Rijeka area	1986	Urban wastewater	UV-Fluoresc. Kuwait oil	"	293(9)	10-964
Rijeka area	1986		Chrysene	"	47(9)	3-113
Sibenik area	1984-86	Industr. wastewater	UV-Fluoresc. Kuwait oil	ug l^{-1}	1,900(14)	270-3,802
Sibenik area	1984-86	"	Chrysene	"	487(14)	18-3,309
Sibenik area	1983-85	Seawater	UV-Fluoresc. Kuwait oil	"	7(66)	<1-510
Sibenik area	1983-85	Seawater	Chrysene	"	1.3(66)	<0.2-25
Sibenik area	1984-85	Sediment	UV- Fluoresc. Kuwait oil	mg kg^{-1} DW	49.5(12)	0.9-115.3
Sibenik area	1984-85	Sediment	Chrysene	mg kg^{-1} DW	9.52(12)	0.15-25.2
Sibenik area	1985	Mussels	UV-Fluoresc. Kuwait oil	mg kg^{-1} WW	9.4(5)	1.7-19.5
			Chrysene		0.86(5)	0.21-1.69

Table 3.3.12 (cont'd)

Investigated area	Investigation period	Samples	Standard and method	Concentration	Average	Range
Split area	1984-85	Urban wastewaters	UV method diesel oil	ug l^{-1}	2,610(40)	17-8,520
Split area	1986	"	IR method HC mixture	"	615(20)	16-3,120
Split area	1984-85	Domestic wastewaters	UV method diesel oil	"	2,440(8)	54-8,600
Split area	1986	"	IR method HC mixture	"	554(8)	120-2,750
Split area	1984-85	Seawater	UV-Fluoresc. Chrysene	"	0.6(36)	ND-2
Split area	1986	Seawater	UV-Fluoresc. Kuwait oil	"	2.5(12)	ND-5.8
Split area	1984-86	Sediment	UV-Fluoresc. Chrysene	mg kg^{-1} DW	29.7(12)	ND-193.7
Split area	1986	Sediment	UV-Fluoresc.	"	904(4)	4-2,267
Montenegrin coastal area	1986	Source (river)	UV-Fluoresc.	ug l^{-1}	1.5	
			Chrysene	"	5.4	
	1986	Seawater	Kuwait oil UV-Fluoresc. Chrysene	"	0.4(2)	0.4-0.4
	1986	Seawater	Kuwait oil	"	1.1(2)	0.8-1.3

ND = Not detected (under sensitivity limit)
Number of samples in brackets

Table 3.3.13

Ratios of summer and nonsummer concentrations of petroleum hydrocarbons in wastewaters of investigated areas.

Area	Year:	1984	1985	1986
Rijeka Area	All samples	0.78	0.59	1.37
	Urban wastewaters	1.23	-	0.04
Split area	All samples	0.44	1.39	3.26
	Urban wastewaters	0.44	1.52	3.24
	Domestic wastewaters	0.44	1.12	3.34

Petroleum hydrocarbons in seawater and estuarine water

Table 3.3.14 compares concentrations of petroleum hydrocarbons in seawater samples from various areas of the Mediterranean Sea with concentrations in the samples analyzed in the framework of the Yugoslav Monitoring Programme. These latter concentrations, both for the open and coastal waters, are slightly lower than in the other areas of the Mediterranean Sea. However, the observed concentration ranges obtained in the Yugoslav Monitoring Programme are significantly higher than in the other areas of the Mediterranean Sea.

The comparison of petroleum hydrocarbon concentrations in seawater at the estuarine (E-4), reference (R-1, R-2), and coastal (C1-C3) stations obtained during the 1983-1985 period of the Sibenik area is presented in Fig. 3.3.16. Petroleum hydrocarbon concentrations in the same subareas obtained at stations R-1 and R-2, and C-1 and C-2 were relatively low. Besides, the subareas, where stations C-3 and E-4 were located, had significantly higher petroleum hydrocarbon concentrations and much higher variations in concentrations. With such very high variations in concentrations during the two year monitoring periods no trend calculations could possibly be carried out. It is obvious that, as in the case of detergent and phenol monitoring for trend fluctuation, more samples should be analyzed. Fig. 3.3.17 presents the frequency of concentration distribution of petroleum hydrocarbons in open waters of the northern Adriatic and the Sibenik area. Both distributions followed the geometrical distribution. However, in the Sibenik area samples with higher petroleum hydrocarbon concentrations were more frequent than in the northern Adriatic. (Picer, M., 1984a; Picer, M., et al.,1985; Picer, M., et al., 1986).

Concentrations of dissolved/dispersed petroleum hydrocarbons (in chrysene equivalents) for the Split area are presented in Table 3.3.12. The most polluted subarea was station 1 (Vranjic). At the reference station the results were near the sensitivity limit of the analytical method used.

During the 1985-86 period, oil slicks and other floating pollutants were observed in the Rijeka Bay. The results are presented in Table 3.3.15. Of 352 observations carried out, in 77 (22%) from the Rijeka Bay, some oil slicks or other floating material were recorded. Moreover, in 13,8% the floating material had a continuous cover. The pollution intensity in most observations was not very high (1/8 showed 61%), but in 5.4% the pollution intensity was very high (8/8).

Table 3.3.14

Polyaromatic hydrocarbons in seawater from the Mediterranean Sea (ug l^{-1}).

Area*	Location	Year	Method of Analysis	Compound(s) or Oil	Average	Min.	Max.	References
I	Coastal and open waters	1976	UV-Fluoresc.	Kuwait crude oil equival.	7.9(23)	4.3	14.6	Faraco and Ros 1979,
II	Coastal and open waters	1975-77	UV-Fluoresc.	Kuwait crude oil equival.	4.3(26)	1.8	18.2	Faraco and Ros 1979,
III	Coastal and open waters	1975-77	UV-Fluoresc.	Kuwait crude oil equival.	17(31)	1.0	123.5	Faraco and Ros 1979,
IV	Coastal and open waters	1975-77	UV-Fluoresc.	Kuwait crude oil equival.	9.3(41)	1.9	20.5	Faraco and Ros 1979,
VI	Coastal and open waters	1977-82	UV-Fluoresc.	Chrysene equiv.	5.1(90)	1.1	38.2	Mimicos et al., 1981,
VI & VIII	Coastal and open waters	1977-79	UV-Fluoresc.	Chrysene equiv.	(about 60 samples)	0.6	28.2	Mimicos et al., 1981,
VII	Coastal and open waters	1980	UV-Fluoresc.	No data	3.7(60)	0.2	20	Gerges and Durgham 1983,
VIII	Coastal and open waters	1980-82	UV-Fluoresc.	Chrysene equiv.	1.9(28)	0.5	11.5	Scoullos et al., 1983,
IX	Coast.waters	1980-82	UV-Fluoresc.	Chrysene equiv.	1.5	0.5	3.5	Sunay et al., 1983.
	Open waters	1980-82	UV-Fluoresc.	Chrysene equiv.		2.0	6.0	

Table 3.3.14 (cont'd)

Area*	Location	Year	Method of Analysis	Compound(s) or oil	Average	Min.	Max.	References
IX	Coast.waters	1983	UV-Fluoresc.	Chrysene equiv.	1.5(9)	0.1	5.6	Saydam et al., 1985,
	Open waters	1983	"	"	1.9(6)	0.8	3.8	
X	Coast. waters	1979-80	UV-Fluoresc.	Chrysene equiv.	6.4(23)	0.7	41.4	Wahby and El Deeb 1981,
	Coast. waters	1981-82	"	"	3.0(39)	0.5	13.0	El Samra et al., 1983,
	Coast. waters 1 m deep	1978-79	"	Iranian crude oil equivalent	7.4(138)	1.1	35.2	Aboul Dahab and Halim 1981a,
	Coast. waters 9.3 m deep	"	"	"	5.5(12)	0.6	9.1	"
	Coast. waters 18.6 m deep	"	"	"	3.7(12)	2.2	4.5	"
	Coast. waters	"	"	"	3.7(32)	0.7	35.2	Aboul Dahab and Halim 1981b.

Table 3.3.14 (cont'd)

Area*	Location	Year	Method of Analysis	Compound(s) or Oil	Average	Min.	Max.	References
T H E A D R I A T I C S E A	Open waters	1983-84	UV-Fluoresc.	Chrysene equiv.	0.2			Anonymous 1985a,
	Open waters	"	"	Kuwait crude oil equivalent	1.0			
	Open waters	1984-85	"	Chrysene equiv.	0.7(25)	0.1	2.0	Picer M. et al., 1985,
	Open waters	"	"	Kuwait crude oil equivalent	2.9(25)	0.5	7.0	Picer M. et al., 1986,
	Open waters	1983-86	UV-Fluoresc.	Chrysene equiv.	0.1(17)	ND	0.5	Anonymous 1987,
	Coastal and estuarine	"	"	Chrysene equiv.	0.8(83)	ND	25.0	Anonymous 1987,
	Open waters	1983-86	UV-Fluoresc.	Kuwait oil	0.8(14)	ND	3	Anonymous 1987,
	Coastal	1983-86	"	Kuwait oil	5.2(62)	ND	510	Anonymous 1987.

ND = Not detected (under sensitivity limit). Number of samples in brackets.
* = See Fig. 3.3.4

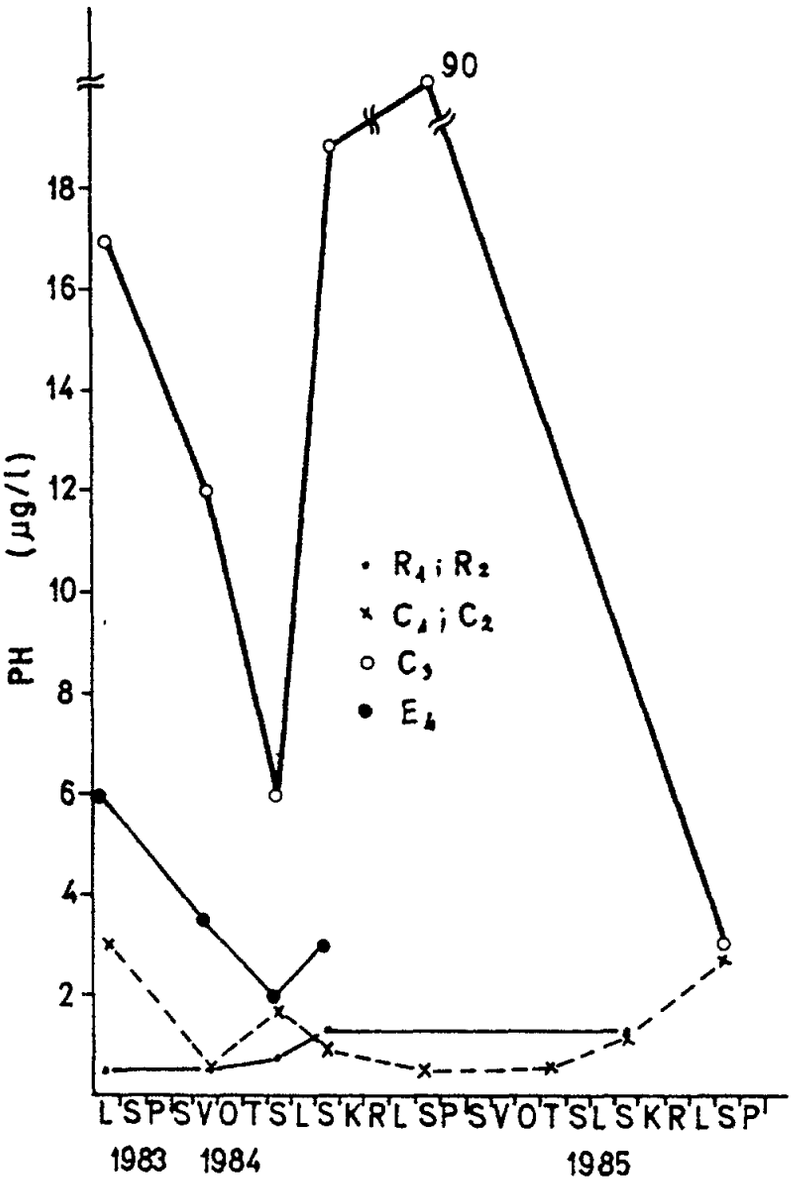


Fig. 3.3.16 Petroleum hydrocarbons at some stations of the Sibenik area in the years 1983-1985

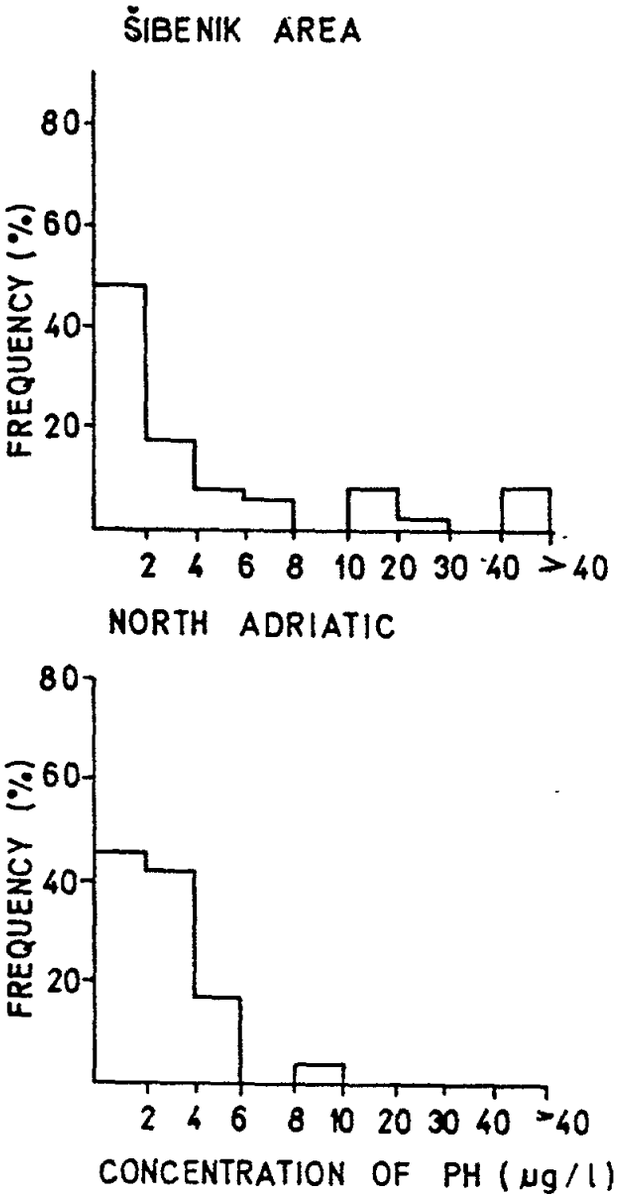


Fig. 3.3.17 Comparison of frequency distribution of petroleum hydrocarbon concentrations between the Sibenik and North Adriatic areas

Table 3.3.15

Oil slicks and other floating pollutants in the Rijeka area 1985-1986.

A)	Status of observation			0	2		
	Number of observations			275	77		
	Frequency (%)			78	22		
B)	Types of pollutants			1	4	1/4	
	Frequency (%)			22	39	39	
C)	Configuration		1	2	2	4	
	Frequency (%)		13.8	75.0	4.2	7.0	
D)	Concentrations	1	2	3	4	6	8
	Frequency (%)	61.0	14.7	9.4	6.7	2.8	5.4

Explanation of codes:

A) 0 = Sea surface observed but no pollutants to report
2 = Pollutants observed and recorded

B) 1 = Thin oil film (may include occasional minor patches or lumps of thick oil)
4 = Other pollutants
1/4 = Thin oil film and other pollutants

C) 1 = Continuous cover
2 = Patches
3 = In a line or lines
4 = Patches and lines

D) The WMO code for ice coverage
1 = 1/8; 2 = 2/8; 3 = 3/8; 4 = 4/8; 6 = 6/8; 8 = 8/8

Petroleum hydrocarbons in sediments

Petroleum hydrocarbons in sediments collected in the framework of the Yugoslav Monitoring Programme were analyzed by using the UV spectrofluorometry method. Table 3.3.16 compares some concentrations of polyaromatics in sediments from various areas in the Mediterranean with those obtained in the Yugoslav Monitoring Programme. As shown, the concentrations of polyaromatics in the samples analyzed for the Yugoslav Monitoring Programme are much higher than those in samples from other parts of the Mediterranean. However, concentrations of some identified polyaromatics as for example benzo(a)pyrene are much lower.

A comparison of distribution frequency for petroleum hydrocarbon concentrations in the northern Adriatic and Sibenik area sediments is shown in Fig. 3.3.18. These frequency distributions are significantly different. The results presented show that the Sibenik sediments were significantly more polluted with petroleum hydrocarbons than the northern Adriatic sediment samples. Although petroleum hydrocarbon levels in the Sibenik area sediments varied significantly, a common picture of the expected pollution sources was obtained (Picer, M., 1984a; Picer, M., 1986; Picer, M., et al. 1986, Picer M. and N. Picer, 1986).

