



**MEDITERRANEAN ACTION PLAN  
MED POL**

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**UNITED NATIONS ENVIRONMENT PROGRAMME**

**MONITORING PROGRAMME OF THE EASTERN ADRIATIC COASTAL AREA**

**Report for 1983-1991**

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## CONTRIBUTORS

The preparation of this report was coordinated by:

**Nenad Mikulic**, M.Sc.  
Nation Coordinator for MED POL  
Republic of Croatia  
Ministry of Civil Engineering and Environmental Protection

This report was prepared by:

**Danilo Degobbis**, Ph.D.  
Centre for Marine Research Rovinj  
“Ruder Boskovic” Institute

**Mladen Picer**, Ph.D.  
Centre for Marine Research Zagreb  
“Ruder Boskovic” Institute

**Biserka Raspor**, Ph.D.  
Centre for Marine Research Zagreb  
“Ruder Boskovic” Institute

**Laszlo Sipos**, Ph.D.  
Faculty of Chemical Engineering and Technology  
University of Zagreb

**Slavko Sobot**, Ph.D.  
Public Health Institute of the Republic of Croatia  
Health Ecology Service Zagreb

**Tomislav Zvonaric**, Ph.D.  
Institute for Oceanography and Fisheries Split

This report was edited by:

**Robert Precali**, M.Sc.  
Centre for Marine Research Rovinj  
“Ruder Boskovic” Institute

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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<sup>2</sup>) of the northern Mediterranean, extending for 800 km into the heartland of the European continent. On its southern side the Adriatic Sea is connected with 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 was estimated in the range of 5 to 10 years (Zore-Armanda and Pucher-Petkoviæ 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 (Buljan and Zore-Armanda, 1976). The shallow northern part (max. depth 75 m) extends southwards in a line joining Ancona (Italy) with Pag Island (Croatia). The central part, with the Jabuka Trench (max. depth 270 m), is separated by the Palagruža Sill (130 m) from the deepest southern part (max. depth 1270 m).

The shallow northern Adriatic receives considerable freshwater discharge (3000 m<sup>3</sup>/s, Cavazzoni Galaverni, 1972), mainly from the Po River (about 50% of the total discharge), one of the major rivers in the Mediterranean area. Many minor rivers, streams, and drainage canals flow into the sea from the northern and western coasts, while underground karstic springs and a few karstic streams are scattered along the east coast. A resident population of 15 million lives in the Po River watershed, on seven million hectares of land, half of which is intensely cultivated. The industrial organic load (expressed in BOD<sub>5</sub>) in this region accounts for 40 million inhabitant equivalents (Anon., 1977). In addition, significant quantities of wastewaters are discharged directly into the sea from the coastal regions, which are densely populated and have well-developed industrial and marine activities. Finally, tourist population increases significantly during the summer period, raising the basic 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 open area, or at least a larger coastal region, started at the beginning of this century, before World War I. Several seasonal cruises with the research vessels "Najade" and "Ciclope" were organized by the Italian-Austrian Permanent International Commission for Research of the Adriatic Sea during 1911-1914. The former Yugoslav Academy of Sciences and Arts in Zagreb sponsored a series of cruises in the Kvarner Region (northeastern Adriatic Sea) in 1913-1914. In the period between World War I and II marine research was mostly localized in coastal areas. After World War II, during the 1955 International Geophysical Year, extended cruises were again carried out. After the 1960s research in the open sea and coastal regions was gradually intensified by oceanographic institutions from both sides of the Adriatic. In addition USA ("Atlantis I"), former URSS ("Akademik Kowalevski" and "Akademik Vavilov"), and French ("Calipso") research vessels visited the Adriatic. A detailed historical review of marine fundamental research activities, with lists of institutions and research vessels was compiled by Zavodnik (1983).

#### 1.1.1. Researches related to pollution and eutrophication in open Adriatic waters

During the 1970s more attention was paid to pollution and eutrophication research in the Adriatic in response to the increased anthropogenic loads, due to the intensive development of agriculture, industry, marine traffic, port activities, and tourism in the area. Investigations performed during 1972-1974 in the open northern and central Adriatic, as well as in the eastern Adriatic coastal area in the framework of the Programme "Jadran III" (Anon., 1976) led to the hypothesis that anthropogenic pollution and eutrophication occurred only in estuarine and restricted harbour areas, in some places with serious consequences for the local ecosystem, while the natural ecological equilibrium of the Adriatic Sea as a whole had not been disturbed. Measurements of pollutant concentrations in the various compartments of the marine ecosystem were performed during subsequent years by various research groups, operating in the Adriatic area, but often with different sampling and analytical techniques, without intercalibration.

Data relevant for eutrophication studies were collected with a fixed sampling and analytical protocol (Gilmartin *et al.*, 1972 *et seq.*) at three (since 1966) to six (since 1972) stations, from the Rovinj coastal waters to the open northern Adriatic as far as the border of Italian national waters, off the Po delta, with a frequency ranging from biweekly to seasonal (Gilmartin *et al.*, 1990). Furthermore, a series of more than a hundred cruises on numerous stations have been performed in the northern Adriatic since 1965 (Franco, 1970, 1972, 1982; Franco and Michelato, 1992). These data are hardly comparable with earlier oceanographic and nutrient data obtained during cruises in 1911-1914 ("Najade" and "Ciclope" cruises; temperature, salinity and dissolved oxygen only), 1955 (Picotti, 1960) and 1960 (Faganelli, 1961), due to different analytical methods and sampling station locations.

Heavy metals and chlorinated hydrocarbons were determined in water, plankton, benthic organisms, fishes and sediment during cruises of the former Yugoslav Navy research vessel "Andrija Mohorovičič" in 1973 and 1976/78 at 30 stations covering the entire Adriatic Sea (Štirn *et al.*, 1974; Paul and Meischner, 1976; Kosta *et al.*, 1978, Stegnar *et al.*, 1978). Additional analyses of heavy metals, DDT and PBCs were performed in northern Adriatic pelagic and benthic fishes (Viviani *et al.*, 1973; Criseting *et al.*, 1973; Gilmartin and Revelante, 1975; Revelante and Gilmartin, 1975). The data obtained have shown that up to the mid 1970s no significant contamination occurred in the Adriatic ecosystem as a whole, although locally increased pollutant levels were measured, particularly for mercury. In a study on Hg, Pb and Cd content of five Adriatic organisms, representing various levels of the food chain (mussels, shrimps, mullets, anchovies and tunas), carried out between 1976 and 1979, higher concentrations were observed in specimens collected in the northernmost part of the Adriatic with respect to the central area (Viviani *et al.*, 1983). More recently (in April 1990), Hg was determined in water, particulate matter, plankton and sediments from the open waters and Italian coastal region along the entire Adriatic (Ferrara and Maserti, 1992).

The lack of a systematic knowledge of pollution and eutrophication trends in the open Adriatic Sea, and the increase of coastal pollution level in both countries, led the Italian and former 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 (ASCOP-Adriatic Scientific Coordinate Programme) with the aim of establishing an essential reference for coastal studies and identifying particular problems and areas where interventions were primarily needed (Accerboni and Jeftić 1980). Relevant to this was the agreement that data obtained and discussed by scientists participating in the joint programme will be officially recognized by the governments of both countries. To achieve the proposed aims a monitoring programme was designed, including the measurement of 75 parameters that characterize the physical, chemical, sedimentological and biological aspects of pollution processes, on a grid of 86 main stations covering the Adriatic international waters. To fully evaluate the collected data, methodology intercalibration exercises, development of data bank services and elaboration of mathematical models were also included.

Unfortunately, the programme was realized with a reduced frequency than that designed and the measurements were never extended to the southern Adriatic area. Moreover, the coordinated work of mixed scientist groups was not fully realized, particularly in more recent years, when the participation of Italian scientists was drastically reduced. In 1979 and in the period 1983-1992, 21 cruises were conducted in the northern Adriatic on 21 main stations, and 12 cruises in the central Adriatic on eight main stations (Anon., 1993). The results did not reveal high or critical pollution levels in both Adriatic regions (Accerboni, 1982; ASCOP Coordinating Board, 1985; Degobbi *et al.*, 1986a; Bregant and Catalano, 1989; Campesan *et al.*, 1989; Fossato *et al.*, 1989; Giordani *et al.*, 1989; Hieke Merlin *et al.*, 1989; Serrazanetti and Viviani, 1989; Precali and Konrad, 1986-1992, 1993; Anon., 1993). Radioactivity was also monitored, and the effects of the Chernobyl accident on the Adriatic ecosystem were well documented (Triulzi *et al.*, 1989, 1991).

Data from the ASCOP and other national (Croatian and Italian) and international (Croatian-USA) research programmes have shown that since the late 1970s and during the 1980s near-anoxia (eg 1977, 1988, 1991) or anoxia (1989) conditions were observed during the autumn in the bottom layer over extended areas in the northern Adriatic Sea, including the more oligotrophic eastern regions (Degobbi *et al.*, 1979, 1990, 1991a; Orel *et al.*, 1993). During these events mass mortality in the benthic macro and meiofauna communities was recorded (eg Jaklin and Zahtila, 1990; Travizi, 1990; Orel *et al.*, 1993). Remarkably, in most cases, the observed bottom oxygen crisis was not apparently related to an unusual increase of organic load (phytoplankton blooms), except in 1977.

Since 1991 some activities of the former Yugoslav-Italian Committee, including the Adriatic monitoring, have been continued by a trilateral committee, composed provisionally by Croatian, Slovenian and Italian delegations. One of the committee's initiatives concerned the compilation of detailed reports on the state-of-art of research and other activities related to environmental protection of the Adriatic area, including the Croatian and Slovenian coastal regions (Ozretić 1992a,b). Unfortunately, no cruises were planned for 1993, although the continuation of systematic monitoring is essential, not only to better evaluate the actual pollution levels and trends at a regional level, but also to define the



strategies of intervention in coastal areas and subsequently to verify the efficiency of the technical measures applied.

#### 1.1.2. Researches related to pollution and eutrophication in the eastern Adriatic coastal waters

In contrast to the open waters, pollution effects are clearly evident in coastal regions, particularly in the northwestern Adriatic (e.g. the Venice Lagoon, Cossu *et al.*, 1987, the Po River delta, Bartoletti *et al.*, 1985, the Emilia Romagna coastal zone, Vollenweider *et al.*, 1992). Even along the deeper, much less urbanized, eastern Adriatic coast, the harbour areas of almost all urban centres were subjected to progressive degradation as evidenced, for instance, by changes in the benthic community structure (Zavodnik, 1977; Ozretić 1992a).

In the Gulf of Trieste, including Slovenian coastal waters, parameters relevant to eutrophication have been measured since the early 1970s (Olivotti *et al.*, 1986). The region was qualified as predominantly oligotrophic. However, an anoxia event, localized in the deeper outer part of the Gulf of Trieste, occurred in late summer 1983, with serious consequences for the bottom fauna (Faganeli *et al.*, 1985; Stachowitsch, 1984, 1992; Malej, 1990; Orel *et al.*, 1993). In this area, near-anoxia conditions were also established in 1987 and 1990, but for shorter periods (Orel *et al.*, 1993). These events were ascribed to particular oceanographic conditions leading to stagnation of a bottom layer, which was physically limited by the geomorphological characteristics of the gulf and a deep pycnocline, rather than to an eutrophication forcing (Orel *et al.*, 1993).

In other semi-enclosed embayments, inadequate wastewater disposal caused a serious alteration of the marine ecological equilibrium, with fish and shellfish kills. Non-toxic "red tide" has occurred during summer in the Pula harbour since the early 1970s (Maretić *et al.*, 1978). Although part of the wastewater discharge was diverted into the open sea, more recent observations and analyses (June and July 1993; CMR-R unpublished data) have shown that this phenomenon is still actual in this harbour. In the Vranjic area of the Kaštela Bay (Split area) non-toxic "red tides" have appeared with increasing frequency and intensity during the 1980s (e.g. Marasović 1990). Furthermore, a potentially toxic dinoflagellate species has been increasingly abundant in the Šibenik Bay phytoplankton bloom (Marasović 1986).

At several points along the Istrian, Kvarner, Rijeka Bay, and Dalmatian coasts, heavy metals were analysed in water, suspended matter, sediments and organisms, primarily in the mussel *Mytilus galloprovincialis* (see Raspor, 1985 and Ozretić 1992a for review). In a restricted (industrialized) zone of Kaštela Bay a significant heavy metal pollution has been recorded, particularly mercury (Vukadin, 1980; Vukadin *et al.*, 1982, Stegnar *et al.*, 1980, 1983; Mikac *et al.*, 1983, 1985; Horvat *et al.*, 1987; Zvonarić *et al.*, 1987, 1989; Zvonarić 1991), but not Cr (Vukadin and Odžak, 1991). Higher heavy metal content was measured in sediment and mussels of areas under the influence of the Zadar, Šibenik, Split, Ploče, and Dubrovnik harbours, compared with the open sea sediment (Zvonarić *et al.*, 1986a,b). In contrast, significantly lower concentrations were reported in the various matrices for other areas: the Slovenian part of the Gulf of Trieste (Kosta *et al.*, 1978), the

Limski Kanal (Martinèæ *et al.*, 1980a,b, 1984, 1986c, 1987b,c; Najdek and Bažuliæ 1983), Raša Bay (Prohiæ *et al.*, 1992), the Rabac area (eastern Istria; Valkoviæ 1980), Bakar Bay and Susak Island areas (Ozretiæ *et al.*, 1990), the Krk Island area (Marjanoviæ *et al.*, 1982), the Krka estuary and Šibenik area (Branica *et al.*, 1985, 1986; Juraèiæ and Prohiæ 1986; Martinèæ *et al.*, 1985a,b, 1986a,b, 1987a, 1989, 1990; Pravdiæ and Juraèiæ 1988, Mikac *et al.*, 1989; Elbaz-Poulichet *et al.*, 1991; Seyler and Martin, 1991), the central eastern Adriatic islands area (Vuèetiæ *et al.*, 1974).

Organic pollutants (petroleum hydrocarbons, chlorinated hydrocarbons, phenols, detergents, total surfactants, methyl mercury) were also determined in several eastern Adriatic coastal areas during the early 1970s but with different methods (see Picer, M., 1985b for review). Thus, data are hardly comparable at a quantitative level. The PCBs and PCTs content in fish from the Gulf of Trieste were higher than in fish from rivers running through non-industrialized areas in Slovenia (Jan *et al.*, 1978). The content of these pollutants was higher in the surface sediment of the Koper area compared with the rest of the Slovenian coastal sediments (Salihoglu *et al.*, 1980). Chlorinated hydrocarbons were determined in water, sediment, mussels and several fish species from several Istrian coastal zones, Rijeka Bay, Bakar Bay, and Lošinj Island areas (Nazansky *et al.*, 1978; Picer, M. *et al.*, 1978a, 1981b, Picer, N. *et al.* 1984; Ahel and Picer, M., 1979; Smodlaka *et al.*, 1980). Significantly higher concentrations were measured only in sediment from restricted wastewater discharge areas. Dissolved/dispersed petroleum hydrocarbon concentrations in waters varied considerably along the Krka River estuary, particularly with respect to the Kornati Islands area (Picer, M., 1984). The lindane content was minimal in sediment samples, collected in 1977 by the RV "Calipso" in the western Istria and Split coastal areas (Villeneuve and Burns, 1982). The organic pollutant levels in sediment and mussels from the Dalmatian coastal region were among the lowest in the Mediterranean, except in restricted zones near the harbours of the major urban centres (Zadar, Šibenik, Split, Ploëe, Dubrovnik; Dujmov *et al.*, 1978, 1985; Vilièiæ *et al.*, 1978; Vuèetiæ and Dujmov, 1980; Picer, M. *et al.*, 1986a; Picer, M., 1986b; Kršiniæ *et al.*, 1991).

Sanitary control of some beaches and mariculture areas started in the early 1970s in the Slovenian, western Istria, Rijeka, Kvarner islands, Zadar, Šibenik, Split, Ploëe, and Dubrovnik coastal areas (e.g. Turk, 1987; Fuks and Devescovi, 1986, 1989; Krstuloviæ 1989; Fuks *et al.*, 1989; Degobbi *et al.*, 1989). More recently (since 1990), the bacteriological monitoring has been intensified, particularly in the northern Adriatic, in the framework of the activity of the "Alpe-Adria" Observatory for the northern Adriatic (Ozretiæ 1992a, pp. 106-107), and in the Dalmatian marine region (Programme "Vir-Konavle"; Krstuloviæ 1987).

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<sup>2</sup>, 60 m deep) ecosystem was undertaken from 1976 to 1980 (Jeftiæ 1981, 1982). Moreover, additional coordinated studies on currents, water exchange mechanisms and rates, toxicological effects of oil products on marine organisms, as well as elaborations of thermal pollution and ecological mathematical models were also performed. The study also provided a baseline to evaluate the efficiency of future sewage and industrial wastewater disposal systems by long submarine outfalls. About 200,000 residents live in the region, with a yearly tourist

presence of four million overnights. Several industries (refineries, a coke plant, power and petrochemical plants, shipyards, an oil terminal, a paper-mill factory) operate along the northern coast of the bay.

During 20 seasonal cruises in Rijeka Bay meteorological parameters, as well as basic physical, chemical and biological parameters in the water and sediment were measured on about 30 stations around the region, including Bakar Bay. Specific pollution parameters (hydrocarbons, chlorinated hydrocarbons, total surfactants, anionic detergents, benzopyrene mono-oxygenase induction, complexation capacity, heavy metals) were measured in samples of water, sediment, plankton, mussels and other benthic organism, collected at the oceanographic stations and along the shore. Increased concentration of pollutants was observed only in a narrow northern coastal zone, including Bakar Bay (Ahel and Picer, M., 1978, 1979; Nazansky *et al.*, 1978; Picer, N. and Picer, M., 1979; Ašovica and Žutić 1981; Picer, M. *et al.*, 1981b; Ahel, 1984). The water sanitary quality on the beaches was significantly influenced by wind conditions (Fuks and Juribašić 1981). Non seasonal phytoplankton blooms were also noticed in some restricted zones with reduced water exchange and increased nutrient input (Smodlaka, 1985). However, the ecosystem of that region was qualified as a whole to have a high self purification capacity for pollutants (Jeftić 1982). Research has also shown that wastes from oil refinery should not produce significant toxic and genetic effect in 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 Rijeka Bay, was also performed in the coastal area (4 km width) of the western Istrian peninsula during 10 seasonal cruises at 28 stations (Jeftić and Degobbis, 1978; Jeftić and Smodlaka, 1978; Jeftić and Lucu, 1979; Ozretić 1981). The results, concerning pollution degree, led to conclusions similar to those of Rijeka Bay. Persistent pollutants were only detected in sediment and organism samples collected in proximity of the Umag, Poreč, 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; Degobbis *et al.*, 1990).

Eutrophication, water sanitary control, and pollutant distribution have been monitored since 1976 in the areas of the main Dalmatia urban and industrial centres and other commercially important areas (Programme "Vir-Konavle"; e.g. Krstulović 1987; Zvonarić *et al.*, 1986a,b; Vilić and Stojanoski, 1987; Vilić 1989).

In 1990 an "Alpe-Adria" Programme was started with the aim of monitoring and studying undesirable phenomena (mucilaginous aggregates, phytoplankton blooms, anoxia events) in the open and coastal waters of the northern Adriatic, including the Kvarner areas (Degobbis *et al.*, 1993).

Several other, limited studies have performed over the last 25 years along the eastern Adriatic coast to acquire basic oceanographic and pollution data in localities in which sewages or industrial wastewaters are disposed, or were planned for future disposal (e.g. Piran, Rabac, Zadar, Šibenik, Split, Omiš, Vela Luka, Dubrovnik, Cavtat coastal areas, and

Šibenik, Kaštela and Maloston bays), or in those proposed for tourist exploitation (e.g. Kvarner islands, several Dalmatian centres), mariculture activities (Limski kanal, Raša, Budava and Klimno bays), and, for the building of a nuclear power plant (Vir Island, Zadar region), as well as in some estuaries (Mirna, Krka, Jadro, Cetina, Neretva rivers). Unfortunately, most of the collected data have not yet been published in open literature, but are presented in technical reports (see lists in Ozretić 1992b).

#### 1.1.3. Proposed technical solutions for wastewater disposal

Several years ago, it was recognized that long submarine outfalls represent an optimal technique for wastewater disposal along the relatively deep eastern Adriatic coasts (e.g. Price, 1980; Margeta, 1986). Sewer and outfall facilities are under construction in most of the urban and tourist centres along the eastern Adriatic coast. In a few localities, such a system has been operating for several years with satisfactory results. A 3,450 m long submarine outfall with a 120 m long diffuser at the depth of 20 m was shown to be efficient in disposing urban waters of the towns of Piran, Portorož, and Lucija, and surrounding tourist facilities (Slovenian coastal area; Avèin *et al.*, 1979; Malej, 1980), without significantly affecting the nutrient budget of the discharge area (Faganeli, 1982). After the provisional submarine outfall began operating, the sanitary quality of some Rovinj beaches significantly improved (Fuks and Devescovi, 1990). The Rabac (eastern Istria) 250 m long outfall, without diffuser, but discharging sewage at a depth of 45 m, efficiently serves 10,000 people in summer, preserving high water quality on the beaches and in the coastal area (Degobbis *et al.*, 1987). Sewages of the city of Dubrovnik and neighbouring tourist resorts are disposed into the sea at a depth of 101 m with a 1,568 m hard polyethylene outfall (0.8 m in diameter) after screening and grease flotation (Margeta *et al.*, 1989).

## **1.2. Overview of the MED POL activities in the former Yugoslavia**

Since 1975 the research and pollution monitoring along the eastern Adriatic coast has been organized at the national level. Namely, the Government of the former Yugoslavia signed in 1976, and ratified in 1977, the Convention for the Protection of the Mediterranean Sea against Pollution (Barcelona Convention).

The obligations of the Barcelona Convention were realized through the Mediterranean Action Plan (MAP). 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 was realized in two phases.

During the realization of the MED POL - PHASE I five research centres from the former Yugoslavia were involved in the following seven pilot Programmes:

- @ 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, PCPs and other Chlorinated Hydrocarbons in Marine Organisms;
- @ MED POL IV: Research on the Effects on 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 institutions participated in the above-mentioned pilot programmes of the MED POL - PHASE I:

- @ Centre for Marine Research Rovinj-Zagreb, "Ruđer Bošković" Institute, Zagreb (MED POL I, II, III, IV, V, VI and VII);
- @ Marine Biological Station, Portorož, 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 programmes started in 1975 and ended in 1980. During this period, most of the institutions have been qualified for specific activities, depending on their research orientation and available instrumentation. They started the research and monitoring measurements planned in the second phase of the MED POL programme with relative ease.

Twelve institutions were involved in the realization of the MED POL PHASE II activities, consisting of research programmes and a monitoring programme.

The following research programmes were realized in the period 1983-1992:

- @ 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; and
- @ JELLYFISH PROGRAMMES.

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

- @ Marine Biological Station, Piran, Institute of Biology, University of Ljubljana (ACTIVITY F, G, H and JELLYFISH PROGRAMME);
- @ "Jožef Stefan" Institute, University of Ljubljana (ACTIVITY D);
- @ Centre for Marine Research Rovinj, "Ruđer Bošković" Institute, Zagreb (ACTIVITY G, H, I, K and JELLYFISH PROGRAMME);
- @ Department for communicable diseases, Pula (JELLYFISH PROGRAMME);

- @ Centre for Marine Research Zagreb, "Ruđer Bošković" Institute, Zagreb (ACTIVITY A, C, F, G, H, K, L and JELLYFISH PROGRAMME);
- @ Department of Physics, "Ruđer Bošković" 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 PROGRAMME);
- @ Biological Institute, Dubrovnik, Institute for Oceanography and Fisheries, Split (ACTIVITY I and JELLYFISH PROGRAMME);
- @ University "Veljko Vlahović", Titograd (ACTIVITY K);
- @ Federal Hydrometeorological Institute, Beograd (ACTIVITY L); and
- @ Institute of Chemistry, University of Beograd, Beograd (ACTIVITY G).

The design of the Yugoslav National Programme of the Monitoring of Pollution in the Adriatic Sea was performed in 1982, and its realization started in 1983.

During the first year of the programme only one institutions from Slovenia and three from Croatia participated in the monitoring. The following year five other institutions joined the programme. Thus, in 1985 and 1986 two institutions from Slovenia, eight from Croatia and two from Montenegro were engaged in the measurements. In this way, pollution was monitored in almost all areas of urban, industrial and touristic importance along the Adriatic coast of former Yugoslavia.

In the following chapters the organization of the programme (participating institutions, methodology, geographic coverage, observation schedules) is described in detail, and the results obtained in the period 1983-1992 is discussed thoroughly. Finally, extended concluding remarks and recommendations for future work will be also presented.

## **2. ORGANIZATION OF THE NATIONAL MONITORING PROGRAMME OF FORMER YUGOSLAVIA**

### **2.1. Participating institutions**

The following institutions participated in the present programme:

- @ Marine Biological Station, Piran, Institute of Biology, University of Ljubljana (MBS-P);
- @ Centre for Marine Research Rovinj, "Ruđer Bošković" Institute, Zagreb (CMR-R);
- @ Institute of Public Health, Pula (IPH-P);
- @ Institute of Public Health, Rijeka (IPH-R);
- @ Institute of Public Health, Zadar (IPH-Z);
- @ Public Health Institute of the Republic of Croatia (IPHC-Z);
- @ Faculty of Civil Engineering Sciences, University of Zagreb (FCES-Z);
- @ Faculty of Chemical Engineering and Technology, University of Zagreb (FCET-Z);
- @ Centre for Marine Research Zagreb, "Ruđer Bošković" 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); and
- @ Institute for Subtropical Cultures and Environment Protection, Bar (ISCEP-B).

#### **Collaborating institutions:**

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

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

Information about the participating institutions and their main research activities are 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)
- @ petroleum hydrocarbons (PH)

#### *Other parameters*

- @ biochemical oxygen demand (BOD<sub>5</sub>)
- @ chemical oxygen demand (COD)
- @ total suspended solids (TSS)
- @ total phosphorus (P)
- @ total nitrogen (N)
- @ faecal coliforms (FC)
- @ anionic detergents (DET)
- @ phenols index (PHE)
- @ total lead (Pb)
- @ total chromium (Cr)
- @ total zinc (Zn)

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

#### *Estuarine water (E)*

- @ faecal coliforms (FC)
- @ total mercury (Hg)
- @ basic oceanographic and meteorological observations (BO&M)
- @ high molecular weight chlorinated hydrocarbons (CH)
- @ total cadmium (Cd)
- @ total phosphorus (P)
- @ total nitrogen (N)
- @ biochemical oxygen demand (BOD<sub>5</sub>)
- @ 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 chlorinated hydrocarbons (CH)
- @ petroleum hydrocarbons (PH)

### *Biological material*

- @ total mercury (Hg)
- @ total cadmium (Cd)
- @ high molecular weight chlorinated hydrocarbons (CH)
- @ petroleum hydrocarbons (PH)
- @ faecal coliforms - edible bivalves only (FC)

## 2.2.2. Sampling and analytical methods

Generally, for all above-mentioned parameters standard sampling and analytical procedures, have been used as proposed by UNEP, and published in UNEP's series of Reference Methods for Marine Pollution Studies. However, in cases where no methods are recommended by UNEP, or in case of shortage of recommended equipment in some institutions, standard, well-known procedures were adopted. Moreover, some institutions also applied 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 obtained data, participating institutions took part in standardization and intercalibration exercises organised on national or international levels.

In this manner the sampling and analytical procedures of determination of the following group of parameters have been 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 of obtaining information about 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 indirectly 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 Limski kanal to Crvevni otok),
- @ Pula area (from Peroj to the Raša Bay).
- @ Rijeka area (from Mošćenica to Crikvenica),
- @ Zadar area (from Diklovac to Punta Bajlo)
- @ Šibenik area (from Skradin to Zlarin),
- @ Split area (from Vranjic to Stobreč),
- @ Dubrovnik area (from Orebić to Cavtat), and
- @ Montenegrin coastal area (from Herceg Novi to Ulcinj).

Reference areas were monitored at:

- @ The Rovinj-Po River profile,
- @ Kornati area,
- @ The Vis Island area,
- @ Montenegrin coastal area.

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

Figs 2.3.1.1-9.2. show in detail each investigated area with sampling stations.

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

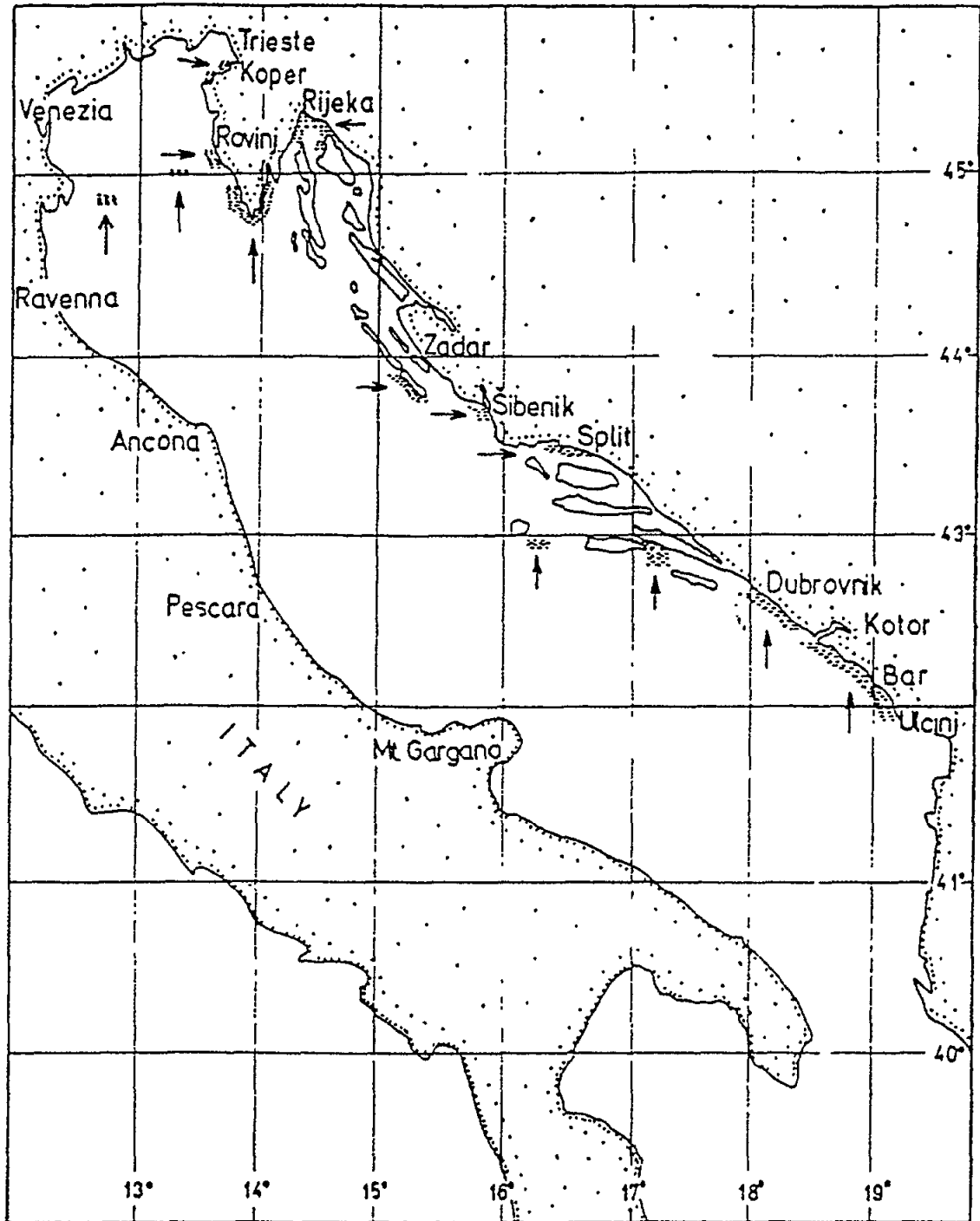


Fig. 2.3.1. The Adriatic Sea - investigated areas.

### 2.3.1. Slovenian coastal area (MBS-P)

Monitoring was carried out along the Slovenian coast including the coastal sea from the Cape of Debeli rtiè to the Cape of Savudrija. It is a part of the Gulf of Trieste which is the northernmost region of the Adriatic sea.

In most of the coast in which the Bay of Koper and the Bay of Piran are situated the flysch topography prevails, with the exception of limestone Savudrian coast. Eastward continuations of the Koper and Piran bays are the flat-bottomed valleys of the river Rižana and the river Dragonja.

The karst topography of the Istrian Peninsula, continues further under water and represents deeper geological basis of the entire region.

The Adriatic Sea here attains 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 line Grado-Savudrija, modulated on a daily period by the local wind field. Semidiurnal tidal currents, are ineffective regarding 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  $6 \text{ m s}^{-1}$ , is, therefore, the main agent for the renewal of the surface waters in this area.

The region is intensively populated (about 50,000 inhabitants), and during the summer it is visited by many tourists. However, sewages are efficiently disposed into the sea by a long submarine outfall.

The pollution sources monitoring was carried out at the following stations (Fig. 2.3.1.1):

Pa, Pb, Ia, Ka, Kb	-	outlets of domestic sewage of Piran, Izola and Koper towns, respectively,
DE	-	outlet of industrial effluents discharged by the "Delamaris" fish canning industry, Izola,
RI, BA	-	stations in the Rižana and Badaševica 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.

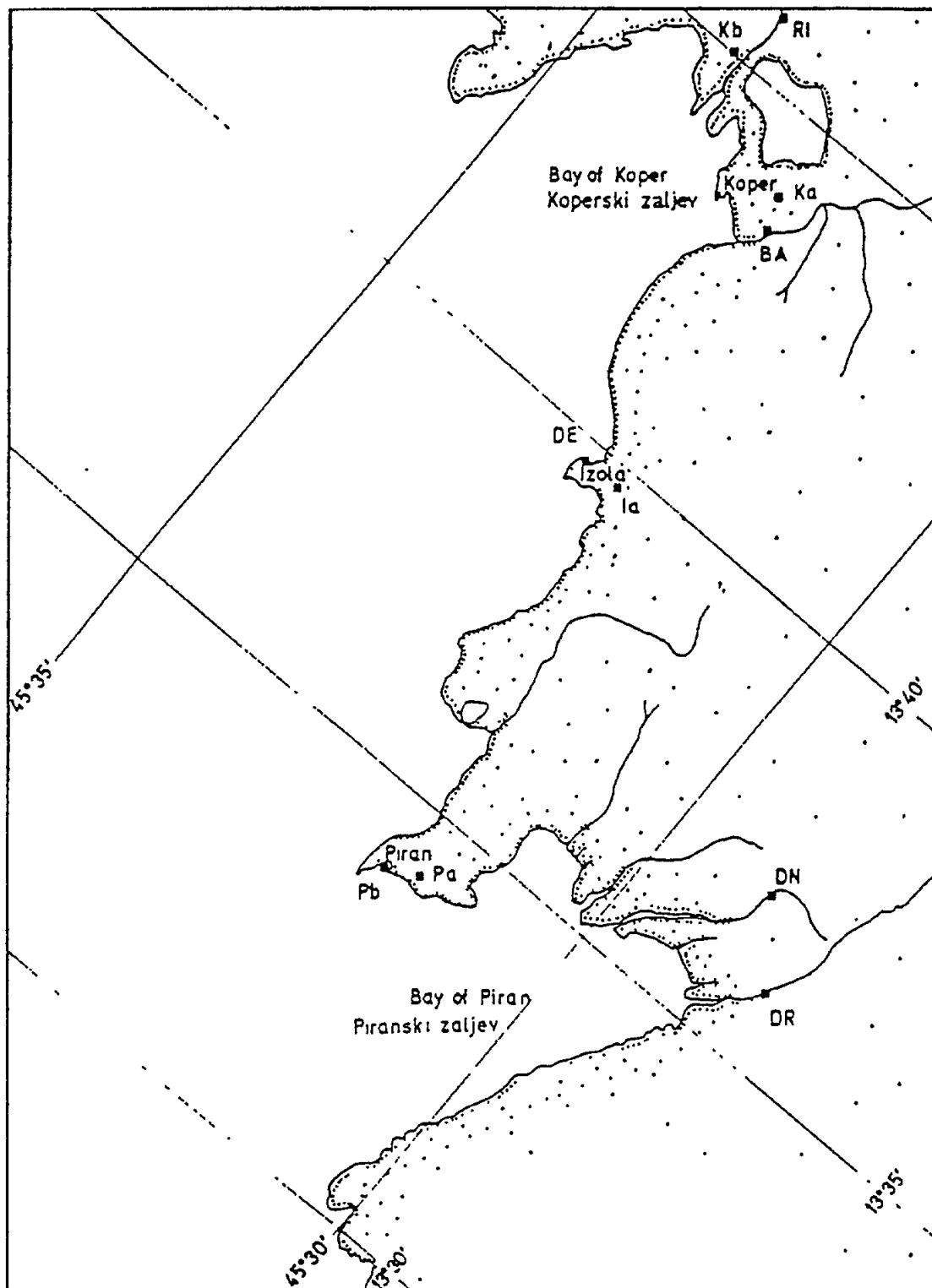


Fig. 2.3.1.1. The Slovenian coastal area - effluent sampling stations.

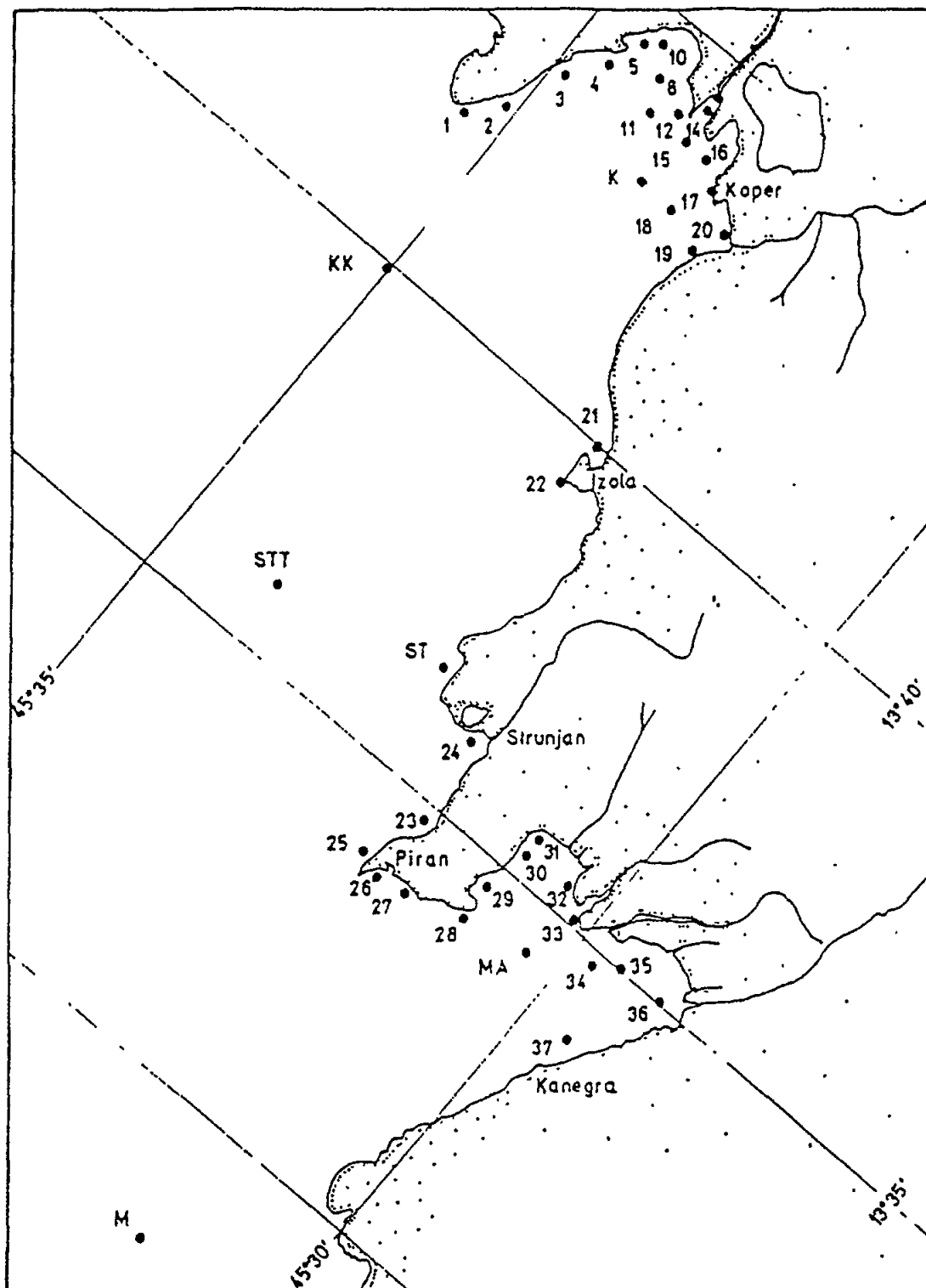


Fig. 2.3.1.2. The Slovenian coastal area - coastal water sampling stations.

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

The coastal waters monitoring stations are shown in Fig 2.3.1.2. At stations 1-37 bacteriological parameters were measured. The stations cover near-shore waters under influence of urban agglomerations, including all public beaches and shellfish rearing localities. At the stations denoted with capital letters monitoring of heavy metals in 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 open waters was controlled. Station M was chosen as a reference station.