Figure 3.3.19 presents all the data on polyaromatic concentrations in monitored sediment samples from the Split area. For the more polluted samples the fluctuations in the results are very high. Such great variations in the concentrations are centainly due to changes in the UV fluorescence methodology applied. However, for the Sibenik area, there were no marked differences in PAH levels in the sediments obtained from the same stations during the 1984-85 period.

Since polyaromatic hydrocarbons (PAH) enter the marine environment from a variety of sources, an attempt was made to record the spectra emission of monoaromatic and polyaromatic sediment fraction extracts to the point of the characteristic absorption maxima. The pyrolitic pollution sources had a characteristic peak at about 400 nm (benzo(a)pyrene), whereas PAH originating from diagenetic sources showed absorption maxima at higher wavelengths (perylene at about 430 nm). The petrogenic PAH occurred at 340-380 nm wavelengths during the recording of the emission spectra. The maxima mentioned are characteristic for the excitation wavelength of 310 nm.

Figure 3.3.20 depicts the emission spectrum of fraction (lower aromatics) in sediment samples from station 1 (the Split area, Vranjic). The determination of 2-4 core PAH and the emission of polycyclic aromatics was noticed. Aromatic compound values with 5 or more benzene rings (0.032 ug g^{-1} dry sediment) were not recorded in fraction IV either. It may be stated that the results are an indication of strong pollution by oil and oil derivatives. For the Split harbour (station 5) the situation was quite the opposite. Figures 3.3.21 and 3.3.22 present the emission spectra for fractions III and IV of sediment extracts. Fraction IV of PAH values was dominant. It may be stated that sediments from the city harbour were polluted by petrochemical products with compounds characteristic for harbour and exhaust gases from internal combustion engines but aromatics originating from the natural sediment matrix could also be found (Aisenshtat, 1973).

Table 3.3.16

Polyaromatic hydrocarbons in sediments from the Mediterranean Sea (ug kg^{-1} dry weight).

Area	Water Depth (m)	Year	Method of Analysis	Compound(s) or Oil	Average	Min.	Max.	References
II	10-1000	1980	GC	Polyaromatics	10,400(20)	500	40,000	Albaiges
	"	"	"	Benzo(a)pyrene	10(20)	ND	64	et al., 1983,
II	10-225	1983	GC-MS	Polyaromatics	851(18)	195	2685	Grimalt
	"	"	"	Benzo(a)pyrene	60(18)	7	168	et al., 1985,
II	250	1981	GC-MS	Polyaromatics (total)	726(4)	599	847	Burns and Villeneuve
		"	"	Chrysene	95(4)	63	121	1983,
II	Coastal waters	?	UV-Fluoresc.	Polyaromatics (total)	60,600(12)	3,700	402,000	Mille et al., 1983,
II& III	Coastal and open waters	?	GC-MS	Chrysene	5.2(17)	ND	14	Arnoux et al., 1983,
II& III	"		"	Benzo(a)pyrene	3.2(17)	ND	9	
VIII	15-28	1980	UV-Fluoresc.	Chrysene equiv.	9,300(9) (wet.wt.)	ND	23,600	Scoullos et al., 1983,
IX	30-90	1980-82	UV-Fluoresc. & GC-MS	Chrysene equiv.	240(16)	40	680	Sunay et al., 1983,
X	19	1981-82	UV-Fluoresc.	Chrysene equiv.	980(8)	100	3,000	El Samra et al., 1983.

Table 3.3.16 (cont'd)

Area*	Water Depth (m)	Year	Method or Analysis	Compound(s) of oil	Average	Min.	Max.	References
The Adriatic Sea	38-69	1967-68	UV-Fluoresc.	Benzo(a)pyrene	25.9(15)	3.3	55.1	Olmo and Molinas 1969,
	12-351	1965-66	UV-Fluoresc.	Benzo(a)pyrene	22.1(5)	11.4	35.0	Piccinetti 1968,
	40-50	1984-85	UV-Fluoresc.	Chrysene equiv.	800(17)	150	3,040	Picer M. et al., 1985, Picer M. et al., 1986,
	40-50	1984-85	UV-Fluoresc.	Kuwait crude oil	3,900(17)	740	18,020	Picer M. et al., 1986,
	Various	1984-86	UV-Fluoresc.	Chrysene	19,600(24)	ND	193,700	Anonymous 1987.
			"	Kuwait oil	476,000(16)	ND	2,270,000	

ND = Non detected (under sensitivity limit); Number of samples in brackets
* = See Fig. 3.3.4

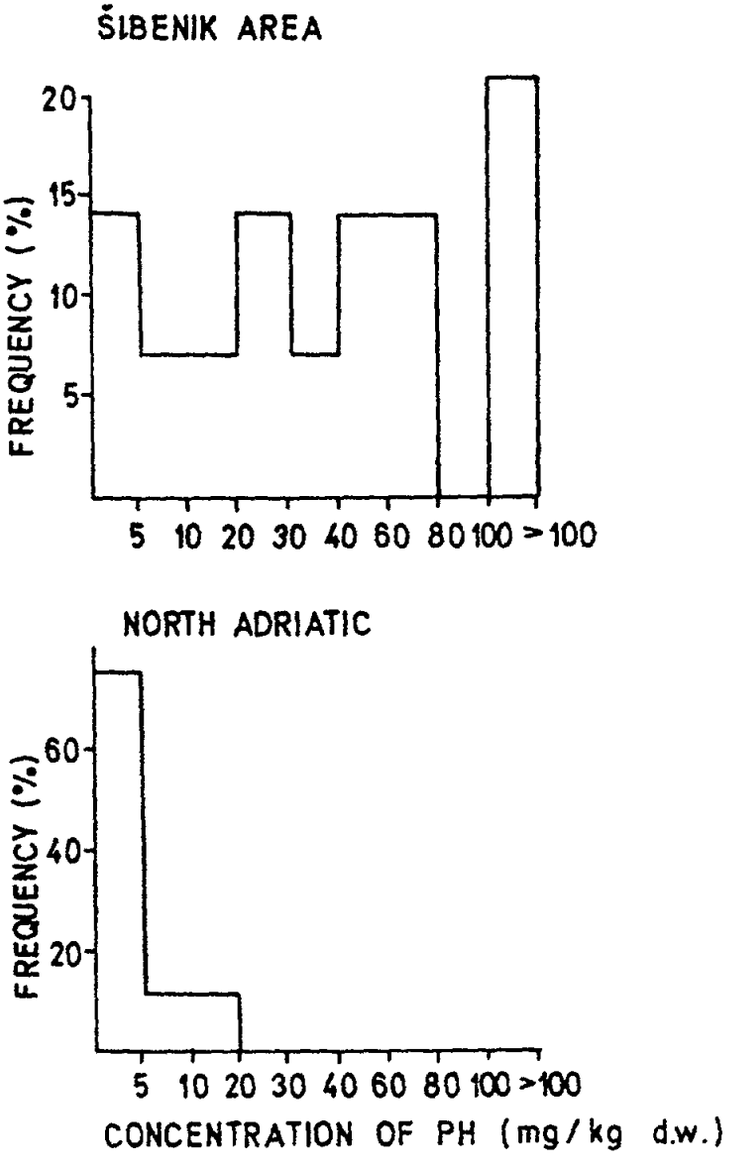


Fig. 3.3.18 Comparison of frequency distribution of petroleum hydrocarbon concentrations between the Sibenik and North Adriatic areas

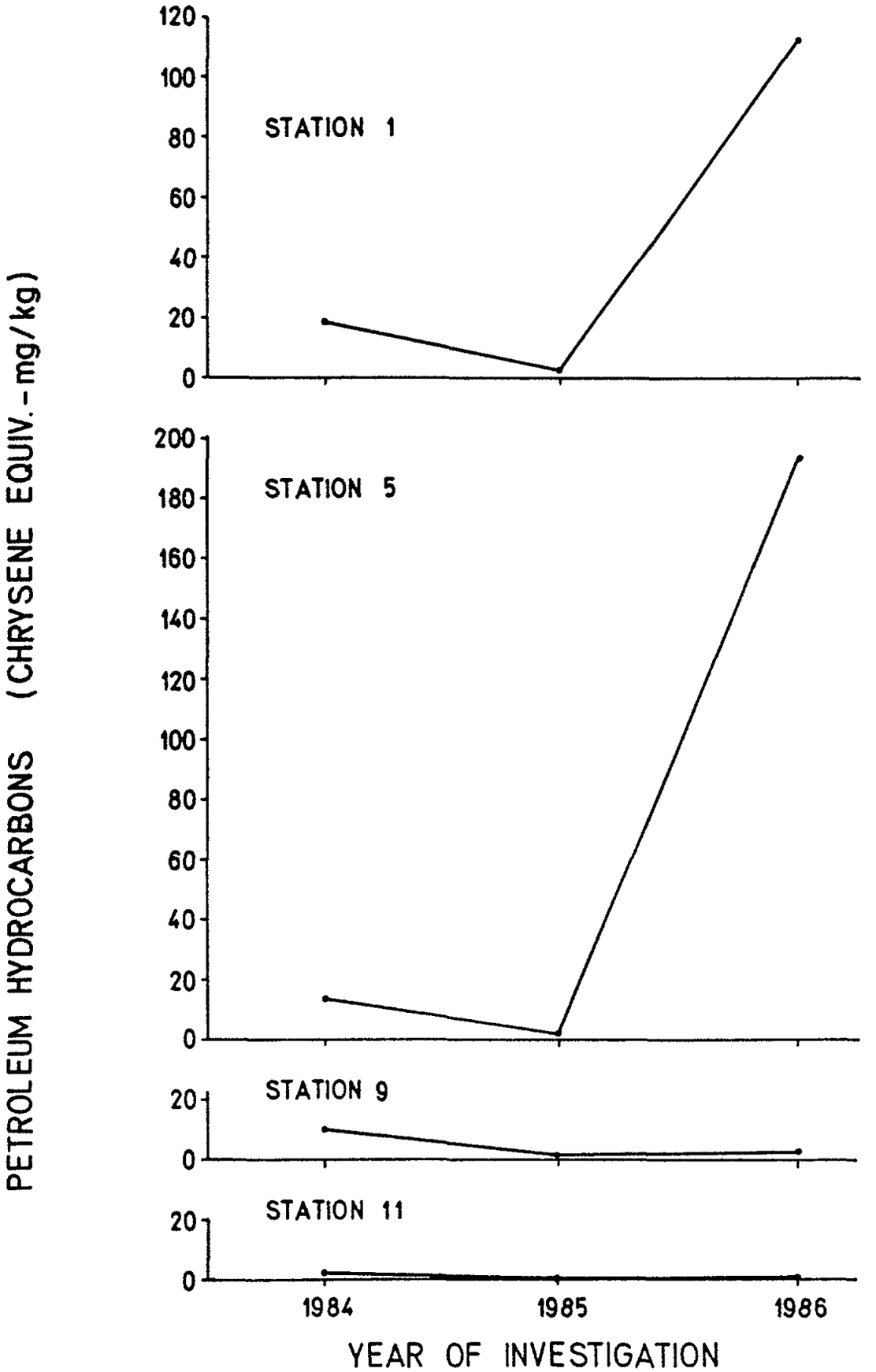


Fig. 3.3.19 Petroleum hydrocarbons (expressed in chrysene equivalents) in sediments of the Split area

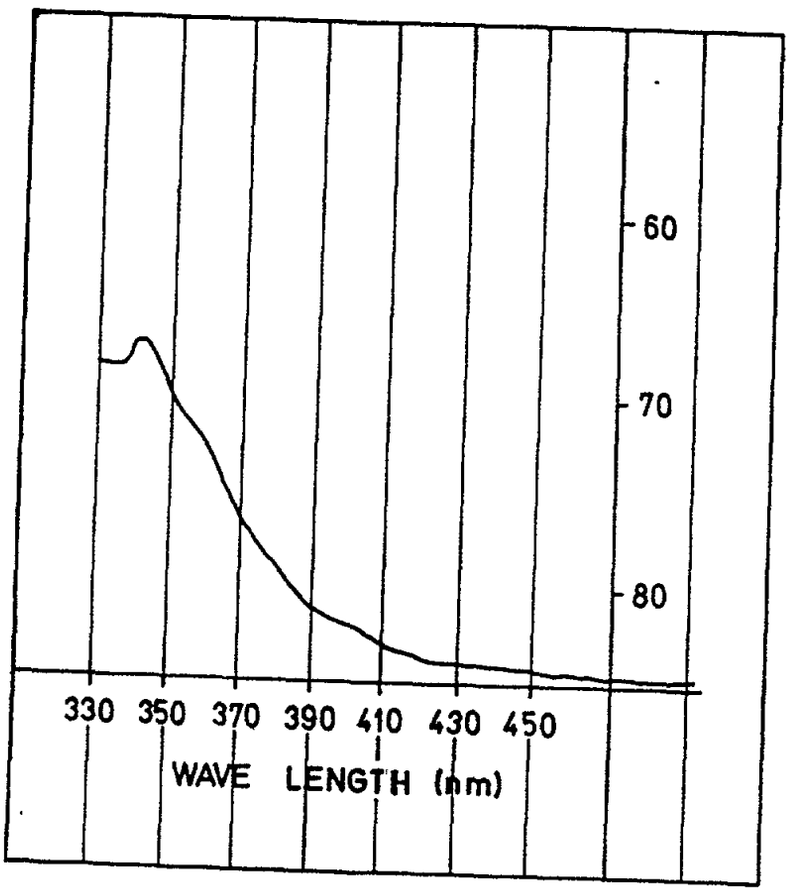


Fig. 3.3.20 Emission fluorescence spectrum of sediment extract from the Split area (Vranjic Station - Fraction III)

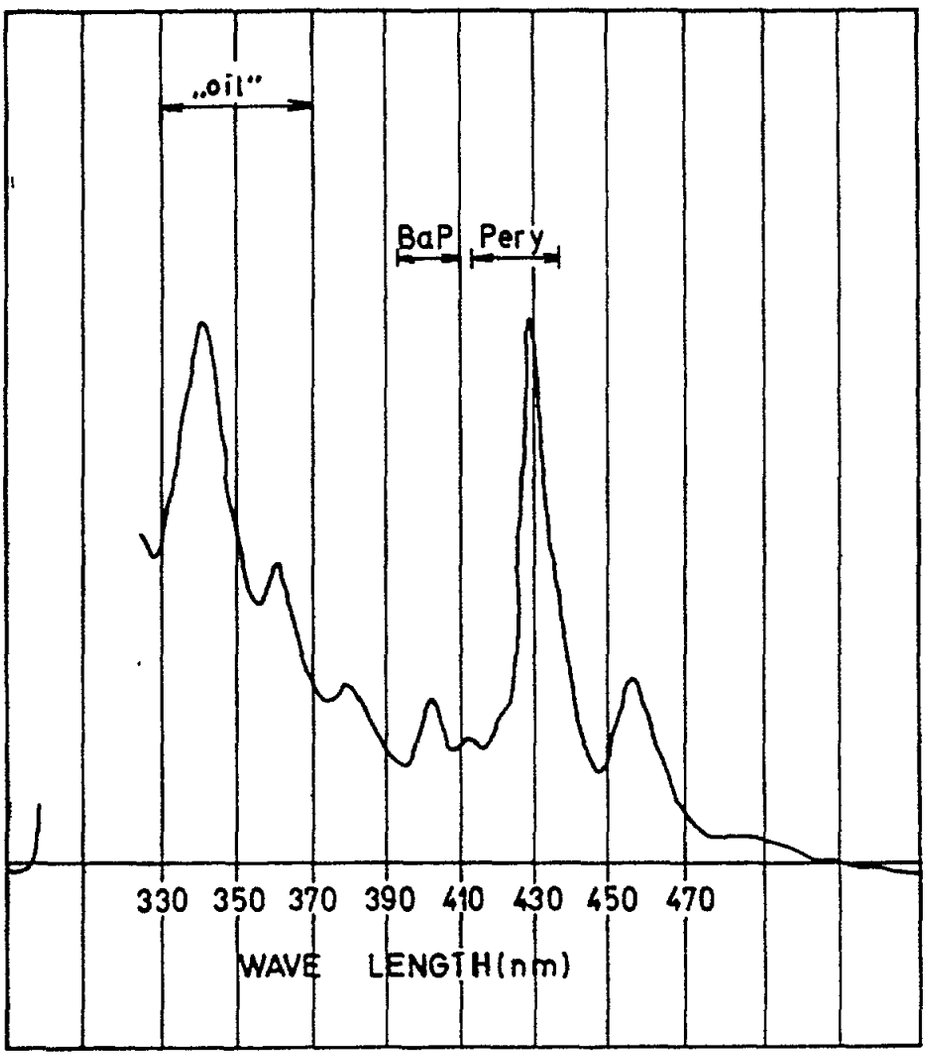


Fig. 3.3.21 Emission fluorescence spectrum of sediment extract from the Split area (Gradska Luka Station, Fraction III)

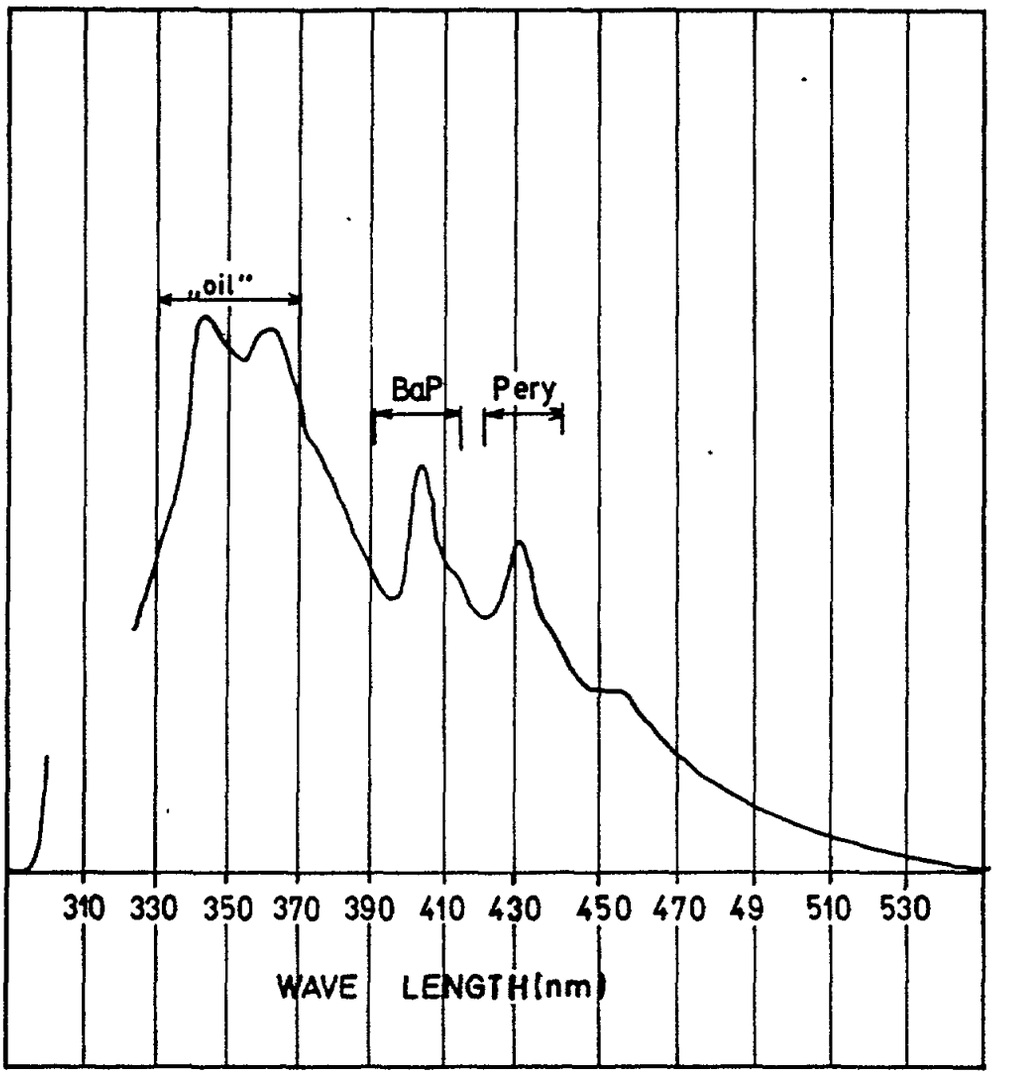


Fig. 3.3.22 Emission fluorescence spectrum of sediment extract from the Split area (Gradska Luka Station, Fraction IV)

At reference station 11 (Vis Island) no significant concentrations of polyaromatics in sediment samples were found.

Petroleum hydrocarbons in mussels

In the framework of the Yugoslav Monitoring Programme petroleum hydrocarbons were monitored only in some samples from the Sibenik area. For the sake of comparison with other Mediterranean areas, Table 3.3.17 presents some of the results of the polyaromatic hydrocarbon determination in various organisms from the Mediterranean Sea. The results are very variable and it is difficult to compare them, except for the benthic organisms from the North Adriatic where the same methodology was applied.

Table 3.3.18 presents the ratios obtained by comparing the petroleum hydrocarbon concentrations in various matrices of the Sibenik and Split areas. Concentration factors between water and sediments in Sibenik have an average of 11,600 when petroleum hydrocarbon concentrations are presented as chrysene equivalents and 12,700 when they are presented as Kuwait crude oil. In the Split area, these concentration factors are about 7 times higher, with extremely wide ranges (from 60 to 514,000). The average of the bioconcentration factor for water/mussel is 4,050 when the polyaromatic fraction of hydrocarbons is expressed as chrysene equivalent and an average of 3,770 when expressed as Kuwait crude oil equivalent. Furthermore, in this case the ranges of bioconcentration factors for the Sibenik area are relatively small (from 2,000 to 6,000). The results show that the analytical methodology used for the polyaromatic fraction of petroleum hydrocarbons in the Sibenik area ecosystem is relatively reliable and can be recommended for other areas as well.

Table 3.3.17

Polyaromatic hydrocarbons in mussels, fish and other ogranisms from the Mediterranean Sea (ug kg^{-1} fresh weight).

Area*	Organisms	Year	Method of Analysis	Compound(s) or oil equiv.	Average	Min.	Max.	References
II	Fish (2 species, muscle)	1983	UV-Fluoresc.	Kuwait crude oil equiv.	6,380(6) (dry wt.)	1,700	11,100	Albaiges et al., 1985,
VIII	Mussels	?	GC	Total poly-aromatics	91(57)			
"	"		"	Carcinogenic polyaromatics	19(57)			Iosifidou et al., 1982,
"	"		"	Benzo(a)pyrene	1			
IX	Fish (5 species, muscle)	1980 1982	GC and UV-Fluoresc.	Chrysene equiv.	130	40	7,300	Sunay et al., 1983,
T	Fish (9	1965-66	UV	Benzo(a)pyrene	71(10)	10	208	Cicatelli 1966,
H	species)		Fluoresc.		282(21)	2	2,200	Piccinetti 1968,
E	Various organ-	"	"	"				
A	isms (12)							
D	species)							
R	Mussels	1975-76	TLC&UV Flu.	Benzo(a)pyrene	11.0(90)	2.1	24.1	Fossato et al.,
I	"	"	"	Perylene	1.7(90)	0.3	3.0	1979,
A	Benthic	1984-85	UV Fluor.	Chrysene equiv.	2860(13) (dry wt)	490	10,300	Picer M. et al., 1985,
T	organisms							
I	"	"	"	Kuwait crude	13,840(13)	2,440	46,800	Picer M. et al.,
C	(10 species)			oil equiv.				1986,
S	Mussels	1985	UV-Fluor.	Chrysene equiv.	900(5)	210	1690	Anonymous 1987.
E	"	"	"	Kuwait crude	8,880(5)	1,700	19,500	
A				oil equiv.				

Number of samples in brackets.
* See Fig. 3.3.4

Table 3.3.18

Petroleum hydrocarbon concentration ratios from various matrices of the Sibenik and Split areas.

Area	Investigation period	Investigated matrix	Number of samples	Type of hydrocarbons	Ratio Average	Ratio Minimum	Ratio Maximum
Sibenik area	1983-84	Sediment/ water	5 17	Chrysene	11,600	275	39,800
	1985	Mussels/ water	2 2	"	4,050	2,100	6,000
	1985	Sediment/ Mussels	2 2	"	23	11	36
	1983-84	Sediment/ water	5 17	Kuwait crude oil	12,700	650	43,200
	1985	Mussels/ water	2 2	"	3,770	1,310	6,220
	1985	Sediment/ Mussels	2 2	"	9.5	5	14
Split area	1984-86	Sediment/ water	12 36	Chrysene	73,000	60	514,000
	1986	Sediment/ water	4 10	Kuwait crude oil	267,000	4,700	769,000

3.4. Faecal coliforms

Coliforms are typical indicators of faecal pollution in the aquatic environment. Concentrations of coliforms in ordinary municipal wastewaters are usually in the 10^7 to 10^8 per 100 ml range, while concentrations of faecal coliforms usually amount to 10-60% of total coliforms.

In the Slovenian coastal area most of the wastewater effluents, which are of domestic, agricultural and industrial origin, are discharged through the Rizana River into Koper Bay(Lenarcic, 1981; Turk et al., 1983). High values for bacterial indicators of faecal pollution were constantly recorded at the mouth of the Rizana river.

The distribution of faecal coliforms and the evaluation of the results, performed according to the WHO/UNEP (1983c) interim criteria, are shown in Table 3.4.1 and Fig. 3.4.1.

Areas I, II and III, extending from the Cape of Debelirtic to the Kanegra on the Savudria peninsula, comprise the sampling stations on all public beaches along the Slovenian coastline. During the Monitoring Programme, 801 samples were collected and 85.6% of the results from these areas contained less than 100 faecal coliforms per 100 ml. Although most of the sampling stations in the recreational areas gave bacteriological values that comply with the WHO/UNEP interim criteria, some of the stations in these areas are under the influence of local sewage effluents.

Area IV comprises 8 sampling stations in the inner part of Koper Bay. This area is influenced by the pollution load of the estuary of the Rizana river and displays transitional characteristics between very high levels of pollution in the estuary and fairly low levels along the recreational zones. The contamination decreases from 80% above the value of 1000/100 ml for stations 13 and 14 near the mouth of the Rizana river to 85.5% below the value of 100/100 ml in the middle of Koper Bay. The area benefits from a favorable tidal mixing which favours the dilution of pollutants to a considerable degree. The pollution level also depends on weather conditions; for example, during May, June and July very low values of bacteria were recorded.

According to the results obtained in the periods 1977-1980 and 1981-1986 the water quality of the Slovenian coastal area did not change, except in the inner part of the Piran Bay where, owing to the installation of a new combined sewage system, improved water quality was recorded.

The sanitary quality of the seawater in the Rovinj area did not satisfy the WHO/UNEP interim criteria at stations 6-8 (Table 3.4.2 and Fig. 3.4.2).

Table 3.4.1

Distribution of faecal coliforms on the Slovenian coast and evaluation according to WHO/UNEP interim criteria (1983).

	Samples (%) exceeding limits of FC/100ml											
STATION	n[a]	10^2	10^3	n[a]	10^2	10^3	n[a]	10^2	10^3	n[a]	102	103
	1983			1984			1985			1986		
Area I[b]	51	13.7	0	58	22.4	3.4	71	16.0	4.2	66	34.8	1.5
Area II[b]	25	16.0	4.0	24	12.5	0	48	16.7	2.1	44	13.6	0
Area III[b]	82	2.4	0	89	6.7	1.1	133	10.5	0.8	110	7.3	0
Area IV[b]	70	32.9	4.3	69	17.4	4.3	93	15.1	2.2	88	35.2	7.9
13	11	100	72.7	18	100	77.8	12	100	100	11	100	90.9
14	11	100	90.9	18	100	77.8	12	100	100	11	100	90.9
36	9	0	0	10	0	0	12	0	0	11	0	0
MA	11	0	0	19	5.3	0	12	0	0	11	0	0
K	11	18.1	0	19	5.3	0	12	16.6	0	11	18.2	0

[a]Number of samples

[b]Area I - stations 1-5, 17
Area II - stations 21-24
Area III - stations 25-33, 37
Area IV - stations 8, 10-12, 15, 16, 18, 20

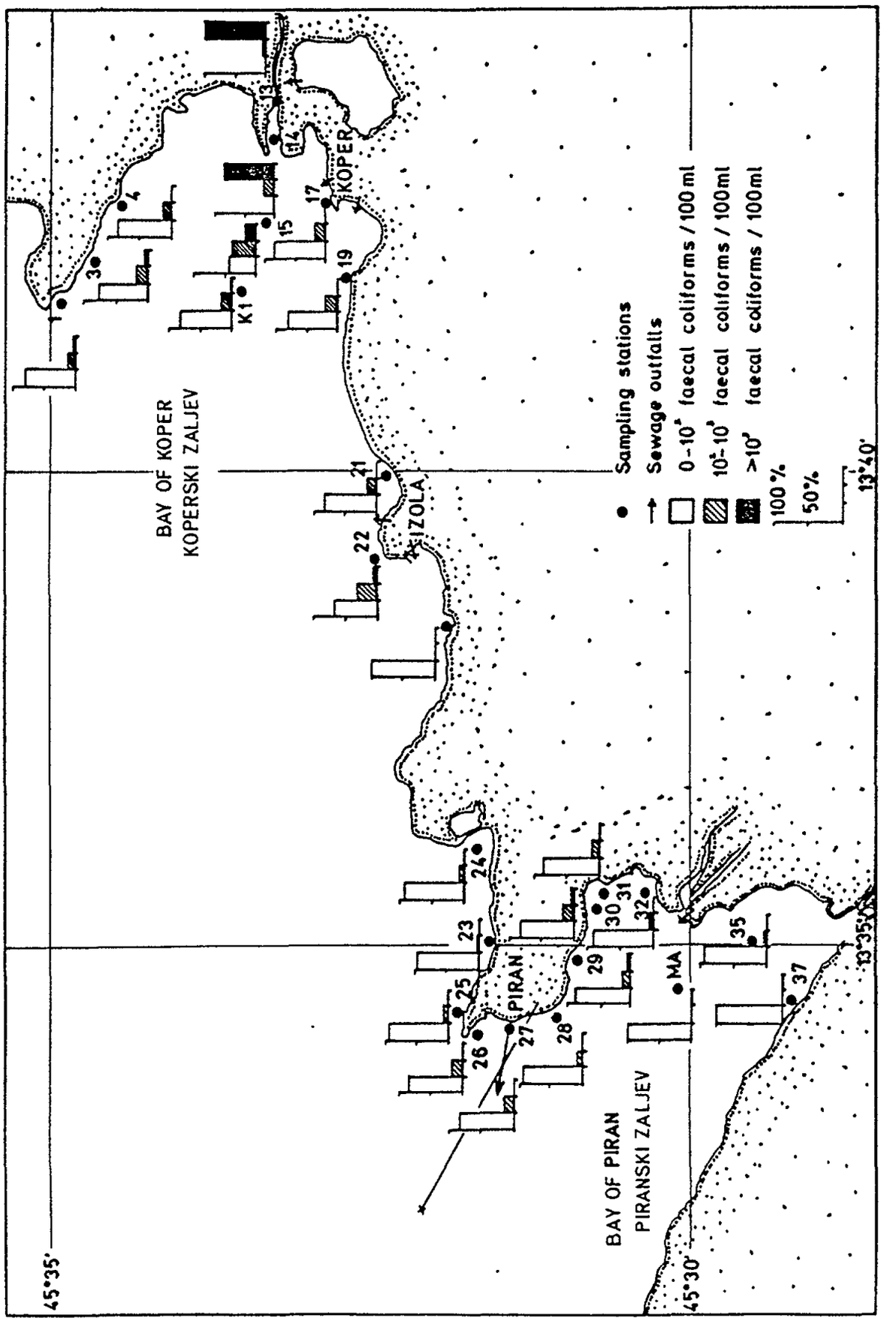


Fig. 3.4.1 Slovenian coastal area - distribution of faecal coliform concentrations

Table 3.4.2

Distribution of faecal coliforms in the Rovinj area and evalutation according to WHO/UNEP interim criteria (1983).