### 2.3.2. Rovinj area (CMR-R)

The Rovinj area is located in the central part of the western Istrian coast, north of the Pula region, and south of the Poreč region. The coast is rocky and relatively deep (up to 30 m a few hundreds metres from the coastline), with many embayments and islands. Along the coastline the only urban centre is Rovinj, a town with a population of about 10,000 inhabitants. However, in summer, an additional 40,000 tourists are accommodated in the town and in tourist villages and camping sites, situated a few kilometres to the north and south of the town. The organic load is then increased several times, while sewage is partially disposed directly onto 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 (Valdibora Bay). Sewages and wastewaters of a tobacco factory are discharged into the southern harbour (Lone Bay), in which a marina with 200 yachts operates. Some of the tourist villages and camp sites dispose of their waters by inadequate submarine outfalls, often near the beaches.

The construction of a modern system for sewage disposal by long submarine outfalls has started ten years ago. Today a 800-metres-long submarine outfall is in use collecting a limited part of the town and tourist facility wastewaters.

The Limski Kanal, located on the border between the Rovinj and Poreč territories is a very narrow (less than 600 m) and relatively long (11 km) inlet on 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 reserved for mariculture. At present, about 200 tons of shellfish and about 200 tons of fish (sea bass, gilt-head bream) are produced. Water quality monitoring is essential for this region, in which an intensive mariculture production besides the restaurants in the inner part, and large tourist centres at the mouth of the inlet coexist. Furthermore, about fifteen springs



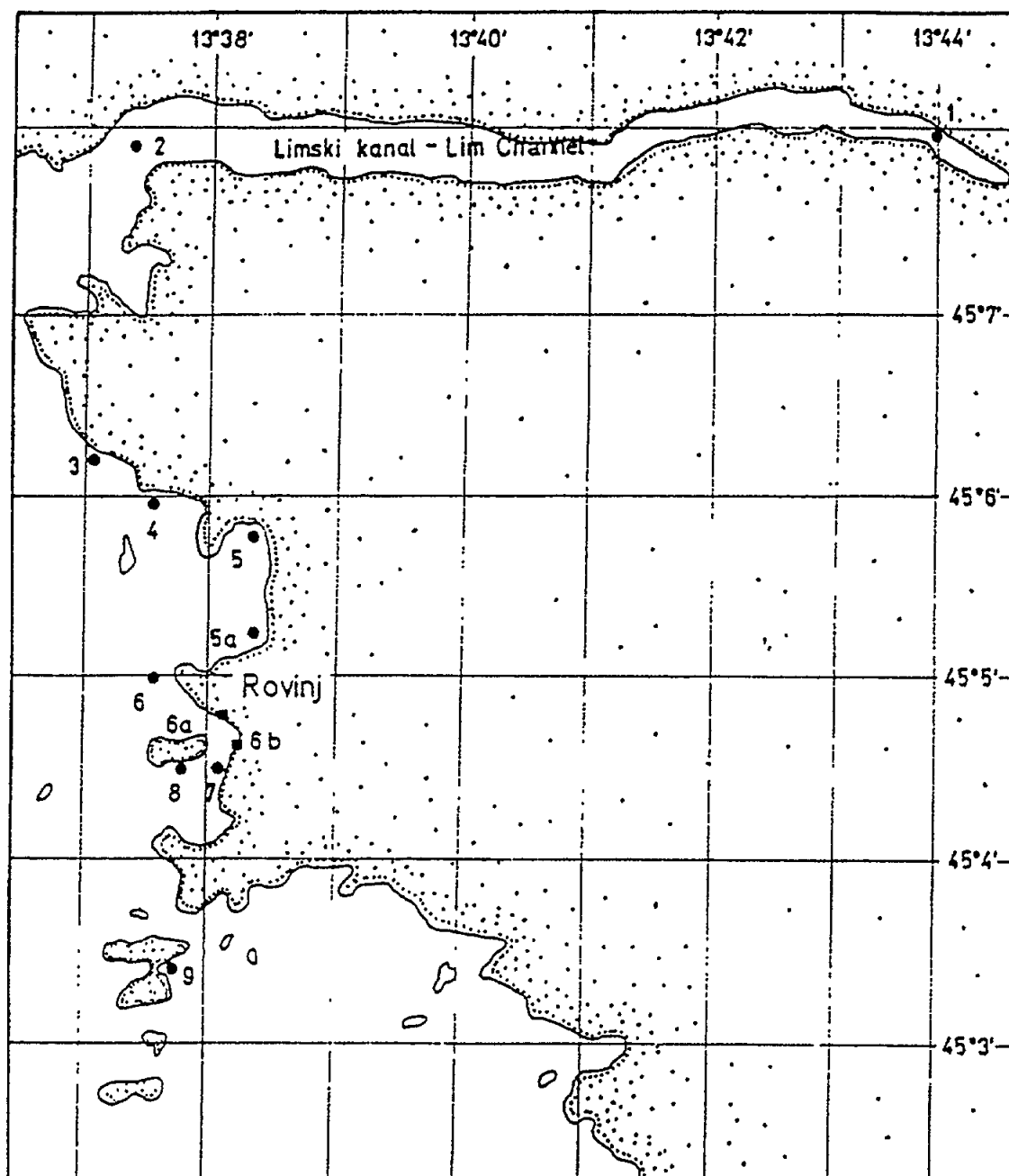


Fig. 2.3.2.1. The Rovinj area - sampling stations.

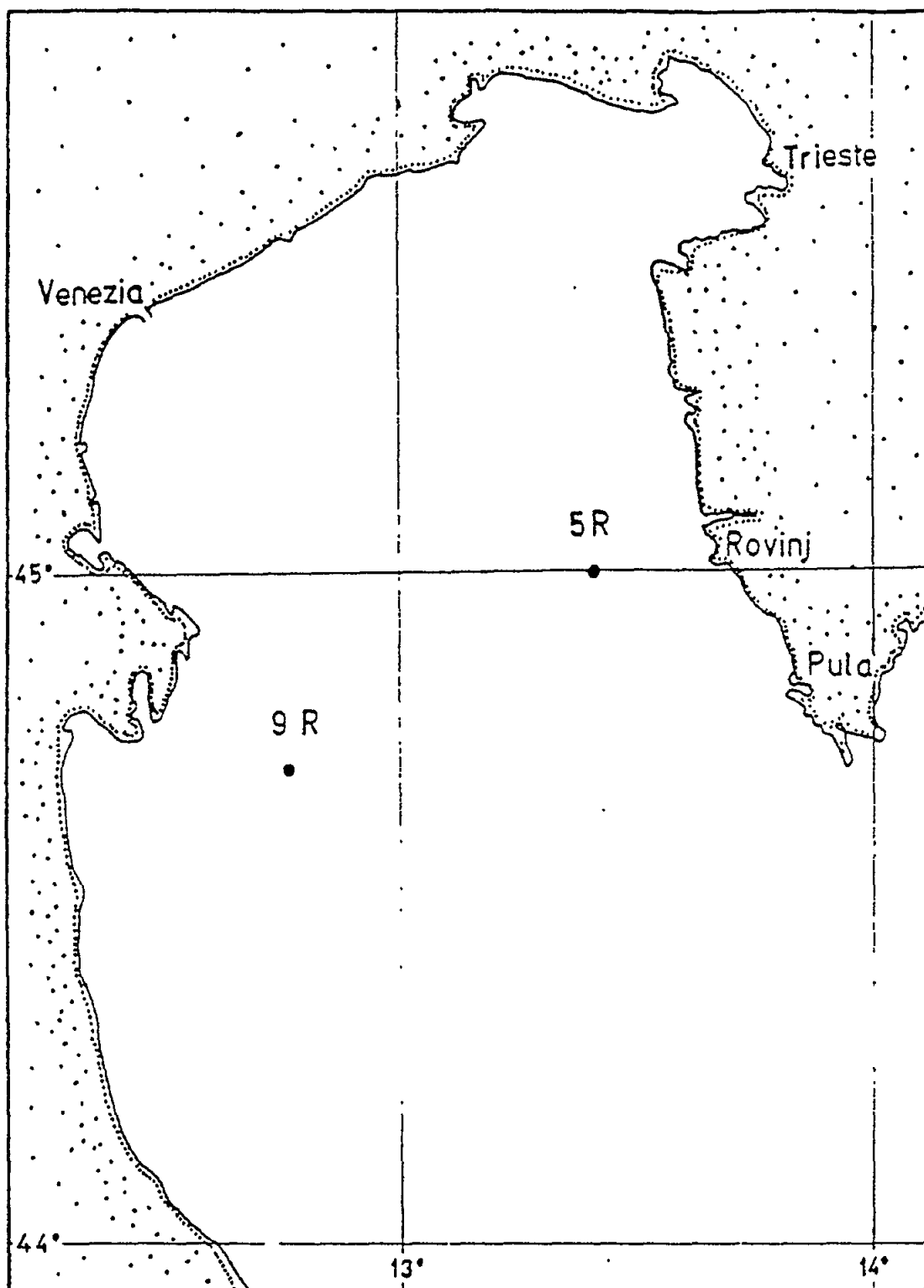


Fig. 2.3.2.2. The Rovinj-Po River Delta profile - sampling stations.

discharge into the Limski Kanal 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 15,000 inhabitants.

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

The sanitary quality of the tourist centres and 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 station, 6A in the main harbour, and 6B at station in the southern harbour, in the discharge area of the tobacco factory wastewaters (Fig. 2.3.2.1).

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 Limski Kanal were performed in the inner part (station 1), in which fish and shellfish are grown and at the entrance of the inlet (station 2) to estimate the influence of the Istrian coastal waters (Fig. 2.3.2.1). The northern Adriatic open waters were monitored at two stations (Fig.2.3.2.2). During winter station 5R, 25 km off Rovinj, is under the influence of oligotrophic waters from the central Adriatic. But in 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 freshwaters, very rich in nutrients and pollutants.

### 2.3.3. Pula area (IPH-P)

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

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

About 75,000 residents live in the town of Pula and in the large suburban areas. 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 camping sites, as well as small and large tourist villages.

The western and southern part of the coast is under the influence of pollution caused by waste waters from industry, urban areas, tourist villages and agriculture. This area also includes the Pula harbour in which  $20,000 \text{ m}^3 \text{ d}^{-1}$  of faecal and industrial waste waters are discharged through 14 outfalls directly onto the coastline.

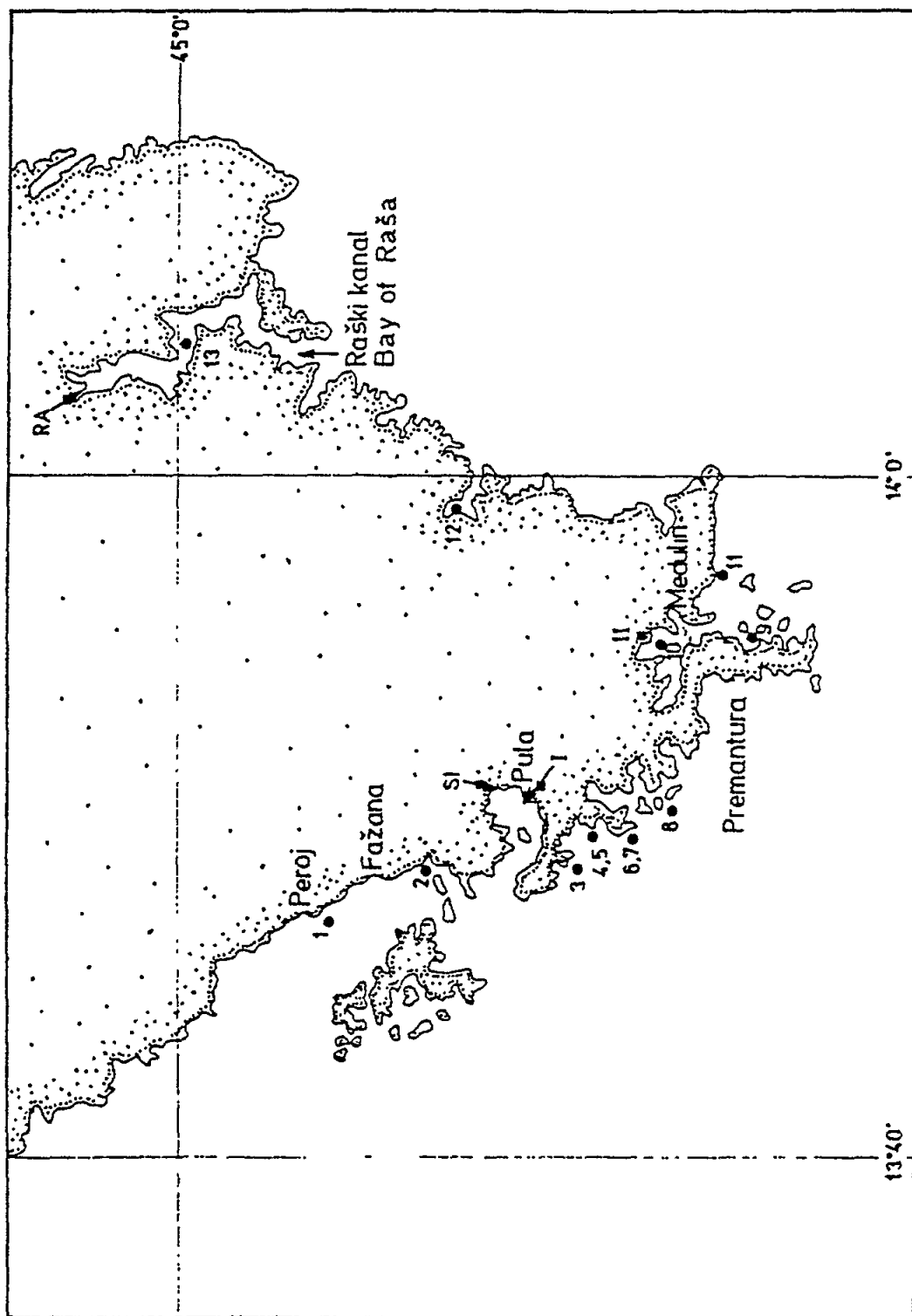


Fig. 2.3.3.1. The Pula area - sampling stations.

In the harbour intensive dinoflagellate blooms (red tide) occur periodically. On the remainder of the western and southern coasts mostly untreated sewages 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.2.3.3.1):

- I - Pula outfall effluents,
- II - Medulin tourist centre outfall effluent,
- Si - chemical industry outfall effluent,
- RA - the Raša 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 with urban, industrial and agriculture wastes carried into this region by karstic groundwaters and by the Raša river.

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

Pollution monitoring in the Pula area coastal waters was carried out at 13 stations (Fig. 2.3.3.1). Eleven stations were located near the next urban and tourist areas:

- 1-2 Peroj and Valbandon areas, with several small and large recreational centres,
- 3,8-11 Valovine, Banjole, Prematura and two sites in Medulin area, in which the urban centres, recreational sites, hotels, bungalows and tourist villages are numerous, and
- 4-7 the Gortan Cove, the tourist areas around hotels Splendid and Brioni,

with about 90,000 inhabitants and tourists during the summer. Two stations were on the eastern part of the Istrian coast, in Budava Cove and Raša Bay. At both stations mussel *Mytilus galloprovincialis* and sediment were also analysed.

#### 2.3.4. Rijeka area (FCES-Z, FCET-Z and IPH-R)

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

Rijeka Bay (about 450 km<sup>2</sup>) with a depth of about 60-65 m, receives large quantities of freshwaters discharged into the sea from mountain streams, coastal and submarine springs and by the Rječina 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 eddy 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 Mošćenička Draga to Bakarac.

About 200,000 residents live in the Rijeka Bay area, including the city of Rijeka and other coastal towns and settlements. During the tourist season the population is doubled. The wastewaters of towns and settlements enter the sea mainly untreated, directly onto the coastline or through inadequate submarine outfalls.

The Liburnian Riviera and Vinodol Channel is an exclusive tourist area. On the northern coast of the Krk Island, tourist and industrial facilities are both present. The major part of the Rijeka coastal area is occupied mostly by harbours and industries.

Among the biggest industrial plants here are oil refineries in Rijeka and Urinj, an oil terminal and a petrochemical complex in Omišalj, all discharging high quantities of wastewaters. 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 points (Fig. 2.3.4.1):

U-1	-	Opatija outfall effluents,
U-2-5	-	Rijeka outfall effluents,
U-6	-	industry outfall and urban effluents mixed,
U-8-12	-	Martinšćica, Bakar, Kraljevica, Crikvenica and Omišalj outfall effluents,
I-1	-	Ika outfall effluents and fish processing plant outfall effluents, mixed,
I-2	-	Urinj oil refinery effluent outfall.

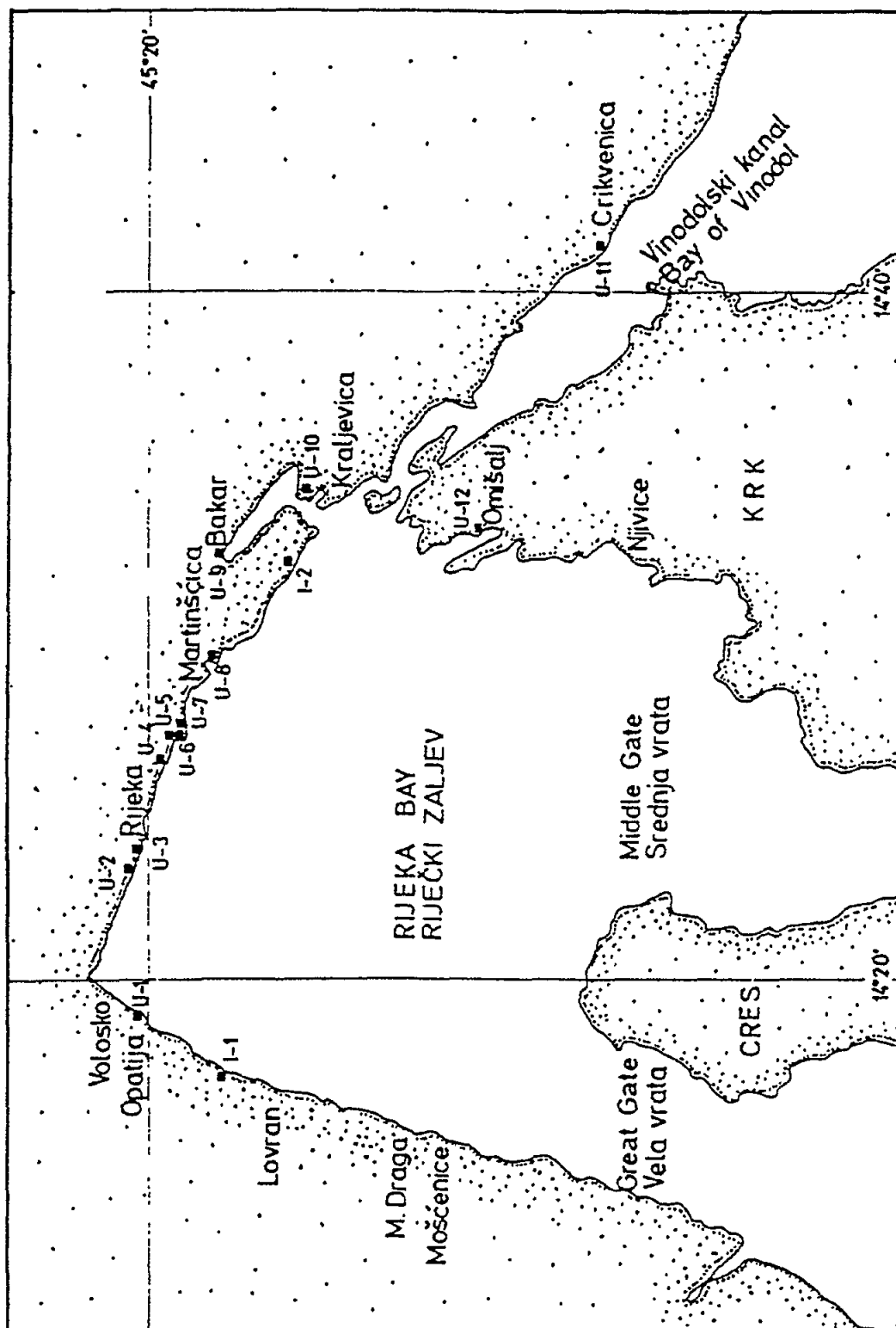


Fig. 2.3.4.1. The Rijeka area - effluent sampling stations.

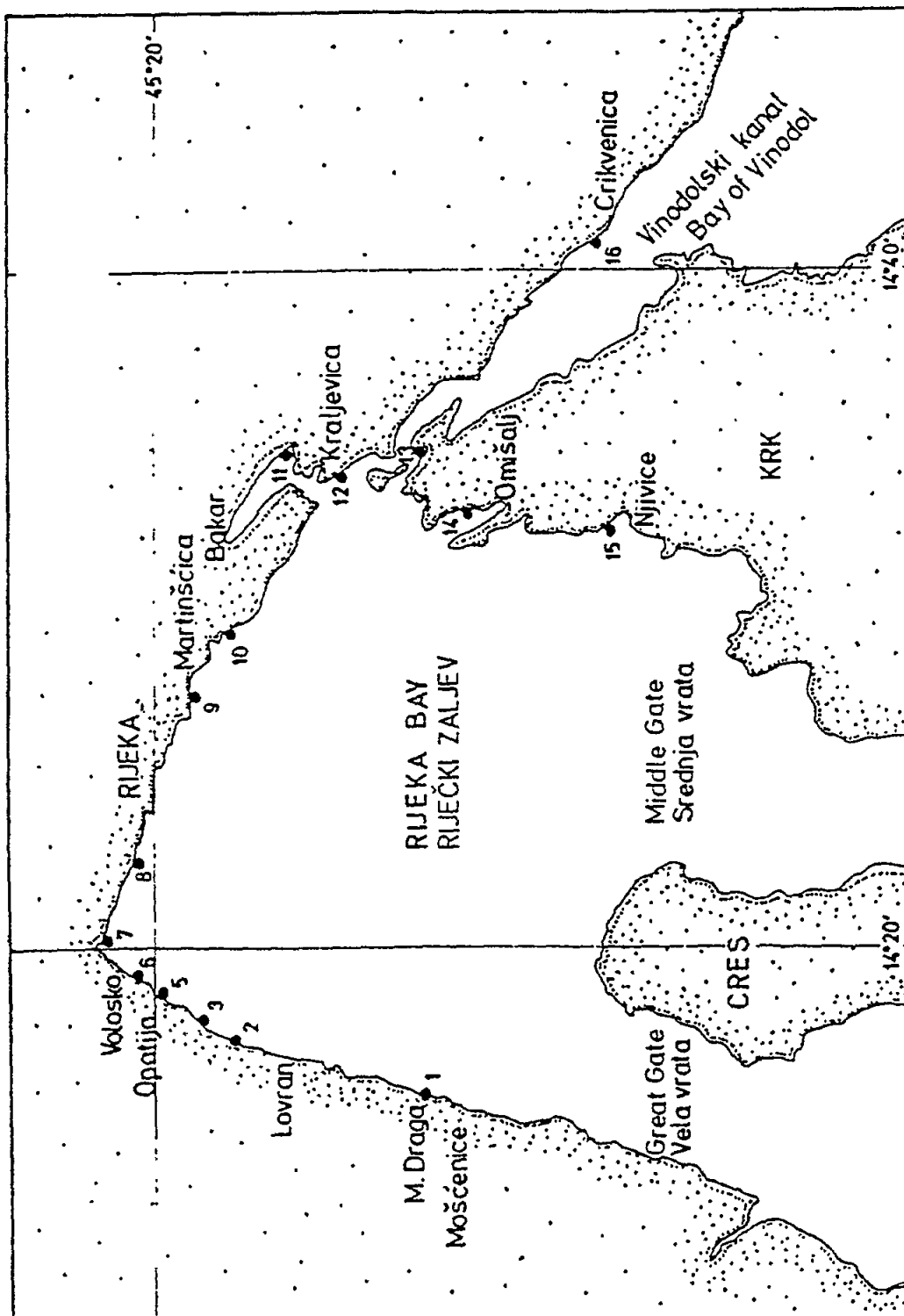


Fig. 2.3.4.2. The Rijeka area - coastal water sampling stations.



The coastal sampling stations are shown in Fig. 2.3.4.2. The stations are distributed along the Liburnian Riviera (stations 1-6), the Rijeka coastal area (stations 7-22), the northern coast of the 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 Mošćenička Draga, Lovran, Opatija, Volovsko, Rijeka, Kostrena, Bakarac, Kraljevica, Omišalj to Njivice, as well as those of Crikvenica in the Vinodol Channel.

#### 2.3.5. Zadar area (IPHC-Z and IPH-Z)

The Zadar area coastline is characterized by a slight slope and many bays, coves, inlets and islands.

Zadar with its large suburbia has a population of about 70,000 residents which doubles during the tourist season. Three marinas, one main harbour, several food processing plants and chemical industries are situated along its coastline. A portion of urban sewage is collected at Kolovare and deposited into coastal waters through a 1,500-metres-long submarine outfall. Many short outfalls discharge the remaining urban and industrial waste waters directly onto the coastline.

Pollution sources were monitored at the following sampling points (Fig. 2.3.5.1):

- I-1 - industrial effluents from a tannery,
- I-2 - industrial effluents from a textile factory,
- U-3 - urban effluents from the Kolovare facilities, and
- I-4 - industrial effluents from a food factory

Fig. 2.3.5.2 shows the coastal sampling stations involved. At stations 1-11 the hygienic safety of coastal waters was monitored, and at stations 6 and 11 mussel and sediment samples collected.

#### 2.3.6. Šibenik area (CMR-Z)

The watershed of the 72.5 km long karstic Krka River and its estuary account for about 2,100 km<sup>2</sup>. The estuary is 25 km long and of complex morphology, with several channels, Lake Prokljan and Šibenik Bay. 53,000 inhabitants live in the region, most of whom (72%) are concentrated in the lower part of the estuary in the town of Šibenik. 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 overnights per year) and mariculture are also developed. The capacity of Skradin marina (upper estuary) is about 100 yachts. In contrast, agriculture and forestry activities are negligible.

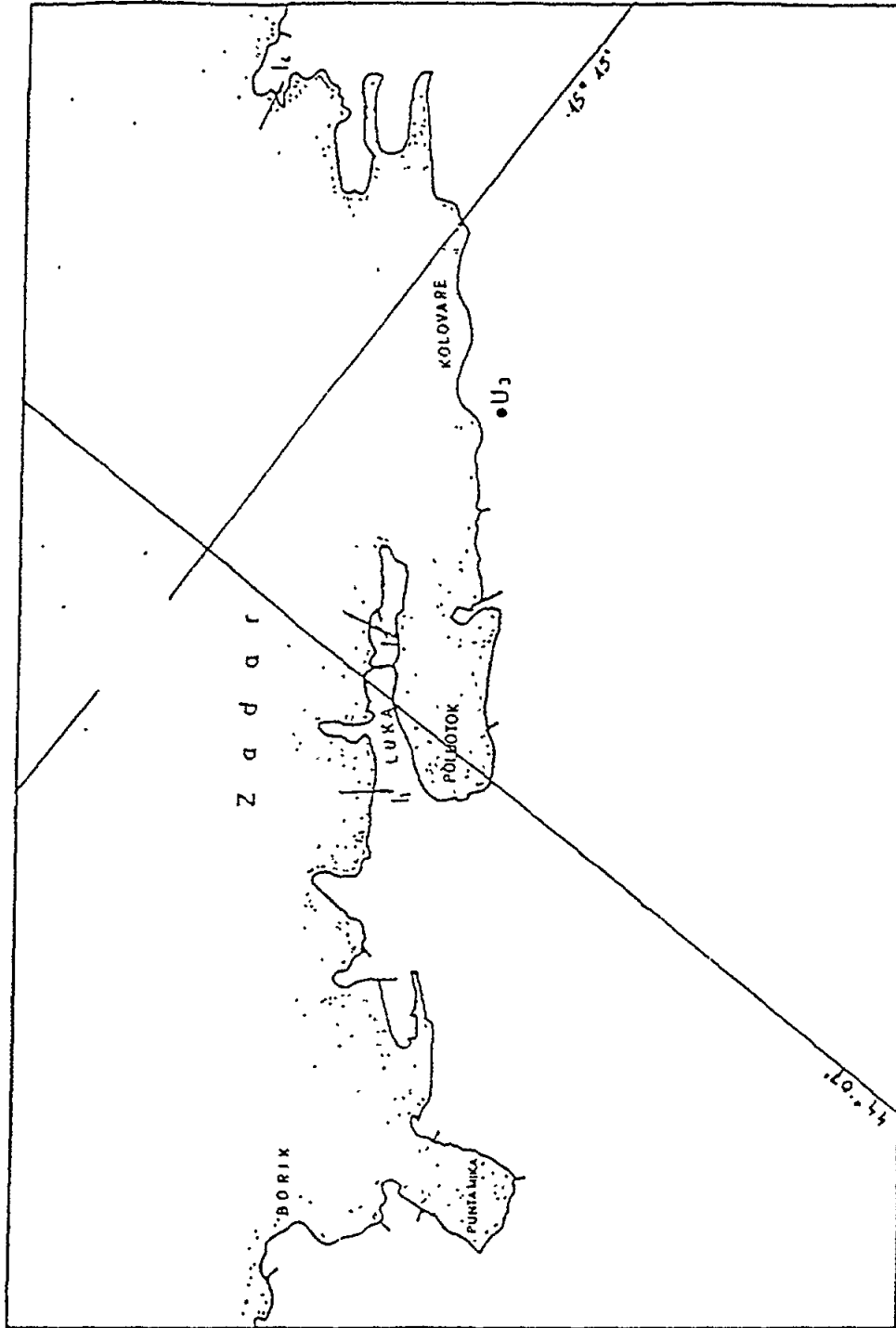


Fig. 2.3.5.1. The Zadar area - effluent sampling stations.

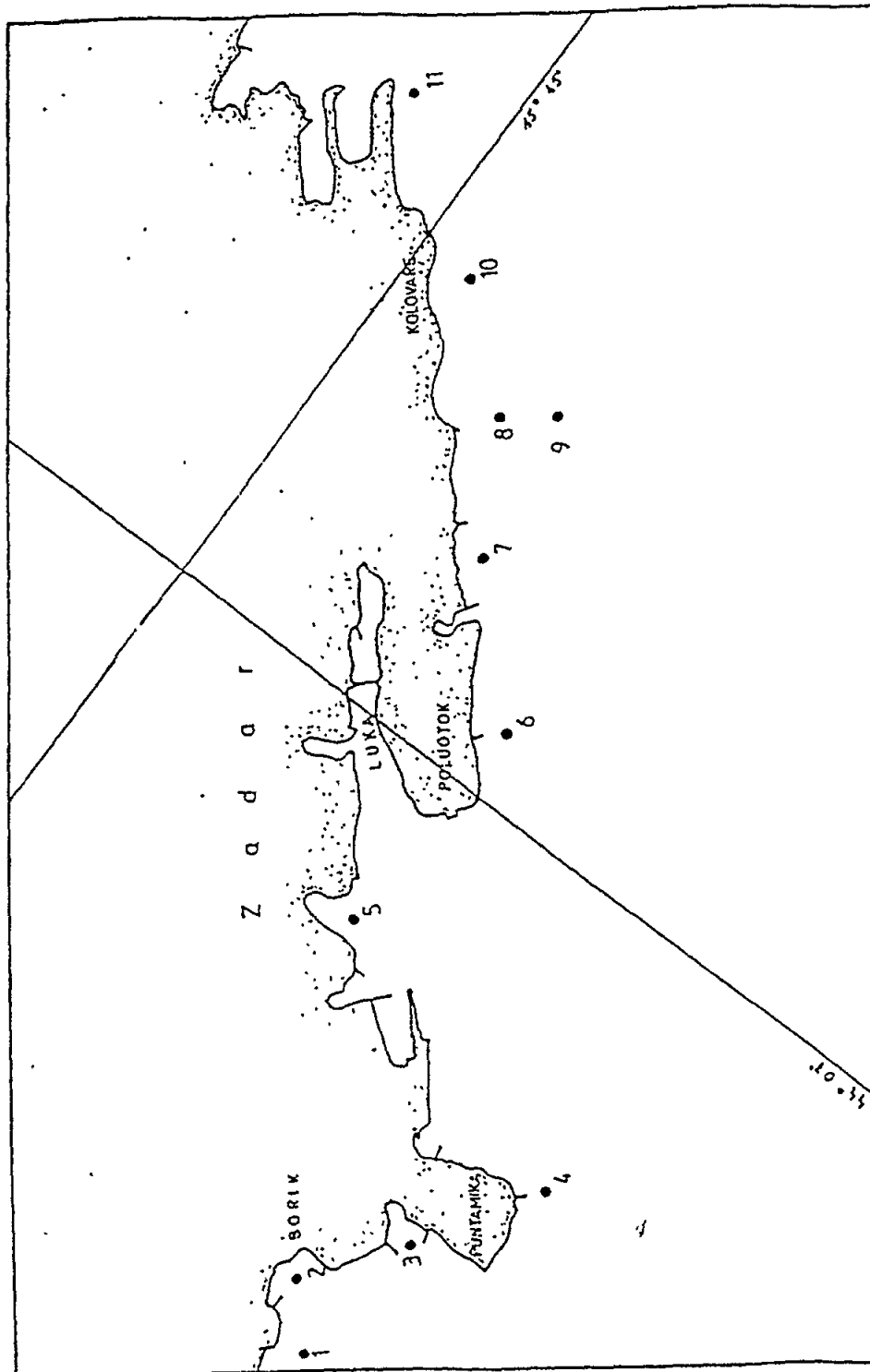


Fig. 2.3.5.2. The Zadar area - coastal water sampling stations.

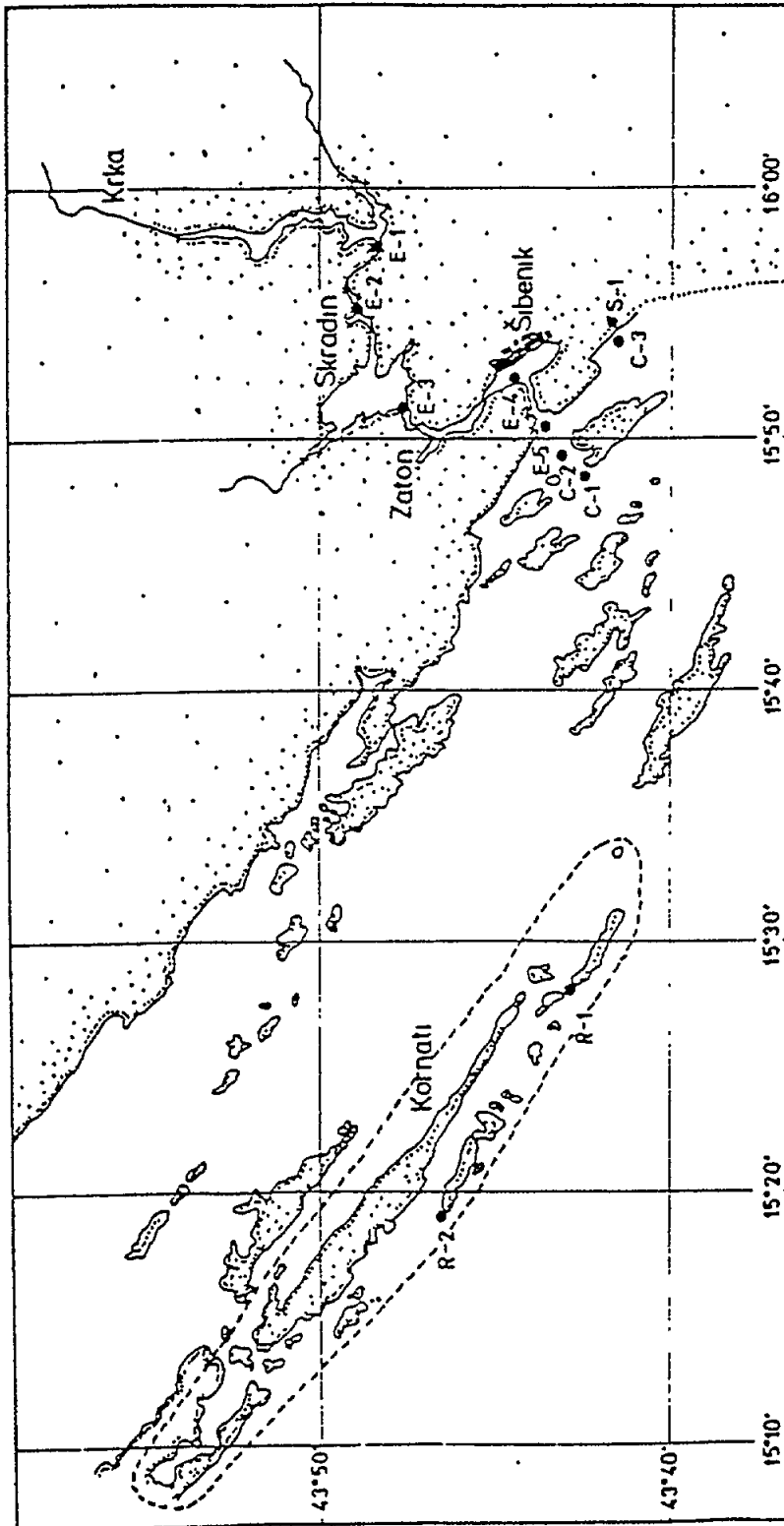


Fig. 2.3.6.1. The Šibenik area - sampling stations.

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

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

Pollution sources were monitored at the sampling point S-1 in the light metal and food processing plant effluent outfall (Fig. 2.3.6.1).

In the monitoring of coastal waters the following stations were included (Fig. 2.3.6.1): 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 near the stations at which other parameters were determined.

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. 2.3.6.1), 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.

### 2.3.7. Split area (IOF-S and IPH-S)

About 250,000 inhabitants live in the Split urban area which is the second largest city on the eastern Adriatic coast. The Split area and the region of the southern Adriatic make a unique geographical area with common Mediterranean characteristics in respect of climate, landscape, culture and economy.

The whole coastal region is bound by the mountain massif that separates the city of Split from its hinterland. To the south of the city lie the Dalmatian islands. Dugi Otok Island is close to the Bay of Kaštela. The inner islands of Brač, Šolta and Makarska are located to the south and border the Split and Brač 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 Marjan Hill, to the east, 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 Kaštela, there is a new commercial and industrial port, cement and chemical plants, shipyards and other factories. To the north of Marjan Hill there is a well-developed, wide Kaštela plain. In several places in the coastal region extending from the city of Split to Makarska there are sheer rocks arising from the flat land.

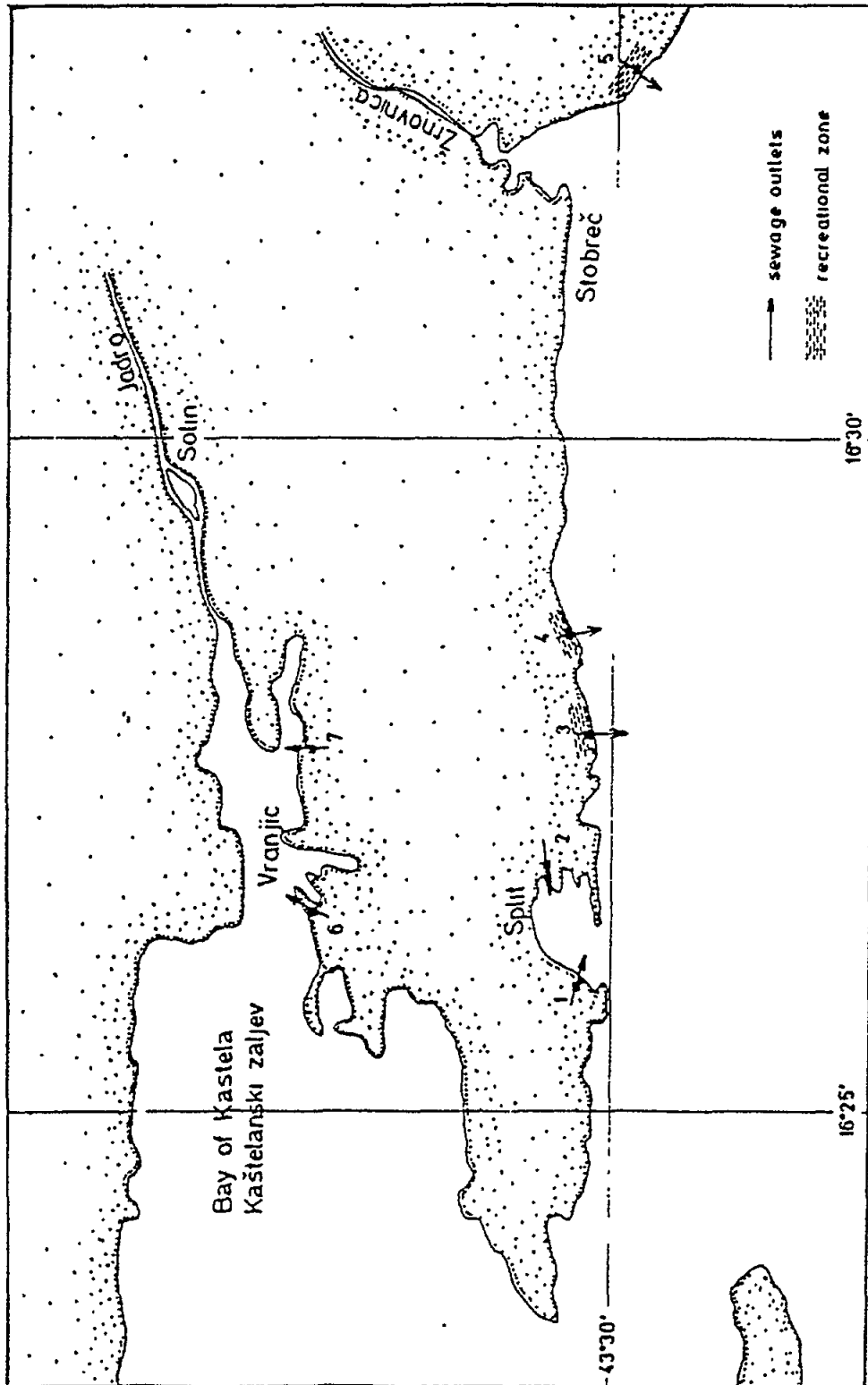


Fig. 2.3.7.1. The Split area - effluent sampling stations.

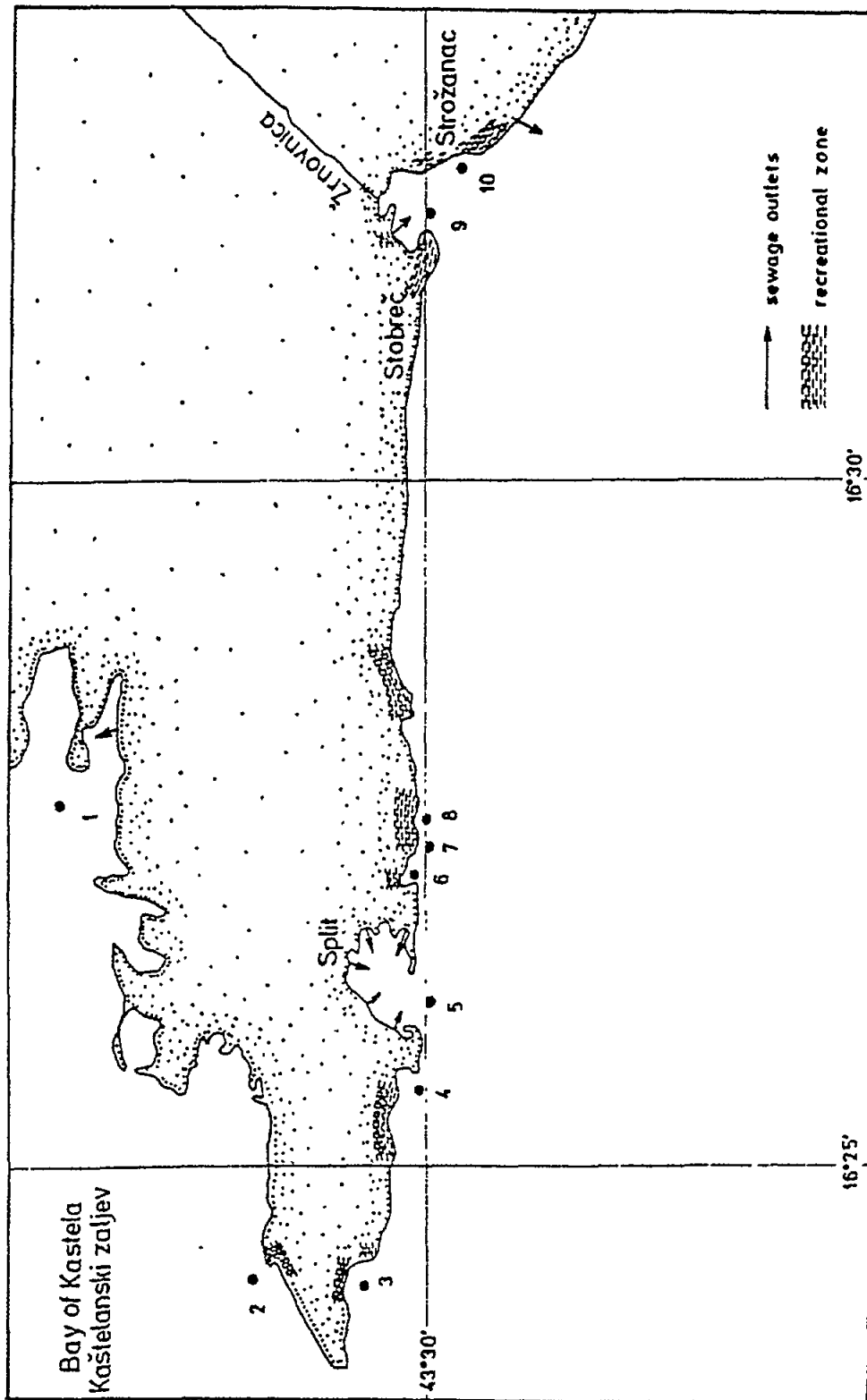


Fig. 2.3.7.2. The Split area - coastal water sampling stations.

Pollution sources were monitored (IPH-S) at 7 stations of the Split sewage system through which urban and industrial effluents are discharged (Fig. 2.3.7.1).

In the Split coastal area, investigations were carried out in the coastal sea region, from the easternmost part of the Bay of Kaštela (the Vranjic basin) to Stobreč, where the estuary of the river Žrnovica is situated. Nutrients, heavy metals, polyaromatic and chlorinated hydrocarbons were monitored to identify effects of industrial (station 1), and urban wastewaters (station 5) as well as of freshwaters in the estuarine area. On the city beaches, besides the basic hydrographic parameters, the sanitary quality of the seawater was also followed up (stations 2-4, 6-10; Fig. 2.3.7.2).

The location of the stations at which mussels (*Mytilus galloprovincialis*) were collected for chlorinated hydrocarbons investigation 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 Kaštela, on the island of Divo, where there are no significant sources of pollution.

As a reference area for all parameters an open sea station, close to the Vis of Island, was chosen (station 11; Fig. 2.3.7.3).

#### 2.3.8. The Klek-Neum area (IOF-S)

The Klek-Neum area represents a separate part, ca. 8 km<sup>2</sup>, of Maloston Bay and Malo More (Fig. 2.3.8.1). On the relatively steep coast, ca. 25 km in length, and rich in vegetation, two bigger settlements - Klek and Neum - are located. The area around Maloston Bay because of its natural characteristics is particularly favourable for shellfish cultivation, and for this reason it was proclaimed by FAO/UNEP as one of the pilot areas for the development of shellfarming on the Mediterranean. In the Klek-Neum area tourism is intensively developing (12,000 tourists can be accommodated), and therefore for the preservation of the sea quality in the Bay, adequate for shellfish cultivation, a proper disposal of urban sewage waters is very important.

For pollution monitoring at four stations water is controlled, and at one station mussels (station 1) are controlled for faecal coliforms presence. At station 3, hydrographical parameters and nutrients are controlled, and in mussels and sediment Cd and Hg measured.



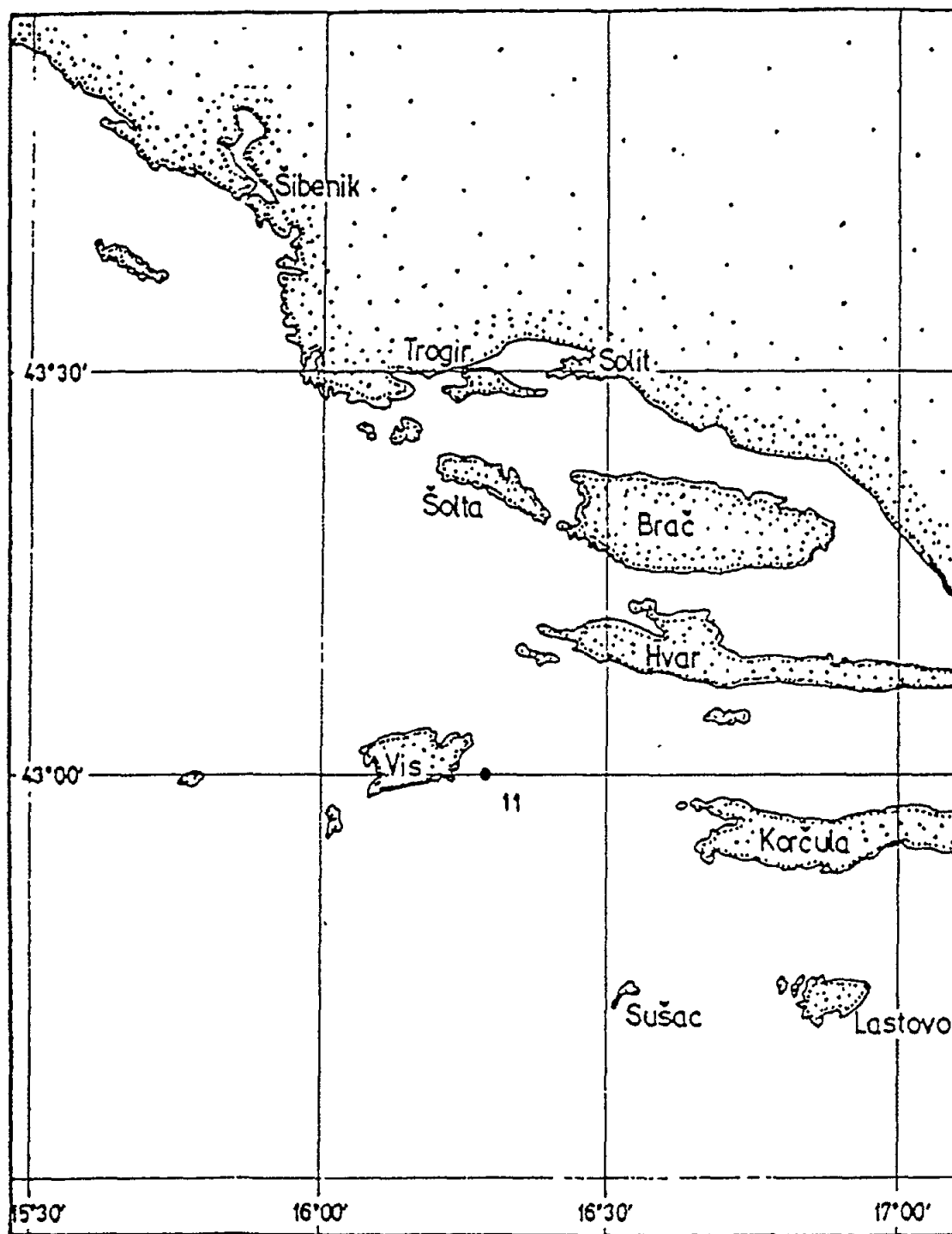


Fig. 2.3.7.3. The Split area - referent sampling stations.

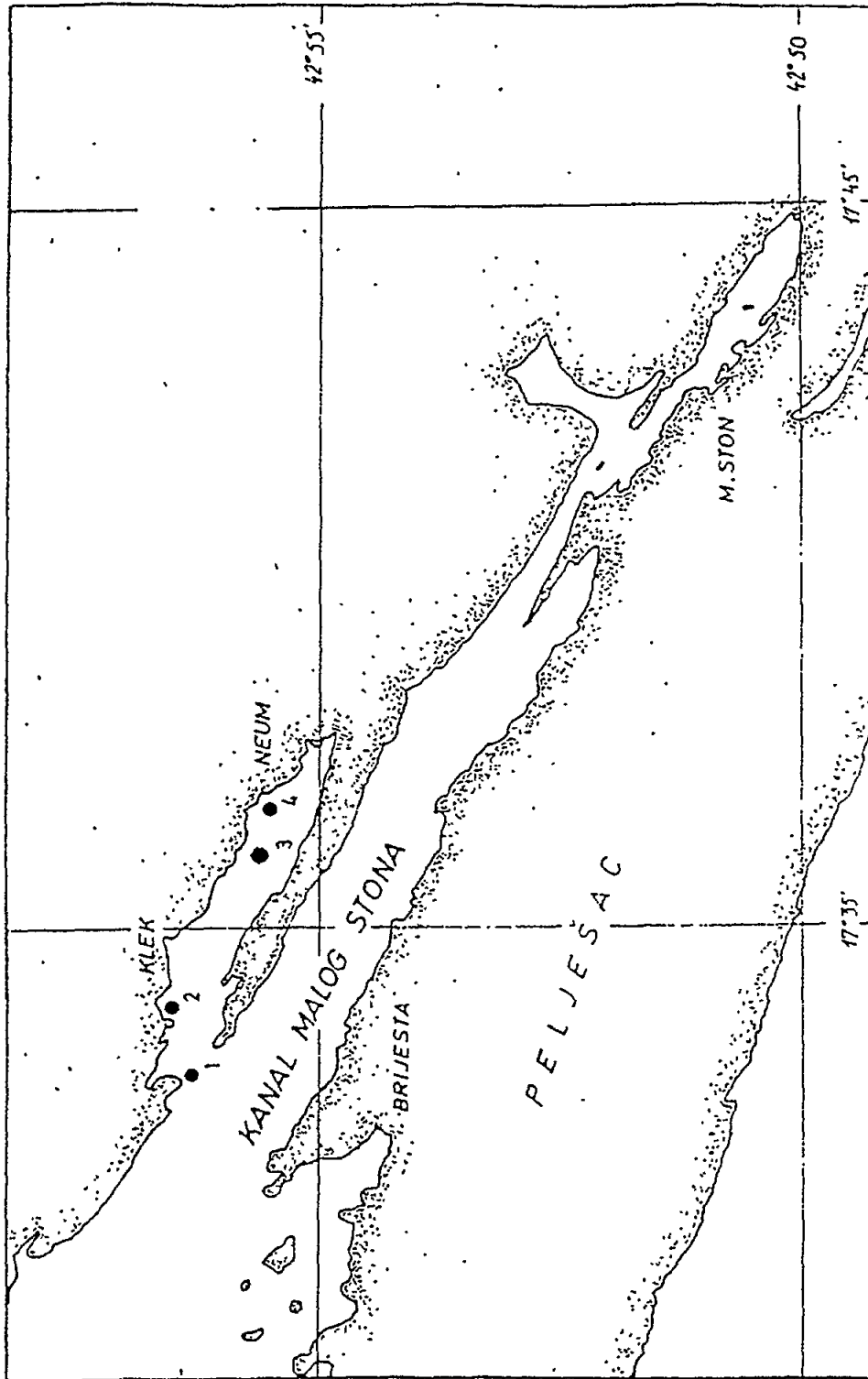


Fig. 2.3.8.1. The Klek-Neum area - sampling stations.

### 2.3.9. Dubrovnik area (BI-D)

The Dubrovnik area covers Maloston Bay, the Pelješac Channel and the area of the town of Dubrovnik with 30,000 inhabitants.

The continental area near the coast is built of highly permeable limestone mass, which has specific hydrogeological characteristics and causes intensive drainage towards the sea through swallow holes and submarine springs during the rainy periods. The transport of allochthonous inorganic and organic materials is especially intensive in the Maloston 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 of 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 the monitoring samples were taken in three areas (at 5 stations): in Maloston Bay, the Pelješac Channel, near the town of Dubrovnik and Cavtat (Fig. 2.3.9.1). Station 1 at Bistrina, an inlet of Maloston 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 of the Neretva River. In the Maloston Bay area a stronger influence of underground freshwaters 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 (Orebiæ) is influenced by a strong current that comes from the south and brings clean oligotrophic eastern Mediterranean and south Adriatic water towards the middle and north Adriatic region. Station 3 is situated on the eastern coast of the island of Daksu near 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 metals and chlorinated hydrocarbons pollution. Station 4 and 5 are near several tourist centres, but are strongly influenced by the open sea waters.

### 2.3.10. Montenegrin coastal area (IBM-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 inland by Orjen, Lovćen and Rumija mountains. Its width is only 10 km in the region of Boka Kotorska and Ulcinj while at Budva is even less than 2 km.

Near 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 Boka Kotorska cuts deeply into the coast.

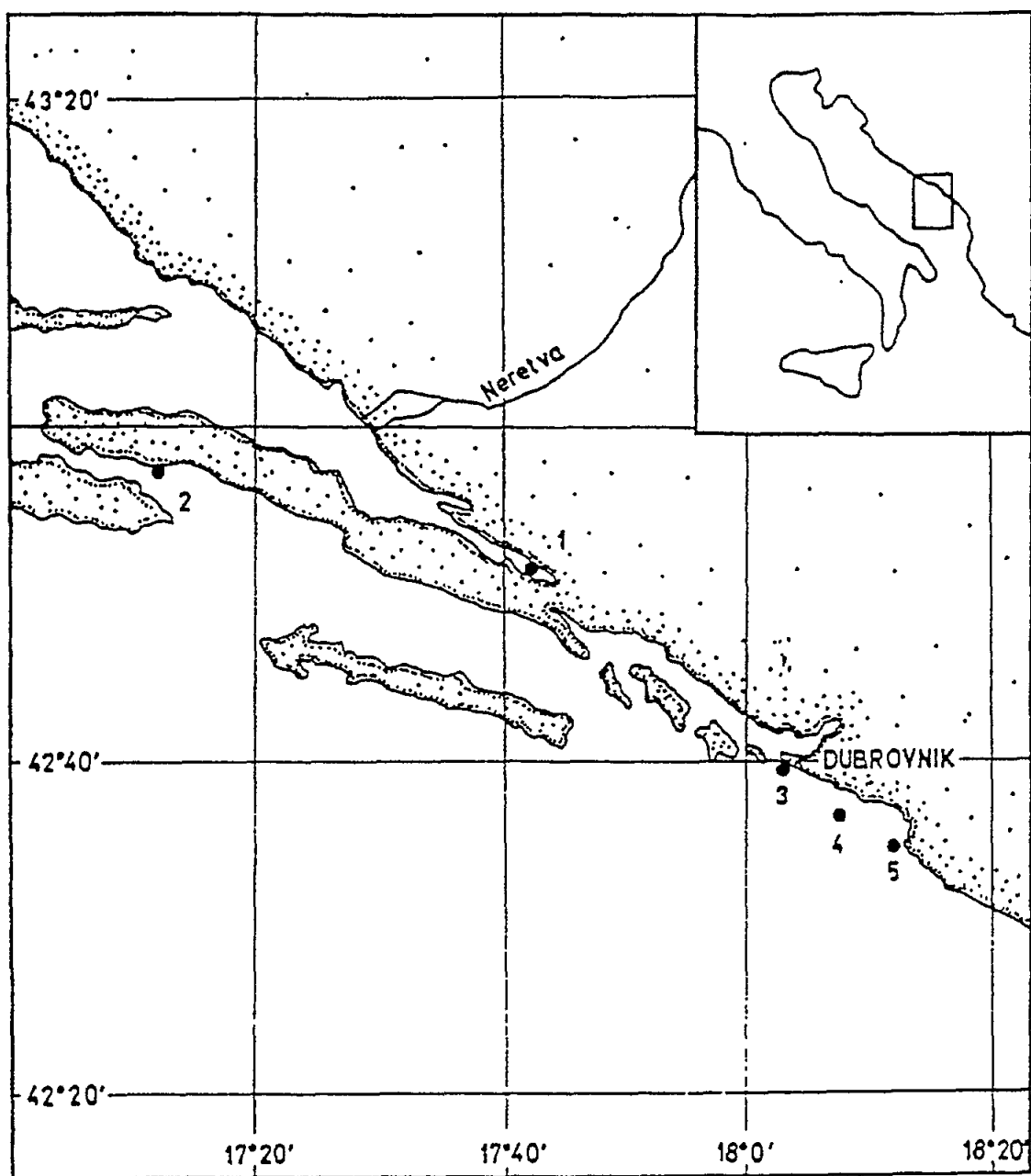


Fig. 2.3.9.1. The Dubrovnik area - sampling stations.

Due to the recent intensive economic development, the coastal region is almost completely urbanized. At present the resident population stands at 120,000, the number doubling in summer during the tourist season.

In the waters of Boka Kotorska (Fig. 2.3.10.1) measurements were carried out off Igalo (station 1) in the entrance zone of the bay, in which open waters mix with 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 I, 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 Sv. Stefan Island (station 6; Fig. 2.3.10.1) the influence of land is minimal.

In the Bar region (Fig. 2.3.10.2) 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 town harbour. The reference station II is located 3 km off Budva.

In the southernmost part of the region (Fig. 2.3.10.2) 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 is 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.

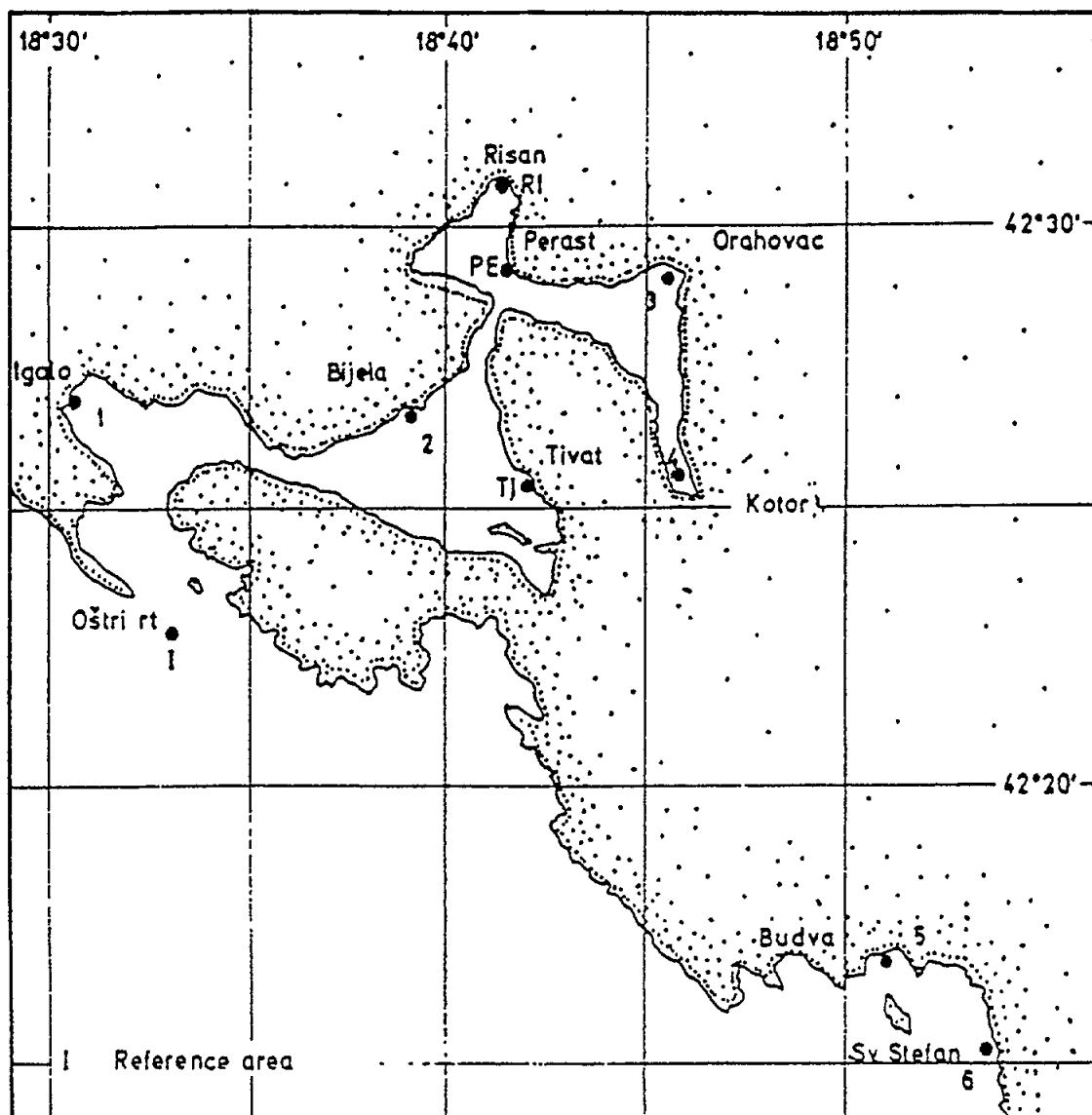


Fig. 2.3.10.1. The Montenegrin coastal area - sampling stations in the Boka Kotorska and Budva area.

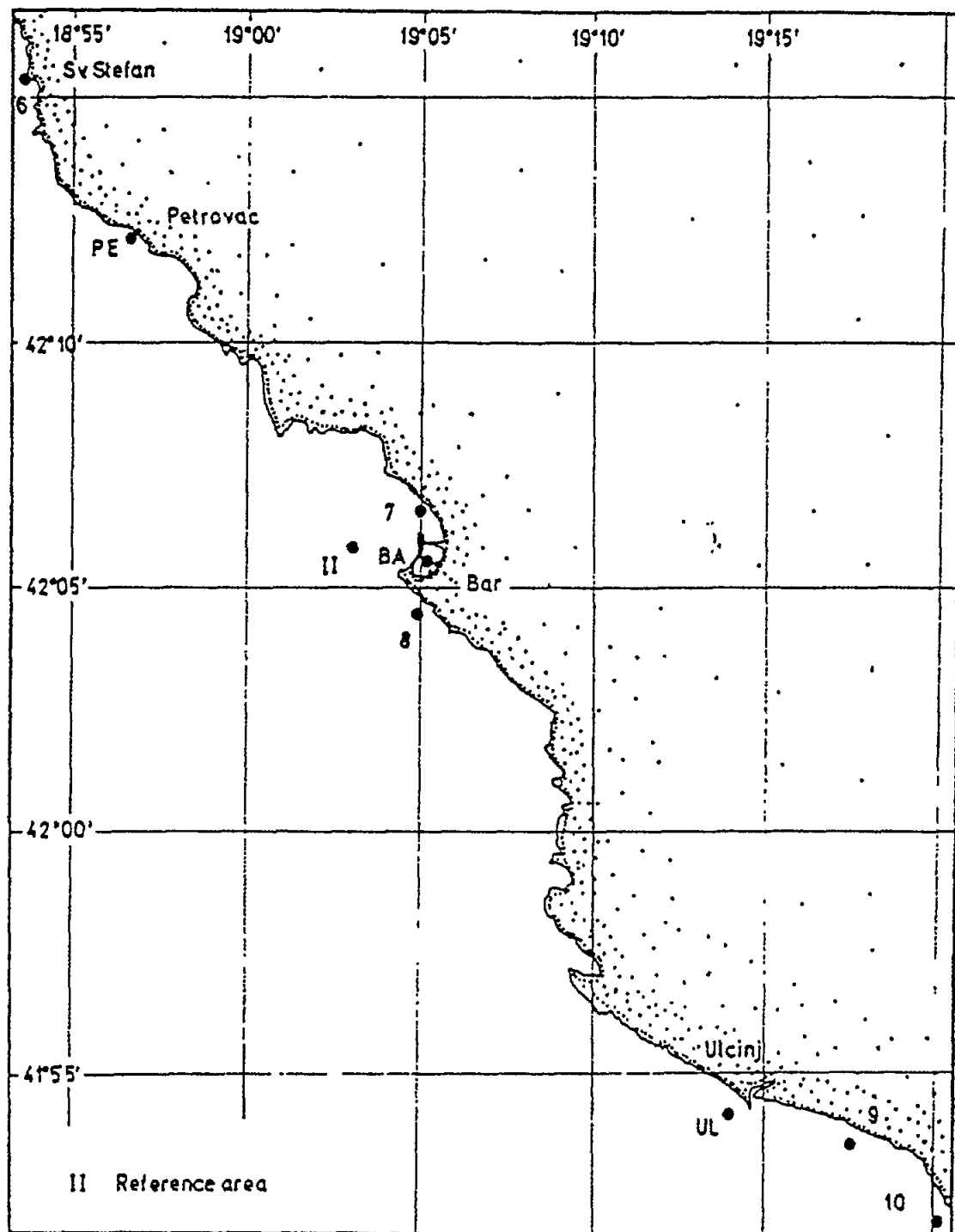


Fig. 2.3.10.2.

The Montenegrin coastal area - sampling stations in the Bar and Ulcinj area.

## **2.4. Measurements frequency**

### **2.4.1. Effluents**

Biochemical (BOD<sub>5</sub>) 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 Šibenik and Slovenian coastal area 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 Šibenik and Montenegrin coastal areas.

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

In the Rijeka, Šibenik, 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 in the Slovenian coastal, Rovinj, Pula, Rijeka, and Split areas.

### **2.4.2. Sea water**

Total nitrogen and total phosphorus in the inner part of the Limski Kanal (stations 1, 15 m; 2, 32 m) were monitored monthly from 1983-1987. These parameters were also measured seasonally in the open northern Adriatic, (5R, 37 m; 9R, 32 m). Total phosphorus was determined seasonally at the Krka River mouth (E1) and its estuary (E2-E5 and E9, 8-42 m), in the Šibenik coastal region in front of the estuary entrance (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, orthophosphate and orthosilicate) basic oceanographic parameters were determined seasonally in the above described regions, as well as at three stations in the Split region (S2, the Vranjic Bay, 22 m; S5, the Split harbour, 10 m; S9 the Žrnovica River estuary, 12 m) and at the reference station near Vis Island (S11, 100 m).

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



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

Phenols and detergents were analysed sporadically in Šibenik and Montenegrin coastal areas.

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

#### 2.4.3. Sediment

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

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

#### 2.4.4. 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 area, from one to three times in the Šibenik area and once in the Montenegrin coastal area.

Chlorinated hydrocarbons were determined seasonally in mussels from the Rovinj, Pula, Šibenik, 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 Šibenik 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 2.4.1-4. the total number of samples collected and each parameter determined in the investigated areas are resumed.

**Table 2.4.1.** Number of data of basic parameters and total nitrogen and phosphorous in the investigated areas in the period 1983-1991.

Type of samples	Parameter	Number of samples in areas								Total
		Slovenian coastal	Rovinj	Northern Adriatic	Pula	Rijeka	Zadar	Šibenik	Split+Klek-Neum	
Effluent	BOD	148	37	-	120	370	59	-	196	<b>930</b>
	COD	90	-	-	91	391	59	-	196	<b>827</b>
	TSS	147	37	-	118	410	59	-	196	<b>967</b>
	TN	148	-	-	122	396	59	-	196	<b>921</b>
	TP	148	-	-	122	396	59	-	196	<b>921</b>
Coastal water	Basin param	-	330	2020	-	-	-	4346	1689	<b>8385</b>
	Nutrients	-	258	1689	-	-	-	5202	1279	<b>8428</b>
	TN	-	236	326	24	-	-	63	-	<b>649</b>
	TP	-	258	334	24	-	-	1041	-	<b>1657</b>

**Table 2.4.2.** Number of data of Hg and Cd mass fractions in suspended matter, sediment and marine organisms from the investigated areas in the period 1983-1991.

Type of samples	Metal	Number of samples in areas										Total
		Slovenian coastal	Rovinj	Pula	Rijeka	Zadar	Šibenik	Split	Klek-Neum	Dubrovnik	Montenegrin coastal	
Suspended matter	Hg	227	-	-	-	-	-	-	-	-	-	<b>227</b>
	Cd	221	-	-	-	-	-	-	-	-	-	<b>221</b>
Sediment	Hg	58	30	15	-	14	75	44	3	2	9	<b>250</b>
	Cd	15	-	15	-	14	80	37	3	2	40	<b>206</b>
Marine organisms	Hg	81	89	65	51	26	127	79	10	87	-	<b>615</b>
	Cd	76	107	63	51	26	117	79	10	87	9	<b>624</b>

**Table 2.4.3.** Number of data of organic pollutants in the investigated areas in the period 1974-1992.

Samples and pollutants	Number of samples in areas										Total	
	Slovenian coastal	Istrain coastal	Pula	Rijeka	Zadar	Šibenik	Split	Dubrovnik	Montenegrin coastal	Northern Adriatic		Central Adriatic
Effluents												
DDT <sub>total</sub>	2	-	-	12	32	-	-	-	-	-	-	46
PCB	2	-	-	12	32	-	-	-	-	-	-	46
Phenols	-	-	112	332	45	-	194	-	-	-	-	683
Detergents	130	-	112	382	45	-	196	-	-	-	-	865
Petr.hydr.	-	-	-	62	-	ag	196	-	-	-	-	267
Seawater												
Phenols	-	-	-	-	-	-	-	-	30	-	-	30
Detergents	-	-	-	-	-	11	-	-	-	-	-	11
Petr.hydr.	-	-	-	-	-	79	72	-	64	153	-	368
Oil slick and other floating materials	-	-	-	719	-	-	-	-	-	-	-	719
Sediment												
DDT <sub>total</sub>	-	73	20	51	8	30	-	14	19	60	12	287
PCB	-	73	20	50	8	30	-	14	19	60	12	286
Petr.hydr.	-	-	-	-	-	30	20	-	5	81	12	148
Organisms												
DDT <sub>total</sub>	-	130	68	79	39	23	64	74	16	-	-	493
PCB	-	131	68	79	39	23	63	74	16	-	-	494
Petr.hydr.	-	-	-	-	-	23	-	-	6	96	-	125

<sup>a</sup> as polyaromatics

**Table 2.4.4.** Number of microbial pollution data in effluents, seawater and marine organisms from the investigated areas in the period 1983-1991.

Type of samples	Number of samples in areas										Total
	Slovenian coastal	Rovinj	Pula	Rijeka	Zadar	Šibenik	Split	Klek-Neum	Dubrovnik	Montenegrin coastal	
Effluent	146	58	121	439	64	-	195	-	-	-	<b>1023</b>
Seawater	3275	945	1128	1387	506	375	915	45	-	570	<b>9146</b>
Marine organisms	58	185	68	52	32	-	98	9	-	-	<b>502</b>

### 3. RESULTS AND DISCUSSION

#### 3.1. Basic parameters, nitrogen and phosphorus

##### 3.1.1. Basic chemical characteristics, total nitrogen, and total phosphorus in effluents

Effluent monitoring has been conducted since 1983 in several regions at 45 temporary or permanent sampling stations: 11 in the Slovenian (MBS-P), 2 in the Rovinj (CMR-R), 7 in the Pula (IPH-P), 14 in the Rijeka (FCES-Z and FCET-Z), 4 in the Zadar (IPH-Z), and 7 in the Split coastal areas (IPH-S). Over 700 samples were collected and analysed in the period 1983-1991. The average annual discharge rate of the investigated effluents (sewages and industrial wastewaters) varied over a large range ( $0.04\text{--}410 \cdot 10^6 \text{ m}^3 \text{ a}^{-1}$ ; Table 3.1.1.1).

Arithmetic means and standard deviations were calculated from basic chemical parameters ( $\text{BOD}_5$ , COD and TSS), total nitrogen, and total phosphorus data obtained in the period 1984-1991 at each effluent sampling station (Table 3.1.1.2). The annual discharge rates of sewages (Fig.3.1.1.1 and Table 3.1.1.3) and industrial effluents (Table 3.1.1.4) in each investigated area were calculated from these means.

A high data variability was observed for the basic chemical parameter ( $\text{BOD}_5$ , COD and TSS), total nitrogen and total phosphorus concentrations in sewages and industrial wastewaters of the major Adriatic urban centres (Table 3.1.1.2). However,  $\text{BOD}_5$  values in sewages were relatively more homogeneous between stations within an area than between different areas. As an example, the lowest variability was observed for  $\text{BOD}_5$  (but also for the other parameters) between the seven sampling points in the Split area (Tables 3.1.1.2), for which the lowest mean value was calculated ( $137.4 \text{ mg dm}^{-3}$ ; Table 3.1.1.3). A relatively low variability and mean value ( $153.5 \text{ mg}$ ) was also found in the Piran area (Table 3.1.1.3). In contrast, the highest mean  $\text{BOD}_5$  values were obtained for the Pula ( $386.3 \text{ mg dm}^{-3}$ ) and Opatija ( $519.6 \text{ mg dm}^{-3}$ ) sewages. In the Izola, Koper, and Medulin sewages intermediate  $\text{BOD}_5$  levels were measured (Table 3.1.1.2).

The chemical characteristics varied more markedly in industrial wastewaters than in sewages, depending on the technological process and relative contribution of biodegradable organic matter. In the wastewaters under the influence of cannery factories at Izola, Rovinj and Ika the average organic load was higher ( $560.8$ ,  $514.6$ , and  $691.5 \text{ mg dm}^{-3}$ , respectively) than in sewages. On the contrary, the  $\text{BOD}_5$  values in the oil refinery (I2, Rijeka) wastewater were significantly lower than in sewages (Table 3.1.1.2 and 3.1.1.4).

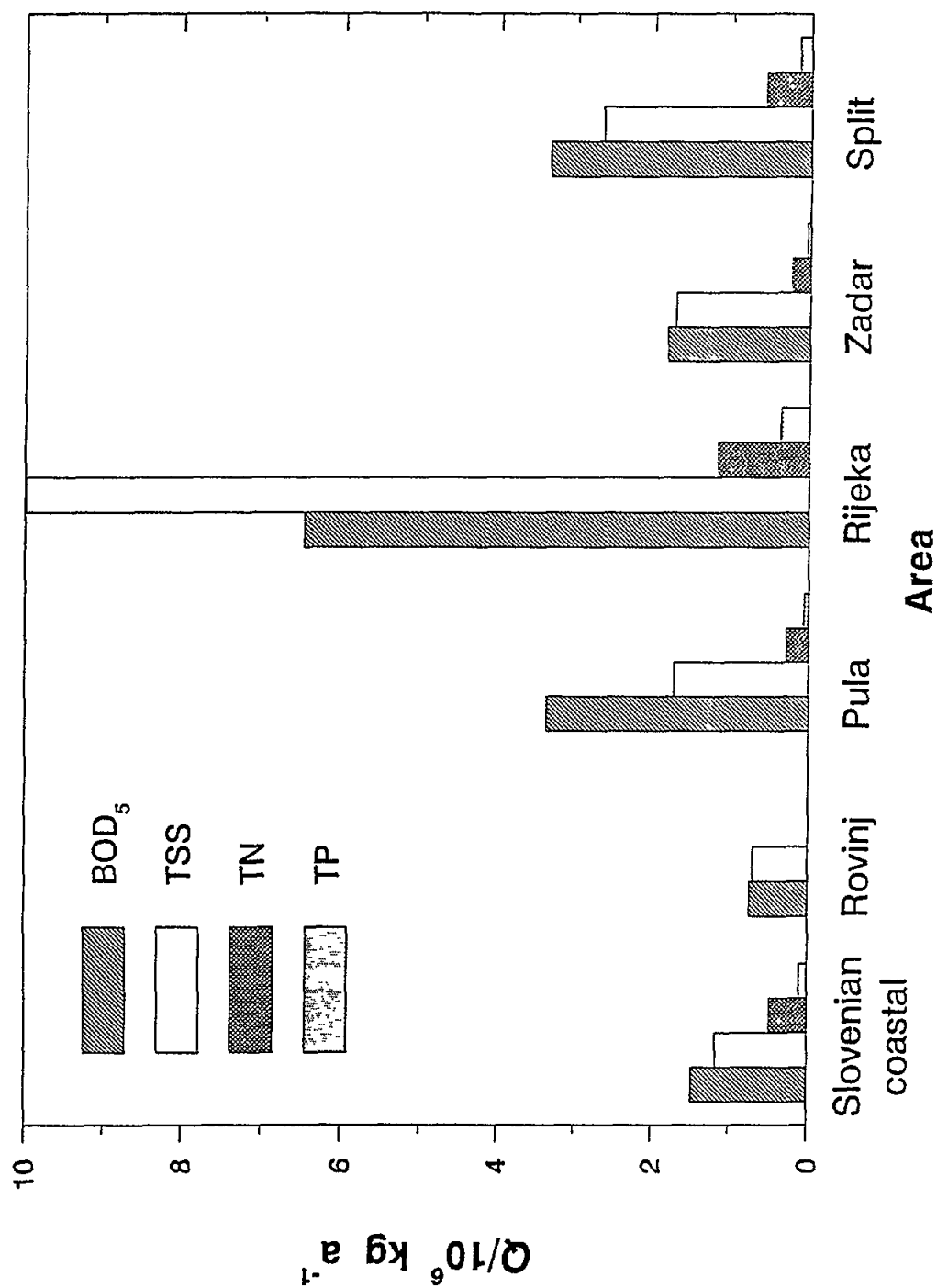


Fig. 3.1.1.1. Annual average discharge rates ( $Q$ ) of biological oxygen demand (BOD<sub>5</sub>), total suspended solids (TSS), total nitrogen (TN), and total phosphorous (TP) in urban effluents from different areas.

**Table 3.1.1.1.** Average annual discharge rate (Q) of investigated effluents (see interested area description for effluent code in chapter 2.3 of this Report).

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Area	Effluent code	Q/10 <sup>6</sup> m <sup>3</sup> a <sup>-1</sup>
))))))))))))))))))		
Slovenian coastal	PA	3.80
	PB	1.00
	IA	0.11
	KA	0.27
	KB	4.40
	BA	63.00
	DE	0.70
	DN	16.00
	DR	30.00
	RI	147.00
Pula	I	4.50
	II	48.00
	SI	0.90
Rijeka	U1	3.20
	U2	0.21
	U3	0.79
	U4	3.15
	U5	0.28
	U6	18.90
	U7	409.97
	U8	0.94
	U9	0.22
	U10	0.79
	U11	2.84
	U12	0.19
	I1	0.04
	I2	1.58
Split	1	2.10
	2	4.90
	3	2.20
	4	2.10
	5	0.08
	6	3.30
	7	3.10
Zadar	I1	5.50
	I2	4.90
	I3	61.30
	I4	3.30
))))))))))))))))))		



**Table 3.1.1.2.** Concentration (c) of organic matter expressed as biological (BOD<sub>5</sub>) and chemical (COD) oxygen demand, total suspended solids (TSS), total nitrogen (TN), and total phosphorous (TP) in sewages and some industrial wastewaters discharged into the sea along the eastern Adriatic coast (N= number of samples,  $\bar{c}$ = average values; std= standard deviation).