	Samples (%) exceeding limits of FC/100ml											
STATION	n^a	10^2	10^3	n^a	10^2	10^3	n^a	10^2	10^3	n^a	10^2	10^3
	1983			1984			1985			1986		
3	10	10	0	16	12.5	0	14	14.3	7.1	16	12.5	0
4	10	20	0	16	6.3	0	14	0	0	16	6.2	0
5	10	30	0	16	6.3	0	14	7.1	0	16	18.8	0
6	10	40	10	16	31.3	0	14	14.3	0	16	18.8	6.2
7	-	-	-	16	43.8	6.3	14	28.6	7.1	16	25.0	12.5
8	10	30	0	16	37.5	6.3	14	42.9	7.1	16	18.8	6.2
9	10	10	0	16	0	0	14	0	0	16	0	0

[a]Number of samples

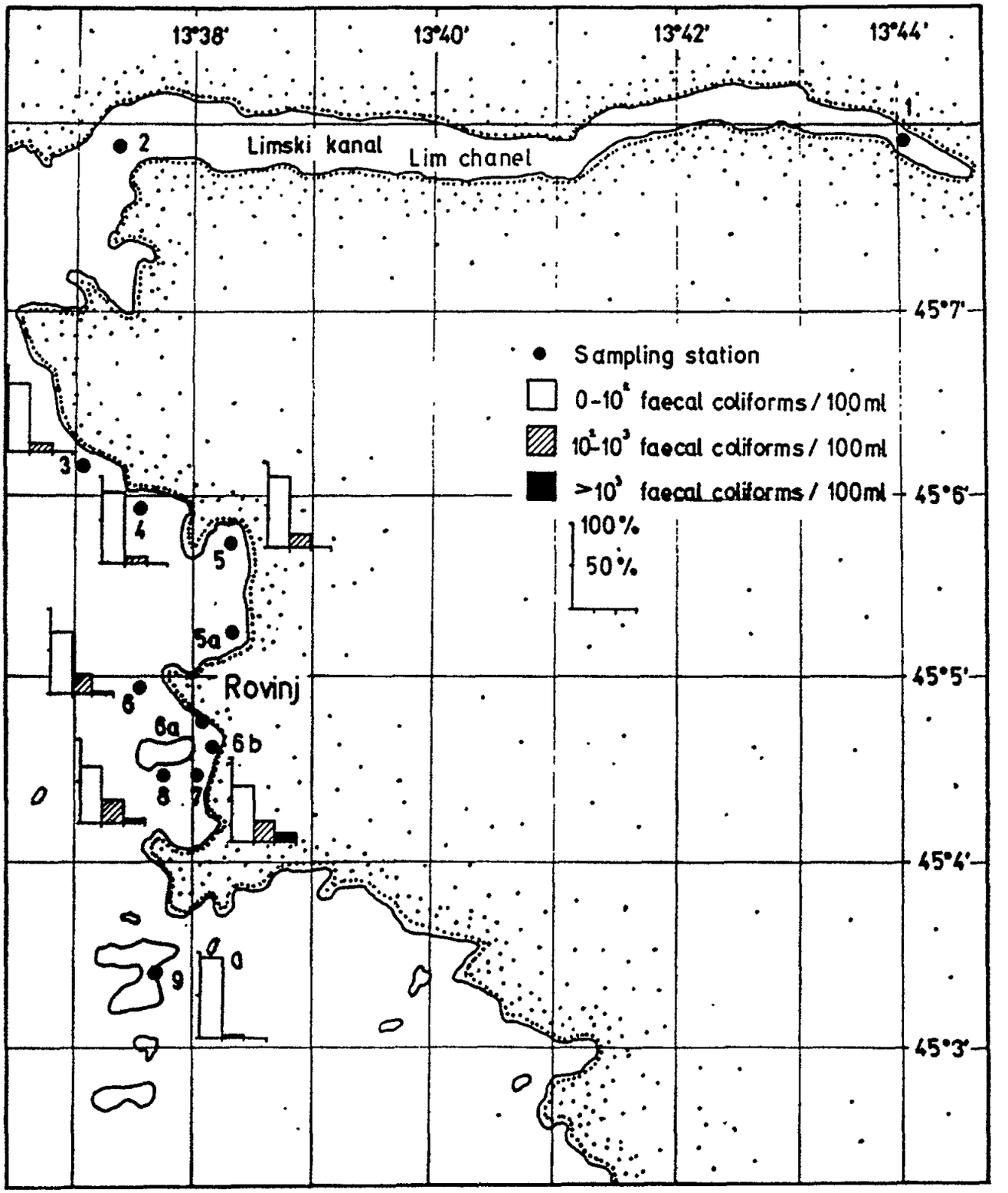


Fig. 3.4.2 Rovinj Area - distribution of faecal coliform concentrations

The increasing number of tourists and inadequate sewage discharges have resulted in a deterioration of the sanitary quality of the coastal waters in the Rovinj area (Fuks 1981a; 1981b). Of all the controlled beaches, only stations 4 and 9 had a high sanitary water quality, owing to the absence of nearby sewage outfalls. The sanitary quality of the water at stations 3 and 6, due to the presence of nearby sewage outfalls and the influence of meteorological and hydrological conditions on sewage dispersion, did not temporarily satisfy the WHO/UNEP interim criteria.

Although the percentage of samples exceeding the limit of the WHO/UNEP interim criteria increased at all the stations, the decrease of the sanitary water quality of the Rovinj recreational waters was not statistically significant during the monitoring period.

In the Pula area the monitoring of the coastal water quality included beaches on its western and southern coasts (Table 3.4.3 and Fig. 3.4.3).

The coast is under the influence of effluents dicharged from industry, urban areas, tourist villages and agricultural areas. The area also includes the harbour of Pula in which 20,000 m^3 of wastewaters (urban and industrial) are discharged daily through 14 sewage outfalls.

The sanitary seawater quality of the beaches (stations 1-11) satisfied the WHO/UNEP interim criteria except on the southern coast (stations 9-11), due to an increase of sewage discharges from the tourist areas in the region.

In the Rijeka area the sanitary quality of seawater is shown in Table 3.4.4 and Fig. 3.4.4

According to the WHO/UNEP interim criteria seawater was of a high quality at the Moscenicka Draga, Lovran, Opatija-Lipovica, Volosko, Zurkovo, Kraljevica, Voz, Omisalj, Njivice and Crikvenica stations (stations 1, 2, 5, 6, 10, 12, 13, 14, 15 and 16).

The sanitary quality of seawater was not satisfactory at stations 3 (Ika), 4 (Opatija-Slatina), 7 (Preluka), 8 (Rijeka-Bivio), 9 (Rijeka-Sablicevo), 11 (Bakarac), due to inadequate sewage treatment.

Generally it can be stated that the sanitary quality of seawater near the city of Rijeka is low, while the seawater in the eastern part of the Rijeka Bay and at the Krk Island has so far been unpolluted.

In the Sibenik area the results show that the Krka River was not noticeably loaded as far as faecal coliforms are concerned (Table 3.4.5 and Fig. 3.4.5).

Table 3.4.3

Distribution of faecal coliforms in the Pula area and evaluation according to WHO/UNEP interim criteria (1983).

	Samples (%) exceeding limits of FC/100ml											
STATION	n^a	10^2	10^3	n^a	10^2	10^3	n^a	10^2	10^3	n^a	10^2	10^3
	1983			1984			1985			1986		
1	-	-	-	11	18.2	0	11	36.4	0	11	9.1	0
2	-	-	-	11	9.1	0	11	0	0	11	0	0
3	-	-	-	11	0	0	11	45.5	9.1	11	9.1	9.1
4	-	-	-	11	0	0	11	0	0	11	9.1	0
5	-	-	-	11	0	0	11	36.4	0	11	9.1	0
6	-	-	-	11	0	0	11	36.4	0	11	9.1	0
7	-	-	-	11	0	0	11	0	0	11	0	0
8	-	-	-	11	0	0	11	0	0	11	0	0
9	-	-	-	11	18.2	0	11	45.5	45.5	11	54.5	45.5
10	-	-	-	11	27.3	0	11	36.4	9.1	11	36.3	18.2
11	-	-	-	11	18.2	0	11	54.4	9.1	11	63.6	63.6
12	-	-	-	11	0	0	11	0	0	11	0	0
13	-	-	-	11	18.2	0	11	0	0	11	0	0

[a]Number of samples

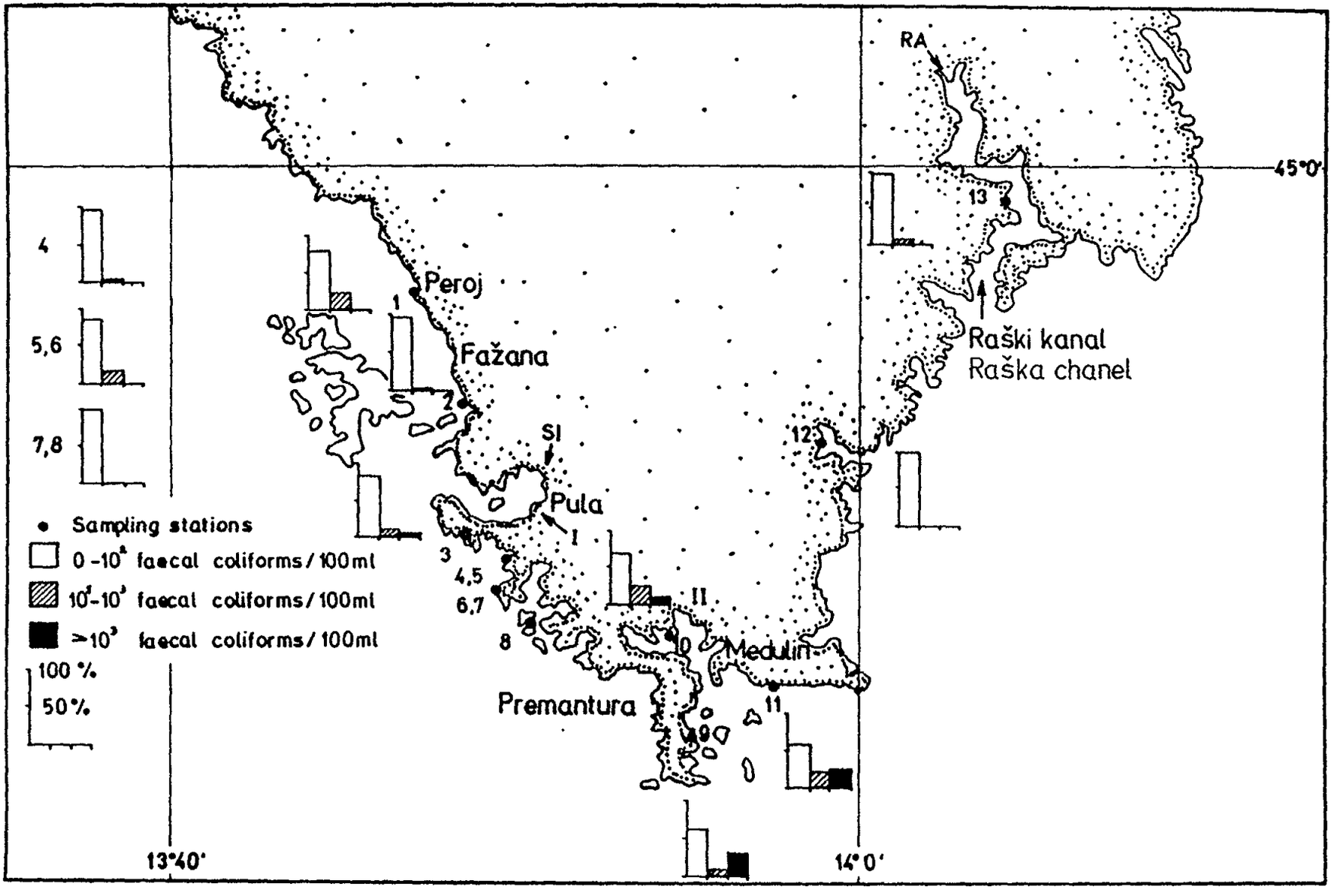


Fig. 3.4.3 Pula Area - distribution of faecal coliform concentrations

Table 3.4.4

Distribution of faecal coliforms in the Rijeka area and evaluation according to WHO/UNEP interim criteria (1983).

	Samples (%) exceeding limits of FC/100ml											
STATION	n^a	10^2	10^3	n^a	10^2	10^3	n^a	10^2	10^3	n^a	10^2	10^3
	1983			1984			1985			1986		
1	-	-	-	11	9.1	0	11	9.1	0	11	9.1	0
2	-	-	-	11	0	0	11	0	0	11	0	0
3	-	-	-	11	45.5	0	11	45.5	27.3	11	72.0	36.4
4	-	-	-	11	81.7	27.3	11	45.5	0	11	54.1	18.2
5	-	-	-	11	36.4	9.1	11	45.5	18.2	11	27.3	0
6	-	-	-	11	27.3	0	11	36.4	0	11	27.3	0
7	-	-	-	11	9.1	0	11	18.2	9.1	11	36.4	18.2
8	-	-	-	11	45.5	44.4	11	9.1	0	11	18.2	9.1
9	-	-	-	11	63.6	55.6	11	63.6	9.1	11	36.4	0
10	-	-	-	11	9.1	0	11	18.2	0	11	0	0
11	-	-	-	11	18.2	9.1	11	36.4	18.2	11	36.4	18.2
12	-	-	-	11	0	0	11	9.1	0	11	9.1	0
13	-	-	-	11	0	0	11	0	0	11	0	0
14	-	-	-	11	9.1	0	11	0	0	11	0	0
15	-	-	-	11	0	0	11	9.1	0	11	9.1	9.1
16	-	-	-	11	0	0	11	0	0	11	9.1	0

[a]Number of samples

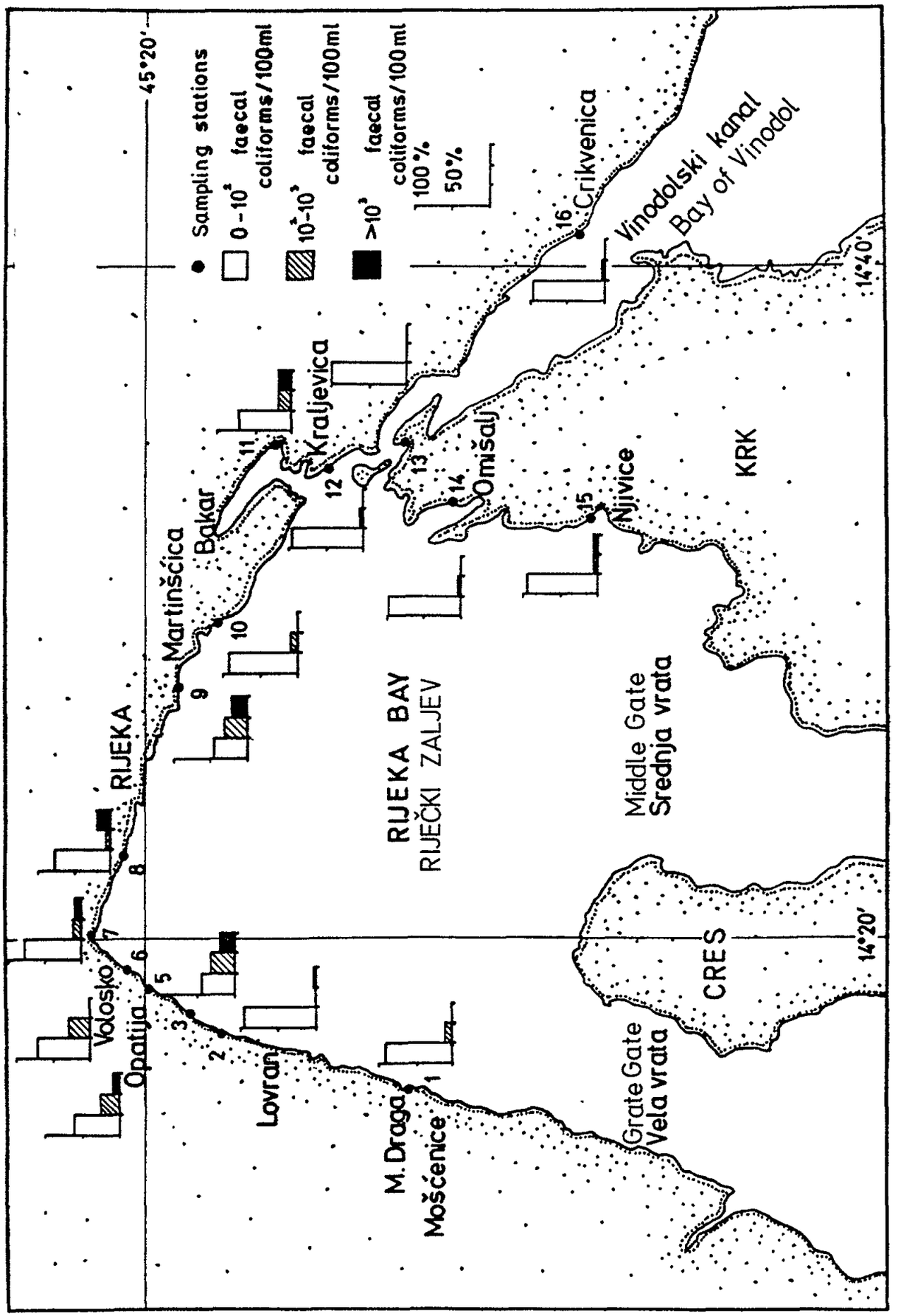


Fig. 3.4.4 Rijeka area - distribution of faecal coliform concentrations

Table 3.4.5

Distribution of faecal coliforms in the Sibenik area and evaluation according to WHO/UNEP interim criteria (1983).

	Samples (%) exceeding limits of FC/100ml											
STATION	n[a]	10^2	10^3	n[a]	10^2	10^3	n[a]	10^2	10^3	n[a]	10^2	10^3
	1983			1984			1985			1986		
E-1	-	-	-	3	33.3	0	9	22.2	0	6	66.6	0
E-2	-	-	-	5	40.0	0	9	55.5	33.3	6	33.3	16.6
E-3	-	-	-	3	0	0	6	50.0	0	2	0	0
E-5	-	-	-	5	0	0	9	0	0	6	0	0
C-2	-	-	-	4	0	0	9	11.1	0	6	0	0
C-3	-	-	-	3	0	0	11	27.3	18.2	6	0	0

[a]Number of samples

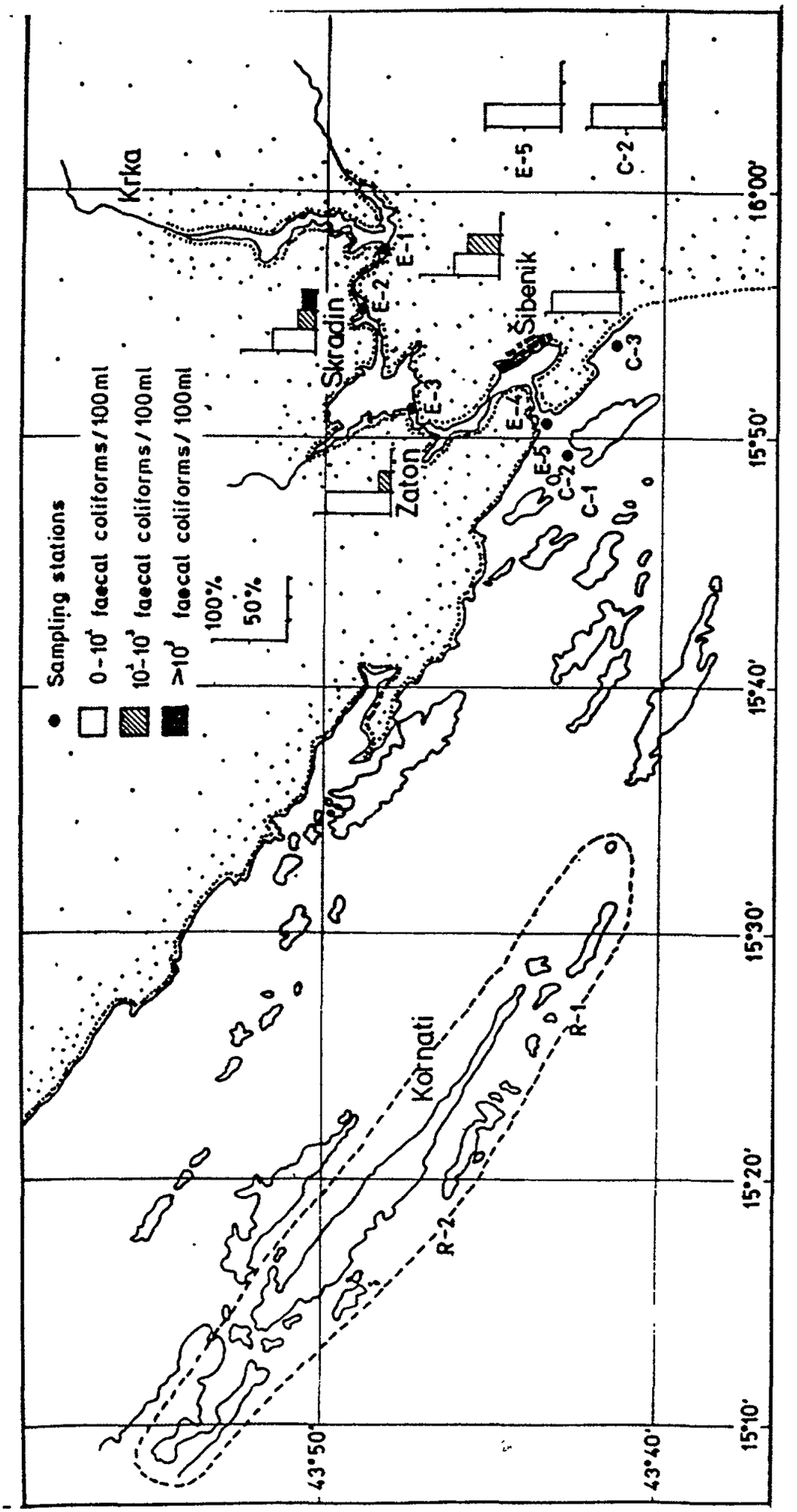


Fig. 3.4.5 Krka estuary and the Kornati archipelago area - distribution of faecal coliform concentrations

A noticeable influence of faecal pollution originating in nearby settlements was recorded at the estuary station E-2 where 16.6% of the samples exceeded the limit of 100/100 ml.

The rest of the beaches (stations E-3, E-5, C-2 and C-3) satisfied the norms for water quality.

The Split coastal area is under a rather strong effect of faecal pollution (Sobot, 1981; Krstulovic and Sobot, 1983; Krstulovic, 1986). This primarily refers to stations 1 (Vranjic Basin), 4 (Zvoncac) and 5 (the city harbour). However, a very strong effect from a heavily polluted harbour was felt over a wider coastal area (stations 6 and 7). It has to be stressed that in 1986 the sanitary quality of seawater on all city beaches deteriorated in relation to previous periods generally. This situation is primarily caused by the malfunctioning of the main underwater outfall.

In the Montenegrin coastal area, most sewage effluents (of urban and industrial origin), entering the sea in the vicinity of larger settlements and harbours, influenced the sanitary quality of coastal waters (Table 3.4.7 and Fig. 3.4.7 and Fig. 3.4.8).

All beaches, except at stations 1 and 10, satisfied the WHO/UNEP interim criteria. Due to the relatively low number of samples collected at all stations, the assessment of the Montenegrin coastal water quality is tentative.

In the Slovenian coastal area, the level of faecal contamination of shellfish did not show a very high sanitary quality (Table 3.4.8 and Table 3.4.9).

Generally, the faecal coliform concentrations in shellfish are higher than could be expected from the sanitary quality of the shellfish growing waters. Although the number of faecal coliforms recorded in samples taken at both stations did not exceed 100 FC/100 ml of water, the sanitary quality of the shellfish growing waters did not satisfy the WHO/UNEP interim criteria.

The seawater in the Lim Channel (stations 1 and 2) was adequate for shellfish growing (Hrs-Brenko, 1983). There were a few results obtained in this area during 1984 that exceeded the limits of interim criteria. Occasionally, the number of the registered faecal coliforms in shellfish collected at station 1 approached the limit, if shellfish is to be sold without previous purification treatment.

The sanitary quality of seawater in the Pula area (station 12) satisfied the criteria required for areas given over to shellfish culture, while at station 13 it deviates periodically from the requested norms. Furthermore, the mussels collected at station 13 did not on occasion satisfy the WHO/UNEP interim criteria. The first results from the Rijeka area (stations 4 and 14) show that the sanitary quality of mussels was satisfactory, but this was not the case for the seawater at station 4.

In the Split area concentrations of faecal coliforms in mussels were high at all monitored stations. It must be stressed that in the Split area there are no locations for shellfish growing and therefore mussels were collected at stations with varying levels of pollution. Because of the high level of faecal pollution in this area, high levels were also obtained for shellfish.

Table 3.4.6

Distribution of faecal coliforms in the Split area and evaluation according to WHO/UNEP interim criteria (1983).

	Samples (%) exceeding limits of FC/100ml											
STATION	n^a	10^2	10^3	n^a	10^2	10^3	n^a	10^2	10^3	n^a	10^2	10^3
	1983			1984			1985			1986		
1	9	100	80.9	11	100	90.9	11	100	72.7	11	100	100
2	9	0	0	11	0	0	11	0	0	11	54.6	36.3
3	9	0	0	11	0	0	11	36.4	0	11	77.9	45.4
4	9	76.6	11.1	11	72.7	0	11	72.7	0	11	90.9	72.7
5	9	100	100	11	100	1000	11	100	100	11	100	100
6	9	23.0	0	11	54.5	0	11	45.4	0	11	100	82.7
7	9	0	0	11	54.5	9.1	11	36.4	0	11	81.8	72.7
8	9	0	0	11	27.3	0	11	18.2	0	11	81.8	63.6
9	9	12.0	0	11	9.1	0	11	63.6	0	11	63.6	63.6
10	9	11.0	0	11	0	0	11	0	0	11	63.6	63.6

[a]Number of samples

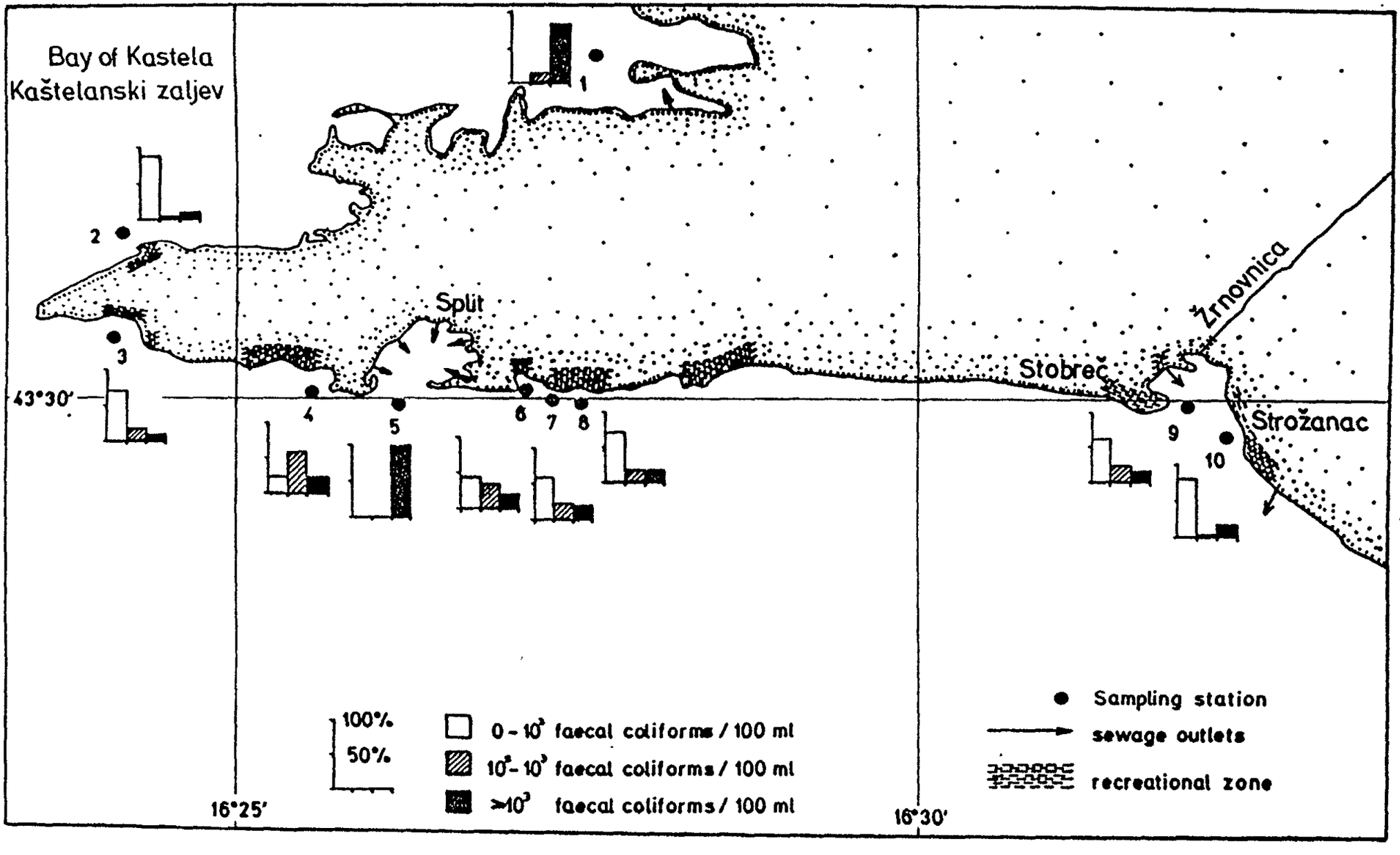


Fig. 3.4.6 Split Area - distribution of faecal coliform concentrations

Table 3.4.7

Distribution of faecal coliforms on the Montenegrin coast and evaluation according to WHO/UNEP interim criteria (1983).

STATION	Samples (%) exceeding limits of FC/100ml											
	n^a	10^2	10^3	n^a	10^2	10^3	n^a	10^2	10^3	n^a	10^2	10^3
	1983			1984			1985			1986		
1	-	-	-	-	-	-	4	50.0	0	9	22.2	0
2	-	-	-	-	-	-	6	0	0	9	11.1	0
3	-	-	-	-	-	-	4	25.0	0	9	11.1	0
4	-	-	-	-	-	-	6	33.3	0	9	33.3	0
5	-	-	-	-	-	-	4	25.0	0	9	0	0
6	-	-	-	-	-	-	6	0	0	9	0	0
7	-	-	-	-	-	-	4	25.0	0	9	33.3	11.1
8	-	-	-	-	-	-	6	16.6	0	9	0	0
9	-	-	-	-	-	-	6	16.6	0	9	0	0
10	-	-	-	-	-	-	4	25.0	0	9	88.8	11.1