Area			Samp. Orig.			c(BOD <sub>5</sub> )/mg dm <sup>-3</sup>			c(COD)/mg dm <sup>-3</sup>			c(TSS)/mg dm <sup>-3</sup>			c(TN)/mg dm <sup>-3</sup>			c(TP)/mg dm <sup>-3</sup>		
Locality			code			N	c̄	std	N	c̄	std	N	c̄	std	N	c̄	std	N	c̄	std
Slovenian coastal																				
Piran			PA	U	17	86.4	76.3	4	71.5	123.0	17	75.9	76.9	17	20.8	11.2	17	4.9	3.2	
Piran			PB	U	17	156.2	91.8	4	275.0	530.0	17	97.9	132.1	17	37.0	19.4	17	7.1	4.3	
Izola			IA	U	17	240.0	84.4	11	84.8	112.0	16	141.3	166.0	17	51.8	52.5	17	13.4	14.9	
Izola			IB	U	3	202.7	241.6	2	412.5	569.2	3	180.5	145.3	3	105.8	106.1	3	17.0	13.6	
Koper			KA	U	7	123.3	98.7	4	258.8	265.5	7	120.1	56.9	7	58.8	60.2	7	11.0	9.3	
Koper			KB	U	9	112.3	68.4	2	10.0	0.0	9	114.5	124.3	9	25.8	9.6	9	6.8	3.1	
Badaševica			BA	Ri	14	6.1	2.6	14	328.0	328.0	14	13.3	23.9	14	3.3	2.6	14	0.3	0.2	
Izola			DE	I	16	560.3	485.7	15	907.6	921.2	16	244.2	240.1	16	49.6	22.6	16	14.5	13.1	
Drnica			DN	Ri	14	4.9	3.5	13	270.9	346.3	14	11.5	20.0	14	3.0	2.0	14	0.2	0.2	
Dragonja			DR	Ri	17	2.1	0.9	16	82.1	106.3	17	17.4	33.3	17	1.3	0.7	17	0.2	0.1	
Rižana			RI	Ri	17	26.3	69.8	5	76.1	44.1	17	23.1	34.7	17	1.3	0.5	17	0.2	0.1	
Rovinj																				
Fish.proc.plant			5AI	U	18	514.6	280.9	-	-	-	18	512.9	595.7	-	-	-	-	-	-	
Tabacco fact.			6AI	U	19	187.6	161.0	-	-	-	19	145.3	86.4	-	-	-	-	-	-	
Pula																				
Pula harbour			I	U	29	429.5	172.6	25	575.3	162.8	29	218.9	208.1	29	34.7	22.9	29	7.8	5.2	
Medulin harbour			II	U	27	343.1	192.7	16	448.2	254.7	28	174.2	124.0	28	29.8	23.1	28	5.5	4.2	
Siporex			SI	I	24	252.3	165.0	10	263.2	200.3	24	283.5	311.3	24	13.3	10.9	24	3.9	12.0	
Pula			5	U	4	322.6	223.1	4	688.7	56.5	4	316.0	85.0	4	49.9	13.8	4	8.0	1.1	
Pula			10	U	4	239.8	111.2	4	369.5	194.5	4	96.5	105.4	4	33.5	14.4	4	5.4	1.0	
Pula			13	U	4	3.5	2.4	4	19.9	12.0	4	73.8	25.0	5	2.7	1.2	5	0.1	0.1	
Raša			RA	Ri	28	5.0	6.2	28	298.9	436.9	25	49.6	48.8	28	1.9	2.4	28	0.4	1.5	

Table 3.1.1.2. continued

ANALIZA KVALITETA VODE U RJEČIŠTU I OKOLIŠU																	
Area	Samp.	Orig.	c(BOD <sub>5</sub> )/mg dm <sup>-3</sup>			c(COD)/mg dm <sup>-3</sup>			c(TSS)/mg dm <sup>-3</sup>			c(TN)/mg dm <sup>-3</sup>			c(TP)/mg dm <sup>-3</sup>		
Locality	code		N	ĉ	std	N	ĉ	std	N	ĉ	std	N	ĉ	std	N	ĉ	std
Rijeka																	
Opatija	U1	U	27	519.6	207.6	29	996.9	449.9	30	380.6	156.3	29	78.9	51.5	29	35.9	31.9
Children clinic	U2	U	25	200.1	76.8	26	354.1	125.2	27	180.8	99.4	27	39.6	27.1	27	16.3	12.1
Kantrida shipyard	U3	U	25	326.6	156.2	26	559.1	291.4	28	318.2	292.4	27	58.0	37.4	27	19.1	14.4
Mlaka	U4	U	27	308.4	102.7	29	588.2	223.0	30	275.4	163.7	28	60.8	35.9	28	15.4	7.4
Customs	U5	U	25	98.2	169.9	27	200.4	332.7	27	357.2	1303.9	27	19.4	15.3	27	5.7	6.8
Brajdica	U6	U/I	37	269.5	289.6	39	586.0	542.6	40	257.7	173.8	39	26.4	30.5	39	10.4	20.8
Rječina	U7	U	27	14.6	14.9	24	42.1	28.8	30	43.1	53.9	27	9.1	22.7	29	2.5	2.3
Martinšćica	U8	U	25	387.2	311.6	27	701.7	405.5	28	331.7	383.5	27	60.9	43.6	26	29.7	71.3
Bakar	U9	U	25	547.9	303.3	27	965.4	570.6	28	2788.7	12128.8	27	127.2	122.0	27	22.8	18.5
Kraljevica	U10	U	25	417.4	165.8	27	774.1	294.8	28	333.3	158.1	27	87.3	58.5	27	22.2	13.0
Crkvenica	U11	U	27	331.9	218.5	28	638.4	333.5	30	355.9	347.0	29	62.0	80.7	29	14.7	6.4
Omišalj	U12	U	23	259.3	151.7	26	511.3	258.2	27	269.8	192.0	26	43.4	23.0	26	14.1	10.7
Ika	I1	I	26	691.5	439.1	29	2519.8	4264.5	30	527.2	829.3	29	110.2	79.7	29	27.4	27.7
INA Urinj	I2	I	26	74.8	103.9	27	218.7	287.6	27	120.4	376.3	27	28.4	34.8	26	3.5	3.9
Zadar																	
Maraska	I1	I	15	372.9	460.1	15	679.7	964.3	15	110.5	137.5	15	6.3	7.9	15	0.6	1.2
Boris Kidrič	I2	I	15	185.7	231.5	15	658.7	588.1	15	113.1	175.9	15	15.1	17.5	15	7.3	20.2
Kolovare	I3	U	15	258.1	136.2	15	475.5	317.2	15	243.5	213.1	15	32.8	11.7	15	5.8	3.9
Kozara	I4	I	14	460.5	313.3	14	1445.9	1213.7	14	339.4	568.7	14	44.2	55.9	14	0.7	0.8
Split																	
Split harbour 1	1	U	28	165.5	119.5	28	280.8	154.5	28	90.0	114.3	28	25.6	24.1	28	5.6	4.0
Split harbour 2	2	U	28	132.7	91.7	28	234.2	137.7	28	121.6	168.7	28	25.5	20.1	28	5.7	4.3
Zenta	3	U	28	127.4	83.9	28	215.6	114.3	28	80.1	79.5	28	24.8	17.6	28	7.7	13.1
Trstenik	4	U	28	124.6	78.0	28	213.9	118.9	28	110.3	107.3	28	21.4	15.1	28	6.0	6.8
Lav	5	U	28	151.8	105.5	28	249.5	135.3	28	114.1	74.2	28	23.7	14.6	28	7.0	7.1
Lora	6	U	28	124.6	88.5	28	226.2	135.5	28	106.4	168.0	28	25.1	21.4	28	5.9	5.3
Duje	7	U	28	135.4	141.0	28	262.4	169.1	28	142.6	302.5	28	17.4	11.3	28	3.9	2.7
ANALIZA KVALITETA VODE U RJEČIŠTU I OKOLIŠU																	

**Table 3.1.1.3.** Average concentrations ( $\bar{c}$ ) and annual discharge rates ( $Q$ ) of organic matter expressed as biological ( $BOD_5$ ) and chemical (COD) oxygen demand, total suspended solids (TSS), total nitrogen (TN), and total phosphorous (TP) in urban effluents (U) from different areas.

Area	$Q(U)$ $10^6 \text{ m}^3 \text{ a}^{-1}$	$\bar{c}(BOD_5)$ $\text{mg dm}^{-3}$	$Q(BOD_5)$ $10^6 \text{ kg a}^{-1}$	$\bar{c}(COD)$ $\text{mg dm}^{-3}$	$Q(COD)$ $10^6 \text{ kg a}^{-1}$	$\bar{c}(TSS)$ $\text{mg dm}^{-3}$	$Q(TSS)$ $10^6 \text{ kg a}^{-1}$	$\bar{c}(TN)$ $\text{mg dm}^{-3}$	$Q(TN)$ $\text{kg a}^{-1}$	$\bar{c}(TP)$ $\text{mg dm}^{-3}$	$Q(TP)$ $\text{kg a}^{-1}$
Piran	9.58	153.5	1.47	-	-	121.7	1.17	50.0	478,867	10.0	96,155
Rovinj	2.11	351.1	0.74	-	-	329.1	0.69	-	-	-	-
Pula	8.73	386.3	3.37	511.7	4.47	196.6	1.72	32.2	281,301	6.7	58,337
Rijeka	18.19	356.8	6.49	667.5	12.14	549.2	9.99	64.4	1,172,213	20.1	365,149
Zadar	7.04	258.1	1.82	475.5	3.35	243.5	1.71	32.8	230,560	5.8	40,489
Split	24.35	137.4	3.35	240.4	5.85	109.3	2.66	23.3	568,433	6.0	145,404

**Table 3.1.1.4.** Average concentrations ( $\bar{c}$ ) and annual discharge rate ( $Q$ ) of organic matter expressed as biological (BOD<sub>5</sub>) and chemical (COD) oxygen demand, total suspended solids (TSS), total nitrogen (TN), and total phosphorous (TP) in industrial effluents (I) from different areas.

Area	$Q(I)$	$\bar{c}(BOD_5)$	$Q(BOD_5)$	$\bar{c}(COD)$	$Q(COD)$	$\bar{c}(TSS)$	$Q(TSS)$	$\bar{c}(TN)$	$Q(TN)$	$\bar{c}(TP)$	$Q(TP)$
Locality	$10^3 \text{ m}^3 \text{ a}^{-1}$	$\text{mg dm}^{-3}$	$10^3 \text{ kg a}^{-1}$	$\text{mg dm}^{-3}$	$10^3 \text{ kg a}^{-1}$	$\text{mg dm}^{-3}$	$10^3 \text{ kg a}^{-1}$	$\text{mg dm}^{-3}$	$\text{kg a}^{-1}$	$\text{mg dm}^{-3}$	$\text{kg a}^{-1}$
Slovenian coastal											
Delamaris (DE)	700	560.3	392	907.6	635	244.2	171	49.6	34723	14.5	10129
Pula											
Siporex (SI)	900	252.3	227	263.2	237	283.5	255	13.3	11996	3.9	3518
Rijeka											
Brajdica (U6)	31500	269.5	8490	586.0	18457	257.7	8117	26.4	832327	10.4	326930
Ika (I1)	631	691.5	436	2519.8	1589	527.2	332	110.2	69531	27.4	17309
INA Urinj (I2)	526	74.8	39	218.7	115	120.4	63	28.4	14915	3.5	1825
Zadar											
Maraska (I1)	97	372.9	36	679.7	66	110.5	11	6.3	614	0.6	53
Boris Kidric (I2)	180	185.7	33	658.7	119	113.1	20	15.1	2719	7.3	1315
Kozara (I4)	114	460.5	52	1445.9	165	339.4	39	44.2	5036	0.7	74

Similar general considerations as for BOD<sub>5</sub> can be also made for COD, TSS, N and P. Thus, BOD<sub>5</sub> value changes usually corresponded to similar changes of the other parameters. This was evident from the fairly constant values of the ratios COD/BOD<sub>5</sub>, TSS/BOD<sub>5</sub>, N/BOD<sub>5</sub> and P/BOD<sub>5</sub> (Table 3.1.1.5), with a few exceptions. Moreover, according to the rule of thumb (COD:BOD<sub>5</sub>:N:P = 200:100:5:1; Junkins *et al.*, 1983), the ratio of COD, BOD<sub>5</sub>, total nitrogen and total phosphorus in the investigated effluents is suitable for their proper biological treatment.

**Table 3.1.1.5.** Mass ratio ( $\alpha$ ) of chemical oxygen demand (COD), total suspended solids (TSS), total nitrogen (TN), and total phosphorous (TP) and biological oxygen demand (BOD<sub>5</sub>).

Area	c(BOD <sub>5</sub> ) mg dm <sup>-3</sup>	$\alpha_{\text{COD,BOD}_5}$ 10 <sup>-2</sup>	$\alpha_{\text{TSS,BOD}_5}$ 10 <sup>-2</sup>	$\alpha_{\text{TN,BOD}_5}$ 10 <sup>-2</sup>	$\alpha_{\text{TP,BOD}_5}$ 10 <sup>-2</sup>
Slovenia coastal	153.5	-	79.3	32.6	6.5
Rovinj	351.1	-	93.7	-	-
Pula	386.3	132.5	50.9	8.3	1.7
Rijeka	356.8	187.1	153.9	18.1	5.6
Zadar	258.1	184.3	94.3	12.7	2.2
Split	137.4	174.9	79.5	17.0	4.3
A rule of thumb	100.0	200.0		5.0	1.0

The wastewaters are generally discharged into the Adriatic sea without any treatment. Thus, considerable amounts of oxygen-consuming substances, suspended matter and nutrients are continuously discharged in the sea. The Rijeka wastewater appears to be the largest source of these substances compared with the effluents from other investigated areas (Table 3.1.1.3 and Fig. 3.1.1.1).

From the results obtained it is difficult to assess with sufficient reliability if long-term changes of the effluent loads occurred in the period 1983-1991. The composition variability of the effluents was typically high, as shown by diel changes (within an order of magnitude) of the COD values at one of the largest discharge points in Rijeka area (Brajčica; Fig. 3.1.1.2). This highlights the need of longer monitoring periods, with a sufficiently large number of samples of the principal effluents with different compositions.

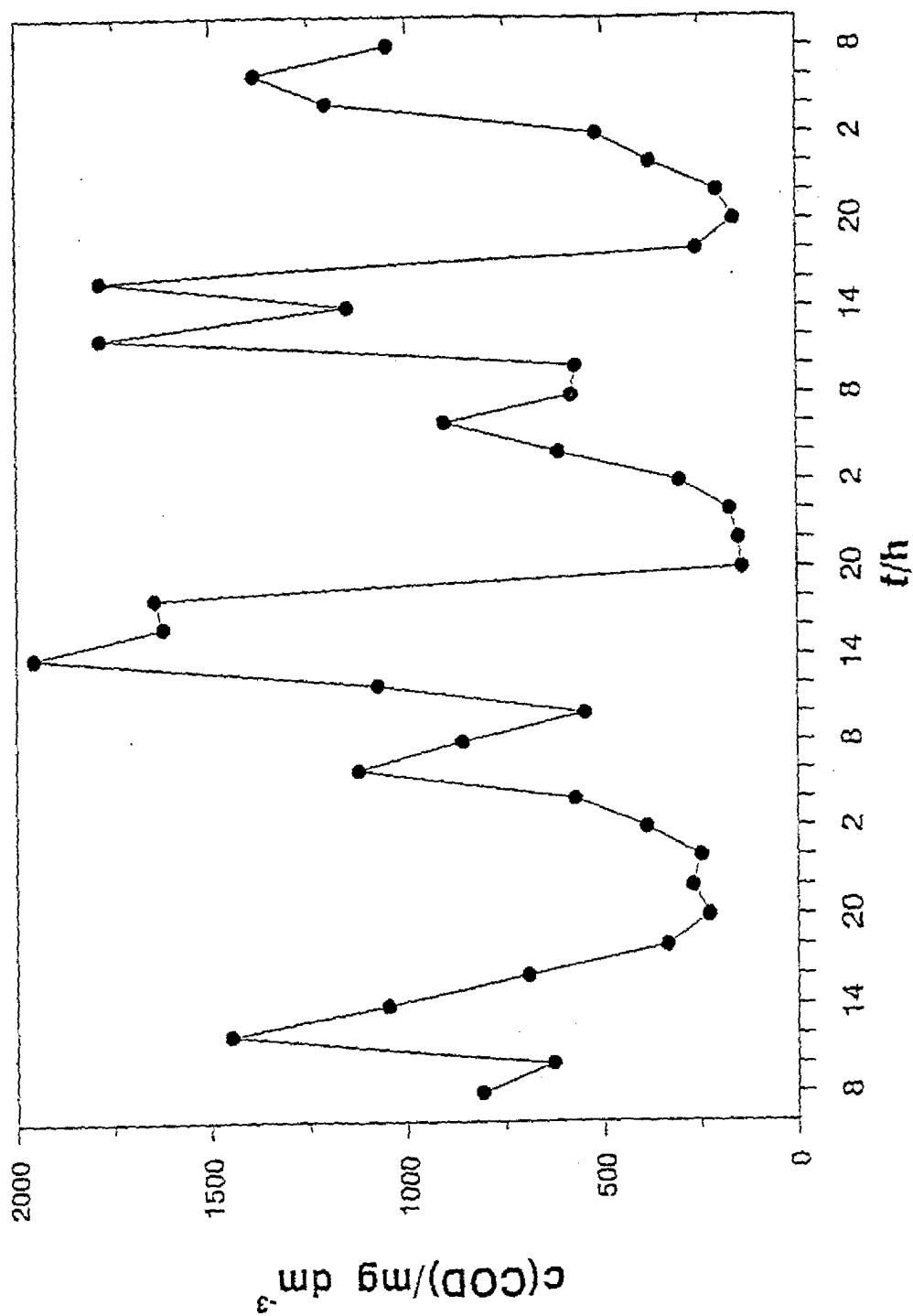


Fig. 3.1.1.2. Diel ( $t$ ) variations of organic matter concentration ( $c$ ) expressed as chemical oxygen demand (COD) at Brajdica (U6) location in the Rijeka area.

### 3.1.2. Nutrient loads in the Adriatic Sea

The computation of loads and budgets is a basic step in the study of eutrophication in a coastal sea, primarily because of the relative importance of the processes controlling the biogeochemical cycles of nutrients. For instance, the ratio of inputs vs recycling rates in the marine ecosystem is an indicator of the impact of land nutrients in a coastal area and useful to estimate its assimilation capacity. The knowledge of the anthropogenic vs natural nutrient input ratio provides useful information to select suitable protection and/or restoration measures.

No more recent nutrient load estimates than those already presented and discussed in the previous report (UNEP, 1988) were available for the Adriatic Sea as a whole. These estimates were reported in papers of Sekuliæ(1985) and Provini *et al.*, (1979). However, some data collected or published meanwhile seem to further support the assumption that the loads calculated by Sekuliæ(1985) for the eastern Adriatic were overestimated, and those for the western area underestimated. For instance, the total nitrogen and phosphorus concentrations measured in urban and industrial waters along the eastern Adriatic coast in the framework of this programme (Table 3.1.1.2.) were lower than the values assumed by Sekuliæ. On the other hand, even the higher load values reported by Provini *et al.* (1979) for the western Adriatic may be underestimated, if inorganic nutrient concentrations and loads of the Po River, the major nutrient point source in the Adriatic, were increased during the 1980s compared to the 1970s (Marchetti *et al.*, 1985, 1989; Tartari *et al.*, 1991; section 4.2 of this Report).

At a regional level nutrient load and budget calculations were improved for the northern Adriatic and the Krka Estuary area.

#### The northern Adriatic Sea

Nutrient budgets were estimated for the northern Adriatic region lying north of the line from the southernmost extension of the Istrian peninsula to the southern border of the Emilia-Romagna region (Fig. 3.1.2.1; Degobbis and Gilmartin, 1990). This region has a surface of 18,900 km<sup>2</sup> (13.6% of the total Adriatic surface), a volume of 635 km<sup>3</sup> (2% of the total Adriatic volume), and an average depth of 33.5 m. Nutrient, primary production and basic oceanographic data, collected by the Centre for Marine Research at Rovinj since 1966, as well as literature data were used in calculations.

Nitrogen, phosphorus, and orthosilicate loads were estimated separately for four major subregions (Fig. 3.1.2.1):

- A) the west Istrian coast (mainly karstic groundwater sources and a few streams in the northern part-Mirna, Dragonja, Rižana);
- B) the region from Trieste to the Po Delta (the Soèa-Isonzo, Stella, Tagliamento, Livenza, Piave, Sile, Brenta, Bacchiglione, and Adige rivers, and various drainage canals);
- C) the Po Delta; and
- E) the Emilia-Romagna coastal region (the Reno, Lamone, Ronco, Montone, and Savio rivers, and numerous streams and drainage canals).

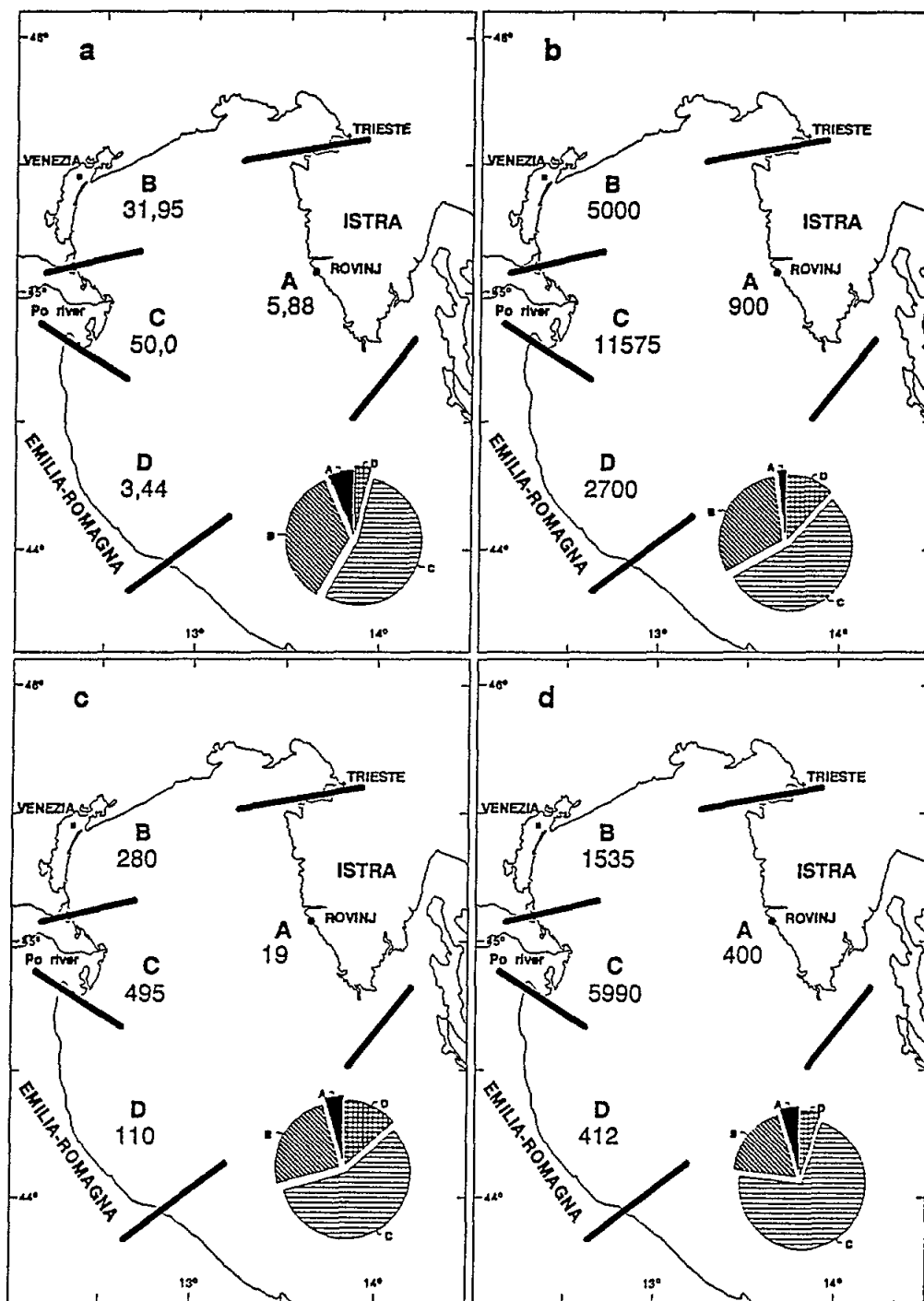


Fig. 3.1.2.1. Mean annual freshwater discharge rate ( $10^9 \text{ m}^3 \text{ a}^{-1}$ ) (a), and total nitrogen (b), total phosphorus (c) and orthosilicate (d) loads ( $10^6 \text{ mol a}^{-1}$ ) from the (A) west Istrian coast, (B) the region from Trieste to the Po Delta, (C) the Po River, and D) the Emilia-Romagna coastal region. The relative contributions of the subregions are represented by pie diagrams.



Calculations (Fig. 3.1.2.1) were based on freshwater discharge data from Cavazzoni Galaverni (1972) and nutrient concentrations in rivers, streams and karstic groundwaters described in the previous report (UNEP, 1988). Nutrient loads in urban and industrial wastewaters of the west Istrian region were based on the same methods used for the western Adriatic coast (Provini *et al.*, 1979), using demographic and other reported data (Anon., 1984). No data were available to estimate Istrian agriculture contribution. However, this activity is poorly developed along the Istrian coast, which also lacks a significant surface drainage.

Average nitrogen and phosphorus compound concentrations, measured in the period 1981-1984 (Marchetti *et al.*, 1985; Table 3.1.1 in the previous report, UNEP, 1988), and orthosilicate concentrations, obtained in 1977-1978 at two fixed stations, 70 and 90 km from the delta (Provini *et al.*, 1980), were used to estimate the Po River inorganic nutrient and total phosphorus contributions. The total loads (Fig. 3.1.2.1) were recalculated assuming that the organic fraction accounts for 26% of the total nitrogen, as suggested in Anon., (1977). These loads, calculated multiplying mean nutrient concentrations with freshwater discharge rate, were higher (up to 20% for total inorganic nitrogen and 40% for orthophosphate) than those estimated by Marchetti *et al.* (1989) for the period 1981-1984, using a more sophisticated Box and Whiskers plot techniques. More recent data (1988-1990; Tartari *et al.*, 1991; Table 3.1.2.1) suggest that actual orthophosphate load may be even lower. Recent organic nitrogen (dissolved and particulate) measurements in the Po waters (1988-1990) have shown that its percentage is 29 (Table 3.1.2.1), ie very close to the value assumed by Degobbi and Gilmartin.

The nutrient inputs in the northern Adriatic are heterogeneously distributed along the coast (Fig. 3.1.2.1). The Po River is the main nutrient point source and significantly affects the open northern Adriatic pelagic ecosystem. Its watershed is very large (75000 km<sup>2</sup>; Cati, 1981) and includes highly developed Italian regions with 15 million residents and an industry equalling an additional 40 million inhabitants (Anon., 1977). In contrast, the influence of minor rivers and groundwater sources is restricted to coastal zones. For example, Istrian freshwater discharges, mainly karstic groundwaters, account for only a small part of the total freshwater discharge into the northern Adriatic and contribute relatively less nitrogen and phosphorus compared with the heavily polluted Po River and Emilia-Romagna streams (Fig. 3.1.2.1).

Other nutrient inputs were estimated using data measured within the northern Adriatic (rainfall contributions) or literature data for similar coastal regions (nitrogen gas fixation). These inputs are probably at least an order of magnitude lower than freshwater contributions (Table 3.1.2.2).

**Table 3.1.2.1.** Nitrogen and phosphorus species mean concentrations (c) and percentages of the total N and P in the Po River in two periods of the eighties.

Species <sup>a</sup>	1981-1984 <sup>b</sup>		1988-1990 <sup>c</sup>	
	c/ $\mu\text{mol dm}^{-3}$	%	c/ $\mu\text{mol dm}^{-3}$	%
TIN	171	74	160	71
DON			38	17
PN			26	12
TN	<sup>d</sup> 231	100	224	100
PO <sub>4</sub>	4.6	46	2.7	49
DOP	0.4	4	0.3	5
PP	4.8	49	2.5	46
TP	9.8	100	5.5	100

<sup>a</sup> TIN-total inorganic nitrogen (ammonium, nitrite, nitrate), DON or DOP-dissolved organic nitrogen or phosphorus, PN or PP-particulate nitrogen or phosphorus, TN or TP- total nitrogen or phosphorus, PO<sub>4</sub>-orthophosphate (dissolved reactive phosphorus).

<sup>b</sup> Used by Degobbis and Gilmartin (1990) to calculate the nitrogen and phosphorus loads in the Po River.

<sup>c</sup> From Tartari *et al.* (1991)

<sup>d</sup> Value calculated assuming an organic and particulate nitrogen mean concentration as measured in other polluted rivers of the world (26% of TN; Anon., 1977).

Nutrient losses were evaluated mostly from data obtained for the region (Table 3.1.2.2). Water mass exchange plays a dominant role as the principal process controlling the nutrient outputs from the northern Adriatic. However, denitrification almost equals water mass exchange as a mechanism of nitrogen loss. In contrast, burial in the sediment represents a significant loss for phosphorus and orthosilicate. Other losses, ie N<sub>2</sub>O and NO production, and fish catch play only small roles in the nutrient budgets of the northern Adriatic.

The annual quantity of nutrients assimilated by phytoplankton (Table 3.1.2.2) was estimated from monthly *in situ* primary production measurements by the <sup>14</sup>C technique in the northern Adriatic, recalculated to nutrient assimilation rates considering nutrient ratios specific for the region, which differ significantly from the oceanic ratios (Degobbis, 1990b). Regeneration rates were estimated from increase in nutrients concentration and decrease of oxygen concentration in the bottom layer during periods when the layer was quasi-isolated by a strong pycnocline. Regeneration occurring in the water column was estimated by subtracting average fluxes from the sediments, measured in the Emilia-Romagna coastal region with similar sediment facies as in the entire northern Adriatic.

**Table 3.1.2.2.** Total nitrogen (TN) and total phosphorus (TP) annual budgets (*B*) for the northern Adriatic Sea (Modified from Degobbi and Gilmartin, 1990).

	$B(TN)$ $10^6 \text{ mol a}^{-1}$	%	$B(TP)$ $10^6 \text{ mol a}^{-1}$	%
<i>Inputs</i>				
Po River	11575	49	495	55
Minor rivers and wastewaters	8600	36	409	44
Rainfall	3300	14	10	1
N <sub>2</sub> fixation	135	1	-	-
TOTAL	23610	100	914	100
<i>Outputs</i>				
Water transport	9220	54	430	59
Denitrification in sediments	7100	42	-	-
Burial in sediments	260	1.5	260	36
Fish catches	370	2	40	5
N <sub>2</sub> O and NO production	200	1	-	-
TOTAL	17150	100	730	100
<i>Recycled</i>				
Assimilated	21300		600	
Regenerated				
in the water column	26900-35900		780-1040	
released from sediments	2500		25	

The results suggested that different nutrient species are regenerated in the northern Adriatic by different mechanisms. Orthosilicate is probably regenerated almost entirely at the sediment-water interface from silica frustules, produced by diatoms, and other phytoplankton and protozoan species, which sedimentation rates are expected to be relatively higher to their dissolution rates. This assumption was supported by a recent seasonal study of relationships between orthosilicate and biogenic silica concentration changes in the water column of the northern Adriatic (Lonèar, 1992). In contrast, nitrogen and phosphorus are mostly regenerated in the water column during the sinking of organic matter, mainly by a microheterotrophic (bacterial and protozoan) food web (Degobbi, 1988).

Concluding, the described calculations pointed out, on a quantitative basis, the important role of nutrient input for the northern Adriatic ecosystem. Total nitrogen and phosphorus inputs from all sources (mostly anthropogenic) approximate nitrogen and phosphorus quantities that are annually recycled in the northern Adriatic ecosystem (Table 3.1.2.2). Such a ratio is rarely encountered, even in heavily polluted estuaries (Nixon, 1981; Kemp *et al.*, 1982) and indicates that the northern Adriatic ecosystem is especially sensitive to seasonal and long-term

variations of eutrophication pressure. Furthermore, a N/P recycling rate ratio of 29 (calculated after denitrification rates were subtracted; Degobbi, 1988) would show a phosphorus limitation of primary production at the ecosystem level (Smith, 1984).

### The Krka Estuary and Šibenik Bay

The Krka River estuary (central Adriatic Sea; Fig. 2.3.6.1), with a surface area of 21.3 km<sup>2</sup>, and a volume of 0.3 km<sup>3</sup> extends 25 km into the heartland of the karstic Dalmatia region of Croatia. The extremely variable freshwater inflow to the estuary is mainly due to the 72 km long Krka River (with a watershed of 2,088 km<sup>2</sup>) in the uppermost part of the estuary (5-550 m<sup>3</sup> s<sup>-1</sup>; Hydrological Bulletins of the Hydrometeorological Institute of Croatia, Annual Reports, 1988, Zagreb). In its last tract the Krka River is considerably widened (up to 1500 m), and receives the Ćikola effluent. River waters enter the estuary through the Skradinski Buk waterfalls. Other minor freshwater sources are the Guduća Creek and the much smaller Ljuljeva and Mokrica creeks in the northernmost part of the Prokljan Lake. In addition, the Jaruga Stream and a series of small karstic groundwater springs discharge waters into the estuary reach that extends from the waterfalls to the town of Skradin. The discharge rates of these minor freshwater sources are not known, but probably are not significant compared to the Krka River inflow. The terrigenous input is low: the average sedimentation rate in the Prokljan Lake is 0.12 mm a<sup>-1</sup> (ranging from 0.06-0.27 mm a<sup>-1</sup>; Juračić 1987).

The estuary receives nutrients from various sources, especially those concentrated in the Šibenik area (UNEP, 1988; B. Sekulić personal communication). Untreated sewages from a local population of 39,000 (38,000 in Šibenik and 1,000 in Skradin), and from an additional tourist population of about 2,000 inhabitant equivalents, were discharged directly to the estuary and coastal sea. In addition, wastewaters from the Knin urban area (40 km from the estuary, 10,000 inhabitants), and Drniš area (20 km from the estuary, 4,000 inhabitants), including a pig farm, were discharged into the estuary tributaries (Krka River and Ćikola Creek). A marina in Skradin (upper estuary) had a capacity of up to 200 boats. In the Šibenik area (lower estuary), moderate port activities, including the unloading of phosphate ores, occurred. In this area industrial wastewater discharges into the estuary and coastal sea amounted to 6·10<sup>6</sup> m<sup>3</sup> a<sup>-1</sup>.

Nutrient enrichment, particularly marked for phosphorus in Šibenik Bay (section 3.1.3 of this report), can be related to direct anthropogenic discharges into the estuary. These discharges were estimated and compared with nutrient inputs from the Krka River and other freshwater sources (Fig. 3.1.2.2). The same methodology adopted by Gržetić *et al.* (1991) was followed, but the most recent data collected in the framework of this project were used (Table 3.1.2.3).

The Krka River represents the largest freshwater source in the investigated area. Nutrient concentrations in this river were on average several times lower than in other Adriatic karstic rivers and groundwaters, which are under anthropogenic influence, and at least one order of magnitude lower than in the heavily polluted Po and Adige rivers (Table 3.1.1 in the previous report; UNEP, 1988).

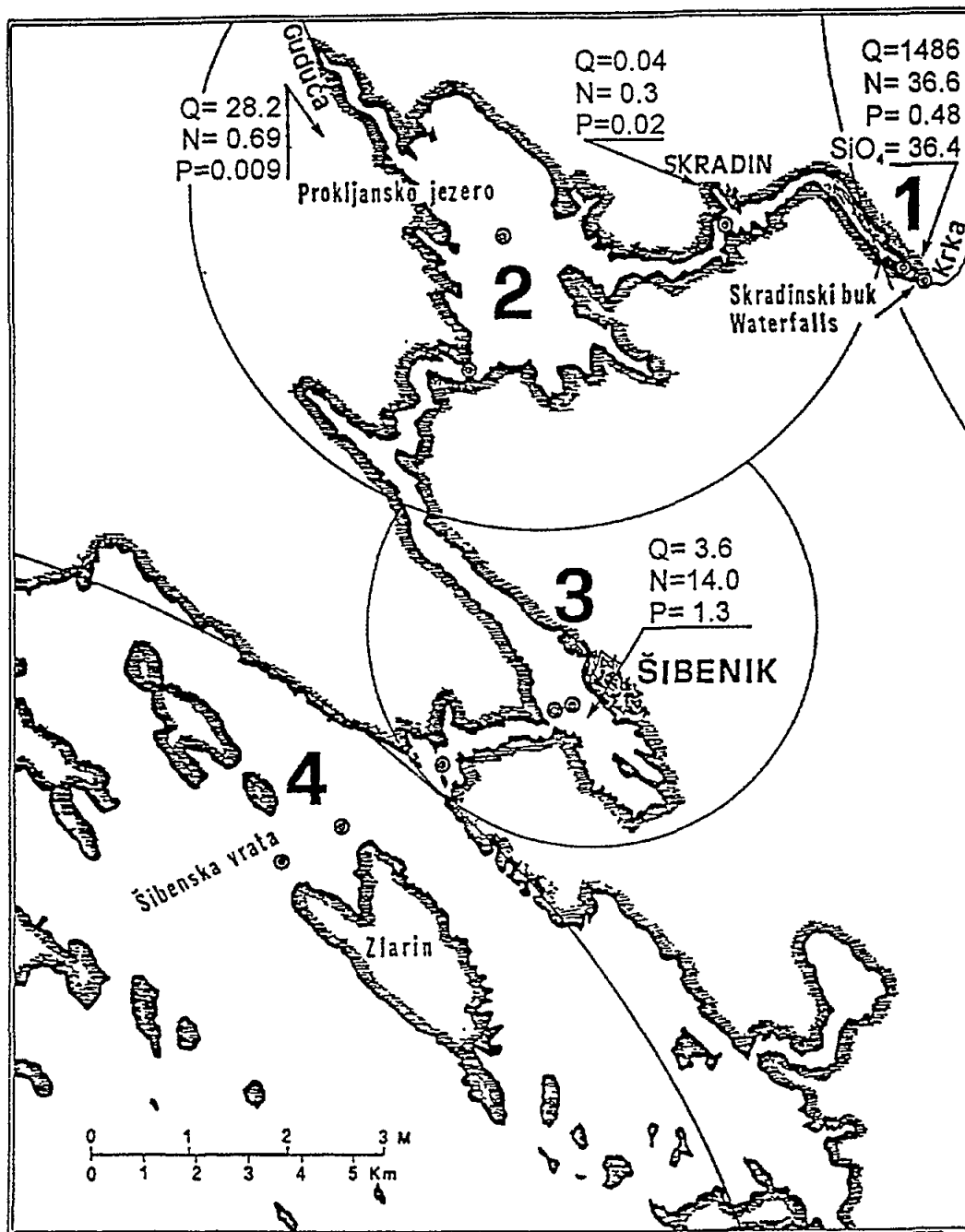


Fig. 3.1.2.2. Mean annual freshwater discharge rate ( $Q/10^9 \text{ m}^3 \text{ a}^{-1}$ ), and total nitrogen (N), total phosphorus (P) and orthosilicate ( $\text{SiO}_4$ ) loads ( $10^6 \text{ mol a}^{-1}$ ) from the Krka River (zone 1), Skradin sewages and Čikola Stream (zone 2), and Šibenik urban area (zone 3). Šibenik coastal waters (zone 4).

**Table 3.1.2.3.** Statistical data (N-number of samples, R-range,  $\bar{x}$ -mean) for basic oceanographic parameters, nutrients, and total phosphorus concentrations (c) in the layer above (AH) and below (BH) the halocline of the characteristic zones in the Krka Estuary and coastal areas (Fig. 3.1.2.2; zone 5 - Kornati Islands area, Fig. 2.3.6.1; period 1983-1991).

Parameter <sup>a</sup>	Zone Layer Stat.	1	2	3	4	5
		AH	AH	BH	AH	BH
$t/^{\circ}\text{C}$	N	45	172	238	74	206
	R	7.80-24.40	4.90-26.40	8.50-28.80	4.50-25.20	10.40-26.00
	$\bar{x}$	15.67	16.01	17.73	15.18	16.67
s-1	N	53	175	238	75	212
	R	0.00-3.40	0.00-37.17	6.04-38.62	3.46-36.61	23.20-38.64
	$\bar{x}$	0.37	7.79	36.07	15.87	36.17
$z_{SD}/\text{m}$	N	15	98	-	73	-
	R	2.0-5.0	1.0-9.0	-	1.0-40.0	-
	$\bar{x}$	4.0	4.8	-	6.9	-
pH	N	41	134	181	62	183
	R	7.71-8.51	7.46-8.44	7.81-8.49	8.16-8.68	7.99-8.53
	$\bar{x}$	8.20	8.29	8.21	8.34	8.27
$n(\text{O}_2/\text{O}_2') \cdot 1$	N	43	160	216	72	192
	R	0.77-1.87	0.63-1.41	0.16-1.76	0.68-1.82	0.67-1.65
	$\bar{x}$	1.09	1.08	1.01	1.17	1.08
$c(\text{PO}_4)$ $\mu\text{mol dm}^{-3}$	N	51	171	234	75	209
	R	0.00-0.66	0.00-0.69	0.00-2.41	0.00-1.48	0.00-1.73
	$\bar{x}$	0.12	0.12	0.17	0.28	0.18

**Table 3.1.2.3. continued**

Parameter <sup>a</sup>	Zone Layer Stat.	1		2		3		4		5
		AH	AH	BH	AH	BH	AH	BH	AH	BH
c(Org. P) μmol dm <sup>-3</sup>	N	49	159	218	70	200	2	117	54	
	R	0.00-0.65	0.00-0.83	0.00-1.42	0.00-1.03	0.00-1.55	0.10-0.23	0.00-0.67	0.03-0.26	
	$\bar{x}$	0.20	0.21	0.22	0.37	0.24	0.17	0.12	0.12	
c(TP) μmol dm <sup>-3</sup>	N	52	167	233	74	209	3	133	58	
	R	0.08-0.87	0.05-1.16	0.03-1.78	0.12-2.05	0.03-2.87	0.17-0.34	0.00-0.92	0.01-0.28	
	$\bar{x}$	0.32	0.32	0.36	0.62	0.41	0.26	0.17	0.13	
c(NH <sub>4</sub> ) μmol dm <sup>-3</sup>	N	50	159	220	71	202	3	129	58	
	R	0.32-4.59	0.00-13.28	0.00-10.35	0.04-3.35	0.00-11.88	0.29-0.67	0.00-6.11	0.00-3.59	
	$\bar{x}$	1.35	1.31	1.21	0.98	0.96	0.44	0.79	0.75	
c(NO <sub>2</sub> ) μmol dm <sup>-3</sup>	N	53	172	235	75	209	3	136	58	
	R	0.01-1.07	0.00-0.95	0.00-2.13	0.02-0.63	0.00-1.05	0.13-0.28	0.00-0.42	0.00-0.35	
	$\bar{x}$	0.33	0.27	0.24	0.26	0.18	0.19	0.09	0.04	
c(NO <sub>3</sub> ) μmol dm <sup>-3</sup>	N	52	171	234	74	209	3	135	55	
	R	0.34-45.17	0.22-46.22	0.00-22.05	0.13-59.18	0.00-45.56	0.57-22.05	0.00-13.91	0.00-1.16	
	$\bar{x}$	15.80	14.75	1.86	11.15	1.99	10.00	1.12	0.23	
c(SiO <sub>4</sub> ) μmol dm <sup>-3</sup>	N	53	170	234	75	209	3	139	59	
	R	0.75-61.23	0.84-49.62	0.00-65.85	0.52-42.05	0.07-25.23	0.94-18.04	0.00-11.04	0.04-3.40	
	$\bar{x}$	25.59	18.95	9.59	11.57	3.67	8.42	1.69	0.93	

<sup>a</sup> *t* - temperature; *s* - salinity; *z*<sub>SD</sub> - Secchi depth; *n*(O<sub>2</sub>/O<sub>2</sub>') - oxygen saturation ratio; PO<sub>4</sub> - orthophosphate; Org. P - organic phosphorus; TP - total phosphorus; NH<sub>4</sub> - ammonium; NO<sub>2</sub> - nitrite; NO<sub>3</sub> - nitrate; SiO<sub>4</sub> - orthosilicate.

The Krka River nutrient inputs were estimated from the average freshwater discharge rate of  $1486 \cdot 10^6 \text{ m}^3 \text{ a}^{-1}$  (calculated for the period 1981-1987 from data reported in the Hydrological Bulletin of the Hydrometeorological Institute of Zagreb, Croatia), and the average total phosphorus and total inorganic nitrogen concentrations measured in zone 1 (Table 3.1.2.3). Total nitrogen input was estimated assuming an organic nitrogen percentage of 29, measured in the Po River (Table 3.1.2.1; Tartari et al., 1991), which probably is overestimated for the less polluted Krka River. These calculated inputs (Fig. 3.1.2.2) include also eventual anthropogenic contributions from the Drniš and Knin areas.

The Guduèa Creek and the Skradin sewage discharges represent additional nutrient inputs in the upper estuary. The Guduèa Creek average flow rate of  $28.2 \cdot 10^6 \text{ m}^3 \text{ a}^{-1}$  was calculated for the period 1983-1987 from data reported in the Hydrological Bulletin cited above. Unfortunately, no nutrient concentration data were available for this stream. Thus, the average Krka River values were used to calculate nutrient inputs from the Guduèa Creek (Fig. 3.1.2.2). A population of 1,000 inhabitants (UNEP, 1988), and physiological human excretion rates per inhabitant of  $320 \text{ mol a}^{-1}$  for nitrogen and  $23 \text{ mol a}^{-1}$  for phosphorus (including detergent use; Provini et al., 1979), the same used in the calculations for the northern Adriatic, were assumed to estimate the inputs from the Skradin area.

Anthropogenic nutrient sources (sewages, industrial wastewaters, port activities) are only important in Šibenik Bay (zone 3). Sewage nitrogen and phosphorus discharge calculations were based on a total population of 38,000 inhabitants and the same coefficients used for the upper estuary. Nutrient fluxes of  $12 \cdot 10^6 \text{ mol a}^{-1}$  for nitrogen and  $0.9 \cdot 10^6 \text{ mol a}^{-1}$  for phosphorus were estimated. About  $1.9 \cdot 10^6 \text{ m}^3 \text{ a}^{-1}$  of industrial wastewaters are discharged annually into Šibenik Bay (Sekulić personal communication). It was accepted that industrial wastewater discharges contained on average  $1.2 \text{ mol m}^{-3}$  of nitrogen and  $0.065 \text{ mol m}^{-3}$  of phosphorus (Bond and Straub, 1974). Inputs of  $1.9 \cdot 10^6 \text{ mol a}^{-1}$  for nitrogen and  $0.1 \cdot 10^6 \text{ mol a}^{-1}$  for phosphorus were calculated from these data. An additional phosphorus input of  $0.3 \cdot 10^6 \text{ mol a}^{-1}$  was assigned to phosphorite losses during unloading in the Šibenik port ( $0.01\%$  of  $840000 \text{ t a}^{-1}$ ; UNEP, 1988), assuming a 10% phosphorus content in the ores. Total inputs to Šibenik Bay (zone 3) are presented in Fig. 3.1.2.2.

A clear relationship was evident between the surface layer nutrient enrichment and nutrient inputs in the Krka estuary zones. While the nitrogen input in the upper estuary (zone 2) is more than three times higher than in Šibenik Bay (zone 3), an inverse ratio was calculated for phosphorus (Fig. 3.1.2.2). This can explain the greater orthophosphate enrichment in Šibenik Bay (mainly because of sewage) in comparison with nitrate. Significantly, nitrate strongly dominated over the other inorganic nitrogen species in all estuarine zones. This suggests that freshwater nitrate contributions (mainly from the Krka River) are more important to the estuary nitrogen budget than sewage ammonium contributions. In fact, extremely high ammonium concentrations (up to  $13 \text{ mmol m}^{-3}$ ; Table 3.1.2.3), indicating direct sewage contamination in the sampling area, were rarely measured.

Data on anthropogenic orthosilicate inputs were not available. Compared with the Krka River contribution (Fig. 3.1.2.2), these inputs are probably not significant for the orthosilicate distribution and budget of the estuary. This was also inferred from orthosilicate concentration changes along the estuary, which were closely related to the salinity gradient (see section 3.1.3. of this Report).



### The Split coastal area

A partial nutrient load calculation was attempted only for the Kaštela Bay (Bariæ 1989). The used nitrogen and phosphorus average concentrations were calculated from direct measurements in the Split city sewages and Jadro Stream waters. Literature concentration data were used to calculate rain nitrogen and phosphorus contributions.

Most of the estimated nitrogen ( $27 \cdot 10^6 \text{ mol a}^{-1}$ ) and phosphorus ( $2.9 \cdot 10^6 \text{ mol a}^{-1}$ ) loads in the bay were related to sources along the eastern coast (including the Vranjic area; station 1). Two sewage outfalls of the Split city (Duje and Lora) are located there, which accounted for two thirds of the total wastewater discharge in the bay ( $9.6 \cdot 10^6 \text{ m}^3 \text{ a}^{-1}$ ) and for 43% of N and 34% of P load. Moreover, the Jadro Stream waters ( $239 \cdot 10^6 \text{ m}^3 \text{ a}^{-1}$ ), which are discharged near Vranjic, contributed for further 27% of the N and 44% of the P load. The P load of this stream included only orthophosphate. This means that the Jadro contribution and consequently the total P-load can be significantly larger than calculated.

Several small sewage outfalls, distributed along the eastern and northern part of the Kaštela Bay coast, accounted for the remaining one third of the total wastewater discharge, and for 21% of N and 17% of P load. The difference (10% of N and 4% P) was calculated as rain contribution ( $837 \text{ mm a}^{-1}$ ).

Nutrient rich wastewaters from food industrial plants are discharged into the southeastern area of Kaštela Bay. Unfortunately, no relevant data to calculate nitrogen and phosphorus loads from this source were available.

#### 3.1.3. Oceanographic characteristics, nutrients, total nitrogen and total phosphorus in the eastern Adriatic coastal region

For a more precise interpretation of data collected in this programme, all available data in the Centre for Marine Research and published results were used to describe the oceanographic characteristics, nutrient cycles, and eutrophication mechanisms in the open northern Adriatic. Data for oceanographic parameters (salinity, temperature, density, dissolved oxygen, pH, total alkalinity, transparency, organic and inorganic suspended solids, basic meteorological data), nutrient and chlorophyll *a* concentrations, potential primary production rates ( $^{14}\text{C}$ ), and phytoplankton counts have been collected since 1966 at a variable number of stations (6-21) and frequency (weekly to seasonally) in the framework of several national and international projects. In some of these projects basic research was combined with monitoring activities applied to marine environment protection. Examples of seasonal variability for some relevant parameters at stations 5R (corresponding to station SJ107 in the CMR-R nomenclature) and 9R (SJ108) are presented in tables and figures of this report.

Oceanographic and nutrient data collected in the framework of this programme (1983-1991), additional chlorophyll *a* and potential primary production ( $^{14}\text{C}$ ) data, and literature results were used to describe the characteristics and eutrophication of the Krka River estuary and Šibenik Bay areas.

For the Split area only data collected for this programme were available (1984-1991), but literature results were also used.

### Open northern Adriatic waters

An extreme variability of nutrient concentrations and primary production was observed in the northern Adriatic Sea (examples for stations 5R and 9R in Table 3.1.3.1), one of the most productive area in the Mediterranean (Sournia, 1973). This variability was due to an alternate dominance of at least two main water types with different chemical compositions and intensity of prevailing biological processes (assimilation, regeneration, nitrification; Gilmartin *et al.*, 1990). The dominance of each water type depends on freshwater discharge, vertical mixing in the water column and horizontal water advection.

**Table 3.1.3.1.** Statistical data (N-number of samples, R-range,  $\bar{x}$ -mean) for basic oceanographic parameters, nutrients, and total phosphorus and total nitrogen concentrations (c) in surface and bottom layers of station 5R (1966-1992) and 9R (1972-1992) in the open northern Adriatic<sup>a</sup>.

Station		5R		9R	
Parameter <sup>b</sup>	Stat.	Surface	Bottom	Surface	Bottom
$t^{\circ}\text{C}$	N	295	204	154	152
	R	7.19-28.12	8.27-19.97	7.17-28.74	6.69-18.73
	$\bar{x}$	17.44	12.80	17.78	12.29
s-1	N	293	200	153	152
	R	29.76-38.68	37.33-38.70	13.10-38.08	36.82-38.79
	$\bar{x}$	36.33	38.08	32.92	37.91
$z_{SD}/\text{m}$	N	275	-	139	-
	R	3.0-29.0	-	0.8-26.0	-
	$\bar{x}$	13.5	-	6.3	-
pH	N	111	111	92	92
	R	8.11-8.58	7.90-8.48	8.13-9.15	7.93-8.41
	$\bar{x}$	8.33	8.22	8.39	8.17

**Table 3.1.3.1.** continued

Station		5R		9R	
Parameter <sup>b</sup>	Stat.	Surface	Bottom	Surface	Bottom
$c(O_2/O_2)^{-1}$	N	266	190	148	147
	R	0.90-1.39	0.04-1.16	0.89-2.37	0.13-1.24
	$\bar{x}$	1.05	0.85	1.18	0.73
$c(PO_4)$	N	228	179	147	147
$\mu\text{mol dm}^{-3}$	R	0.00-0.26	0.00-0.59	0.00-1.11	0.00-1.18
	$\bar{x}$	0.04	0.07	0.14	0.22
$c(\text{Org. P})$	N	228	179	147	147
$\mu\text{mol dm}^{-3}$	R	0.00-0.55	0.00-0.67	0.00-1.38	0.00-0.61
	$\bar{x}$	0.14	0.13	0.27	0.14
$c(\text{TP})$	N	181	147	107	110
$\mu\text{mol dm}^{-3}$	R	0.03-0.62	0.02-0.71	0.10-1.53	0.05-1.28
	$\bar{x}$	0.18	0.20	0.40	0.36
$c(NH_4)$	N	174	166	146	143
$\mu\text{mol dm}^{-3}$	R	0.00-2.80	0.00-2.88	0.00-9.10	0.01-8.80
	$\bar{x}$	0.52	0.75	0.86	1.78
$c(NO_2)$	N	214	178	148	147
$\mu\text{mol dm}^{-3}$	R	0.00-1.47	0.01-2.86	0.00-1.93	0.01-3.47
	$\bar{x}$	0.17	0.34	0.39	0.48
$c(NO_3)$	N	214	178	148	146
$\mu\text{mol dm}^{-3}$	R	0.00-10.40	0.02-6.94	0.03-44.51	0.04-27.97
	$\bar{x}$	0.75	0.90	4.68	1.87
$c(\text{Org. N})$	N	89	87	75	66
$\mu\text{mol dm}^{-3}$	R	0.77-10.58	0.13-10.36	0.75-36.55	0.13-8.63
	$\bar{x}$	3.89	3.49	6.05	2.96
$c(\text{TN})$	N	104	103	89	87
$\mu\text{mol dm}^{-3}$	R	1.61-13.86	2.02-12.44	2.55-59.28	1.45-17.86
	$\bar{x}$	5.35	5.67	11.32	6.55
$c(SiO_4)$	N	227	179	148	147
$\mu\text{mol dm}^{-3}$	R	0.00-14.30	0.24-31.59	0.00-45.10	0.77-36.08
	$\bar{x}$	2.44	7.47	5.78	11.71

<sup>a</sup> data collected in this programme and prior 1983 CMR-R data.

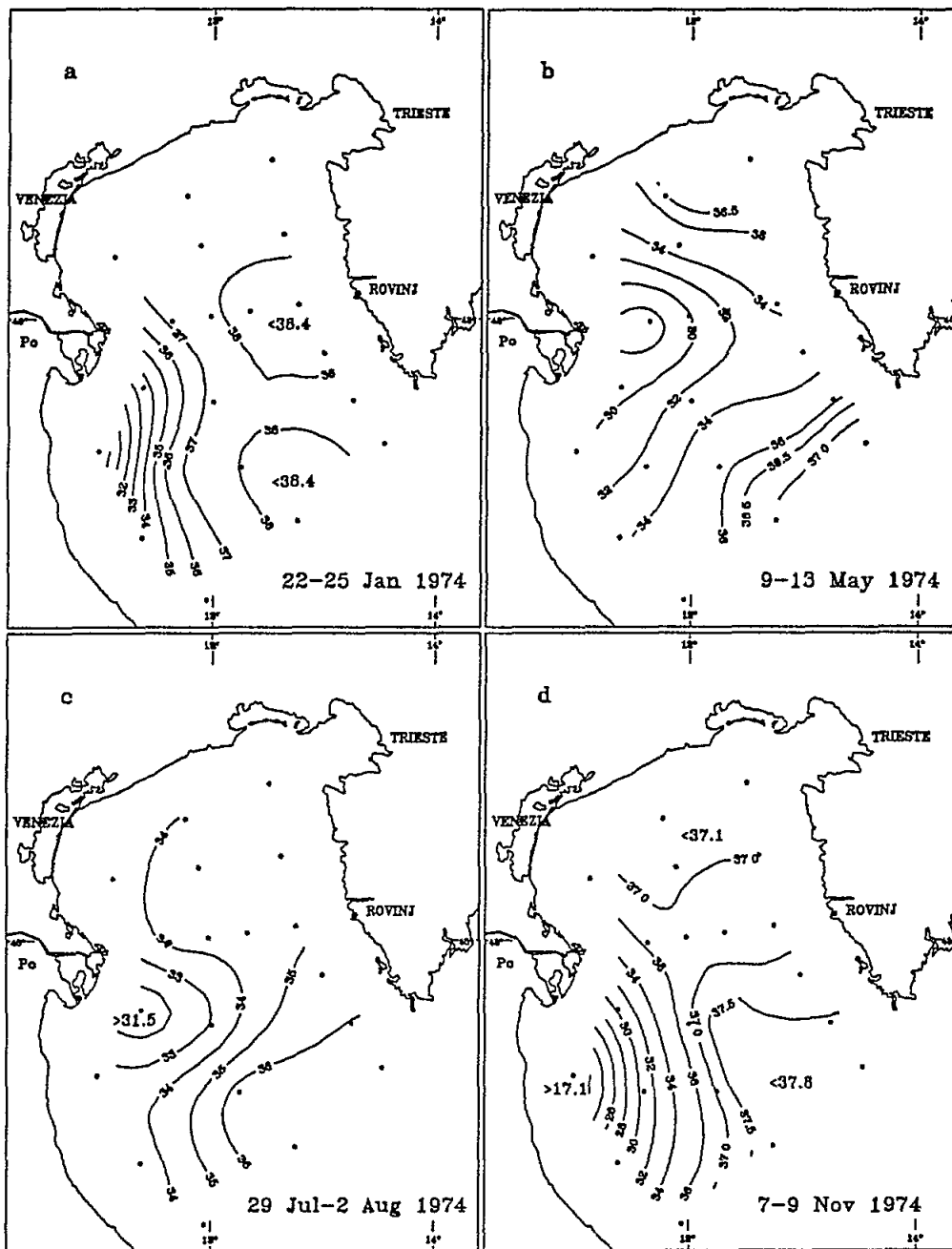
<sup>b</sup>  $t$  - temperature;  $s$  - salinity;  $z_{SD}$  - Secchi depth;  $c(O_2/O_2)$  - oxygen saturation ratio;  $PO_4$  - orthophosphate; Org. P - organic phosphorus; TP - total phosphorus;  $NH_4$  - ammonium;  $NO_2$  - nitrite;  $NO_3$  - nitrate; Org. N - organic nitrogen; TN - total nitrogen;  $SiO_4$  - orthosilicate.

High salinity oligotrophic waters ( $s=37.5-38.6$ ;  $c(O_2/O_2^i)=95-125\%$ ;  $c(TIN)=0-10$ ,  $c(PO_4)=0.0-0.2$ , and  $c(SiO_4)=0-14 \mu\text{mol dm}^{-3}$ ; Degobbis, 1988), which originate in the central Adriatic, occupy most of the northern Adriatic, including the area of station 5R (Table 3.1.3.1), at least from late autumn to early spring. In contrast, lower salinity eutrophic waters ( $s=17-35$ ;  $c(O_2/O_2^i)=90-260\%$ ;  $c(TIN)=0-47$ ,  $c(PO_4)=0.0-0.7$ , and  $c(SiO_4)=0-59 \mu\text{mol dm}^{-3}$ ; Degobbis, 1988) are formed in the surface layer of the northwestern Adriatic coastal area, including the area of station 9R (Table 3.1.3.1), due to river nutrient contributions, mainly with the Po River (Degobbis and Gilmartin, 1990).

During January/February alpine river water discharge is at a minimum and a prevailing cyclonic circulation in the northern Adriatic transports low salinity waters in a relatively narrow coastal region along the Italian coast (Fig. 3.1.3.1). Thus, higher nutrient concentrations can be observed in this region, in which station 9R is generally included (Fig. 3.1.3.2), compared with most of the northern Adriatic that is occupied with well mixed and oxygenated high salinity waters, with low nutrient concentrations (see examples for station 5R; Fig. 3.1.3.2). Organic phosphorus and organic nitrogen concentrations are low in both water types (Fig. 3.1.3.2), because of limited phytoplankton nutrient assimilation, mainly due to low irradiance and unstable conditions in the water column.

Very often, a major phytoplankton bloom, generally dominated by diatoms, develops in February/March, primarily on nutrient reserves regenerated since late autumn and early winter. Bloom development is usually additionally supported by river nutrient input (due to an increased discharge rate; Cati, 1981), at least in the northwestern part of the Adriatic. This is shown by an inorganic nitrogen concentration increase (mainly nitrate), at station 9R (Fig. 3.1.3.2). In contrast, orthophosphate assimilation prevails over river contribution, with a decrease in the concentration level. As a result of the blooms, organic phosphorus and nitrogen concentrations are increased. In the surface layers off the Istrian coast (station 5R; Fig. 3.1.3.2) nutrient concentrations increased in April and are probably mainly due to regeneration of nutrients, contributed by rivers in the preceding month.

Regularly, in May/June the river discharge rate increases markedly, due to snow melting in the Alps. River nutrient contributions exceed assimilation and cause concentrations to increase again. Simultaneously the water column stratification is intensified due to sea surface heating and freshwater runoff (Fig. 3.1.3.3). Light level and temperature favour photosynthesis, and the most strongly developed phytoplankton crops of the year occur in the warmer surface layer (chlorophyll a concentration up to  $32 \text{ mg m}^{-3}$ , primary production ( $^{14}\text{C}$ ) up to  $143 \text{ mg m}^{-3} \text{ h}^{-1}$ ; Gilmartin and Revelante, 1980; Smolaka, 1986), resulting in a maximum concentration of the organic phosphorus and nitrogen forms (Fig. 3.1.3.2); water transparency is drastically reduced and surface pH significantly increased. Nanoplankton fraction generally dominates these spring blooms, but the microplankton one can also contribute significantly.



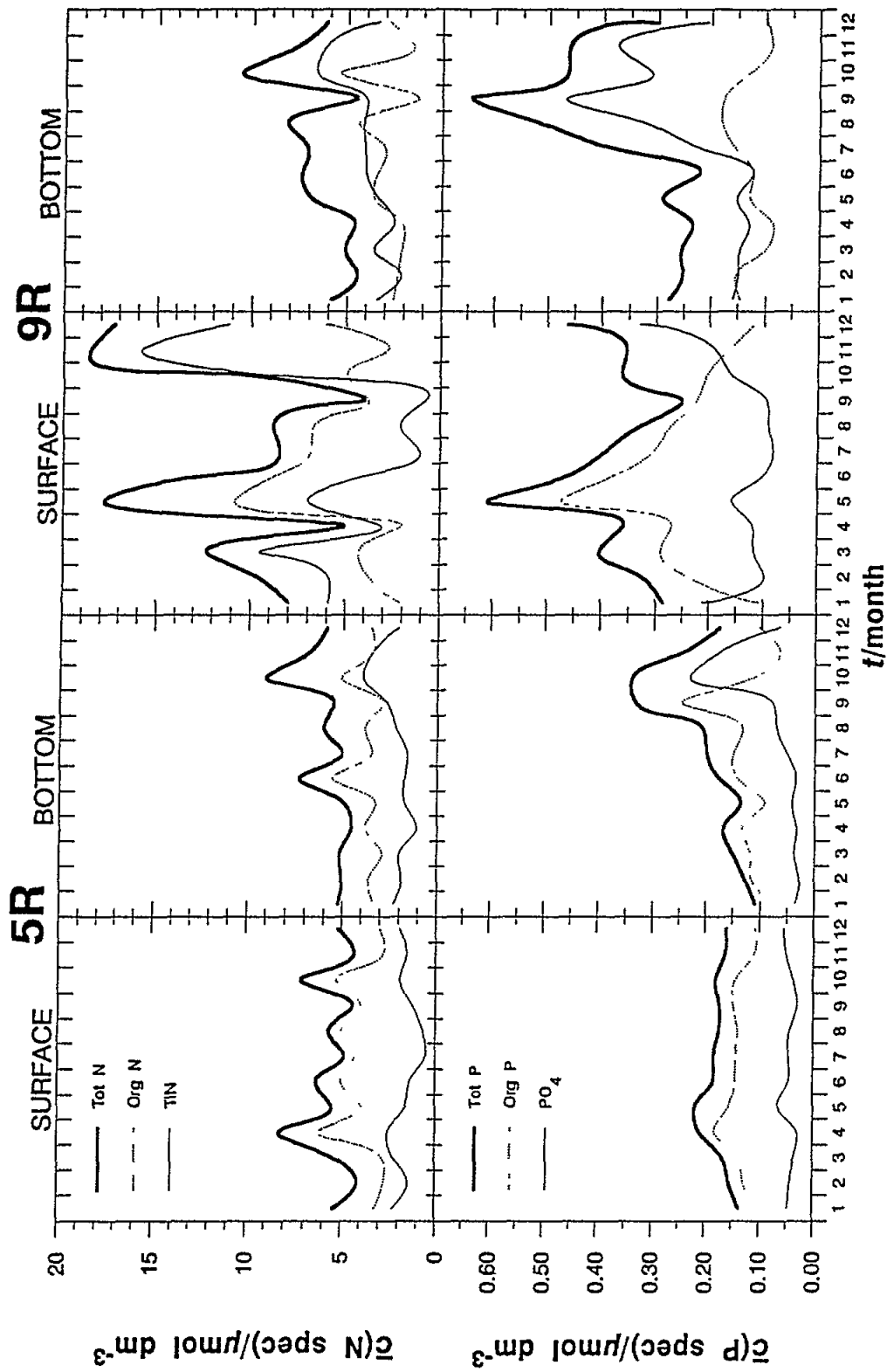


Fig. 3.1.3.2. Monthly means ( $\bar{c}$ ) of total, inorganic and organic nitrogen (N; period 1981-1992) and phosphorus (P) in the surface and bottom layers of the stations 5R (period 1970-1992) and 9R (period 1977-1992) in the open northern Adriatic.

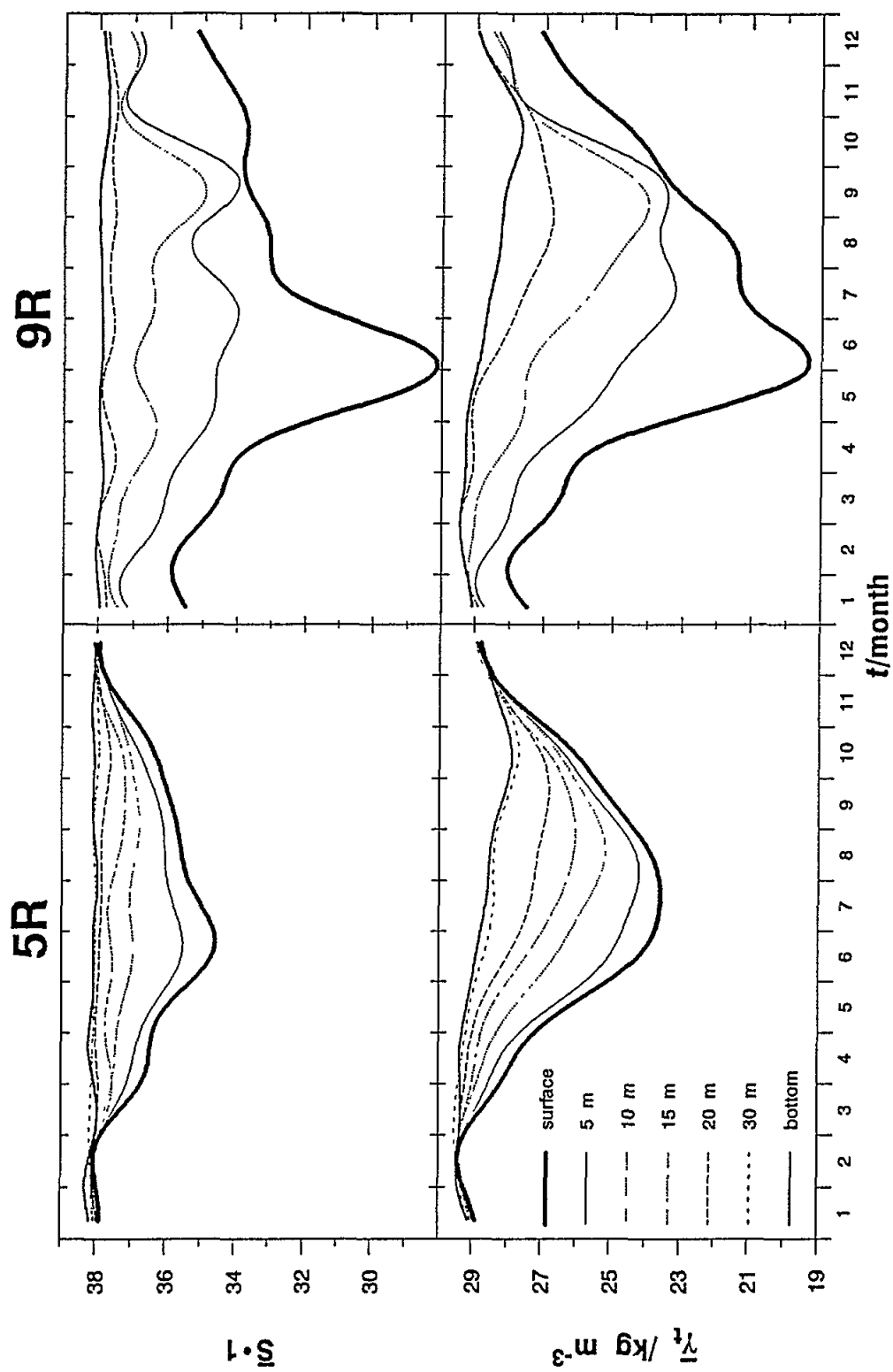


Fig. 3.1.3.3. Average year model of salinity ( $s$ ) and density excess ( $\gamma_t$ ) for several depths at station 5R (period 1966-1992) and 9R (period 1972-1992) in the open northern Adriatic.

Remarkably, if no new contributions of freshwater nutrients occur, all orthophosphate in the lower salinity surface layer can be biologically utilized (ie completely transformed into organic compounds) during these spring blooms in the northwestern part of the Adriatic, often before inorganic nitrogen species and orthosilicate are exhausted (Ivanè and Degobbi, 1988).

At present, the circulation pattern starts changing to a summer type characterized by a semi-closed cyclonic gyre in the northernmost part of the Adriatic. Consequently, low salinity water (Fig. 3.1.3.1), river nutrients and the products of increased primary production are distributed and recycled over a major part of the region up to early autumn (examples of total P and total N distribution in Fig. 3.1.3.4), significantly affecting the biomass and composition of the plankton communities (Gilmartin and Revelante, 1983; Revelante and Gilmartin, 1976, 1983, 1988; Revelante *et al.*, 1985; Benovì *et al.*, 1984; Fuks and Devescovi, 1985). These changes are less intensive in the eastern part (station 5R), where nutrient biological utilization prevails, reducing the concentrations of the inorganic forms, while organic phosphorus and nitrogen still remain relatively high (Fig. 3.1.3.2).

River freshwater discharge is generally at a minimum during summer, but the northern Adriatic is strongly isolated, due to the typical semi-closed circulation, and a warmer, less saline surface layer spread over the region. Therefore, surface salinity remains lower than in winter during all the summer (Fig. 3.1.3.1). No phytoplankton biomass accumulation occurs in this season in the surface layer, but supersaturated oxygen values, minimal nutrient concentrations and moderate primary production rates indicate that significant primary production occurs. Moreover, organic phosphorus and nitrogen concentrations even at lower than spring values, remain significantly higher than in winter (Fig. 3.1.3.2). A rapid nutrient recycling throughout a microheterotroph-nanophytoplankton food web probably can explain the observed typical summer conditions.

In summer and early fall the stratification of the water column is strongly developed, and the bottom layers are isolated from the surface by marked pycnoclines (Fig. 3.1.3.3). In these layers assimilation rates are severely limited by available light and regeneration processes prevail: dissolved oxygen concentration decreases, due to community respiration (both in water column and at the sediment-water interface) and nutrients accumulate up to concentrations an order of magnitude higher than in the spring (Fig 3.1.3.2). The pH decreases down to a minimum as a consequence of CO<sub>2</sub> development during remineralization of organic matter. These processes are generally more intense at the station near the Po Delta, but in the last five years oxygen depleted waters appeared with increasing frequency also in the eastern, more oligotrophic parts (station 5R; Degobbi *et al.*, 1991a; section 4.2 of this report). Organic phosphorus and nitrogen concentrations are relatively high (Fig. 3.1.3.2), very probably due to sedimentation of organic matter, produced in the upper part of the water column. These concentrations decrease in the fall, when remineralization processes prevail over sedimentation.



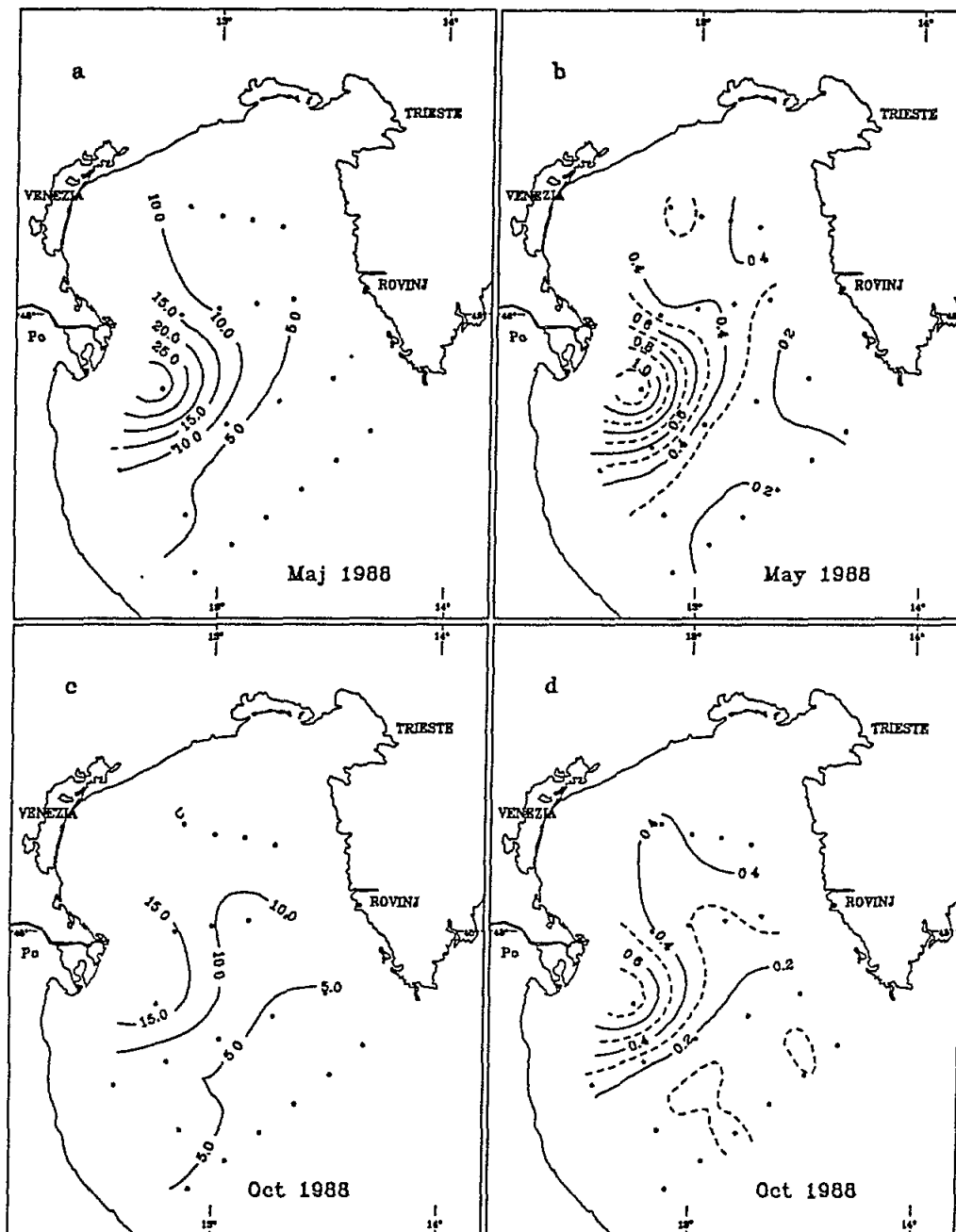


Fig. 3.1.3.4. Total nitrogen (TN; left) and total phosphorus (TP; right) concentrations (c) in the surface layer of the open northern Adriatic in May and October 1988 (CMR-R, unpublished data).

In the autumn the river discharge generally increases again, and simultaneously the winter circulation is reestablished in the region, increasing surface salinity in most of the northern Adriatic (Fig. 3.1.3.1). Increased vertical mixing occurs, due to sea surface cooling, allowing some reoxygenation of the bottom layer. As a result, regenerated nutrients, accumulated in the bottom layer during the summer, are brought into the upper layers. Nutrient input by these two mechanisms induced a fall phytoplankton bloom, dominated by nanoplankton fraction and diatoms, which do not develop fully, due to reduced mean light intensities in the euphotic zone. For this reason, regeneration prevails over assimilation, increasing nutrient concentrations and decreasing organic phosphorus and nitrogen concentrations (Fig. 3.1.3.2). Through vertical and horizontal water mixing reoxygenation is reached in December, when isopycnal conditions (Fig. 3.1.3.3), as well as homogeneous distributions of nutrient concentration and phytoplankton abundance can be observed throughout the water column of the most part of the northern Adriatic.

Relationships among various nutrient species, as well as nutrients (TIN - total inorganic nitrogen = ammonium + nitrite + nitrate,  $\text{PO}_4$  - orthophosphate,  $\text{SiO}_4$  - orthosilicate) and apparent oxygen utilization (AOU) were studied using a linear regression analysis of an extended set of concentration data collected in the northern Adriatic between 1972 and 1981 (Degobbis, 1990b). A stoichiometric model of nutrient regeneration was developed from bottom layer data during periods of marked water column stratification (from late spring to early fall). This model ( $\text{AOU:TIN:SiO}_4:\text{PO}_4 = -610:15:47:1$ ; by atoms) differs significantly from a widely accepted "oceanic" model ( $-276:16:15:1$ ; Redfield *et al.*, 1963). Apparently, in the northern Adriatic much less nitrogen and phosphorus are regenerated when the same amount of oxygen is consumed to oxidize organic compounds. This is probably due to denitrification (reduction of a part of regenerated  $\text{NO}_3^-$  ions to  $\text{N}_2$  after their diffusion from bottom water into the anoxic sediment), different regeneration rates of phosphorus and nitrogen (occurring mainly in the water column) vs biogenic silica (mainly on the sediment), and a phosphorus disproportion in decomposing organic matter from primary and secondary production.

In water masses, mainly the surface layers, in which freshwater nutrient input and phytoplankton assimilation were dominant, the nutrient atomic ratios ( $\text{TIN/PO}_4=62$ ,  $\text{SiO}_4/\text{TIN}=1.1$ , and  $\text{SiO}_4/\text{PO}_4=65$ ) were significantly different from ratios in subeuphotic regeneration layers ( $\text{TIN/PO}_4=15$ ,  $\text{SiO}_4/\text{TIN}=3.3$ , and  $\text{SiO}_4/\text{PO}_4=48$ ). These differences were ascribed to high values in river waters and to a faster utilization of phosphorus by autochthonous phytoplankton compared with nitrogen and particularly silicon. Mean ratio value ranges in the Po River, calculated from data collected from various authors in the period 1973-1981 (UNEP, 1988; Table 3.1.1 in the Report; Degobbis, 1988; Table 2.25 in the Thesis), were  $\text{TIN/PO}_4=40-47$ ,  $\text{SiO}_4/\text{TIN}=0.8-1.0$ , and  $\text{SiO}_4/\text{PO}_4=35-38$ .

### The Krka River estuary, the Šibenik coastal area and the Kornati Islands reference region

Estuaries are important sites for primary production, and are characterized by highly variable hydrographic conditions and nutrient concentrations (eg Kemp *et al.*, 1982; Wolfe and Kjerfve, 1986). These characteristics were preliminary evidenced in the Krka estuary area already in 1949 (Buljan, 1969), and successively in 1973-1974 (Buljan *et al.*, 1980), and were ascribed mainly to the influence of hydrological and meteorological variability, as well as to anthropogenic nutrient inputs. Since 1983 the region has been investigated with a multidisciplinary approach in the framework of several national and international projects, including this programme. Most of the results were presented at an international symposium, whose proceedings were published in 1991 issues of Marine Chemistry (Vol. 32, Nos. 2-4).

The region is a stratified salt-wedge estuary (Gržetić 1990), exposed to a small, but significant influence of tides (average amplitude 20 cm with maxima up to 50 cm). The surface low salinity layer is isolated from the high salinity deeper layer by a very sharp, 10-50 cm thick halocline layer, the depth of which varies from 2-5 m (Gržetić and Marguš, 1989). Oscillations of the halocline depth were observed when strong wind was blowing ( $>20 \text{ m s}^{-1}$ ), but mixing between surface and deeper layers was not significant (Legović *et al.*, 1991a). Wind driven surface currents induced vertical mixing of opposite directions in the surface and lower saline layer, respectively. Such a mixing favours oxygen renewal in the bottom layers.

Five subregions were identified in the estuary with different salinity, transparency, oxygen saturation, pH, and nutrient concentration ranges (Fig. 3.1.2.2 and Table 3.1.2.3; Gržetić *et al.*, 1991).

The Krka River (depth up to 4 m) enters the estuary in zone 1 (station E-0, about 100 m upstream of the Skradinski Buk waterfalls, and station E-1, about 200 m downstream). In this zone only a slight mixing between fresh and saline waters occurred (salinity never higher than 3; Table 3.1.2.3). The highest variability of salinity and oxygen saturation values were observed in the upper estuary (zone 2, station E-2, in front of Skradin, stations E-9 and E-3 in the central and southern parts of the Prokljan Lake, respectively; depths up to 24 m). Compared with zone 2, zone 3 (the lower estuary) is more saline and better oxygenated, and includes stations E-4 and E-4a in Šibenik Bay, and station E-5 at the estuary mouth (depth up to 40 m). In zone 4, the coastal area in front of the estuary mouth (stations C-1 and C-2 in the Šibenska Vrata area, depth up to 40 m), estuarine water influence is still noticeable (salinities as low as 20; Table 3.1.2.3), particularly in winter and spring. In contrast, salinity ranges were minimal in the Kornati Islands area (zone 5), and the water column was well aerated. This zone (stations R-1 and R-2, depth up to 38 m) can be considered as a reference area not influenced by the estuary.