[a]Number of samples

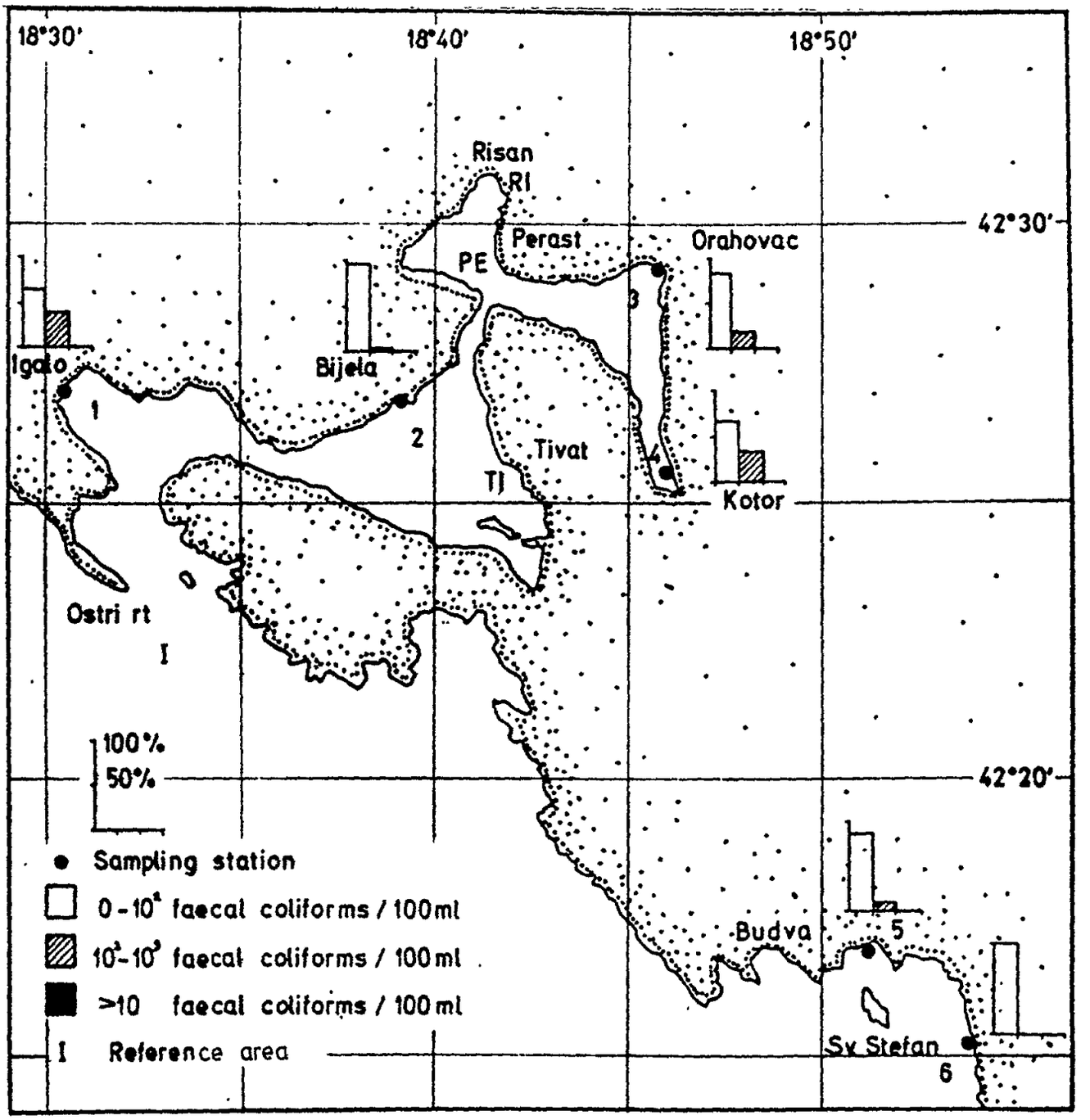


Fig. 3.4.7 Gulf Kotor area - distribution of faecal coliform concentrations

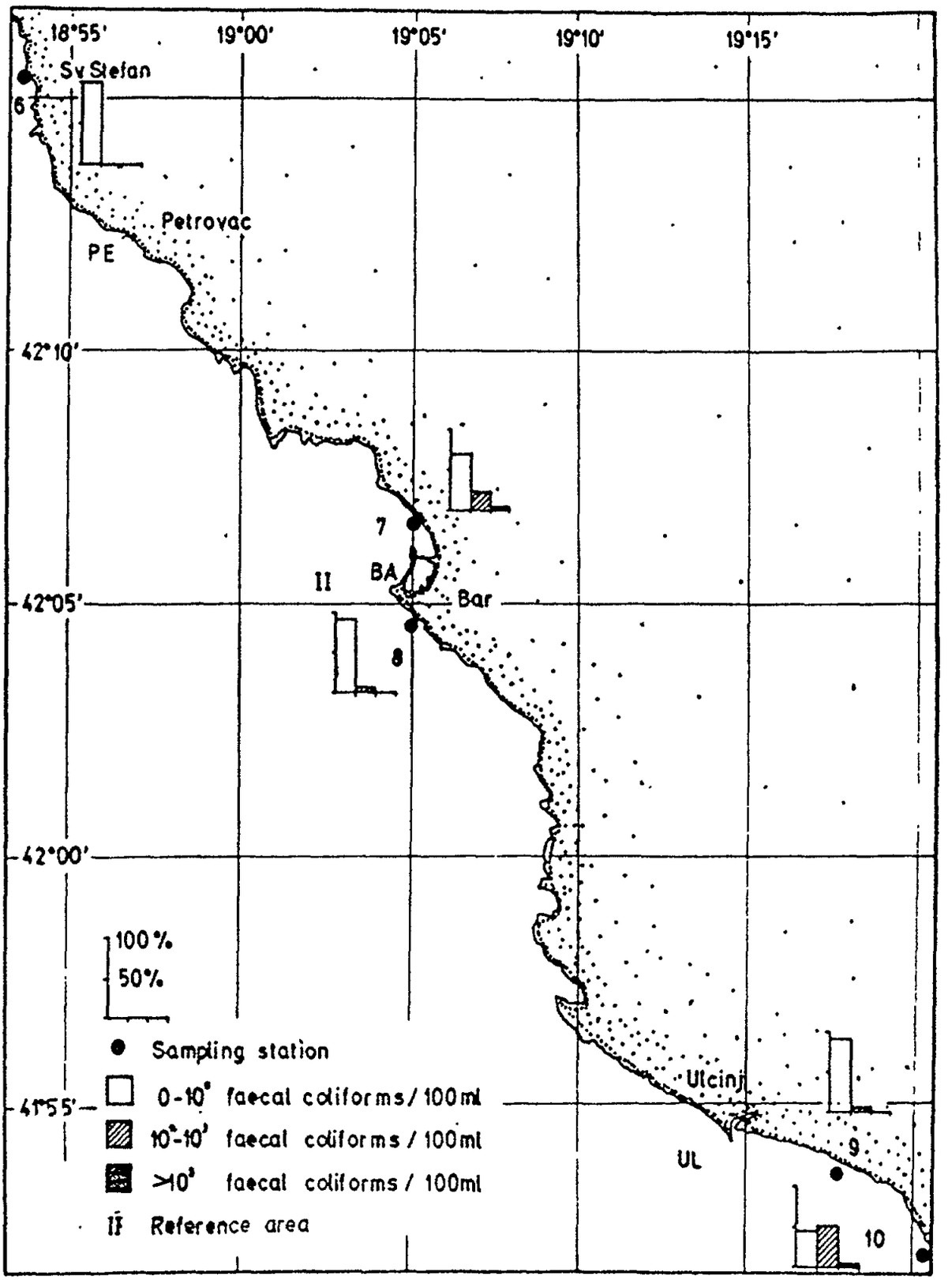


Fig. 3.4.8 Montenegrin coastal area - distribution of faecal coliform concentrations

Table 3.4.8

Review of microbial pollution in mussels.

AREA	Percentage (%) of samples containing: (n FC/g FW)											
	0-2	3-10	10	0-2	3-10	10	0-2	3-10	10	0-2	3-10	10
	1983			1984			1985			1986		
Slovenian coast												
Piran Bay	33.3	0	66.7	25.0	0	75.0	25.0	0	75.0	0	0	100
Strunjan Bay	33.3	0	66.7	50.0	0	50.0	50.0	0	50.0	25.0	0	75.0
Rovinj												
Station 1	-	-	-	78.6	21.4	0	80.0	20.0	0	100	0	0
Station 2	-	-	-	100	0	0	100	0	0	100	0	0
Pula												
Station 12	-	-	-	100	0	0	75.0	0	25.0	100	0	0
Station 13	-	-	-	42.9	14.3	41.8	50.0	50.0	0	75.0	25.0	0
Rijeka												
Station 4	-	-	-	-	-	-	-	-	-	100	0	0
Station 14	-	-	-	-	-	-	-	-	-	100	0	0
Split												
Stat. 1	-	-	-	0	0	100	0	0	100	0	0	100
Stat. 4	0	0	100	0	0	100	0	0	100	0	0	100
Stat. 9	53.3	23.4	23.3	0	0	100	0	0	100	0	0	100

Table 3.4.9

Review of microbial pollution of seawater at the mussel sampling stations.

AREA	Percentage (%) of samples containing: (FC/100ml)											
	0-10	11-100	100	0-10	11-100	100	0-10	11-100	100	0-10	11-100	100
	1983			1984			1985			1986		
Slovenian coast												
Piran Bay	66.7	33.3	0	100	0	0	75.0	25.0	0	100	0	0
Strunjan Bay	100	0	0	100	0	0	75.0	25.0	0	75.0	25.0	0
Rovinj												
Station 1	-	-	-	85.7	14.3	0	90.0	10.0	0	95.5	4.5	0
Station 2	-	-	-	92.9	7.1	0	100	0	0	95.5	4.5	0
Pula												
Station 12	-	-	-	90.9	9.1	0	100	0	0	100	0	0
Station 13	-	-	-	72.7	9.1	18.2	50.0	50.0	0	75.0	25.0	0
Rijeka												
Station 4	-	-	-	-	-	-	-	-	-	0	75.0	25.0
Station 14	-	-	-	-	-	-	-	-	-	100	0	0
Split												
Station 1	-	-	-	0	0	100	0	0	100	0	0	100
Station 4	0	0	100	0	0	100	0	25.0	75.0	0	0	100
Station 9	44.4	44.4	11.2	50.0	50.0	0	0	50.0	50.0	0	0	100

4. CONCLUSIONS

4.1. State of pollution

4.1.1. The trophic state of the investigated region

The Mediterranean is a typical oligotrophic sea with nutrient concentrations, particularly phosphorus, much lower than in the western Atlantic Ocean, with which water exchange occurs (e.g. McGill, 1963). This is also valid for most of the Adriatic Sea, including the Yugoslav coastal region. Thus any local increase even if small of the nutrient load may accelerate the natural rate of the assimilation-regeneration cycle in the receiving zone and significantly influence the oxygen budget of the water column.

The Lim Channel and the Krka Estuary regions possess unique natural and biological characteristics (e.g. Vatova and Milo di Villagrazia, 1950; Sekulic and Lovric, 1986), but are quite loaded with nutrients. Both regions are under the influence of various human activities within their watersheds. Tourism and mariculture require high water quality. But for mariculture, unlike tourism, extreme oligotrophic conditions characterized by clear, blue water are not favourable. Urban and industrial nutrient loads, as well as other pollutants, should be under strict control; a monitoring programme of the coastal waters and effluents in such areas should be given high priority. Anthropogenic loads must be eliminated or significantly reduced in recreational and mariculture areas. In addition, intensive fish growing may also load the ecosystem with nutrients, regenerated from excretion products and food remains. Combined cultures of fish and shellfish should help control the trophic equilibrium (e.g. Filic et al., 1987).

The monitoring of Sibenik and Split harbours as well as other closed areas in the vicinity of urban centres has shown a visible impact of sewage on the receiving waters (turbidity, discoloration, smell, solid wastes) and the urgent need for adequate wastewater disposal is evident.

Control of the eutrophication processes in the open northern Adriatic area is an urgent problem. Therefore monitoring activities should be intensified in the framework of the Yugoslav-Italian collaboration, but coordinated actions in the Yugoslav northern Adriatic coastal regions should also be undertaken in the framework of the National Programme.

4.1.2. Heavy metals

According to the data reported, the level of effluent pollution in the Slovenian area is the highest with respect to Zn (average values 940-15,500 ug l^{-1}) and in the Split area with respect to Cd (average values 2.75-8.51 ug l^{-1}) and Pb (average values 38.3-43.6 ug l^{-1}) in comparison with other areas (average values 12-302, 0.04-4.26 and 1-20 ug l^{-1}, for Zn, Cd and Pb respectively). The average Hg concentrations in effluents of the investigated areas range between 0.1 and 3.38 ug l^{-1}. However, since significant differences in heavy metal contents of effluents of the same origin were observed among various areas, as well as in effluents from the same area but in different years of investigation, the need for standardization and intercalibration of the sampling and analytical methods became apparent.

Concerning the heavy metal concentrations reported for estuarine and seawater samples, it can be concluded that the average dissolved Cd concentration in the Adriatic coastal waters (8.3-42.2 ng l^{-1}) is slightly higher than the reported concentration range of Cd for the open western Mediterranean (4-17 ng l^{-1}) and lower than that for oceans (10-70 ng l^{-1}). Moreower, the average concentration range of Hg in the Yugoslav Adriatic coastal waters (1.3-7.0 ng l^{-1}) fits well within the concentration range of Hg (1.3-7.2 ng l^{-1}), recently reported for the open Ligurian Sea. Thus, despite the fact that the coastal and estuarine Adriatic waters are under the impact of urban, industrial and recreational centres, their Cd and Hg contents indicate no significant pollution if compared with the above mentioned areas.

The average Hg concentrations in mussels (Mytilus galloprovincialis) were relatively uniform, with values generally between 20 and 40 ug kg^{-1} WW in all areas, except for Kastela Bay in the Split area, where extremely high values (730 ug kg^{-1} WW) were recorded. However, a systematic decrease of the average Hg concentration from 532 to 35.3 ug k^{-1} WW and of Cd concentration from 114 to 27.6 ug kg^{-1} WW was recorded for the period between 1983 and 1986. The average Cd concentrations in mussels were the highest in the Slovenian coastal area (164-266 ug kg^{-1} WW).

Extremely high Hg concentrations were found in certain sediment samples of the Rovinj harbour (100-4380 ug kg^{-1} DW) and Split area - Kastela Bay (120-4800 ug kg^{-1} DW); this would indicate that there is an unknown local pollution source in Rovinj; there is also contamination by a chlor-alkali plant in Split.

4.1.3. Organic pollutants

The inflow of chlorinated hydrocarbons in the coastal Yugoslav waters was monitored in 12 wastewater samples in the Rijeka area. In comparison with some older data from various areas in the world (100 and even more DDTtotal ug l^{-1}), the observed concentrations are very small (0.008 DDTtotal and 0.069 PCB ug l^{-1}). However, those older results are doubtful because the analytical methods used were in many cases not reliable. Our results show that in urban wastewaters there are significant concentrations of DDTs and PCBs, the latter being about ten times higher than the former.

The concentration levels of DDTs and PCBs in the sediment samples analyzed are lower than in the other Mediterranean areas. In some sediment samples a few very high concentrations, especially of DDTs (higher than 30 ug kg^{-1} DW), significantly increased the average value for the whole area monitored. It is quite probable that these high values are the consequence of an inadequate use of the analytical procedure applied.

Mussel contamination, analyzed for chlorinated hydrocarbons, is considered as the lowest in the whole Mediterranean Sea. Here again, there are some higher values for DDTs, but they do not greatly affect the average of the whole area, as was the case for sediment concentrations.

In some industrial wastewaters phenols in effluents were high (16.5 mg l^{-1}), as expected, but phenol concentrations in other urban wastewaters were in the range of slightly loaded wastewaters (averages between 10 and 20 ug l^{-1}). The observed, relatively high, concentrations of phenols in seawater (with maximum 42 ug l^{-1}) have to be considered with caution because the methodology used was probably not sufficiently selective.

The anionic detergent concentrations in wastewaters are in the expected ranges for moderately loaded urban wastewaters. From this it follows that concentrations of these pollutants in the Sibenik area estuary and the coastal waters are in the expected ranges. The relatively higher concentrations of these pollutants in the Montenegrin coastal waters (maximum 122 ug l^{-1}) could be attributed to the method used which was not specific enough to estimate anionic detergents in seawater.

Petroleum hydrocarbons in some industrial wastewaters had very high concentrations (more than 15 mg l^{-1}), while in mixed urban and even domestic waters these pollutants were present in somewhat smaller concentration ranges (about 1 mg l^{-1}). Some preliminary data show that the polyaromatic fractions of total hydrocarbons are variable and depend upon the source of pollution.

The observed levels of the polyaromatic fractions of petroleum hydrocarbons (mainly between 1 and 3 ug l^{-1}) classify the Yugoslav seawater as less polluted if compared with other Mediterranean waters, even though the levels varied significantly and referred to two areas only.

In the Sibenik area the sediment proved to be a much better matrix as against seawater in order to obtain a realistic pollution picture of polyaromatic fractions. Unfortunately, the observed concentration averages of the Yugoslav coastal area are not reliable enough, because in the analysis of some sediment samples from the Split area an inadequate analytical procedure was used.

Although only a limited number of data on polyaromatic hydrocarbon pollution in mussels from the Sibenik area was obtained, it seems that the methodology used is quite reliable for the assessment of the polyaromatic hydrocarbon load of the investigated marine ecosystem.

4.1.4. Faecal coliforms

The influence of faecal pollution in wastewater was registered in all monitored areas.

Although most of the sampling stations in the recreational areas of the Slovenian coastal zone gave bacteriological values that comply with the WHO/UNEP interim criteria, some of the stations in this area are under the influence of local sewage effluents (near the Rizana river).

Even though a decrease in the sanitary quality of some beaches in the Rovinj and Pula areas was recorded, it has to be stressed that the quality of seawater satisfied the proposed criteria, except for the southern part (Medulin), where there was inadequate wastewater discharge.

The sanitary quality of coastal seawaters near the city of Rijeka is low, while in the eastern part of the area and around the Krk Island seawater is so far unpolluted.

The estuarine beaches monitored in the Sibenik area satisfied the criteria, except at Skradin.

The coastal waters in the Split area are under quite a strong faecal pollution influence and some sites designated for bathing and recreation did not fully meet the criteria for those purposes (near the main harbour).

The effects of the wastewater discharged into the Montenegrin coastal area are evident in the lower sanitary quality of a few beaches near larger settlements (Bar), but the rest of the beaches meets the proposed criteria.

The sanitary quality of the shellfish collected off natural sites in the Slovenian coastal area and at Split is not satisfactory, while in the Pula area the standard is met only occasionally. It has to be pointed out that the shellfish sanitary quality did not satisfy requirements for controlled commercial growing sites and therefore a continuous sanitary control is required.

4.2. Trends

Trends of eutrophication processes become evident only on a longer time scale. In fact, the parameters which characterize these processes (e.g. nutrient and dissolved oxygen concentrations, phytoplankton biomass and activity) are naturally subject to large fluctuations, both on a seasonal and on annual basis.

In the Northern Adriatic an increasing frequency of nonseasonal phytoplankton blooms, followed by significant oxygen consumption in the bottom layer, is suspected. However, a more sophisticated elaboration of the existing data-time series is needed.

Nevertheless, a clear trend of nutrient concentration increase in the freshwater discharged into the Lim Channel was shown by comparing long term data series (1968-1986).

Cell count data indicated an increased phytoplankton biomass in Sibenik Bay, significantly loaded with orthophosphate. Moreover, changes in the phytoplankton community have also been observed in the past ten years, characterized by a shift of the relative abundance from diatoms to dinoflagellates. Unfortunately, data series for other relevant chemical and biological parameters were much shorter (since 1983) and cannot support these findings with sufficient reliability. In most of the investigated areas the data series are too short to allow conclusions about eutrophication trends.

Owing to a relatively low number of sampling stations and sampling frequencies, some differences in sampling and analytical techniques used for different areas (resulting in relatively large variations in the obtained data values), as well as to a relatively short period of investigation, no significant pollution trends could be recognized on the basis of the data reported on heavy metal concentrations in effluents, estuarine and sea water, suspended particles, biological material and sediment samples. The exception is Kastela Bay in the Split area where a significant decrease of the mercury and cadmium content in mussels was recorded in the last three years of the monitoring period.