Nutrient concentrations in the Krka Estuary (zones 2 and 3) varied markedly and were one or two orders of magnitude higher than in the Kornati Islands area (zone 5; Table 3.1.2.3). Chlorophyll *a* concentrations in the estuary varied within two orders of magnitude ( $0.2\text{-}23 \text{ mg m}^{-3}$ ). *In situ* primary production (measured in incubator in spring 1989) ranged from  $2\text{-}108 \text{ mg m}^{-3} \text{ h}^{-1}$  (Gržetić *et al.*, 1991). These chlorophyll *a* and primary production values

were not as high as those typical of heavily eutrophied estuaries, where chlorophyll *a* concentration can increase up to  $180 \text{ mg m}^{-3}$  and primary production up to  $500 \text{ mg m}^{-3} \text{ h}^{-1}$  (eg Sirois and Fredrick, 1978; Bennett *et al.*, 1986; Degobbis *et al.*, 1986b). However, chlorophyll *a* concentrations within the Krka Estuary were at least an order of magnitude higher than in the coastal sea ( $0.1\text{-}2.4 \text{ mg m}^{-3}$  in zone 4).

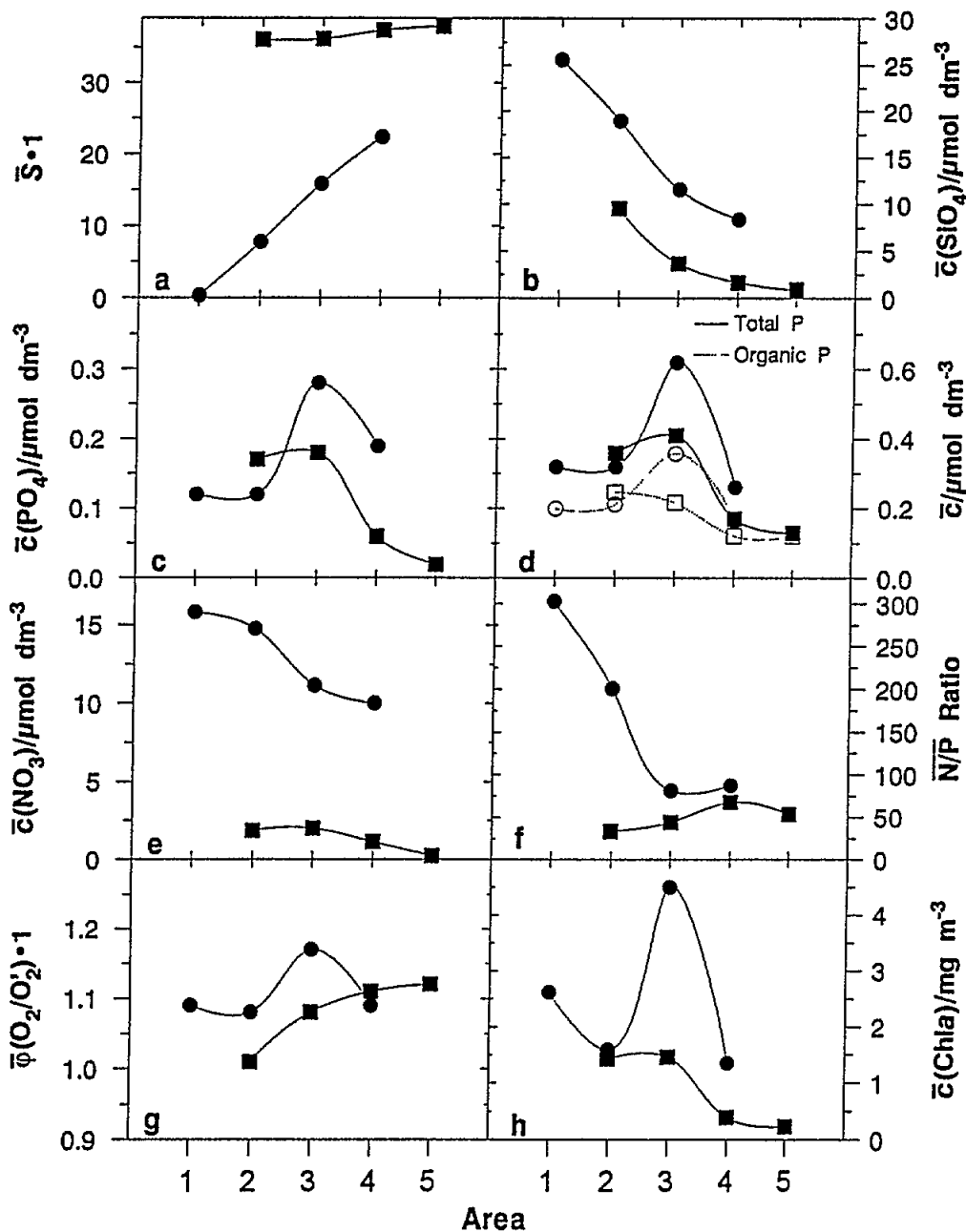
Finally, water transparency was greatly reduced (1-15 m), and pH variability increased (7.5-8.6) within the estuary, compared with the coastal sea, and in particular with the Kornati Islands area (14-26 m and 8.2-8.3 respectively; Table 3.1.2.3).

The distribution of the most relevant parameters (eg salinity, dissolved oxygen, nutrients) along the estuary were represented graphically for each cruise in the Annual Reports on "Long-term Pollution Monitoring and Research of the Krka Estuary and Kornati Archipelago" of the Centre for Marine Research in Zagreb, as a contribution to this programme. Thus, in this report mean values were calculated from all data for the layer above and that below the halocline in each zone, to highlight the main relationships occurring among these parameters (Fig. 3.1.3.5).

Marked differences in average salinity and nutrient concentrations were observed above and below the halocline (Fig. 3.1.3.5). Average orthosilicate and inorganic nitrogen species concentrations decreased gradually from the Krka River to the coastal sea, with a clear inverse relationship with surface salinity. In contrast, orthophosphate and total phosphorus concentrations were on average much higher in zone 3 (Šibenik Bay) than in the other zones, including the Krka River waters.

These nutrient distribution differences can be better described by the total inorganic nitrogen vs orthophosphate concentration ratio, which was very high (mean around 180) in the Krka River, but it was several times lower in Šibenik Bay and coastal sea (Fig. 3.1.3.5). Very high  $\text{TIN}/\text{PO}_4$  ratios are typical of unpolluted or slightly polluted karstic rivers and estuaries of the northern Adriatic, in contrast to heavily polluted streams (eg Rječina River; Table 3.1.1 in the previous report; UNEP, 1988).

Different seasonal patterns of surface concentration were noticed for each nutrient species. The highest orthosilicate and nitrate concentrations were observed in winter and the lowest in summer, corresponding to maximum and minimum freshwater discharge rates. Freshwater inflow is generally also significant in the spring (salinity ranges as large as in winter), but intense phytoplankton assimilation reduced nitrate and orthosilicate concentrations. In contrast, in this season phosphorus anthropogenic input prevailed over biological utilization, particularly in Šibenik Bay, where very low  $\text{TIN}/\text{PO}_4$  ratio values were observed (Table 3.1.3.2).



**Fig. 3.1.3.5.** Means (1983-1991) of (A) salinity ( $\bar{s}$ ); (B) orthosilicate ( $\text{SiO}_4$ ), (C) orthophosphate ( $\text{PO}_4$ ), (D) total phosphorus (TP), and (E) nitrate ( $\text{NO}_3$ ) concentrations ( $\bar{c}$ ), (F) total inorganic nitrogen (TIN) vs. orthophosphate concentration ratio, (G) oxygen saturation ratio ( $\bar{\varphi}$ ), and (H) chlorophyll *a* (Chla) concentration ( $\bar{c}$ ) in the layers above (●) and below (■) the halocline in the characteristic zones of the Krka Estuary and Šibenik coastal areas (Fig. 3.1.2.2).

**Table 3.1.3.2.** Examples of orthophosphate concentration ( $c$ ) and of extremely low total inorganic nitrogen (TIN) vs orthophosphate ( $\text{PO}_4$ ) concentration ratio at the Šibenik Bay (zone 3) stations.

Station	Date	$z/\text{m}$	$c(\text{PO}_4)$ $\mu\text{mol dm}^{-3}$	$\frac{c(\text{TIN})}{c(\text{PO}_4)}$
E4a	08.07.85	0.0	0.4	5.3
E4a	16.05.86	8.0	1.5	5.8
E4a	24.06.88	0.0 2.5	0.7 0.3	7.8 2.3
E4a	05.08.88	0.0 3.7	0.5 0.4	2.0 1.7
E4a	20.10.88	0.0 2.0	0.5 0.6	2.8 2.8
E4a	13.08.89	0.0	0.4	2.3
E4a	01.10.90	0.0 1.5	0.5 0.6	2.1 1.5
E5	02.07.84	0.0	0.2	2.3
	02.03.89	0.0	0.4	8.4
E5	02.03.89	6.0	0.1	5.1

Remarkably, 19% of 70 data available for this ratio, obtained in the layer above the halocline of Šibenik Bay were lower than 10. In contrast, in the upper estuary and coastal area only 4% of 207 data were in this range. So low ratios were considered representative of marine environments, in which nitrogen limitation of phytoplankton growth prevails (eg Hecky and Kilham, 1988).

Average salinities of the layer below the halocline were similar in zones 2 and 3, and were only slightly lower than in the coastal sea (about 1; Fig. 3.1.3.5). Estuarine nutrient concentrations in this layer were much higher than in the coastal sea. These distributions suggest that a "nutrient trap" mechanism (eg Officer, 1983) is functioning in the Krka Estuary.

Below the halocline, oxygen saturation varied significantly and undersaturation dominated the greater part of the year (except spring). Oxygen saturation minima were measured in fall near the bottom of the upper estuary. In the low oxygen layer significant nutrient accumulation occurred. Average N/P ratios were much lower below the halocline than in the surface layer (Fig. 3.1.3.5). Relationships between apparent oxygen utilization (AOU) and inorganic nutrient species concentrations were studied applying linear regression analysis (Gržetić *et al.*, 1991). The ratios between AOU and the various nutrient species were calculated from the regression line slopes. These ratios for the Krka Estuary ( $\text{AOU}:\text{TIN}:\text{SiO}_4:\text{PO}_4 = -690:15:40:1$ ) were close to those calculated for the northern Adriatic

Sea (-610:15:47:1; Degobbis, 1990b). This suggests that similar nutrient recycling mechanisms occur in both regions.

Total nitrogen was determined in the Krka Estuary only in May 1988 (examples in Fig. 3.1.3.6). The organic nitrogen (up to  $11.5 \mu\text{mol dm}^{-3}$ ; 50% of total N), as well as organic phosphorus (up to  $1.3 \mu\text{mol dm}^{-3}$ ; 80% of total P) concentrations were at a maximum in the Šibenik Bay surface layer (station 4a), where an intense phytoplankton bloom was observed (chlorophyll *a* concentration up to  $23 \text{ mg m}^{-3}$ ). Similar values can be observed during spring bloom in the area off the Po Delta (station 9R; Table 3.1.3.1). However, high concentrations were also measured at the halocline interface in the upper estuary (Fig. 3.1.3.6). In fact, this interface is greatly enriched with dissolved organic matter (forming organic films), suspended matter and viable cells of selected phytoplankton species (Žutić and Legović 1987; Vilićević *et al.*, 1989; Cauwet, 1991). In the layers above the halocline in the upper estuary, and below the halocline in the entire estuary, as well as in the coastal area (stations C-1 and C-2) the values for organic nitrogen and phosphorus were much lower ( $0.3\text{-}7.7$  and  $0.06\text{-}0.3 \mu\text{mol dm}^{-3}$ , respectively), but generally accounted for the most of the total N and P concentrations.

Concluding, the variability of nutrient concentration (in time and space), observed in the Krka River estuary, can be related to the combined influence of several processes: the nutrient biological assimilation/regeneration cycle, freshwater discharge, anthropogenic contribution, horizontal and vertical advection, and others. Some of these processes can prevail over others in different parts of the water column (separated by a marked halocline), and/or in different zones of the estuary. Thus, in the surface layer external nutrient inputs and phytoplankton utilization alternately dominate during the seasonal cycle. Nitrogen and orthosilicate inputs are higher in the upper estuary than in Šibenik Bay, but phosphorus input, as well as phytoplankton biomass and activity are higher in the bay. In the lower saline layer nutrient regeneration processes prevail over nutrient exchanges between the estuary and coastal sea, and horizontal advection within the estuary. As a consequence, different oxygen consumption and nutrient accumulation rates occurred in the various investigated zones: the highest were observed in the upper estuary, the lowest in the coastal sea.

#### The Split coastal area and Vis Island reference station

While oceanographic characteristics, nutrient cycles, primary production and phytoplankton ecology have been studied since the 1960s in a central area of Kaštela Bay, in the more polluted eastern part systematic researches started only in 1980, when a "red tide" event was observed for the first time (section 4.2 of this report).

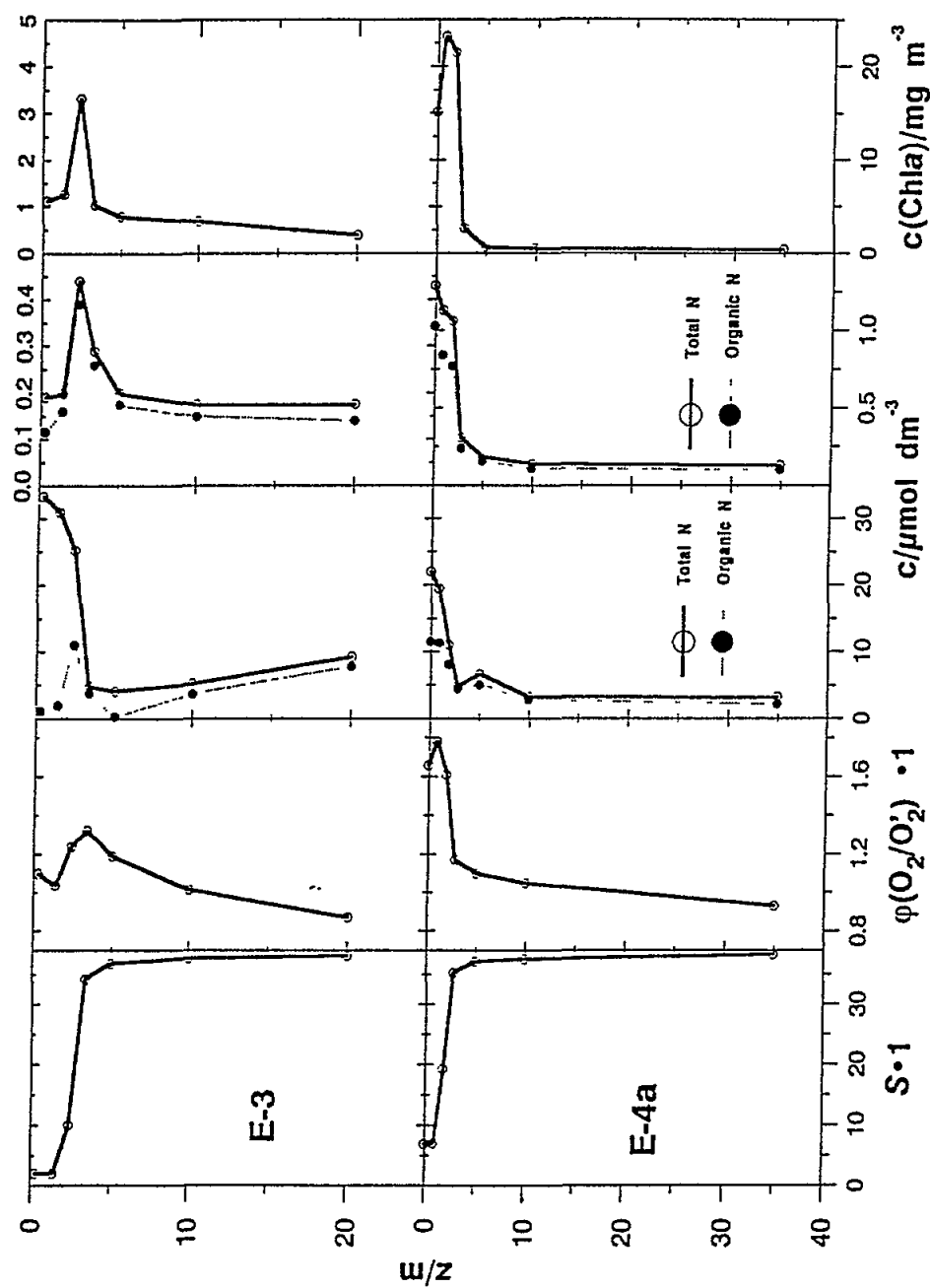


Fig. 3.1.3.6. Vertical distribution of salinity (s), oxygen saturation ratio ( $\phi$ ), total and organic nitrogen and phosphorus, and chlorophyll a concentrations (c) at stations E-3 (upper Krka Estuary) and E-4a (Šibenik Bay) on 13-14.05.1988 (CMR-R, unpublished data).



Significant variations in the distribution of surface salinity have been observed in Kaštela Bay, due to seasonal changes in the freshwater input from various sources and water column stratification, as well as correlated with wind influence (Zore-Armanda, 1980). Wind is also a dominant factor driving water circulation within the bay and water exchange between the bay and the Brač Channel (Gaillardet *et al.*, 1987). When the NE bora blows a cyclonic circulation is established in surface layer, which flows out from the bay. In contrast, under the SE "jugo" anticyclonic motions are induced with an input of surface waters in the bay from the Brač Channel. In summer, eddy circulation patterns are caused by "maestral" blowing, with a reduced exchange with the open sea. In these conditions "red tides" can develop (Marasovič *et al.*, 1991). Western and NW flows are dominant in the surface layer of the Brač and Split Channel, influenced by the main eastern Adriatic current. In the deeper layers compensation currents (E and NE) are the most frequent.

A reduced water exchange in the Vranjic area (station 1), compared with the area of station 5, may explain the observed patterns in the fluctuation of some parameters. Both regions are under a strong and variable influence of sewages, with a water transparency several times lower and an increased variability of salinity, pH, oxygen saturation, and nutrient concentrations in respect to the central area of Kaštela Bay (Barić 1989), and particularly to the reference station near Vis Island (Table 3.1.3.3). But, although in both Split areas the salinity varied in a similar ranges, nutrient concentrations, particularly orthophosphate (evidently originated from sewages), were higher at station 5 than in the Vranjic area. The TIN/PO<sub>4</sub> mean surface ratio is almost doubled at station 1 (33), compared with station 5 (only 18), and only slightly lower than at reference station 11 (39). In contrast, in the Vranjic area the oxygen saturation varied extremely, in much larger ranges than at station 5. The area of this station is open to the Brač Channel, and a significant portion of nutrients can be dispersed without having an impact on the marine ecosystem. On the contrary, in the Vranjic area, particularly during spring and summer, the residence time of the contributed nutrients is sufficient to induce intense phytoplankton blooms, in which oxygen supersaturations up to 180% can be measured, and as a consequence a very high microheterotrophic activity in the bottom layer can lead to near-anoxic conditions (15% of oxygen saturation, Table 3.1.3.3). In fact, in this area chlorophyll *a* concentration can vary in the same range as in Šibenik Bay (Marasovič and Vukadin, 1982), while in central Kaštela Bay the values are lower than 2 mg m<sup>-3</sup>.

In the Žrnovica estuary and Klek-Neum Bay the salinity ranges were only a little lower than in the two other studied Split areas. However, the water transparency was much higher (although significantly lower than at the reference station), and the ranges for nutrient concentration and ratios, and oxygen saturation were much smaller or even similar to those measured at the reference station (Table 3.1.3.3).

**Table 3.1.3.3.** Statistical data (N-number of samples, R-range,  $\bar{x}$ -mean) for basic oceanographic parameters and nutrients concentrations (c) in the surface and bottom layers of stations in the Split area (1984-1991).

Parameter <sup>b</sup>	Station <sup>a</sup> Layer Stat.	1		3		5		9		11	
		Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
$t/^{\circ}\text{C}$	N	30	29	12	12	29	27	29	26	26	26
	R	9.87-26.58	10.68-22.62	13.70-25.70	14.80-19.45	10.68-24.84	10.59-24.13	10.37-24.95	10.53-20.15	12.97-24.70	12.82-17.44
	$\bar{x}$	18.81	16.00	20.85	17.08	18.11	17.74	17.96	16.69	19.80	14.17
s-1	N	30	30	12	12	29	27	29	26	26	26
	R	28.98-37.89	36.92-38.81	32.17-38.34	36.26-38.54	30.86-38.27	32.20-38.56	32.75-38.44	35.46-38.78	36.39-38.95	38.49-38.87
	$\bar{x}$	35.46	37.73	35.42	37.71	36.23	36.97	36.08	37.56	38.25	38.69
$z_{SD}/\text{m}$	N	24	-	10	-	21	-	21	-	25	-
	R	1.0-11.5	-	5.0-15.0	-	2.0-9.0	-	6.0-15.0	-	14.5-37.0	-
	$\bar{x}$	4.6	-	10.3	-	4.4	-	10.4	-	23.4	-
pH	N	28	28	12	12	26	24	26	23	26	26
	R	7.66-8.45	7.79-8.34	8.14-8.39	8.05-8.27	7.96-8.42	7.98-8.37	7.99-8.32	8.01-8.31	8.18-8.33	8.07-8.28
	$\bar{x}$	8.27	8.20	8.25	8.20	8.24	8.24	8.22	8.21	8.23	8.19
$n(\text{O}_2/\text{O}_2') \cdot 1$	N	29	28	12	12	25	24	27	24	25	25
	R	0.66-1.77	0.15-1.06	0.95-1.33	0.82-1.23	0.76-1.23	0.77-1.11	0.82-1.26	0.82-1.27	0.88-1.24	0.76-1.00
	$\bar{x}$	1.13	0.85	1.14	1.01	1.00	0.98	1.07	1.05	1.04	0.88
$c(\text{PO}_4)$ $\mu\text{mol dm}^{-3}$	N	22	21	12	12	22	20	24	19	25	25
	R	0.04-1.02	0.02-0.17	0.03-0.15	0.03-0.16	0.05-1.54	0.05-0.73	0.05-0.47	0.03-0.20	0.00-0.13	0.03-0.24
	$\bar{x}$	0.16	0.08	0.07	0.08	0.42	0.18	0.10	0.08	0.05	0.08

**Table 3.1.3.3.** continued

Parameter <sup>b</sup>	Station <sup>a</sup>	1		3		5		9		11	
	Layer Stat.	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
$c(\text{NH}_4)$ $\mu\text{mol dm}^{-3}$	N	23	25	12	12	23	21	24	20	25	25
	R	0.35-3.12	0.37-2.74	0.12-2.34	0.22-2.46	0.32-8.25	0.28-6.00	0.28-3.85	0.03-2.13	0.24-2.55	0.22-2.32
	$\bar{X}$	1.10	1.11	1.01	1.35	2.47	1.73	1.20	0.97	0.97	0.83
$c(\text{NO}_2)$ $\mu\text{mol dm}^{-3}$	N	25	26	11	11	24	22	24	21	25	25
	R	0.03-0.47	0.04-0.63	0.04-0.13	0.03-0.24	0.06-0.97	0.05-0.56	0.04-0.46	0.04-0.51	0.03-1.98	0.02-2.63
	$\bar{X}$	0.13	0.13	0.09	0.09	0.26	0.17	0.13	0.14	0.17	0.21
$c(\text{NO}_3)$ $\mu\text{mol dm}^{-3}$	N	22	23	9	9	21	19	22	17	22	22
	R	0.52-2.14	0.09-1.81	0.00-1.98	0.35-1.30	0.31-2.55	0.40-3.09	0.28-3.20	0.30-3.09	0.27-1.40	0.05-5.49
	$\bar{X}$	1.13	0.88	0.74	0.85	1.19	1.21	1.04	1.12	0.74	1.11
$c(\text{TIN})$ $\mu\text{mol dm}^{-3}$	N	20	22	8	8	20	18	20	16	22	22
	R	1.31-4.79	1.24-3.56	0.54-2.78	0.69-3.76	1.24-8.16	1.25-9.21	1.34-4.80	1.51-4.30	1.01-3.32	1.18-6.02
	$\bar{X}$	2.40	2.12	1.92	2.26	3.45	3.15	2.49	2.30	1.91	2.17
$c(\text{SiO}_4)$ $\mu\text{mol dm}^{-3}$	N	17	17	12	12	15	15	16	16	18	18
	R	1.38-5.26	1.90-6.85	0.58-4.30	0.42-7.85	1.25-5.75	0.78-3.05	0.90-4.10	0.36-2.70	0.08-10.04	1.08-9.64
	$\bar{X}$	3.12	3.76	1.93	3.36	2.98	1.76	1.87	1.52	1.39	3.05

<sup>a</sup> 1 - Vranjic area; 3 - Klek-Neum Bay; 5 - Split main harbour; 9 - Žrnovica Estuary; 11 - reference station near Vis Island,

<sup>b</sup>  $t$  - temperature;  $s$  - salinity;  $z_{SD}$  - Secchi depth;  $n(\text{O}_2/\text{O}_2')$  - oxygen saturation ratio;  $\text{PO}_4$  - orthophosphate;  $\text{NH}_4$  - ammonium;  $\text{NO}_2$  - nitrite;  $\text{NO}_3$  - nitrate;  $\text{TIN} = \text{NH}_4 + \text{NO}_2 + \text{NO}_3$ ;  $\text{SiO}_4$  - orthosilicate.

#### 3.1.4. Eutrophication and phytoplankton blooms

Ecologically speaking, and in the broadest sense, eutrophication means a substantially increased biomass beyond the prevailing conditions in a given ecosystem, due to an unusually rich supply of nutrients to the euphotic layer. Unpolluted river discharges and upwelling induce natural eutrophication in marine environment. Sewage and manure discharges, as well as land drainage from agriculture areas are responsible for anthropogenic eutrophication. Since the physiological process is the same, it is difficult in some cases to estimate the relative contributions of different mechanisms (eg natural vs anthropogenic nutrient discharges of a polluted river). However, while naturally slower eutrophication processes generally allow the ecosystem to adjust to increased trophic conditions, rapid anthropogenic influences often led to ecosystem disequilibrium and to stressed environment with possible harm to living resources.

Periodical increased "ingression" of Levantine intermediate waters from the Ionian Sea, approximately every nine years (Buljan and Zore-Armanda, 1976), represents a mechanism of natural eutrophication of central and southern Adriatic regions. During such an event the nutrient inputs to the Adriatic Sea can be as great as the yearly contributions of the Po River, (Zore-Armanda and Pucher-Petkoviæ 1976). Increased sardine catch (within 20%) followed "ingression" events with three year delays (necessary for fish growth).

Anthropogenic eutrophication was identified in several Adriatic coastal regions (UNESCO, 1988). Along the eastern Adriatic coast anthropogenic eutrophication-related phenomena, apparently related to inadequate wastewater disposal, have been reported within the harbour area of larger urban or industrial centres (Pula, Rijeka, Šibenik, Split) and in some semi-enclosed embayments with reduced water exchange (eg Bakar Bay, Novigradsko More, Karinsko More, Kaštela Bay and Boka Kotorska; Maretiæ *et al.*, 1978; Smoldaka, 1985; Pucher-Petkoviæ *et al.*, 1988; Vilièi 1989; Marasoviæ 1990; Degobbis, 1990a). These phenomena ranged from relatively small, but significant increases of primary production or phytoplankton bloom frequency to "red tide" events and near anoxic conditions in bottom layers. In addition, combined natural and anthropogenic eutrophication at a regional level in the northern Adriatic periodically affected the western Istrian coastal ecosystem.

The periodical "red tides" due to *Noctiluca miliaris*, observed during late 1970s and early 1980s in the Rovinj area (CMR-R, unpublished data), as well as in the gulfs of Trieste (Fonda-Umani, 1985; A. Malej, personal communication) and Venice (Bianchi *et al.*, 1981), were probably not related to anthropogenic influence. These blooms were usually quickly dispersed by currents and wind.

#### Eutrophication of the open northern Adriatic and influence on the western Istrian coastal region

The northern Adriatic is one of the most, if not the most eutrophied region of the Mediterranean. Eutrophication impact on the northern Adriatic ecosystem results from the combined influence, and changing relative importance, of external nutrient input cycle (mainly anthropogenic), the degree of water column stratification, and water advection, as they control and/or moderate biological assimilation and regeneration processes in the water column and at the sediment-water interface.

The Po River freshwater discharge is the primary factor governing eutrophication processes in the northern Adriatic ecosystem. Not only does it represent the major nutrient input to the marine ecosystem, but also significantly influences the water column stratification characteristics and the general circulation in the Adriatic. This is particularly marked during late spring when discharge rates are increased, the nutrients regenerated during the winter are mostly exhausted in the previous blooms, and the northern Adriatic behaves as a stratified semi-enclosed sea. The conditions of eddy circulation, with reduced water exchange, dominate throughout the summer and the first part of the autumn. This increases the residence time of the produced organic matter in the region and the oxygen demand for its decomposition.

Thus, the monitoring of late spring blooms can provide an index of regional eutrophication and allow an early warning of possible near anoxia or anoxia events in the subsequent summer and fall, when river discharge rate is low (Smodlaka, 1986; Degobbi, 1989).

The phytoplankton succession of the late spring and early summer blooms are dominated by diatoms (*Skeletonema costatum*, *Nitzschia* and *Chaetoceros* species), unidentified nanophytoplankton (probably mostly nanoflagellates), or, but less frequently, by dinoflagellates (*Prorocentrum* and *Gonyaulax* species; Revelante and Gilmartin, 1976, Gilmartin and Revelante, 1980; Lalami-Taleb *et al.*, 1985; Filipiæ 1990; CMR-R, unpublished results). Very intensive cyanobacteria blooms can also occur. For instance, in June and July 1991 the cyanobacteria concentration (up to  $10^9 \text{ dm}^{-3}$ ) was an order of magnitude higher than in 1990 and 1992 (D. Fuks, personal communication). Some diatom and dinoflagellate species, which dominated the blooms during the 1970s, were substituted by other species during the 1980s (section 4.2 of this report).

The freshwater nutrient impact on the northern Adriatic ecosystem can vary greatly in different years. Periodically (eg in 1977), unusually high Po River nutrient discharges greatly increased organic matter production and decomposition rates (Degobbi *et al.*, 1979). Freshwaters "flooded" the entire area, up to the western Istrian coasts, markedly increasing the stratification of the water column. The sedimented excess organic matter caused a higher than normal oxygen demand and created near-anoxic conditions in the bottom waters of the open northern Adriatic (oxygen saturations 13-40% in September).

In other cases, vertical and horizontal water mixing can be reduced significantly because of long periods of calm weather (eg in 1988, 1989, and 1991), increasing the nutrient residence time and its effect on the ecosystem of this region (Degobbi, 1989; Degobbi *et al.*, 1991a; CMR-R, unpublished results). Consequently, near-anoxic conditions occurred in bottom layers, culminating in the November 1989 anoxia event with mass mortality of benthic macro- (Jaklin and Zahtila, 1990) and meio-fauna (Travizi, 1990) over about 1,000 km<sup>2</sup> area, and significant damages to the biological communities over at least 3,500 km<sup>2</sup>. Interestingly, in these years the most critical conditions occurred in the eastern part of the open northern Adriatic, which from available data can be considered as an oligotrophic area (Degobbi *et al.*, 1990; Gilmartin *et al.*, 1990), and the most recent data confirmed this evaluation (Degobbi *et al.*, 1990; CMR-R, unpublished data). At this time the western Istrian coastal region was influenced significantly, with 8-15% oxygen saturation measured near the bottom. Thus, this event is most probably due to changes in the circulation of bottom water masses during the fall. In this case, it does not make sense to apply an

"oxygen index" (ie a quantitative number), maybe suitable for some lakes with reduced water exchange, as a criterion of the eutrophication degree of the northern Adriatic, as proposed recently (eg Justiæ 1991).

In the summers of 1988, 1989, and 1991, after more than 50 years (Fonda-Umani *et al.*, 1989), mucilaginous material appeared in the northern Adriatic in very large quantities (Degobbis, 1989; Stachowitsch *et al.*, 1990; Degobbis *et al.*, 1991b; CMR-R, unpublished data). Suspended and sinking aggregates (up to 3-4 m in maximum dimension) created serious problems for fisheries. Large quantities of sticky gelatinous masses, floating primarily on sea surface, were deposited on beaches by wind and currents, reducing their suitability for bathing.

Initially, considerable controversy surrounded the origins and development mechanisms of the aggregates, but now there is a consensus that they represent a buildup of organic and inorganic material from a matrix, which probably originated as phytoplankton (diatom) polysaccharide exudates. A phytoplankton hypertrophic exudate production may be caused by stress conditions due to increased environmental variability (Degobbis *et al.*, 1991b; section 4.2 of this Report). Mucous material aggregation and accumulation was favoured by conditions of extremely reduced vertical and horizontal water mixing, due to unusually long periods of calm weather during the summer, characterized by high atmospheric pressure (M. Orliæ personal communication). Even if the mucilage hypertrophy has a natural origin, the key role of phytoplankton can suggest that eutrophication may be important. In fact, the intensity and duration of the phenomenon were particularly marked in the northern Adriatic compared with the rest of the Adriatic or the Tyrrhenian Sea.

#### Eutrophication in the Krka Estuary area

In the Krka estuary, as in the other karstic estuaries of the Adriatic Sea, natural inorganic nitrogen/orthophosphate ratios are much higher than in the open sea (section 3.1.3 of this report). Thus, only a relatively small anthropogenic phosphorus addition may be critical for the ecosystem equilibrium, causing undesirable eutrophication processes. The increase of phytoplankton biomass and primary production rates in Šibenik Bay (section 3.1.2 of this report) can be related to sewage phosphorus enrichment. In this bay significantly higher chlorophyll *a* concentrations (up to 26 mg m<sup>-3</sup>; Gržetiæ *et al.*, 1991; Denant *et al.*, 1991) were observed, compared to the inner estuary area, and particularly in respect to the coastal and Kornati Islands regions. In fact, these values are similar to those measured off the Po Delta. Moreover, substantial changes in the phytoplankton community, dominant species composition occurred during the summer blooms in the last two decades (section 4.2 of this report).

Interestingly, even if the organic production was higher in Šibenik Bay, compared to the upper estuary, the oxygen content in the bottom layer was apparently less affected (minimum oxygen saturation ratio 78% and 16%, respectively; Table 3.1.2.3). This is most probably related to the water exchange near the bottom, which is more intensive in Šibenik Bay which is directly connected to the coastal sea. Preliminary current measurements indicated that below the halocline the resultant flow was directed towards the Krka mouth, i.e. contrary to the surface water flow (compensation current; Gržetiæ 1990; Legoviæ *et al.*, 1991a).

In October 1988, in the southern part of the Prokljan Lake, the oxygen saturation was very low (locally below 10%), and a significant mortality of benthic organisms was observed (Legović *et al.*, 1991b). Increased oxygen consumption was related to the decay of a very intense bloom, dominated by the dinoflagellate *Gonyaulax polyedra*, which occurred immediately below the halocline in conditions of a minimal advection, due to an unusually low freshwater discharge rate (Legović *et al.*, 1991c).

#### Plankton blooms in the Split area

In the Vranjic basin (station 1) very intense dinoflagellate blooms ("red tides"), mainly due to dinoflagellate *Gonyaulax polyedra*, occurred several times during the 1980s, in late spring and/or summer, when the water exchange was strongly reduced (Marasović 1990). *Prorocentrum micans* and *Eutreptiella pescheri* also contributed significantly to the blooms. Benthic organism and fish kills were observed in 1980, 1985, and 1987 during "red tide" events, probably due to a drop in dissolved oxygen concentrations in the bottom layer (saturation down to 10%; Marasović 1990).

In 1984 a "red tide", due to *P. micans* and *E. pescheri*, was observed in the right side of the entrance to Kaštela Bay (station 5), including the Split main harbour.

The freshwater influence in the Žrnovica Estuary and Klek-Neum Bay (indicated by surface salinity variations) is probably as significant as in the other Split coastal areas. However, nutrient and oxygen concentrations were rather similar to those observed at the reference station, near Vis Island. Nutrient concentrations in freshwaters discharged into these two areas may be lower than in those discharged into the Vranjic and Split harbour areas, and/or water exchange is more effective reducing their impact on the marine ecosystem.

Composition changes in the phytoplankton community of the Split area and Kaštela Bay in the last decades, which may be related to eutrophication, are described in the section 4.2 of this report.

## 3.2. Heavy metals

### 3.2.1. Heavy metals in effluents

A summary of results obtained from heavy metal analyses in effluents was based on calculations of geometric means and standard deviations (Tables 3.2.1.1-3). These statistical parameters were more convenient with respect to arithmetic means and standard deviations, because heavy metal concentrations varied within large ranges.

On average, the heavy metal concentrations measured in the various investigated areas, did not generally differ substantially (Table 3.2.1.1). Significantly higher concentrations were only measured for Cd in Split, Pb in Rijeka, Cr in Zadar and Zn in the Slovenian effluents, compared with other regions. However, if the very high Cr concentrations in the effluents from the Zadar tannery are excepted, no serious effluent contaminations with other heavy metals can be assessed. In fact, the differences for Cd, Pb, and Zn concentrations were more probably due to different sampling techniques and sensitivities of the analytical methods applied, than to contamination processes. Consequently, the assumption that no significant changes of heavy metal concentration occurred in effluents during the period 1983-1991 should be founded.

Based on the geometric means calculated from the data (Table 3.2.1.1) the annual discharge rates of the investigated heavy metals by urban (Table 3.2.1.2) and industrial (Table 3.2.1.3) effluents were calculated. The effluents from the Split area represented the most significant Hg and Cd pollution source in respect to effluents from the other investigated areas (Fig. 3.2.1.1).

### 3.2.2. Heavy metals in suspended matter

Cd and Hg concentrations and mass fractions in suspended matter were measured in the surface layer during the period 1983-1986 and in surface and bottom layers in 1987-1990 in the Slovenian coastal area only. Cr, Cu, Fe, Mn, Ni, Pb, and Zn concentrations were also determined in 1989 at all stations. In 1990 these metals were analysed at station F only, in surface and bottom layer samples, as well as in particles collected by "sediment traps". This experiment was designed to estimate heavy metal sedimentation fluxes and mass balances in the marine ecosystem.

The highest total Hg geometric mean (GM) concentration in surface samples was obtained for 1985 ( $13.2 \text{ ng dm}^{-3}$ ) and the lowest in 1990 ( $3.9 \text{ ng dm}^{-3}$ ; Table 3.2.2.1; Fig. 3.2.2.1). Most part of the values were included in the range reported for a coastal area of the northern Tyrrhenian Sea, which is influenced by anthropogenic Hg ( $1.5\text{-}8.0 \text{ ng dm}^{-3}$ , Ferrara *et al.*, 1986).

While the maximum absolute Cd concentration was measured in 1988 ( $156 \text{ ng dm}^{-3}$ ), the highest GM concentration ( $25.7 \text{ ng dm}^{-3}$ ) was recorded in 1989 (Table 3.2.2.1; Fig. 3.2.2.1). The 1990 values (although for station F only) were also significantly increased in respect to the period 1983-1988. This suggests that



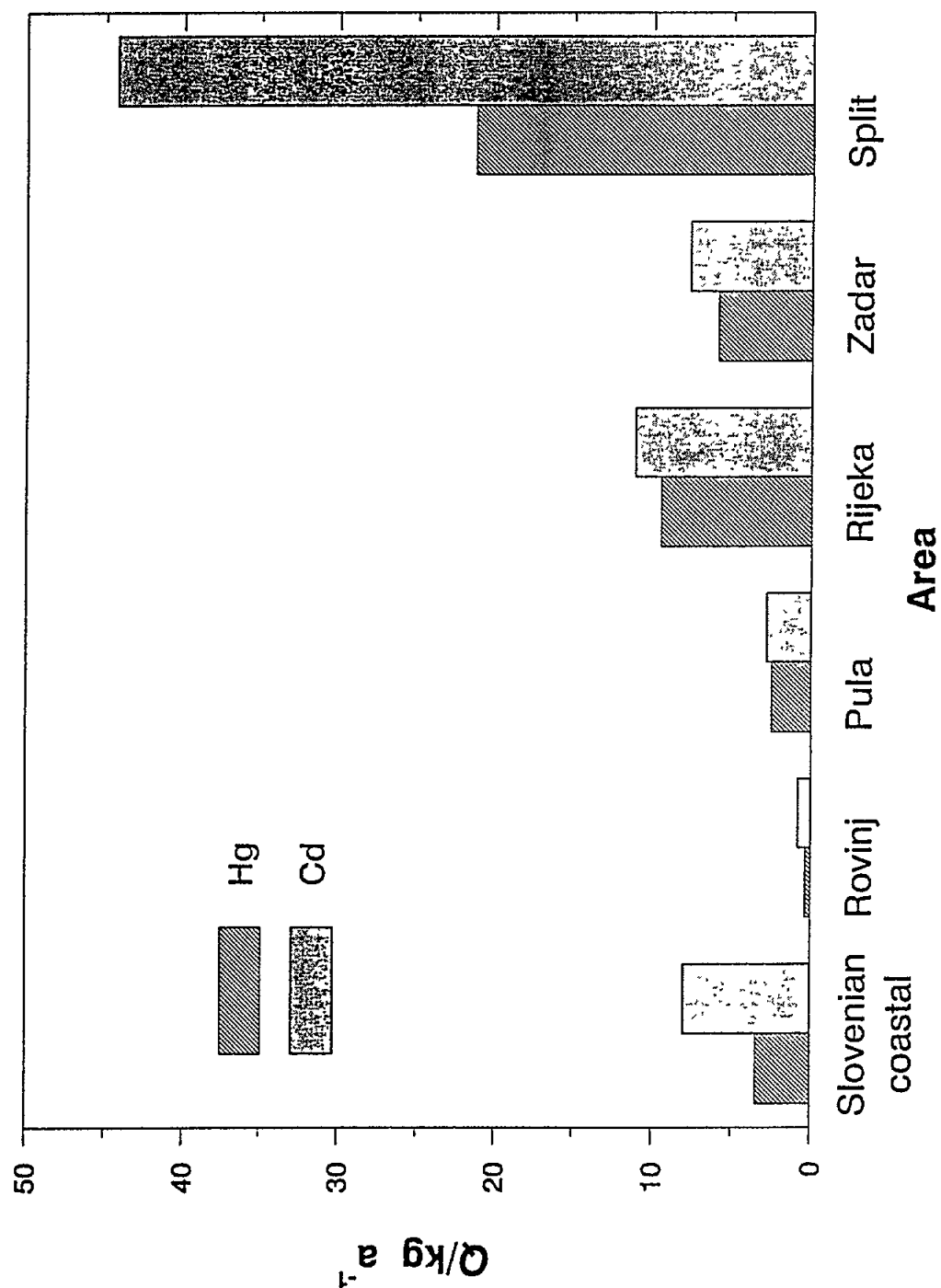


Fig. 3.2.1.1. Annual average discharge rates (Q) of Hg and Cd in urban effluents from different areas.