A comparison of the concentration levels of organic pollutants in effluents, seawater, sediment and mussel samples measured in the framework of the programme during each of the three, and for some parameters, four years was not sufficient to evaluate any statistically significant trend. Average concentrations varied greatly due to large fluctuations of the parameter values, while the sampling frequency was too low and the reliability of the various procedures used for particular analyses not always high. However, when the DDT, and especially PCB, concentration levels in mussels recorded during the Yugoslav Monitoring Programme were compared with data levels obtained earlier (prior to 1980) a decreasing concentration trend became evident.

Generally, it can be stated that the sanitary quality of the coastal seawater in the controlled areas did not change during the monitoring period except in the Split area, where a significant lowering of the sanitary quality was noted.

4.3. Evaluation of the Monitoring Programme

Along the approximately 1200 km long Yugoslav coast, very rich in embayments and islands, a large range of environmental problems exists. In some regions (e.g. Kastela Bay, harbour areas of the major urban centres) pollution manifestations are clearly visible and restoration measures are urgently needed. Some other regions should be effectively preserved because of their unique natural characteristics. Areas, in which various and often contrasting human activities are developing, should be managed optimally in order to minimize pollution and thus the negative consequences of these same activities.

Therefore, the need for a comprehensive, coordinated and systematic long-term pollution monitoring programme of the Yugoslav coastal region was recognized a few decades ago. Finally, the Yugoslav National Monitoring Programme started in 1983 under the auspices of the UNEP Mediterranean Action Plan, after a preparation period (organization, training and education, equipment) which lasted several years.

Such an activity is essential primarily in order to provide data for a priority programme of preservation and restoration measures and a list of areas which need more urgent intervention. Another significant advantage of the Programme was to engage and coordinate almost all the scientific and technical potential in the country (oceanographic, environmental and chemistry institutes, universities, public health institutes), qualified to solve complex environmental problems at national and international level as well.

Naturally, even when the Programme had already been in operation for several years, some of the activities were still insufficient or inadequate, partly because of short-term limited technical and financial means. This will be briefly discussed in the following paragraphs.

To understand fully the mechanisms and evaluate the eutrophication and pollution trends with sufficient accuracy, a region must be monitored comprehensively. Effluent data (concentrations and discharge rates) may provide information about the changes in pollutant loads, while the coastal water investigations should identify eventual consequences of these changes, which may be different in various marine systems. The effluents on the Yugoslav Adriatic coast are mostly diffuse (numerous wastewater outfalls, groundwater springs) and cannot all be included in the monitoring programme. Thus, load calculations based on empirical coefficients, tested by direct measurements, represent an essential and complementary activity in the framework of a monitoring programme. In addition, several processes involving nutrients and pollutants occur in the sewage and at the wastewater-seawater interface, leading to a significant loss from the water phase through various physico-chemical and biological processes. A knowledge of these processes is needed in order to calculate the actual quantities of pollutants that reach the marine ecosystem. Great efforts should be made to monitor industrial wastewater discharges, since the concentration variability, depending on the technological process, is very high.

Unfortunately, such a complex approach was not applied fully in all the investigated areas and in most of them the sampling frequency, limited to seasonal measurements, was not adequate, particularly as concerns effluents (both wastewater and natural freshwater).

Along the Yugoslav Adriatic coast pollution is a diffused environmental problem, since in almost all urban centres wastewater is not adequately discharged into the sea. Unfortunately, some highly urbanized areas (e.g. near the cities of Zadar, Dubrovnik and Kotor as well as the Mirna, Cetina and Neretva River estuaries) were not included in the monitoring programme.

Furthermore, the analytical techniques used were not completely standardized and intercalibrated. Nor were sampling and sample storage techniques fully standardized. Various sampling techniques were used and in some regions the parameters were determined immediately after collection, while in other areas samples were stored frozen and analyzed in the laboratories ashore.

There are very large discrepancies in the number of data regarding parameters for organic pollutants in various matrices and different areas of the country. For example, there are only 5 data on petroleum hydrocarbon concentrations in mussels and 365 on detergents in wastewaters. Moreover, wastewaters were monitored at 14 outlets in the Rijeka area, not at all in the Rovinj, Dubrovnik and Montenegrin areas, while in the Sibenik area only one outlet was monitored. Six small rivers were monitored but the most important rivers from the pollution source point of view were not. This limits the comparison of the various investigated areas and makes impossible a global evaluation of organic pollution in the Yugoslav coastal region.

In conclusion, the results obtained to date are not yet sufficient to get accurate quantitative information on nutrient and pollutant loads, particularly as concerns contributions through the atmosphere, as well as the eutrophication degree and levels of most pollutants in the Yugoslav Adriatic coastal area. However, the results have been used for qualitative considerations which were highly indicative and useful for planning future research programmes and monitoring activities.

5. RECOMMENDATIONS

1. Standardization and intercalibration activities are of primary interest and must be continued as intensively as possible. They must include sampling and sample storage techniques and analytical procedures for all parameters and matrices.

2. To ensure a more effective realization of the intercalibration exercises needed and to improve data quality control, specialized expert groups with major analytical experience on each parameter set should be formed. These groups should periodically, at least every three years, carry out detailed measurements in all investigated areas. Thus, the data already existing and those that will be collected in the future could be evaluated better and additional results would be achieved.

3. A pollutant and pollution source inventory for the entire Yugoslav coast should be compiled as soon as possible.

4. Future monitoring of the input of some volatile pollutants from the atmosphere to the sea is highly recommended.

5. More effort should be focused on the harmonization of monitoring programmes to obtain optimal results. Each parameter included in the National Programme should be monitored in all investigated areas simultaneously in effluents and coastal waters. Station distribution and measurement frequency should be adjusted according to the pollutant loads expected in each area. Efforts should be made to integrate the monitoring activities with data on pollutant dispersion processes in order to get a better estimate of the effects of pollutants on the coastal marine ecosystem.

6. Effluent monitoring should be widened by measuring flow rates and daily variations of parameter values.

7. The effects of external nutrients on the biological cycle of the investigated areas should also be monitored by including in the parameter set at least those that characterize phytoplankton biomass and activity (Chlorophyll *a* and primary production).

8. In order to assess more fully microbial pollution, faecal streptococcus monitoring should be introduced. This parameter has also been included in the WHO/UNEP criteria as a suitable indicator.

9. The monitoring programme should be revised as concerns those parameters, that were often below the detection limit of the analytical method used.

10. It would be very useful to make a priority list of areas and parameter groups so that an optimal design of future monitoring activities, based on actual possibilities, could be drawn.

11. Various efforts (e.g. Yugoslav-Italian cooperation, UNEP programmes, the Yugoslav and Italian National programmes) should be integrated and used to strengthen eutrophication and pollution monitoring programmes in the northern Adriatic, including the western coastal region of Istra and the Gulf of Trieste.

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A N N E X I

INSTITUTIONS PARTICIPATING IN MED POL AND THEIR MAIN RESEARCH ACTIVITIES

The Marine Biological Station at Piran (MBS-P) was founded in 1969 as a department of the Institute of Biology of the University of Ljubljana in order to study the marine ecosystem of the northern Adriatic and to monitor pollution. The main activities of the Centre have lately been focused on research of pollution sources and their effects on the chemical and biological characteristics of coastal ecosystems. Systematic faecal pollution monitoring and heavy metal measurements in sediments, biological material and suspended particles were also included in the station's programmes. At the present time research carried out at the Centre is focused on:

- research of suspended organic matter of various origins;
- phytoplankton blooms;
- jellyfish aggregations;
- ecological and physiological marine organism monitoring;
- ecology and biocoenoses of coastal sediment (macro- and meiobenthos).

For EEC purposes MBS-P is included in the project Bottom Layer Oxygen Depletion in the Gulf of Trieste - Natural Phenomenon or Pollution Induced Modification. Since 1973 the Centre has participated in numerous national and international pollution monitoring and research programmes.

The Centre for Marine Research Rovinj (CMR-R) was founded in 1891 and has since 1969 been affiliated with the "Ruđjer Boskovic" Institute in Zagreb. CMR-R is involved in basic research in marine biology and oceanography in the Adriatic Sea as well as pollution monitoring and mariculture development. In particular the following activities are carried out at the present time:

- research on the processes within and between trophic levels (primary and secondary organic production, the cycle of biogenic elements);

- studies of water mass dynamics;

- flora, fauna and biocoenoses (taxonomy, ecology and biocoenoses in clean and polluted environments);

- ecological, physiological and genetic research on marine organisms (basic physiological and biochemical characteristics of marine organisms and effects of pollution);

- pollution and sanitary water quality monitoring;

- eutrophication studies;

- research related to shellfish and fish mariculture.

Marine eutrophication studies, pollution of selected marine organisms and sediments with heavy metals, chlorinated insecticides and polychlorinated biphenyls and sanitary control of organisms and seawater have been included in long-term investigation programmes since 1972. Such investigations, financially supported by the Self-management Community of Interest for Scientific Research of SR Croatia, other national sources and international organizations (e.g. UNEP, WHO, NSF, EPA, Smithsonian Institution), have been conducted over the entire Adriatic. However, the CMR-R research efforts are mainly focused on the more polluted and eutrophied northern Adriatic coastal and open waters. CMR-R is equipped with the research vessel "Vila Velebita".

The Institutes of Public Health in Pula, Rijeka and Split (IPH-P, IPH-R, IPH-S), founded in 1939, 1926 and 1933 respectively, are organizations whose main activities are connected with research and development of public health. Some of them collaborate with University Schools of medicine and the World Health Organization. The Institutes have participated in various basic and applied research programmes concerning public health and environmental protection. For example, they have participated in the"Jadran-III" programme for the acquisition of data on environmental pollution (seawater and fresh water sanitary conditions) so that adequate restoration measures can be taken. The Institutes have also carried out ecological investigations in the framework of programmes launched by other organizations.

The Faculty of Civil Engineering Sciences of the University of Zagreb (FCES-Z) founded in 1919; together with the Faculties of Civil Engineering Sciences in Split, Rijeka and Osijek they constitute the Civil Engineering Institute, Zagreb. The basic activity of the Faculty is scientific and applied research and teaching at graduate and postgraduate levels in the area of civil engineering. The Department for Hydrotechnics of the Faculty performs activities covering hydraulic engineering, including laboratory and field research on water quality, tests on procedures for water purification on physical models on a semi-technical and technical scale and it also solves problems of wastewater disposal into the sea. It is for these reasons that the Faculty was included in the present programme and carried out investigations of wastewater quality in the Rijeka area.

The Centre for Marine Research Zagreb (CMR-Z), founded in 1969, is an interdisciplinary centre of the "Rudjer Boskovic" Institute with laboratories in Zagreb and Sibenik. The activities of the Centre are focused on basic and applied research on the physical, chemical and biological processes in natural and polluted waters with the following programme:

- research on the natural characteristics and impact on natural waters, research on physical, chemical and biological parameters and pollution monitoring at selected oceanographic stations in the Adriatic, particularly in the northern Adriatic and Sibenik areas;

- research on the biogeochemical cycle of microconstituents and radionuclides in natural and polluted waters, characterization of the physico-chemical state and processes in water, sediment and interface;

- research on power plants and other pollution sources, effects on the quality of surface and underground waters and ecosystem dynamics;

- research on organism reaction to genotoxic compounds in the water and evaluation of harmful effects on water systems and use of water;

- investigation of biodegradation processes of organic matter;

- ecologic modelling and computerized processing of experimental data;

- research and development of aquaculture, intensive growing of fish and shellfish in freshwater, estuaries and sea water;

- development, application and automation of specialized instruments.

CMR-Z collaborates with other national and international organizations. A close collaboration is maintained with universities and institutes in Italy, Czechoslovakia, Austria, France, Switzerland, West Germany, the USA, Great Britain and Japan, and with United Nations agencies (FAO, IAEA, IOC, UNDP, UNEP, UNESCO, WHO).

For over a decade CMR-Z has been organizing postgraduate studies in oceanology under the supervision of the University of Zagreb. CMR-Z scientists also teach at other undergraduate and postgraduate departments of the University. CMR-Z organizes specialized courses and international meetings on research, exploitation and protection of the sea.

The main activities of the Institute for Oceanography and Fisheries in Split (IOF-S), founded in 1930, consist of basic and applied oceanographic research including:

- hydrography (morphological, geological, chemical and physical properties of the sea);

- flora and fauna (taxonomy, ecology, pollution influence on communities);

- quantitative production evaluation for fisheries application;

- fisheries and mariculture research;

- pollution problems and coastal sea protection (particularly in the central and southern Adriatic).

Since 1976 IOF-S has been carrying out the project "Monitoring of Coastal Water Quality (Vir-Konavle)" as a basis for all other specific investigations to solve pollution problems in smaller areas. IOF-S is the owner of the research vessel "Bios".

Each year for the past three years, IOF-S has organized a special fisheries course for developing countries. Most of its scientists participate in common Mediterranean projects (FAO, IOC, UNEP, WHO).

Biological Institute in Dubrovnik (BI-D), founded in 1948; its main activities concern biological oceanography, terrestrial botany and ornithology. Its primary research activities are focused on zooplankton, ecology and biomass systematics. These studies include research on the effects of some pollutants on zooplankton populations and on some zooplankton species. The research vessel "Baldo Kosic II" is at its disposal for field studies.

The Institute of Marine Biology in Kotor (IMB-K) was founded in 1961 with the main objective to study the marine food web of the southern Adriatic. IMB-K consists of hydrographic, planktologic, benthic, ichthyologic and microbiological laboratories. Its activities were widened through the Laboratory for Molecular Biology and Neurophysiology. IMB-K is affiliated with the "Veljko Vlahovic" University of Titograd.

The Institute for Subtropical Cultures and Environment Protection at Bar (ISCEP-B), founded in 1937, is the oldest scientific institution of Montenegro. Its activities concern inter alia studies of chemical processes in natural waters, soil and foodstuff, in particular:

- determination and study of decay processes of pesticides, polychlorinated biphenyls, heavy metals in natural and polluted waters, organisms and sediment;

- studies of pollution processes by phenols, oil and oil products, and detergents in natural waters.

The ISCEP-B is affiliated with the Agricultural Institute of the "Veljko Vlahovic" Institute in Titograd.

A N N E X II

SAMPLING AND ANALYTICAL METHODS

1. Basic parameters, nitrogen and phosphorus

1.1. Basic parameters, nitrogen and phosphorus in effluents

Effluent analyses were performed on composite samples taken automatically or by hand every 15 minutes for two hours, mostly by standard analytical methods, as recommended by the American Public Health Association (Anon., 1971) or for the Pula samples by the Association of Official Analytical Chemists (Anon., 1980).

Appropriately diluted samples for BOD_5 determination were incubated at 20°C for 5 days and the oxygen changes were measured with a Winkler titration technique, COD was determined by refluxing the samples with a mixture of dichromate, sulfuric acid and mercuric sulfate for 2 hours and by back titration of dichromate with a standard solution of ferrous ammonium sulfate. The results are expressed in an equivalent oxygen consumption.

Total suspended solids were determined by weighing, after filtration the samples through Millipore HA membrane filters (0.45 um pore size) and drying at 105°C.

Total nitrogen was analyzed in the Rijeka and Split samples by a Kjeldahl-type treatment of samples by analyzing and determining the released ammonia by a phenol-hypochlorite spectrophotometric method (Scheiner, 1976), and the released orthophosphate by a molybdenum blue spectrophotometric method with ascorbic acid as a reducing reagent (Murphy and Riley, 1962). The samples from Slovenia were oxidized with persulfate and the released nitrate and orthophosphate were measured spectrophotometrically (Jorge and Valderrama, 1981). The analyses of the Pula region samples were performed as recommended by Strickland and Parsons (1972).

Measurements of pH were performed with pH-meters and glass electrodes.

1.2. Basic parameters, nitrogen and phosphorus in sea water

Basic hydrometeorological observations were performed with standard WMO techniques (Anon., 1959, 1962). Sea temperature was measured with Richter and Wiese reversing thermometers, attached to PVC Niskin bottles used to collect water samples for chemical analyses, or with an Interocean STD probe (Split region).

Oxygen analysis, pH and total alkalinity measurements were carried out immediately after sample collection. For nutrient analysis water samples from the open northern Adriatic, most of them from the Lim Channel, were also analyzed aboard the ship immediately after collection. The samples from the other regions were stored frozen at -20°C until analysis could be carried out in the laboratories ashore.

Salinity was measured in the laboratory on shore with a high precision Beckman RS-7 bench salinometer, or in situ with an Interocean STD probe (Split region). Dissolved oxygen concentration was measured using Winkler titration procedures, while pH and total alkalinity were measured with potentiometric methods (Strickland and Parsons, 1972) using high precision pH meters and glass electrodes.