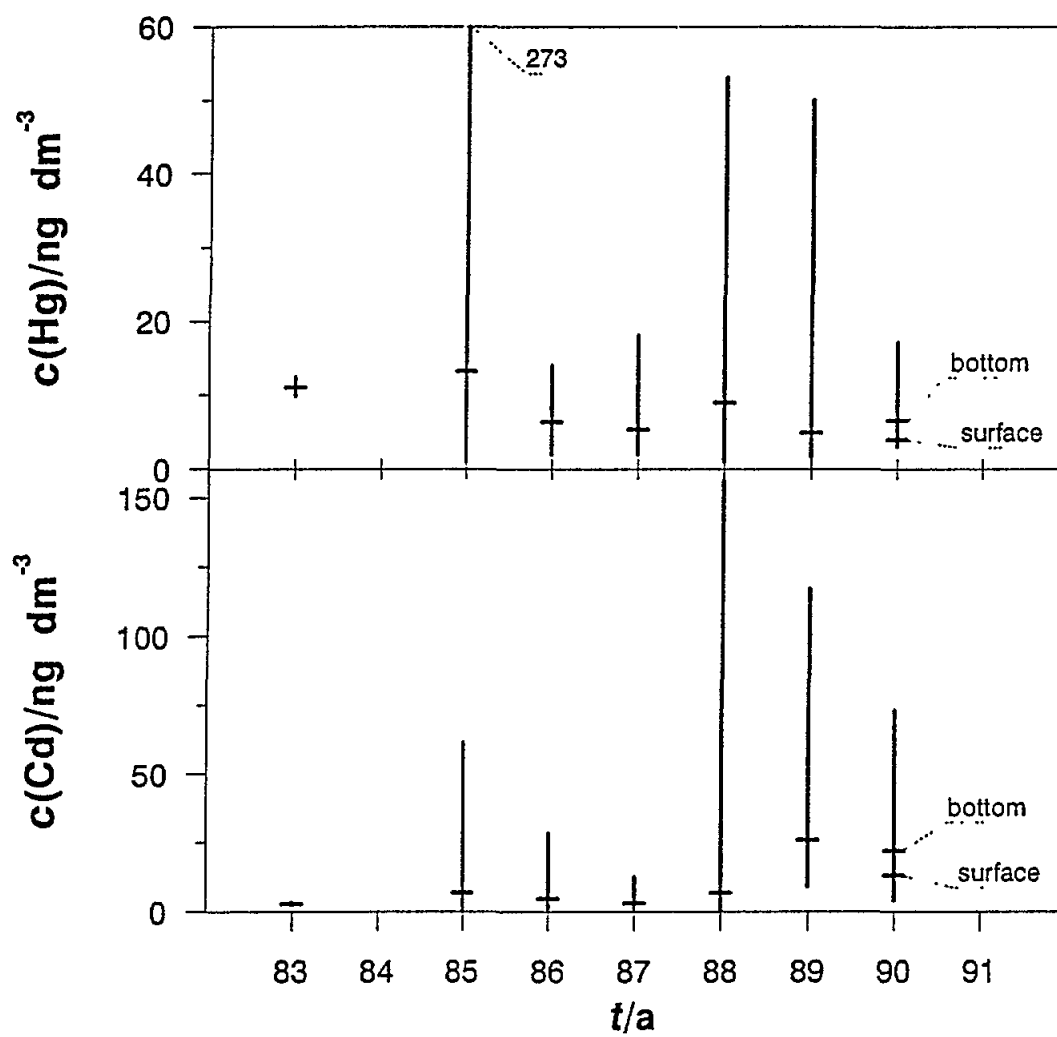


Fig. 3.2.2.1. Concentrations ( $c$ , GM with ranges) of Hg and Cd for different years ( $t$ ) in suspended particles from the Slovenian coastal area.

**Table 3.2.1.1.** Heavy metals concentration (c) in sewage and some industrial waste waters discharged into the sea along the Adriatic coast (N= number of samples, GM= geometric mean; GSD= geometric standard deviation).

Area Locality	Samp. Orig.		c(Hg)/ $\mu\text{g dm}^{-3}$			c(Cd)/ $\mu\text{g dm}^{-3}$			c(Pb)/ $\text{mg dm}^{-3}$		
	code		N	GM	GSD	N	GM	GSD	N	GM	GSD
Slovenian coastal											
Piran	PA	U	13	0.1	4.5	13	0.7	2.9	13	5.0	2.4
Piran	PB	U	13	0.2	3.2	13	0.5	3.3	13	5.3	2.0
Izola	IA	U	13	0.3	3.1	13	1.1	3.0	13	5.9	2.1
Koper	KA	U	4	0.4	1.5	4	1.2	3.1	4	10.5	1.6
Koper	KB	U	8	0.1	2.5	8	0.5	1.9	8	4.4	2.1
Badaševica	BA	Ri	13	0.1	2.8	13	0.5	3.8	13	5.9	3.2
Izola	DE	I	12	0.3	2.2	12	1.1	3.0	11	5.8	1.9
Drnica	DN	Ri	13	0.1	1.8	13	0.5	4.5	13	3.5	3.5
Dragonja	DR	Ri	13	0.1	2.9	13	0.3	2.3	12	2.7	3.0
Rižana	RI	Ri	11	0.1	3.0	11	0.4	6.8	9	2.7	6.0
Rovinj											
Fish.proc.plant	5AI	U	13	0.2	2.0	18	0.4	4.4	-	-	-
Tabacco fact.	6AI	U	12	0.1	2.7	19	0.3	3.0	-	-	-
Pula											
Pula harbour	I	U	29	0.3	7.4	28	0.4	3.3	20	4.5	9.6
Medulin harbour	II	U	28	0.3	7.0	28	0.2	2.9	16	2.7	13.7
Siporex	SI	I	24	0.4	19.1	23	0.5	4.1	16	1.3	8.8
Pula	5	U	4	0.1	1.0	4	0.1	1.5	4	5.7	2.2
Pula	10	U	4	0.1	1.0	4	0.1	1.0	-	-	-
Pula	13	U	5	0.1	1.0	5	0.1	1.0	-	-	-
Raša	RA	Ri	28	0.2	3.5	28	0.3	3.1	16	0.8	6.5
Rijeka											
Opatija	U1	U	15	0.6	1.9	19	0.7	5.5	16	35.9	1.8
Children clinic	U2	U	15	0.6	2.8	17	0.6	3.5	13	12.1	3.2
Kantrida shipy.	U3	U	15	0.6	3.2	17	0.7	3.4	14	23.3	4.8
Mlaka	U4	U	15	0.7	2.6	20	0.5	3.5	17	30.5	3.0
Customs	U5	U	15	0.4	2.6	19	0.5	4.4	15	16.8	3.2
Brajdica	U6	U/I	14	0.6	2.8	17	0.8	4.5	13	10.5	2.9
Rječina	U7	U	15	0.6	2.9	21	0.7	4.2	17	11.8	4.3
Martinševica	U8	U	16	0.4	2.5	16	0.6	4.3	12	25.9	2.2
Bakar	U9	U	16	0.5	1.9	10	0.3	6.6	7	32.6	1.3
Kraljevica	U10	U	16	0.4	2.6	15	0.5	7.3	12	37.5	3.1
Crkvenica	U11	U	15	0.3	2.0	19	0.8	3.3	15	22.3	2.7
Omišalj	U12	U	15	0.4	2.9	17	0.6	2.9	13	9.1	2.6
Ika	I1	I	15	0.7	3.2	20	0.5	5.6	16	12.3	4.9
INA Urinj	I2	I	12	0.6	2.6	19	0.4	3.3	16	29.8	2.9
Zadar											
Maraska	I1	I	14	1.4	9.0	10	0.4	9.4	12	3.7	31.1
Boris Kidrič	I2	I	15	3.6	5.8	12	0.7	11.8	13	1.2	31.2
Kolovare	I3	U	15	0.8	6.9	11	1.1	16.6	12	2.0	27.3
Kozara	I4	I	14	0.8	10.3	11	0.4	10.1	11	2.0	20.7
Split											
Split harbour 1	1	U	28	0.8	4.5	27	1.4	7.4	27	10.1	10.7
Split harbour 2	2	U	28	0.9	4.6	28	1.9	6.0	28	5.6	15.3
Zenta	3	U	28	0.8	3.2	27	1.4	7.9	28	5.4	15.2
Trstenik	4	U	28	0.9	3.7	26	1.2	7.1	26	3.9	14.9
Lav	5	U	28	1.0	3.4	28	1.8	6.7	27	6.0	15.0
Lora	6	U	28	0.9	3.5	28	2.4	4.6	28	6.6	9.8
Duje	7	U	28	0.9	4.1	28	2.5	5.6	28	6.3	14.7

**Table 3.2.1.1.** continued

Area Locality	Samp. Orig.		c(Cr)/ $\mu\text{g dm}^{-3}$			c(Zn)/ $\mu\text{g dm}^{-3}$			c(Cu)/ $\text{mg dm}^{-3}$		
	code		N	GM	GSD	N	GM	GSD	N	GM	GSD
Slovenian coastal											
Piran	PA	U	6	6.4	2.6	13	1742.9	4.7	6	8.4	7.3
Piran	PB	U	6	7.4	3.7	13	625.7	21.3	6	13.2	2.0
Izola	IA	U	6	6.6	3.1	13	1532.8	6.6	6	19.6	2.7
Koper	KA	U	-	-	-	4	7527.5	3.1			
Koper	KB	U	3	16.3	1.5	8	1539.7	4.1	3	12.1	1.4
Badaševica	BA	Ri	13	10.0	2.8	13	1233.9	5.3	6	50.9	10.6
Izola	DE	I	12	16.9	3.2	12	3009.7	3.1	6	52.8	2.0
Drnica	DN	Ri	11	6.5	3.7	13	850.6	6.5	6	38.6	8.6
Dragonja	DR	Ri	11	1.8	4.1	13	582.9	29.2	6	4.2	-
Rižana	RI	Ri	6	1.5	3.4	11	646.5	11.1	6	9.2	28.1
Pula											
Pula harbour	I	U	3	0.1	1.0	16	254.9	3.3	9	63.2	7.0
Medulin harbour	II	U	4	0.1	1.0	11	143.7	7.9	4	47.2	3.1
Siporex	SI	I	4	0.1	1.0	11	46.9	5.8	4	16.7	1.8
Pula	5	U	-	-	-	4	331.7	1.6	4	24.7	1.8
Raša	RA	Ri	4	0.1	1.0	12	14.8	11.5	4	10.9	1.2
Rijeka											
Opatija	U1	U	-	-	-	19	229.5	2.4	14	39.9	1.4
Children clinic	U2	U	-	-	-	17	178.9	2.7	9	29.7	2.7
Kantrida shipy.	U3	U	-	-	-	17	118.2	3.1	10	38.2	1.6
Mlaka	U4	U	-	-	-	21	171.1	3.2	14	46.2	1.8
Customs	U5	U	-	-	-	19	97.3	4.6	12	28.9	2.2
Brajdica	U6	U/I	-	-	-	17	71.5	4.7	12	25.9	2.4
Rječina	U7	U	-	-	-	20	97.6	2.3	13	24.4	2.3
Martinševica	U8	U	-	-	-	16	303.1	2.7	11	34.7	2.0
Bakar	U9	U	-	-	-	10	323.0	2.7	7	56.3	1.6
Kraljevica	U10	U	-	-	-	15	226.8	2.7	9	38.9	1.5
Crkvenica	U11	U	-	-	-	19	203.8	3.0	12	36.7	1.8
Omišalj	U12	U	-	-	-	16	124.5	1.8	10	24.0	1.7
Ika	I1	I	-	-	-	19	177.0	2.1	12	38.1	1.8
INA Urinj	I2	I	-	-	-	19	129.9	2.8	13	16.7	2.4
Zadar											
Maraska	I1	I	12	9.3	33.7	13	265.4	1.9	-	-	-
Boris Kidrič	I2	I	12	9.8	30.9	13	209.1	1.9	-	-	-
Kolovare	I3	U	11	4.4	42.0	15	235.7	3.0	-	-	-
Kozara	I4	I	14	6693.2	6.4	14	276.2	2.4	-	-	-
Split											
Split harbour 1	1	U	28	3.2	9.0	28	66.9	3.0	-	-	-
Split harbour 2	2	U	28	5.6	5.7	28	72.1	2.8	-	-	-
Zenta	3	U	28	6.6	3.0	28	60.0	3.0	-	-	-
Trstenik	4	U	28	4.8	8.2	28	67.2	2.7	-	-	-
Lav	5	U	28	3.6	10.3	28	66.8	2.7	-	-	-
Lora	6	U	28	6.5	6.4	28	56.8	2.9	-	-	-
Duje	7	U	28	4.8	5.6	28	72.0	2.9	-	-	-

**Table 3.2.1.2.** Geometric mean of concentrations ( $\bar{c}$ ) and the annual discharge rates (Q) of heavy metals in urban effluents and of urban effluents (U) at different areas.

Area	$\frac{Q(U)}{10^6 \text{ m}^3 \text{ a}^{-1}}$	$\bar{c}(\text{Hg})$ $\text{mg dm}^{-3}$	$Q(\text{Hg})$ $\text{kg a}^{-1}$	$\bar{c}(\text{Cd})$ $\text{mg dm}^{-3}$	$Q(\text{Cd})$ $\text{kg a}^{-1}$	$\bar{c}(\text{Pb})$ $\text{mg dm}^{-3}$	$Q(\text{Pb})$ $\text{kg a}^{-1}$	$\bar{c}(\text{Cr})$ $\text{mg dm}^{-3}$	$Q(\text{Cr})$ $\text{kg a}^{-1}$	$\bar{c}(\text{Zn})$ $\text{mg dm}^{-3}$	$Q(\text{Zn})$ $\text{kg a}^{-1}$	$\bar{c}(\text{Cu})$ $\text{mg dm}^{-3}$	$Q(\text{Cu})$ $\text{kg a}^{-1}$
Piran	9.58	0.36	3.41	0.84	8.02	5.33	51.06	6.45	61.79	2161.6	20708	9.2	88.4
Rovinj	2.11	0.14	0.30	0.37	0.79	-	-	-	-	-	-	-	-
Pula	8.73	0.28	2.45	0.32	2.80	3.61	31.55	0.10	0.87	199.3	1740	55.2	481.7
Rijeka	18.19	0.52	9.45	0.61	11.12	23.97	435.98	-	-	195.0	3548	37.0	673.9
Zadar	7.04	0.84	5.91	1.09	7.67	2.01	14.16	4.35	30.63	235.7	1660	-	-
Split	24.35	0.87	21.28	1.82	44.27	6.27	152.75	5.03	122.60	66.0	1606	-	-

**Table 3.2.1.3.** Geometric mean of concentrations ( $\bar{c}$ ) and the annual discharge rates (Q) of heavy metals in industrial effluents and of industrial effluents (I) at different areas.

Area Locality	$\frac{Q(I)}{10^9 \text{ m}^3 \text{ a}^{-1}}$	$\bar{c}(\text{Hg})$ $\mu\text{g dm}^{-3}$	$Q(\text{Hg})$ $\text{kg a}^{-1}$	$\bar{c}(\text{Cd})$ $\mu\text{g dm}^{-3}$	$Q(\text{Cd})$ $\text{kg a}^{-1}$	$\bar{c}(\text{Pb})$ $\mu\text{g dm}^{-3}$	$Q(\text{Pb})$ $\text{kg a}^{-1}$	$\bar{c}(\text{Cr})$ $\mu\text{g dm}^{-3}$	$Q(\text{Cr})$ $\text{kg a}^{-1}$	$\bar{c}(\text{Zn})$ $\mu\text{g dm}^{-3}$	$Q(\text{Zn})$ $\text{kg a}^{-1}$	$\bar{c}(\text{Cu})$ $\mu\text{g dm}^{-3}$	$Q(\text{Cu})$ $\text{kg a}^{-1}$
<b>Izola</b>													
Dlamaris (DE)	0.70	0.27	0.2	1.08	0.8	5.79	4.1	16.92	11.8	3009.71	2106.8	52.81	37.0
<b>Pula</b>													
Siporex (SI)	0.90	0.42	0.4	0.47	0.4	1.35	1.2	0.10	0.1	46.91	42.2	16.73	15.1
<b>Rijeka</b>													
Brajdica (U6)	31.50	0.59	18.6	0.78	24.6	10.50	330.8	1.00	31.5	71.55	2253.7	25.94	817.2
Ika (I1)	0.04	0.69	0.0	0.52	0.0	12.29	0.5	1.00	0.0	177.05	6.7	38.15	1.4
INA Urinj (I2)	1.58	0.60	0.9	0.37	0.6	29.77	47.0	1.00	1.6	129.92	205.3	16.65	26.3
<b>Zadar</b>													
Maraska (I1)	0.10	1.44	0.1	0.40	0.0	3.74	0.4	9.25	0.9	265.43	25.7	-	-
Boris Kidriè (I2)	0.18	3.58	0.6	0.73	0.1	1.21	0.2	9.78	1.8	209.07	37.6	-	-
Kozara (I4)	0.11	0.77	0.1	0.42	0.0	2.05	0.2	6693.18	763.0	276.15	31.5	-	-

**Table 3.2.2.1.** Mean year statistical data (N-number of samples, range, GM-geometric mean, GSD-geometric standard deviation) for heavy metal (HM) concentration (c) and mass fraction (w) in suspended matter (dry weight) from the Slovenian coastal area.

Metal	Year	Layer	Range c(HM)/ng dm <sup>-3</sup>	N	GM c(HM)/ng dm <sup>-3</sup>	GSD	GM w <sub>w</sub> (HM)·10 <sup>6</sup>	GSD
<b>Hg</b>	1983.	surface	9.9-12.3	2	11.0	1.2	-	-
	1985.	"	<1-273	45	13.2	4.1	7.7	5.2
	1986.	"	2-14	48	6.3	1.7	1.6	1.7
	1987.	surf.& bott.	2-18	46	5.3	1.6	1.2	1.9
	1988.	"	<1-53	48	8.9	4.2	3.9	2.7
	1989.	"	1.6-50	32	4.8	2.9	-	-
	1990.	surface	3-7	3	3.9	1.5	1.8	1.8
	1990.	bottom	4-17	3	6.5	1.9	1.7	1.7
<b>Cd</b>	1983.	surface	2.1-3.2	2	2.6	1.4	-	-
	1985.	"	<0.1-61	52	6.6	5.9	2.9	4.7
	1986.	"	<0.7-28	37	4.4	3.0	1.2	3.5
	1987.	surf.& bott.	0.8-12	44	2.9	2.3	0.7	2.7
	1988.	"	<0.1-156	48	6.7	4.0	1.5	5.4
	1989.	"	9.0-117	32	25.7	1.7	-	-
	1990.	surface	4-53	3	12.8	2.9	6.3	2.9
	1990.	bottom	7-73	3	21.7	2.6	5.0	2.8
<b>Cr</b>	1989.	surf.& bott.	<sup>a</sup> BDL-296	27	114.9	2.4	-	-
	1990.	surface	13-61	3	35.6	2.0	16.0	2.1
	1990.	bottom	97-240	3	138.0	1.5	33.9	1.4
<b>Cu</b>	1989.	surf.& bott.	32-1702	32	217.3	2.4	-	-
	1990.	surface	66-132	3	86.8	1.4	39.0	1.5
	1990.	bottom	415-4056	3	1442.2	2.6	353.9	2.8
<b>Fe</b>	1989.	surf.& bott.	2410-38400	32	10010.0	2.2	-	-
	1990.	surface	2446-13764	3	6035.1	2.0	2716.9	2.4
	1990.	bottom	60681-103191	3	74481.2	1.3	18275.9	1.3
<b>Mn</b>	1989.	surf.& bott.	106-1302	32	521.3	2.0	-	-
	1990.	surface	862-1641	3	1099.6	1.3	495.2	1.1
	1990.	bottom	1091-2734	3	1701.0	1.5	417.6	1.4
<b>Ni</b>	1989.	surf.& bott.	10-348	28	71.9	2.2	-	-
	1990.	surface	<sup>a</sup> BDL-172	3	29.4	10.9	15.9	7.1
	1990.	bottom	203-1537	3	660.6	2.4	162.2	2.6
<b>Pb</b>	1989.	surf.& bott.	8-752	32	121.0	3.1	-	-
	1990.	surface	60-132	3	95.2	1.4	42.6	1.3
	1990.	bottom	563-3124	3	1266.3	2.0	310.3	2.1
<b>Zn</b>	1989.	surf.& bott.	292-134800	32	2481.4	5.8	-	-
	1990.	surface	208-2133	3	581.8	2.6	262.0	3.3
	1990.	bottom	2843-8315	3	5197.7	1.6	1275.8	1.6

<sup>a</sup> BDL - Below Detection Limit

related to the Cd biogeochemical cycle, some changes might occur recently in the area, which should be investigated and additionally monitored.

The other heavy metals were measured over a wider area (six stations) in 1989, but at a single station (F) in 1990 (Table 3.2.2.1). Thus, temporal and spatial changes could not be evaluated. However, these data indicated that significant differences in the particulate heavy metal contents in the water column can occur. While in the period 1987-1989 the surface and bottom values were similar, in 1990 the concentrations measured in the bottom layers were higher than in the upper part of the water column, particularly for Cu, Fe and Zn: the bottom/surface layer concentration ratios amounted to 1.7 for Hg, Cd, and Mn, 3.9 for Cr, 9 for Zn, 12-13 for Fe and Pb, 17 for Cu, and up to 23 for Ni. For some metals (Hg, Cd, and Mn) these differences were exclusively due to accumulation of sedimented particles, because the mass fraction values in the suspended particles collected in the surface and bottom layers were approximately the same. In contrast, an enrichment of particles with the other metals during sedimentation also contributed to the increase of total bottom concentrations. In fact the bottom/surface mass fraction ratios varied from 2 for Cr, 5 for Zn, and 7 for Fe up to 9 for Cu and 10 for Ni (Table 3.2.2.1).

A preliminary estimate of heavy metal sedimentation fluxes during 1990 varied substantially, depending on the species: up to four orders of magnitude between Hg (and Cd) and Fe (Table 3.2.2.2). Moreover, the seasonal variability of the fluxes was different for the various metals. As an example, the ratio of maximum vs minimum flux values varied from only 1.2 for Pb up to 138 for Cu. For most of the metals the maximum fluxes were recorded in October. Additional measurements should be performed to obtain reliable data useful for mass balance calculations.

**Table 3.2.2.2.** Preliminary results on heavy metal (HM-Hg, Cd, Cr, Pb, Cu, Zn, Ni, Mn, Fe) flux ( $f$ , from sediment trap data, 1 m above bottom) at station F in the Slovenian coastal area.

Flux	$f(\text{HM})/\mu\text{g m}^{-2} \text{ d}^{-1}$								
	Hg	Cd	Cr	Pb	Cu	Zn	Ni	Mn	Fe
Min.	4.2	11.5	99	$7.1 \cdot 10^3$	$0.9 \cdot 10^3$	$18.0 \cdot 10^3$	$0.9 \cdot 10^3$	$3.1 \cdot 10^3$	$186 \cdot 10^3$
Max.	42.1	29.7	1840	$8.4 \cdot 10^3$	$117.6 \cdot 10^3$	$36.4 \cdot 10^3$	$2.8 \cdot 10^3$	$42.0 \cdot 10^3$	$1359 \cdot 10^3$
Mean	17.0	19.2	705	$7.7 \cdot 10^3$	$40.6 \cdot 10^3$	$24.6 \cdot 10^3$	$1.7 \cdot 10^3$	$26.1 \cdot 10^3$	$620 \cdot 10^3$



### 3.2.3. Heavy metals in sediments

Hg and Cd mass fractions in sediments (dry weight) from the investigated areas were measured in the period 1983-1991, and elaborated in term of ranges, geometric means and geometric standard deviations (Table 3.2.3.1; Figs 3.2.3.1-5). In addition, Cr, Cu, Fe, Ni, Pb, and Zn were determined in 1989 and 1991 in selected areas (Table 3.2.3.2). The monitoring of heavy metals in sediments from the Slovenian, Rovinj, Dubrovnik and Montenegrin coastal areas was interrupted in 1989.

A significant increase of Hg geometric mean (GM) mass fraction in sediment of the Slovenian coastal area was observed during the investigation period (Fig. 3.2.3.1). This change might be related to the influence of local polluted rivers and streams, which discharge to the Gulf of Trieste, particularly the Soča (Isonzo) River. However, these increased values were still within ranges measured in the northern Adriatic proper and in the Italian coastal area, but they were an order of magnitude higher than in the central Adriatic proper (Table 3.2.3.3). This suggested that local Hg pollution of the Slovenian area sediments is not more marked than at the regional level.

**Table 3.2.3.3.** Value range for different heavy metal (HM-Hg, Cd, Pb, Cu, Zn) mass fractions ( $w$ ) in sediment (dry weight) from two areas in the Adriatic Sea (Branica and Raspor, 1989), and the mean values (with SD) of Hg, Cd and Pb along the Italian coast (Giordano *et al.*, 1992).

Area	$w_{dw}(HM) \cdot 10^9$		$w_{dw}(HM) \cdot 10^6$		
	Hg	Cd	Pb	Cu	Zn
Northern Adriatic	240-600	140-350	25-50	20-22	105-130
Central Adriatic	37-42	230-260	20-27	19-23	76-100
Italian coast	230±41	160±120	41.1±37.3		

The Hg content in the Split area sediments (GM mass fractions from  $1101-2839 \cdot 10^{-9}$ ) and Šibenik areas ( $458-620 \cdot 10^{-9}$ ) was higher than in the other investigated areas. The highest values for Cd were measured in the Montenegrin coastal sediments (GM mass fractions from  $1236-1538 \cdot 10^{-9}$ ; Table 3.2.3.1; Figs 3.2.3.2 and 3.2.3.4).

A relatively high Hg GM mass fraction was calculated for the Rovinj area (except in 1987). However, it should be emphasized that this high mean was due to extremely high values measured at one heavily polluted station in the Rovinj harbour, very close to an effluent discharge source, which cannot be considered representative for the whole area.

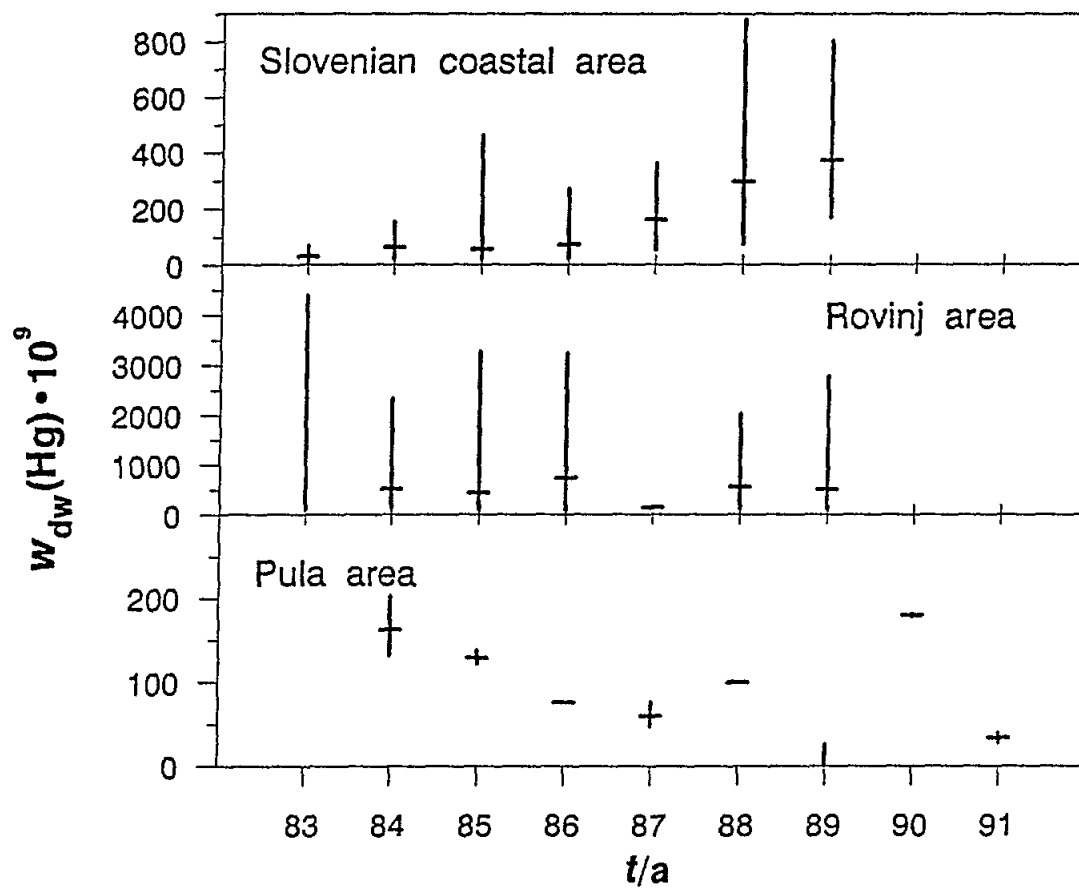


Fig. 3.2.3.1. Hg mass fractions ( $w$ , GM with ranges) for different years ( $t$ ) in sediment from different sampling areas in northern Adriatic.

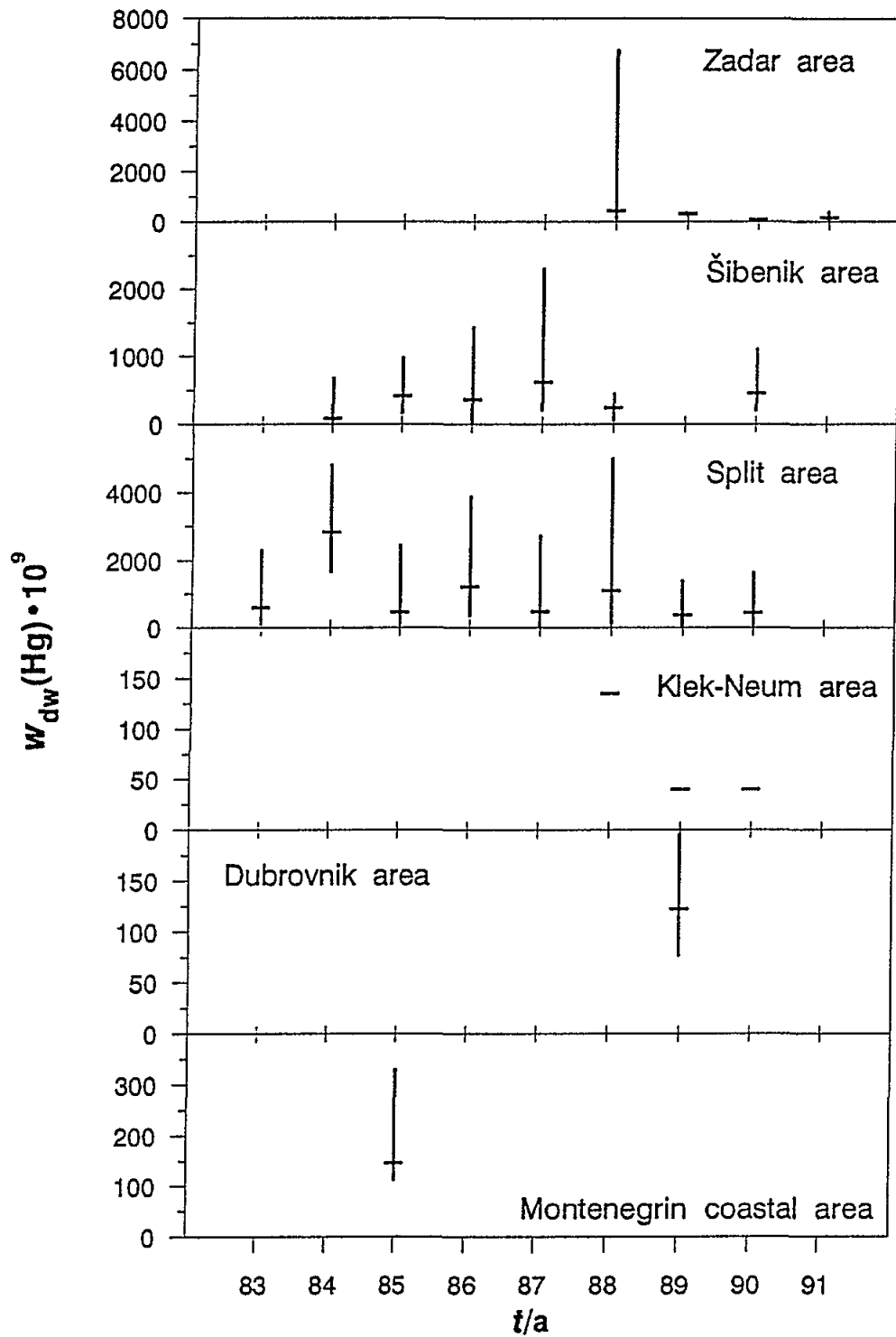


Fig. 3.2.3.2. Hg mass fractions ( $w$ , GM with ranges) for different years ( $t$ ) in sediment from different sampling areas in central and southern Adriatic.

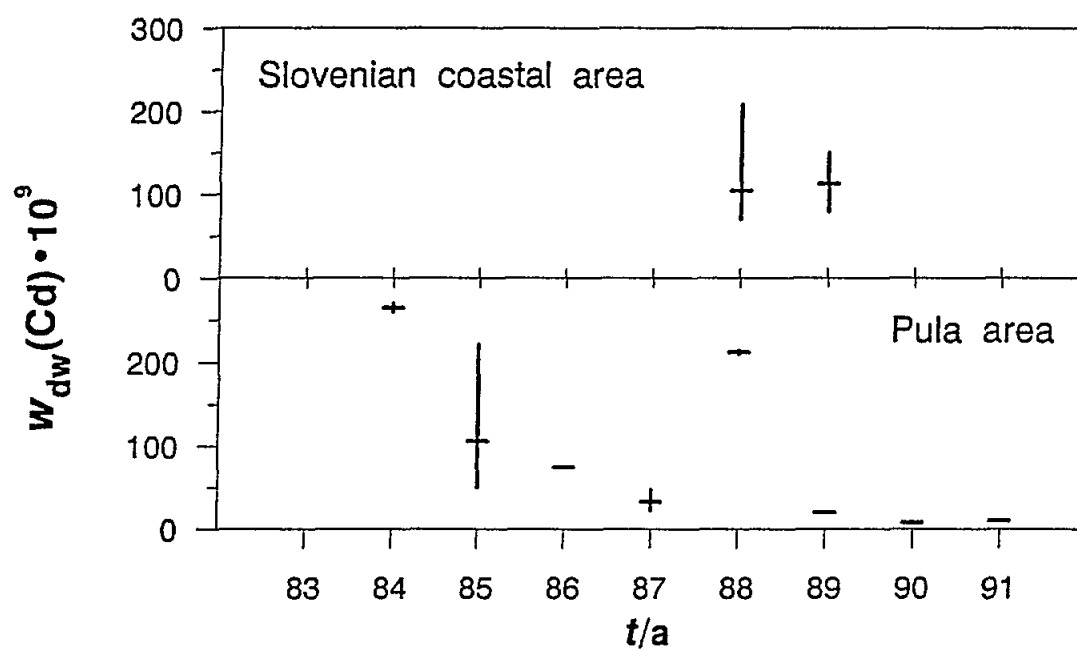


Fig. 3.2.3.3. Cd mass fractions ( $w$ , GM with ranges) for different years ( $t$ ) in sediment from different sampling areas in northern Adriatic.

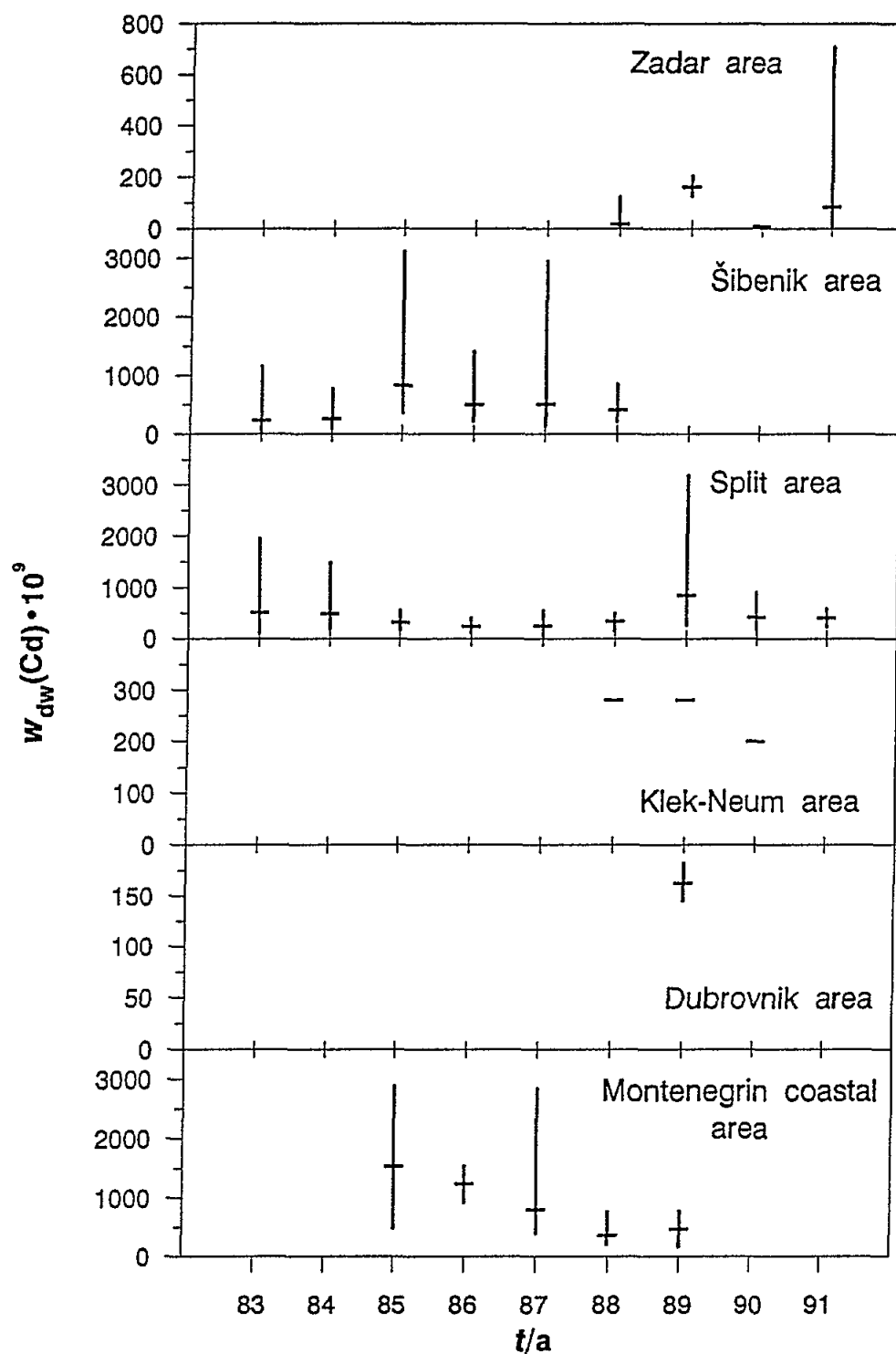


Fig. 3.2.3.4. Cd mass fractions ( $w$ , GM with ranges) for different years ( $t$ ) in sediment from different sampling areas in central and southern Adriatic.