Nutrient concentrations were determined with spectrophotometric methods commonly used in oceanography (Strickland and Parsons, 1972). Reactive phosphorus was analyzed with a molybdenum blue technique with ascorbic acid as reducing reagent (Murphy and Riley, 1962). The ammonia of Krka estuary and Split region samples was analyzed with a phenol hypochlorite method with natrium nitroprusside as a catalyst and citrate as a complexing reagent (Solorzano, 1969 and Head, 1971 respectively). Northern Adriatic and Lim Channel samples were analyzed using a modification of this method (Ivancic and Degobbis, 1984). Nitrite was measured as a pink azo dye obtained after reaction with sulfanilamide and N-naftil-ethylenediamine (Benaschneider and Robinson, 1952). Nitrate was reduced to nitrite in a column filled with copperized cadmium filings (Wood et al., 1967).

Total phosphorus and nitrogen were analyzed after UV irradiation of the samples and determination of released orthophosphate and nitrate (Armstrong and Tibbits, 1968). Total phosphorus in the samples from the Krka estuary and the Sibenik region was determined after persulfate oxidation (Menzel and Corwin, 1965).

Spectrophotometers with 10 cm cells were used. A Technicon autoanalyzer was used for the Split region samples.

2. Heavy metals

2.1. Heavy metals in wastewaters, estuarine waters and seawater

Several techniques have been used for the determination of heavy metals in wastewaters. MBS-P determined heavy metals in effluents by atomic absorption spectrophotometry (AAS). The samples were acidified (HCl suprapure) to about pH 2.5, stored in a deep-freezer, filtrated (1.0 um GF/C Whatman glass filters) and the heavy metal content was determined in both solution and suspension. CMR-R determined Hg in effluents by using cold vapour atomic absorption spectrophotomery (CVAAS) after digestion of the samples with a mixture of KNO_3 and $KMnO_4$ (Horvat et al., 1986), while Cd was determined by AAS in samples digested with HNO_3. IPH-P determined Cd and Hg in wastewaters by AAS and CVAAS, respectively, after sample digestion with a mixture of HNO_3 and H_2SO_4. FCES-Z determined Hg using the same CVAAS technique (in collaboration with IPH-R), but Zn, Cd and Pb were determined through differential pulse anodic stripping voltammetry (DPASV) on a hanging mercury drop electrode (HMDE) in samples digested with HNO_3 in the presence of H_2O_2. IPH-S determined Hg with CVAAS (Deutsche Einheitsverfahren, 1980) while Cd, Zn, Cr and Pb were determined by AAS.

CMR-Z and BI-D in the Sibenik and Dubrovnik areas respectively determined Zn, Cd, Pb, Cu and complexing capacity in seawater samples by using DPASV, while Hg (upon preconcentration on a gold wire) through flameless AAS, using Perkin-Elmer model 410 equipment (Martincic, D., 1981; Martincic et al., 1980; Plavsic et al., 1982; Martincic et al., 1985a,b; Branica et al., 1985). The samples were collected by a diver into 1000 ml Nansen bottles (CMR-Z) or into 500 ml Nalgene bottles fixed on a fiberglass handle (BI-D). Special care was taken to avoid contamination of samples. Immediately after collection, samples for Hg analysis were acidified with redistilled supra-pure HNO_3 to pH 2, while those for the determination of "ionic" Zn, Cd, Pb and Cu were analyzed at natural pH and subsequently acidified to pH 2 (for Zn pH 4.7) to determine their "total" heavy metal content.

Heavy metal content (Pb, Cd, Cu and Zn) in water samples from the Montenegrin coastal area was determined through AAS (PAY UNICAM SP 9) in air-acetylene flame, preceded by extraction with methylisobutylketone (MIBK) from the APDC complex at optimal pH, while Hg was determined through the CVAAS method after extraction with dithyzone from previously destroyed samples (Cunningham et al.,1974).

2.2. Heavy metals in suspended particles

MBS-P sampled sea water into Niskin bottles for the Cd and Hg determination in suspended particles (Forstner and Wittman, 1983). Suspended particles were separated by filtration on 0.45 um pore size Millipore filters washed in 1% hot HNO_3. The filter content was destroyed with a wet procedure in PTFE vessels according to UNEP/FAO/IAEA, 1983. Metal concentrations were determined through atomic absorption UNEP/FAO/IAEA, 1983, spectrophotometry on a Varian CRA and CVT system.

2.3. Heavy metals in biological material

In the Slovenian coastal area the sampling, storage and preparation of organisms for analyses were carried out according to UNEP/FAO/IAEA, 1983 procedures. Two fish muscle tissue parts of a single specimen were analyzed. Hg and Cd contents were analyzed in two samples separated from the composite sample consisting of the homogenized edible part of 10 mussels. The determination of the metal concentration was carried out through the AAS method on a Varian CRA and CVT system.

In the Rovinj coastal area, mussel samples for Hg determination were deep-frozen immediately after sampling and stored until analysis. First, the biometry data were determined and afterwards a sample of 6 mussels was prepared from the soft tissue out of which two subsamples were used for metal analysis. Hg and Cd contents in mussels and zooplankton were determined through the NAA method, as described in the sediment methodology.

In the Budava and Rasa bays, mussel samples were collected from commercial growing areas. Cd, Pb and Cu concentrations were determined through the flame AAS technique. An aliquot separated from the composite sample, consisting of the homogenized edible part of 30 mussels, was previously destroyed at 480° C. The Hg concentration was determined through the AAS flameless technique (cold vapour technique) in mussel samples in which the organic matter was previously destroyed (Price,1979).

In the Sibenik area, at the biological stations, 25 mussels (3-4 cm in length) were sampled in polyethylene bags. In the laboratory, immediately after sampling, the edible part was separated from the shells with a titanium knife in a clean bench atmosphere. The edible part was weighed and homogenized in a mixer. A 0.5 to 10 g homogenate was digested for ca. 15 minutes at 120°C in closed Erlen-Meyer quartz bottles to which 2-4 ml concentrated HNO_3 and 0.5 ml concentrated $HClO_4$ were added. Hg and other metals in the biological material were analyzed as described for sediment analysis.

In the Split area close to the coast, mussels were sampled manually, stored in polyethylene bags and deep-frozen (-15°C) until analysis. At JSI-LJ, the samples were treated following the UNEP procedures (UNEP/FAO/IAEA,1983). The metals were analyzed as described for sediments in the Split area.

Mussel and plankton samples were collected in the Malostow Bay, the Peljesac Channel and the Dubrovnik area. Oysters, Ostrea edulis, were sampled only in the Malostow Bay. The samples collected were stored in polyethylene bags and deep-frozen. The tissue was separated from the shell and homogenized. An aliquot from the homogenized sample, consisting of at least 25 mussels, was digested with a mixture of concentrated redistilled suprapure HNO_3 (4 ml) and $HClO_4$ (0.5 ml). Plankton samples were collected with a plankton net (200 ug pore size) dragged horizontally in the surface layer (0-5m) at 2 Nm speed for 15-30 min. The samples were stored in 500 ml polyethylene bottles at 6±2°C and deep-frozen in the laboratory until analysis. Before analysis, the samples were dried until constant weight was achieved. A 200 mg sample was digested with concentrated HNO_3 and $HClO_4$. In mussels, oysters and plankton the Cd, Pb and Cu concentrations were analyzed by an electrothermal AAS method, using a Perking-Elmer AAS model 3030, HGA-40 and AS-1. Zn was analyzed by FAAS using a Perking-Elmer AAS model 5000 and AS-50, while Hg, concentrated on a gold wire, was analyzed through the flameless AAS technique using a Perkin-Elmer AAS model 410.

Heavy metals in the biological material from the Montenegrin coastal area were determined through an AAS (PAY UNICAM SP 9) method upon digestion of the homogenized samples in quartz with a mixture of HNO_3 and $HClO_4$ (5 ml:0.2 ml).

2.4. Heavy metals in sediments

In the Slovenian coastal area, sediment samples were collected with a corer with an acrylic glass tube. The composite sediment sample consisted of 4-5 samples taken from the surface layer of only 3-4 cm. Before destruction, the samples were dried, deep-frozen and homogenized in a porcelain bowl. A part of the homogenate was destroyed with a mixture of HNO_3 and $HClO_4$ (6:1). Hg and Cd were determined in two subsamples separated from the composite sample through an AAS method using a Varian CRA and CVT system.

Sediment samples from the Rovinj coastal area were prepared for metal analysis with a wet sieving procedure through a nylon net (250 um pore size). Hg and Cd contents were determined with a NAA method after sample and standard treatment (in a Triga Marck II reactor) in a flux of 2×10^{12} n cm^{-2} s^{-1} over 15-20 hours. After wet digestion and carbonate extraction ^{115}Cd was separated (Ravnik et al.1978), while ^{197}Hg was separated in the gaseous phase and afterwards selectively tied to Se (Kosta and Byrne, 1974).

In the sediments from the Budava and Rasa Bays Cd, Hg, Pb and Cu concentrations were determined through the AAS method after wet digestion with a $HNO_3/H2SO_4$ mixture.

In the Sibenik area, sediment samples were taken by divers using an acrylic glass tube (diameter 6 cm, length 15 cm) which was closed at both sides; it was kept in the same position and brought to the laboratory. Under clean bench conditions the <75 um granule fractions were separated by wet sieving. Sediment samples were dried until constant weight in a clean bench atmosphere at room temperature. The dry sample, 0.2 to 0.5 g in weight, was destroyed with a mixture of concentrated acids (0.5 ml $HClO_4$, 5-10 ml HNO_3, 5-10 ml HF) in closed teflon containers at 160°C. The sampler and polypropylene containers for storing <75 um fractions were conditioned for at least 10 days in a plankton bag (200 um) in sea water at a 30 m depth. For Hg analysis, sediment samples weighing 1-2 g were destroyed in quartz still with cut stoppers. The stoppers were tightened to avoid loss of Hg during digestion in a mixture of 9 ml concentrated HNO_3 and 1 ml concentrated $HClO_4$ at 200°C for 1.5 hours. The acid was redistilled before use.

The mineralized sediment samples were analyzed for Cd, Pb and Cu contents through an electrothermal AAS method (Perkin-Elmer, model 3030, HGA 400 and AS-1), while Zn was determined through the FAAS technique (air-acetylene, Perkin-Elmer, model 4000). Due to the matrix effect, for Cd and Pb analysis through AAS, the L'vov procedure was adopted (Martincic et al., 1985b; Martincic et al., 1985a).

In the Split and Vis areas (station 11) surface layer (0-5 cm) sediment samples were collected from the RV "Bios" using a gravitation probe with a corer. The samples were stored in polyethylene bags and deep-frozen (-15°C) until analysis. The sediment was prepared for analysis at JSI-LJ according to the recommended procedures (UNEP/FAO/IAEA,1983). Total Hg and Cd contents were determined through a destructive neutron activation analysis at JSI-LJ. For Hg analysis aliquots (0.5 g) of homogenized sediment samples were put into quartz ampulae (for Cd polyethylene ampulae) and, maintaining the appropriate standards, treated in a Triga Marck II reactor for 15-20 hours and separated with the volatilization technique (Kosta and Byrne,1974; Kosta and Byrne,1969) with diethylditicarbamate.

Sediment samples from the Maloston Bay, the Peljesac channel and the Dubrovnik area were collected and metal concentrations determined as described above for the Sibenik area. Samples were prepared with the wet sieving procedure using nylon sieves of <75 um and <1000 um pore size.

Heavy metals in sediments from the Montenegrin coastal area were sampled with a grab sampler and determined with the AAS (PAY UNICAM SP 9) method after digestion, along the same lines as for the biological material analysis.

3. Organic pollutants

3.1. Halogenated hydrocarbons

Chlorinated insecticides and polychlorinated biphenyls were determined with the ECD gas chromatography.

CMR-R extracted organic materials from sediment samples through Soxhlet extraction with n-hexane. Biological samples were extracted through a blender extraction with n-hexane/acetone mixture.

Silica gel separation was used for the separation of chlorinated insecticides from PCBs in sediment extracts (FAO, 1983). In the biological material, separation of insecticides and PCBs was performed after saponification with KOH.

IPH-P analyzed chlorinated halogenated hydrocarbons in biota and sediment samples after Soxhlet extraction with n-hexane (Fossato, 1981). Sulphur was separated on a Cu column (Blumer, 1957). Chlorinated insecticides were separated on a silica gel column (Snyder and Reinert, 1971).

For the determination of chlorinated hydrocarbons in wastewaters CMR-Z filtrated about 2.5 l of samples through a glass fiber, Whatman GF/C filter paper, by using a modified commercial apparatus for ultrafiltration (Picer N. et al., 1986). The filtrate was twice extracted with 60+40 n-hexane (fluoresc.grade), the solid phase was freeze dried and extracted with n-hexane in a Soxhlet apparatus for 8 hours.

CMR-Z extracted chlorinated hydrocarbons from sediment samples by Soxhlet extraction with n-hexane/acetone mixture and from biota samples by blender extraction with petroleum ether b.p. 40 to 60°C. Wastewater, biota and sediment sample extracts were cleaned with an alumina and silica gel column (Picer M. et al., 1978b; Picer M. and Ahel, 1978). To purify sediment and wastewater extracts from sulfur an additional cleaning step was used with KCN solution in acetone. The methods described were intercalibrated several times with other Mediterranean laboratories and laboratories from around the world (Picer M. et al., 1976, Picer M. et al., 1978a.

PHI-R analyzed chlorinated hydrocarbons in mussels after Soxhlet extraction, H_2SO_4 cleaning and florisil separation.

3.2. Phenols

Volatile phenols in wastewater samples were determined with a standard 4-aminoantipyrene method. Quantification was performed through spectrophotometry after distillation and reduction with 4-aminoantipyrene and chloroform extraction of acidified water samples. This parameter was analyzed in four laboratories. IPH-P, FCES-Z, IPH-S and ISCEP-B used the standard USA method (Anonymous, 1976).

3.3. Anionic detergents

Anionic detergents were determined with a standard method using methylene blue. Prior to the methylene blue reaction, CMR-Z concentrated anionic detergents from a water sample through a nitrogen stream in a Vickbold concentrator (Kozarac et al., 1975). This preconcentration step also gives separation of anionic detergents from interference materials. Other laboratories used direct chloroform extraction with certain modifications. MBS-P, IPH-P, FCES-Z and ISCEP-B adopted the standard USA method (Anonymous, 1976), while IPH-S used the procedure for anionic detergent determination described in the German literature (Hill, 1970).

3.4. Petroleum hydrocarbons

Petroleum hydrocarbons were determined through three different methodological approaches.

Infrared spectrophotometry was used for petroleum hydrocarbon determination in wastewaters collected in the Rijeka area. Lipoid organics were extracted with freon. The polar fraction was separated from the nonpolar fraction on an alumina column. As a quantitative standard, a mixture of n-heptane, i-octane and benzene was used (Anon., 1981).

IPH-S applied UV spectrophotometry after extracting organics from water samples and cleaning the extract on an alumina column. Diesel D-2 oil was used as a standard (Lur'e and Rybnikova, 1974).

CMR-Z and IOF-S used UV spectrofluorometry for the determination of petroleum hydrocarbons in water and sediments recommended by IOC (IOC, 1984; IOC, 1982). Some improvements on this method were described and applied during water sample analysis in the Sibenik and Kornati areas (Picer M. and Hocenski, 1983; Picer M., 1984b; Picer M. et al., 1986a). As standards, solutions of chrysene and Kuwait crude oil in hexane were used. For the determination of oil and other floating materials IPH-R adopted the method recommended by IOC (IOC, 1984).

4. Faecal coliforms

Sea water samples were taken with sterile glass samplers (30-50 cm below sea surface) or with sterile ZoBell samplers (IOF-S). Samples were treated in the ship laboratory immediately after collection or were transported in portable refrigerators to laboratories ashore and analyzed within 6 hours.

Effluent samples were collected from sewage collectors. Three separate samplings were carried out during the morning and a composite sample was made. The multiple test tube method was used to estimate the faecal coliform number in the samples.

Faecal coliform counts were performed after membrane filtration and incubation on M-FC-agar or ENDO-agar (IPH-R, IMB-K) or using a multiple test tube method (IPH-P). Samples were incubated for 24 hours at 44.5°C (WHO/UNEP, 1983a). The colonies produced by faecal coliforms were blue. The same procedure was adopted for samples inoculated on liquid media and shellfish meat (WHO/UNEP, 1983b).

Mussels were collected from commercial aquaculture facilities and autochthonous areas. In mussels faecal coliform determination was performed using the multiple test tube method with the MacConkey or Lactose media (IPH-P). After incubation at 36°C for 24 hours, a transfer from all positive tubes was made to the MacConkey medium and then incubated at 44.5°C for 24 hours. The confirmation of indol production was carried out in transfers from all positive tubes. Records of positive findings were completed in the most probable number term - MPN (WHO/UNEP, 1983b).

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