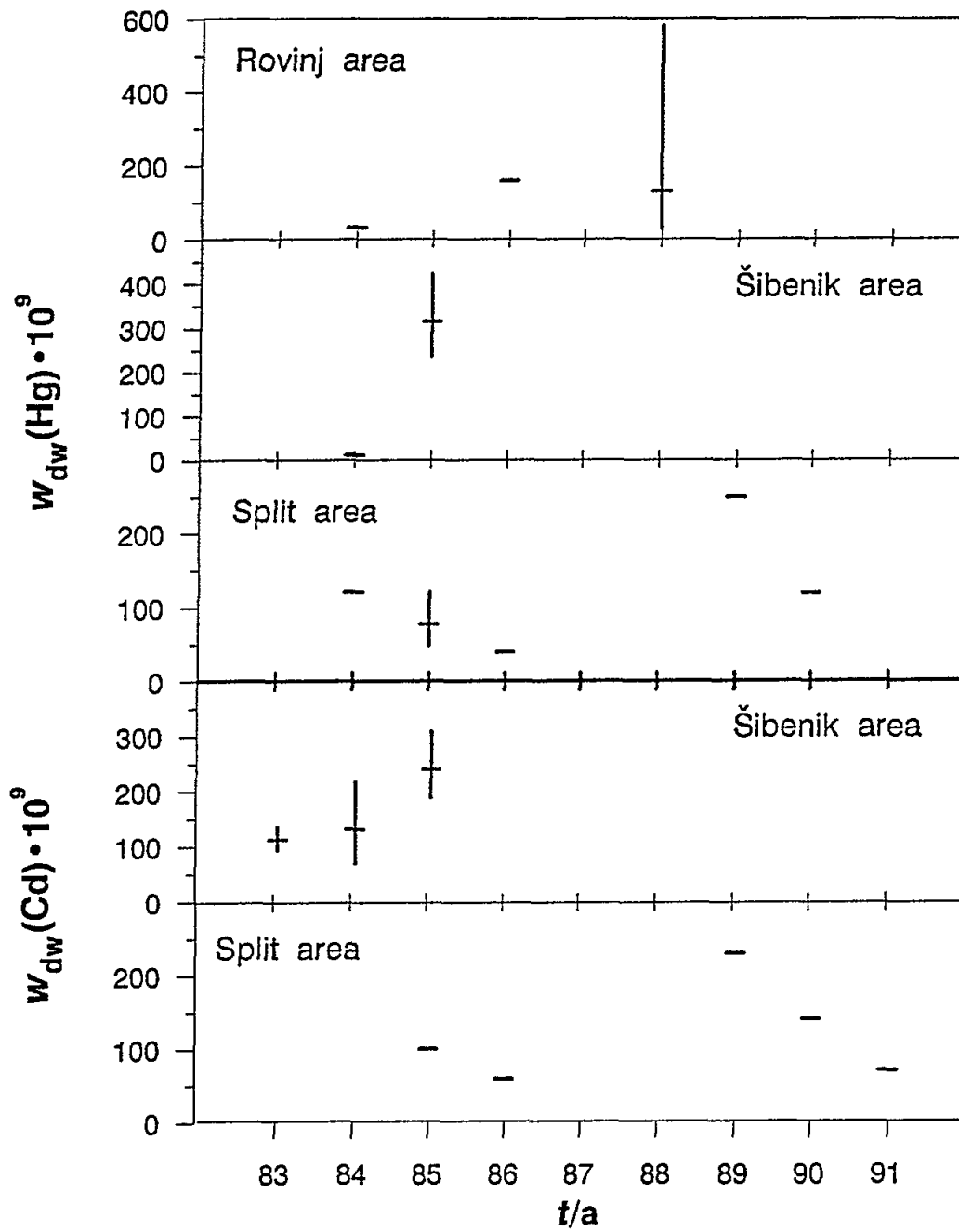


Fig. 3.2.3.5. Hg and Cd mass fractions ( $w$ , GM and ranges) for different years ( $t$ ) in sediment samples from reference areas.

**Table 3.2.3.1.** Mean year statistical data (N-number of samples, range, GM-geometric mean, GSD-geometric standard deviation) for Hg and Cd mass fraction ( $w$ ) in sediment (dry weight) from different areas.

Year	$w_{dw}(\text{Hg}) \cdot 10^9$				$w_{dw}(\text{Cd}) \cdot 10^9$			
	N	Range	GM	GSD	N	Range	GM	GSD
<b>Slovenian coastal area</b>								
1983.	5	10-66	32	2.1	-	-	-	-
1984.	5	24-155	64	2.0	-	-	-	-
1985.	12	24-463	59	2.5	-	-	-	-
1986.	12	26-270	73	2.1	-	-	-	-
1987.	12	55-363	161	1.8	-	-	-	-
1988.	6	76-880	296	2.4	9	71-209	105	1.5
1989.	6	171-802	373	1.9	6	80-150	113	1.2
<b>Rovinj area</b>								
1983.	-	110-4380	-	-	-	-	-	-
1984.	5	150-2330	526	3.7	-	-	-	-
1985.	5	100-3270	449	4.3	-	-	-	-
1986.	5	100-3240	745	6.0	-	-	-	-
1987.	2	140-170	154	1.2	-	-	-	-
1988.	4	130-2030	565	4.0	-	-	-	-
1989.	5	119-2780	517	4.4	-	-	-	-
<b>Reference locations</b>								
1984.	1	34	-	-	-	-	-	-
1986.	1	162	-	-	-	-	-	-
1988.	2	30-580	132	8.1	-	-	-	-
<b>Pula area</b>								
1984.	2	132-202	163	1.4	2	260-270	265	1.0
1985.	2	122-138	129	1.1	2	51-221	106	2.8
1986.	1	76	-	-	1	75	-	-
1987.	2	48-76	60	1.4	2	23-47	33	1.7
1988.	2	-	100	-	2	210-215	213	1.1
1989.	2	<1-25	-	-	2	<20	-	-
1990.	2	178-182	180	1.0	2	7.3-8.1	8	1.1
1991.	2	28-40	34	1.3	2	10	-	-
<b>Zadar area</b>								
1988.	8	148-6760	436	3.7	8	<10-120	18	2.6
1989.	2	291-353	320	1.1	2	129-204	163	1.4
1990.	2	88-95	91	1.0	2	<10	-	-
1991.	2	76-377	169	3.1	2	10-707	84	20.3

**Table 3.2.3.1.** - continued

Year	$w_{dw}(\text{Hg}) \cdot 10^9$				$w_{dw}(\text{Cd}) \cdot 10^9$			
	N	Range	GM	GSD	N	Range	GM	GSD
<b>Sibenik area</b>								
1983.	-	-	-	-	8	42-1145	227	2.9
1984.	32	5-667	89	4.1	32	97-765	263	1.9
1985.	8	170-973	409	1.8	8	361-3103	831	2.3
1986.	7	25-1420	361	3.7	7	224-1400	501	1.9
1987.	7	219-2295	620	2.1	7	154-2940	507	2.4
1988.	8	74-443	240	1.8	8	218-848	410	1.7
1990.	5	211-1095	458	2.0	-	-	-	-
Reference locations								
1983.	-	-	-	-	2	94-136	113	1.3
1984.	6	10-16	12	1.2	6	71-218	133	1.5
1985.	2	237-422	316	1.5	2	189-308	241	1.4
<b>Split area</b>								
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
1985.	9	90-2430	461	4.0	9	182-540	313	1.3
1986.	3	380-3860	1207	3.2	3	120-400	238	1.9
1987.	6	33-2720	472	7.1	6	50-550	250	2.7
1988.	3	150-4970	1101	6.1	3	160-490	335	1.9
1989.	3	60-1380	370	5.1	3	270-3180	852	3.5
1990.	3	80-1620	452	3.6	3	180-900	418	1.9
1991.	4	240-580	410	1.5	-	-	-	-
Reference locations								
1984.	1	122	-	-	-	-	-	-
1985.	2	50-122	78	1.9	2	-	100	-
1986.	1	40	-	-	-	-	60	-
1989.	1	250	-	-	1	230	-	-
1990.	1	120	-	-	1	140	-	-
1991.	1	70	-	-	-	-	-	-
<b>Klek-Neum area</b>								
1988.	1	135	-	-	1	280	-	-
1989.	1	40	-	-	1	280	-	-
1990.	1	40	-	-	1	200	-	-
<b>Dubrovnik area</b>								
1989.	2	77-195	122	1.9	2	145-182	162	1.2
<b>Montenegrin coastal area</b>								
1985.	9	113-328	146	1.4	10	490-2880	1538	2.0
1986.	-	-	-	-	7	910-1530	1236	1.4
1987.	-	-	-	-	8	400-2840	802	2.7
1988.	-	-	-	-	10	210-760	358	1.5
1989.	-	-	-	-	5	170-770	465	1.8



**Table 3.2.3.2.** Mean year statistical data (N-number of samples, range, GM-geometric mean, GSD-geometric standard deviation) for heavy metal (HM-Cr, Cu, Fe, Ni, Pb, Zn) mass fraction ( $w$ ) in sediment (dry weight) from different areas.

Metal	Sampling area	Year	$w_{dw}(HM) \cdot 10^6$			
			N	Range	GM	GSD
<b>Cr</b>	Slovenian coastal area	1989.	7	23-58	39.1	1.4
<b>Cu</b>	Slovenian coastal area	1989.	6	9-40	21.7	1.7
	Split area	1991.	4	14-48	22.9	1.7
	Split area -reference locations	1991.	1	5	-	-
	Klek-Neum area	1991.	1	17	-	-
	Dubrovnik area	1989.	2	22-33	26.9	1.3
	Montenegrin coastal area	1989.	7	8-51	18.7	2.0
<b>Fe</b>	Slovenian coastal area	1989.	6	17-46	27.0	1.4
<b>Ni</b>	Slovenian coastal area	1989.	6	38-179	82.1	1.8
<b>Pb</b>	Slovenian coastal area	1989.	6	14-22	17.6	1.2
	Split area	1991.	4	10-69	26.4	2.2
	Split area -reference locations	1991.	1	11	-	-
	Klek-Neum area	1991.	1	32	-	-
	Dubrovnik area	1989.	2	26-39	31.6	1.3
	Montenegrin coastal area	1989.	8	4-65	17.9	2.7
<b>Zn</b>	Slovenian coastal area	1989.	6	92-170	114.0	1.3
	Split area	1991.	4	131-265	204.3	1.4
	Split area -reference locations	1991.	1	66	-	-
	Klek-Neum area	1991.	1	265	-	-
	Dubrovnik area	1989.	2	56-73	63.9	1.2
	Montenegrin coastal area	1989.	9	11-144	33.9	2.5

Hg and Cd mass fractions in sediment from the Pula area were relatively low, but significantly differed from one year to another, without a regular pattern. This was probably due to a rather small number of analyses and insufficient information on pollution sources. Therefore, no reliable conclusion on actual content of these metals in sediment from this area could be drawn.

Shorter data series (1988-1991) were available for Hg and Cd contents in sediments of the Zadar area compared with other investigated areas. Besides some extreme values (in 1988 for Hg, and in 1991 for Cd) the mass fraction values were mostly low and close to the levels measured at reference stations. More data would be necessary to assess possible pollution trends by these two metals in the Zadar area.

In the Šibenik area total metal contents were determined in sediments from estuarine (stations E2, E4) and coastal locations (station C1, near Zlarin). Relatively high GM mass fraction values (up to  $620 \cdot 10^{-9}$ ) were obtained when high analysis results ( $1095\text{--}2295 \cdot 10^{-9}$ ) for samples collected at the station in front of Šibenik harbour (E4) were included in the calculations. In contrast, the values from the Skradin and Zlarin Island area samples (stations E2 and C1, respectively) were significantly lower ( $210\text{--}350 \cdot 10^{-9}$ ), and varied within ranges measured at the reference stations.

The highest Hg mass fraction, measured in the Split area during 1990, amounted to  $1620 \cdot 10^{-9}$  (station 1). Although considerably lower than the maximum values measured in previous years (Fig. 3.2.3.2), this value was still significantly higher than those obtained for the reference stations. This indicates that Hg accumulated in sediments will probably still represent a significant potential pollution source for several years in future, although the industrial emission of elementary Hg in Kaštela Bay was stopped.

The sediment Cd content in the Split area varied significantly during the investigated period with a maximum in 1988. The values were generally so high that the reduction or elimination of the pollution source(s) should be recommended. High Cd mass fractions were also measured in the sediments of the Montenegrin coastal area, with maxima in 1985 and 1988.

Comparing the results (GM values) of heavy metal analyses in sediments from the different investigated areas (Tables 3.2.3.1-2) with value ranges obtained from samples collected in the northern and central Adriatic proper, and in the Italian coastal region (Table 3.2.3.3), the following considerations can be drawn (see also the Fig. 3.2.3.6):

- @ In the Slovenian coastal area Hg, Cd, Cu and Zn values were within the ranges for the northern Adriatic proper sediments;
- @ In the sediments of the central and southern Adriatic coastal areas the contents of all determined metals were higher than the "probably background mass fractions" (ie the proper sediment mass fractions; Table 3.2.3.3). This was particularly marked for Hg. Remarkably, the Hg contents in the sediment samples of the reference stations from the Šibenik and Split areas, although lower than in the near coastal area, were also significantly higher than in the proper samples;
- @ The Cd mass fractions in sediments from Montenegrin, Split and Šibenik areas were higher with respect to the other investigated areas;
- @ While the Zn mass fractions were higher in the Split and Klek-Neum areas, the Cu values exceeded the range measured in the proper sediments only in the Dubrovnik area.

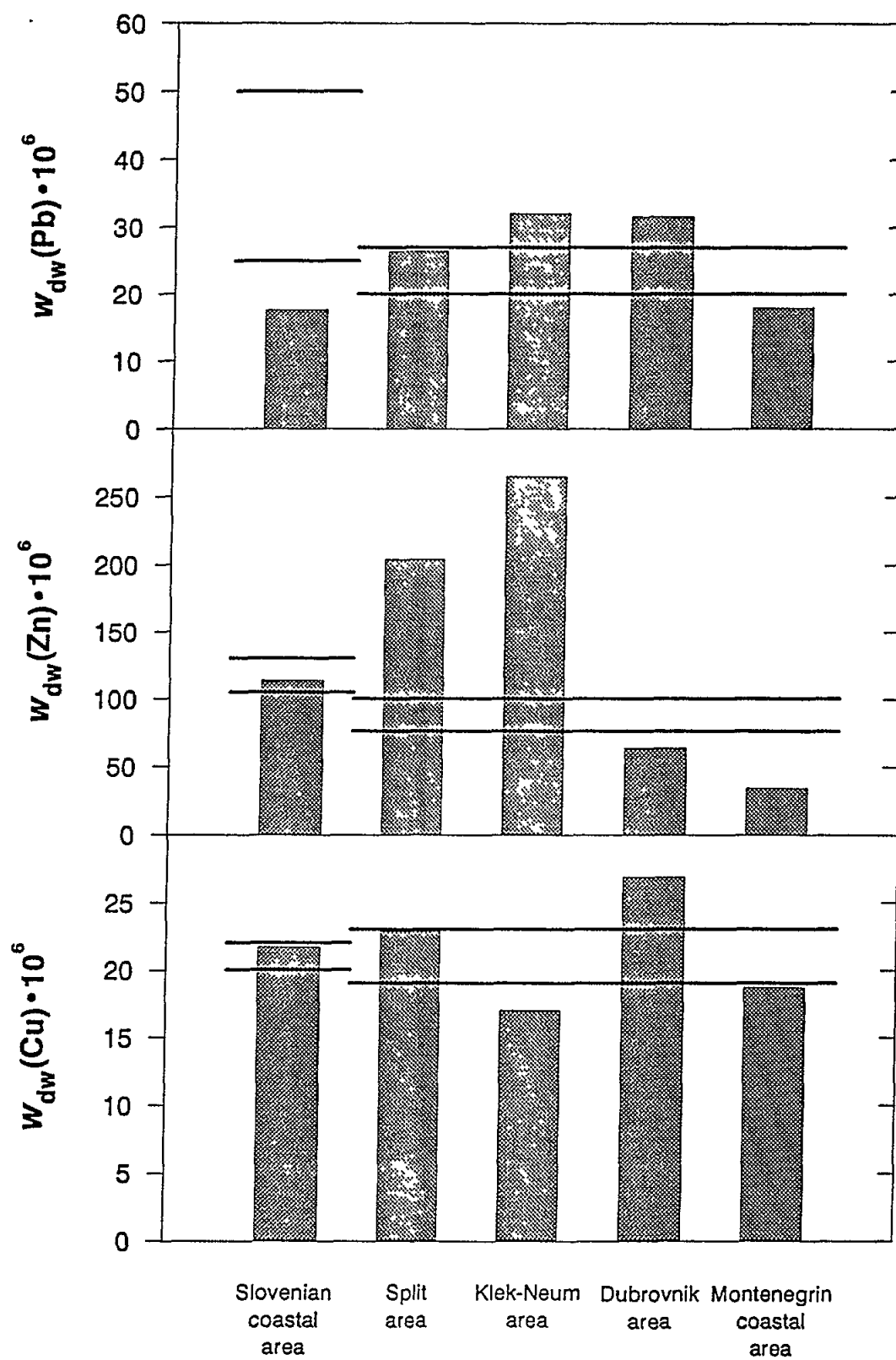


Fig. 3.2.3.6. Mass fractions for Pb, Zn, and Cu ( $w$ , GM) in sediment from different areas and value ranges from northern and central Adriatic.

Despite the above mentioned differences in the metal contents, which may be mostly related to variations of sediment binding properties, the sediments of the most part of the eastern Adriatic coastal area should be considered unpolluted or low polluted. In contrast, a significant pollution influence was recorded in restricted zones of some harbour (eg Rovinj and Šibenik) and industrial areas (eg Kaštela Bay).

#### 3.2.4. Heavy metals in biological material

During the period 1983-1991 the Hg and Cd contents of *Mytilus galloprovincialis* were monitored in almost all investigated areas. In addition, in the Dubrovnik, Montenegrin and Slovenian areas other heavy metals (Zn, Pb, Cu) and marine organisms (*Ostrea edulis*, *Pagellus erythrinus*, plankton) were also monitored. A statistical elaboration of the data obtained since 1983 is presented in Tables 3.2.4.1-3. Furthermore, Hg and Cd geometric mean (GM) mass fractions in mussels, collected along the eastern Adriatic coast are also graphically represented in Figs. 3.2.4.1-5.

The mussel total Hg and Cd contents were no longer measured in the Slovenian coastal area after 1988. The measurements were also stopped in the Dubrovnik and Montenegrin coastal areas after 1989. In 1990, methyl Hg, instead of Cd, was monitored in *Mytilus galloprovincialis* from the Šibenik area.

During 1991, total Hg and Cd were measured in mussels from the Pula, Rijeka, Zadar and Split areas. In the Rovinj area only Cd was analysed, but in the Rijeka area Pb was determined in addition to Cd and Hg.

Comparing heavy metals GM mass fractions in shellfishes from the various investigated areas the following considerations could be drawn:

- @ In more recent years the Hg mass fractions in mussels from most of the investigated areas (except the Zadar area) were lower compared with the previous period. Such a trend is encouraging, and was particularly evident in Kaštela Bay (Split area). Namely, some earlier data have shown that during the period 1983-1986 the mean Hg mass fraction in mussels (fresh weight) dropped from 532 to  $33 \cdot 10^{-9}$  (Anon., 1987). Since 1987 a slight increase was recorded (from 49 to  $59 \cdot 10^{-9}$  in 1989), but the lowest mean value ever recorded in the past nine years of investigation was measured in 1991 ( $29 \cdot 10^{-9}$ ). This decrease can be related to the interruption (since May 1990) of Hg emissions from a chlor-alkali plant, located in Kaštela Bay. The Hg actually present in mussels originated from reserves, previously deposited in sediments, which now act as a Hg source to the water column of the area, because of a gradual sediment selfpurification process (Zvonariæ 1991).
- @ The mass fractions of organic bound Hg (methyl Hg) in mussels from the Krka River estuary (measured only in 1990) ranged from  $2.2\text{--}6.0 \cdot 10^{-9}$ . Even if present in a relatively high percentages of total Hg (19-33%), the mussels can be consumed, because the total Hg contents were far below the safety limits.

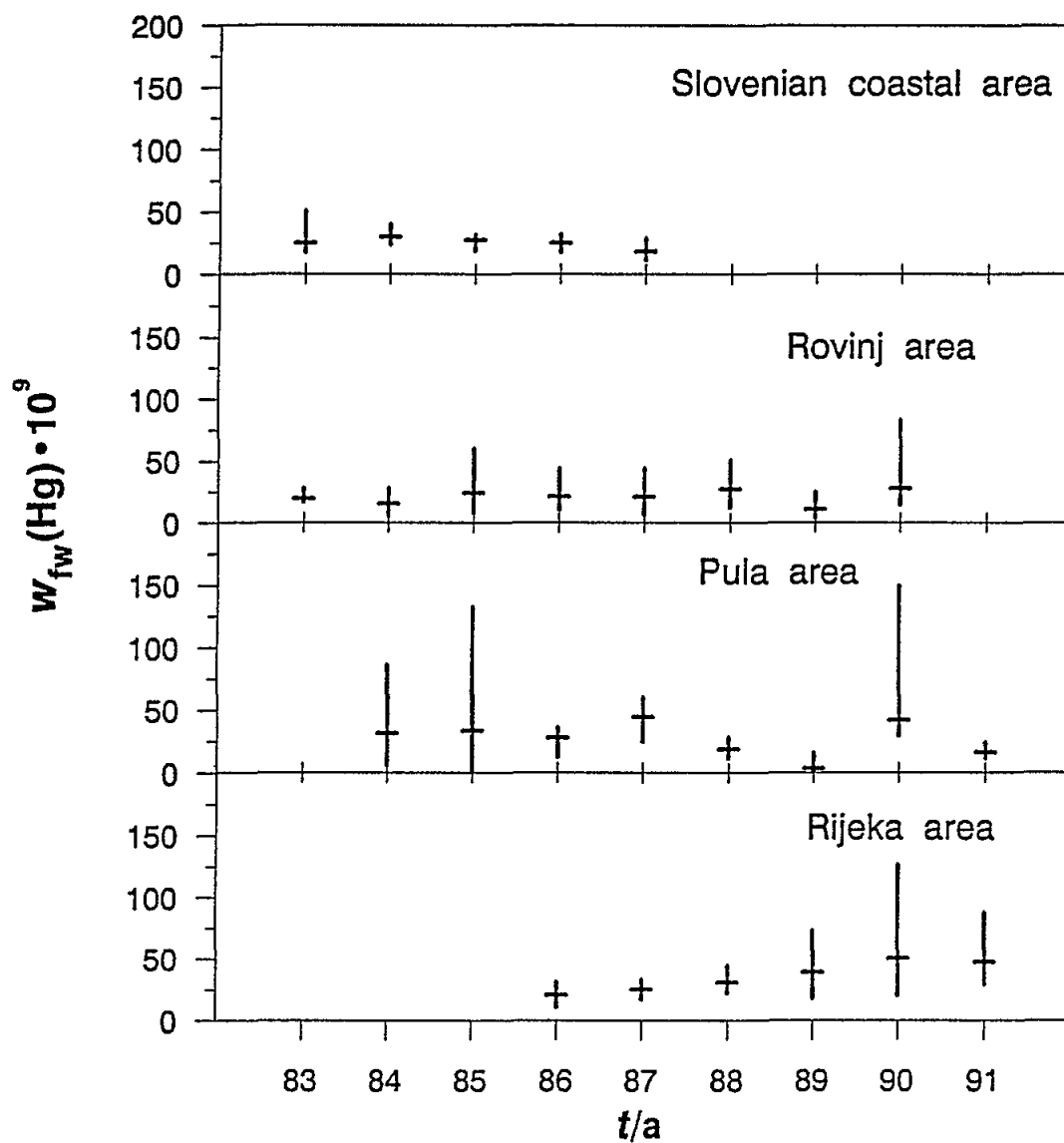


Fig. 3.2.4.1. Hg mass fractions ( $w$ , GM with ranges) for different years ( $t$ ) in *Mytilus galloprovincialis* from different sampling areas in northern Adriatic.

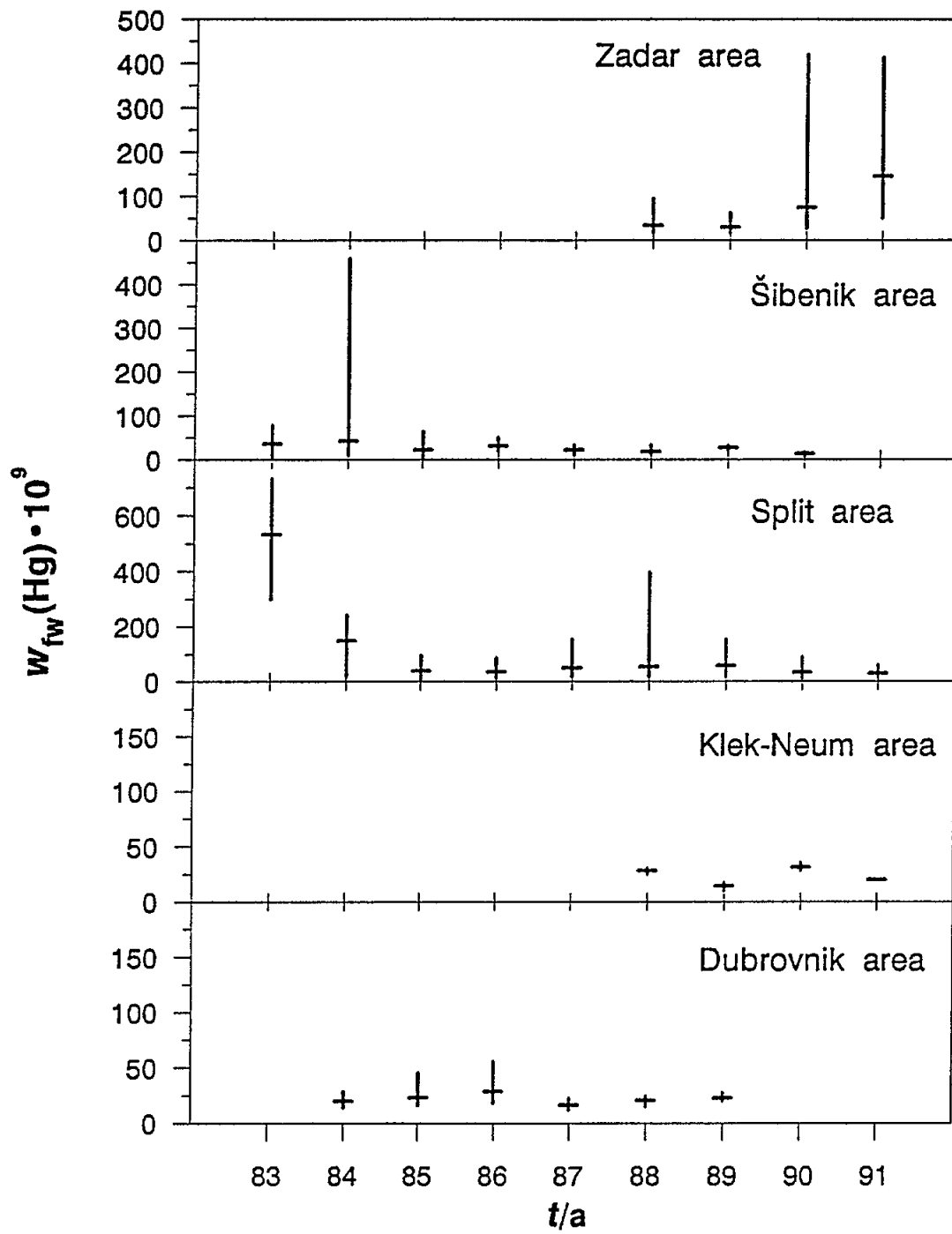


Fig. 3.2.4.2. Hg mass fractions ( $w$ , GM with ranges) for different years ( $t$ ) in *Mytilus galloprovincialis* from different sampling areas in central and southern Adriatic.

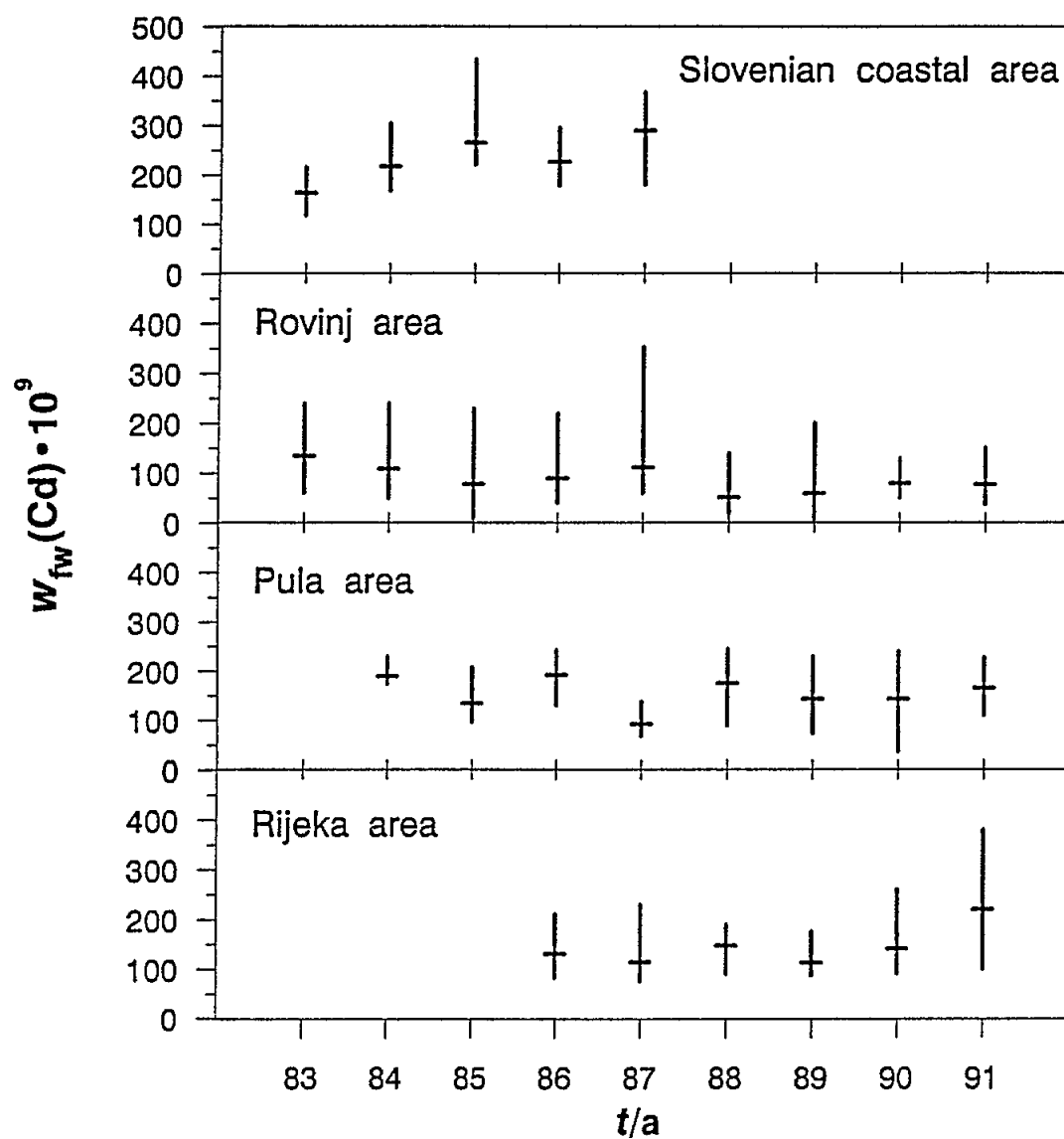


Fig. 3.2.4.3. Cd mass fractions ( $w$ , GM with ranges) for different years ( $t$ ) in *Mytilus galloprovincialis* from different sampling areas in northern Adriatic.

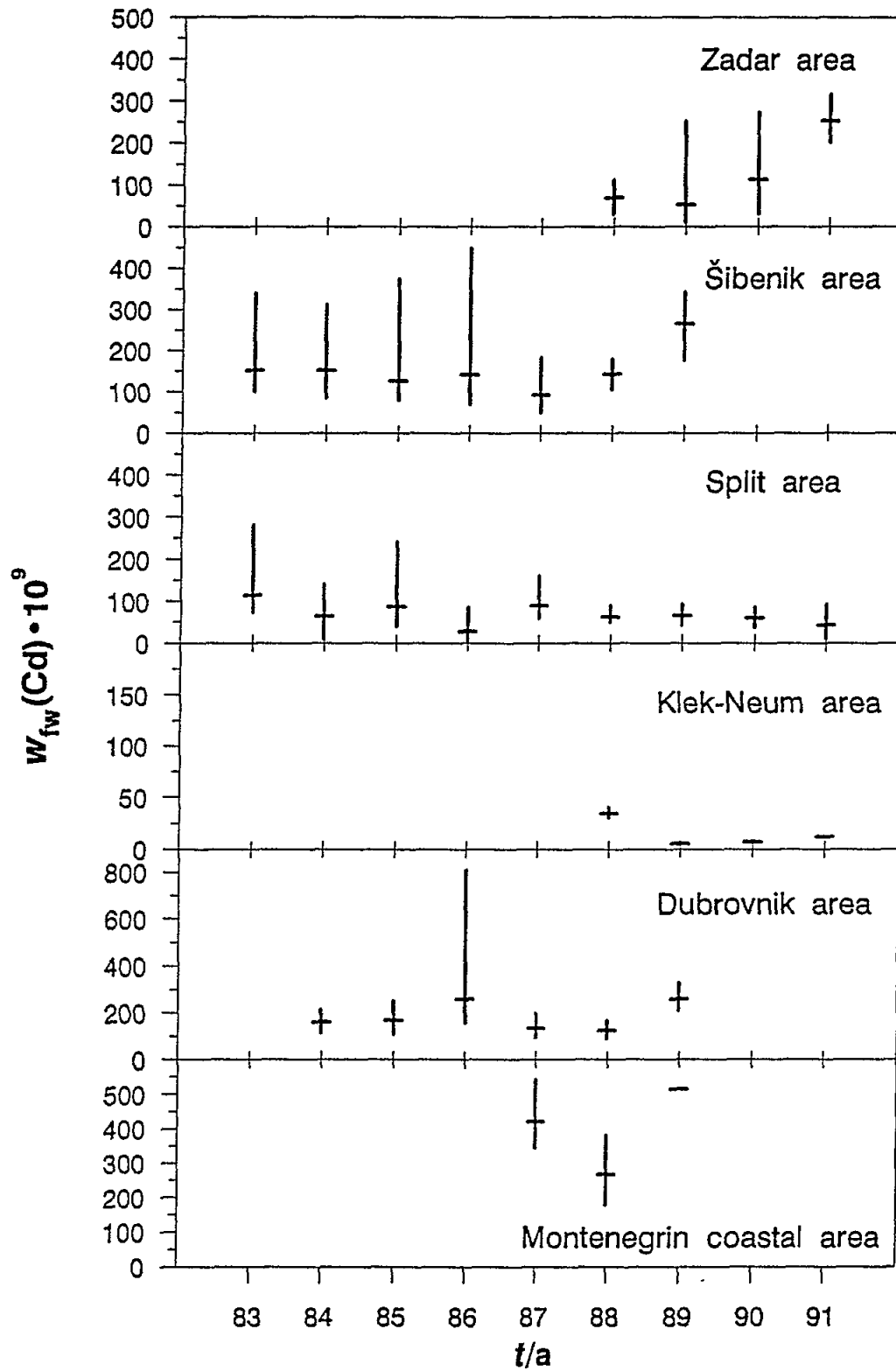


Fig. 3.2.4.4. Cd mass fractions ( $w$ , GM with ranges) for different years ( $t$ ) in *Mytilus galloprovincialis* from different sampling areas in central and southern Adriatic.



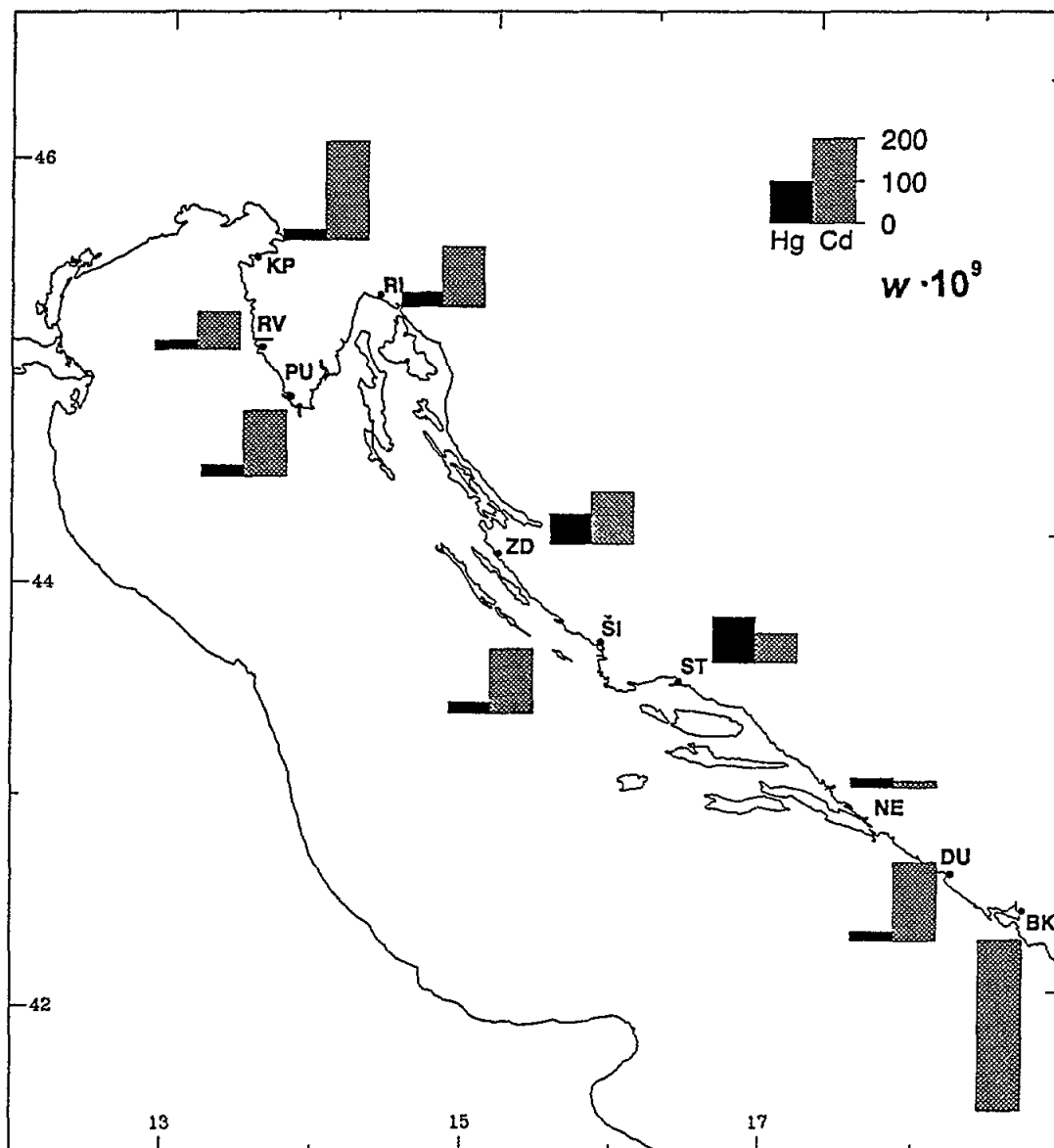


Fig. 3.2.4.5. The GM of Hg and Cd mass fractions ( $w$ ) in *Mytilus galloprovincialis* along the eastern Adriatic coast for the 1983-1992 period.

**Table 3.2.4.1.** Mean year statistical data (N-number of samples, range, GM-geometric mean, GSD-geometric standard deviation) for Hg and Cd mass fraction ( $w$ ) in *Mytilus galloprovincialis* (fresh weight) from different areas.

Year	$w_w(\text{Hg}) \cdot 10^9$				$w_w(\text{Cd}) \cdot 10^9$			
	N	Range	GM	GSD	N	Range	GM	GSD
<b>Slovenian coastal area</b>								
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
1987.	16	12-29	18.4	1.3	16	181-367	290	1.2
<b>Rovinj area</b>								
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	79	3.4
1986.	10	11-44	21.4	1.5	10	41-219	90	1.5
1987.	5	7-44	21.8	2.1	5	60-353	112	2.0
1988.	10	13-51	27.6	1.6	10	20-140	52	2.0
1989.	10	4-25	11.3	1.9	10	8-200	60	2.4
1990.	17	15-83	28.6	1.7	17	51-130	80	1.3
1991.	-	-	-	-	20	38-150	77	1.4
<b>Pula area</b>								
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
1987.	7	25-60	44.6	1.3	7	70-138	92	1.3
1988.	8	12-28	19.1	1.4	8	90-245	176	1.4
1989.	8	1-16	3.7	2.6	8	75-230	144	1.5
1990.	8	30-150	42.3	1.6	8	38-240	144	1.6
1991.	8	12-24	16.6	1.3	8	110-227	165	1.3
<b>Rijeka area</b>								
1986.	8	11-31	20.7	1.4	8	84-210	131	1.4
1987.	8	17-33	25.3	1.3	8	75-230	114	1.5
1988.	8	22-44	30.9	1.3	8	91-190	148	1.2
1989.	7	18-73	38.8	1.6	7	88-176	112	1.3
1990.	12	20-126	50.4	1.8	12	91-260	142	1.4
1991.	8	29-87	47.2	1.5	8	100-380	221	1.5

**Table 3.2.4.1.** - continued

Year	$w_w(\text{Hg}) \cdot 10^9$				$w_w(\text{Cd}) \cdot 10^9$			
	N	Range	GM	GSD	N	Range	GM	GSD
<b>Zadar area</b>								
1988.	8	18-94	33.9	1.7	8	30-110	69	1.5
1989.	8	17-62	29.9	1.5	8	10-250	52	3.0
1990.	8	27-419	75.4	2.7	8	30-273	113	2.0
1991.	2	51-412	145.5	4.4	2	202-314	252	1.4
<b>Šibenik area</b>								
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
1987.	16	11-33	22.2	1.4	16	50-182	92	1.4
1988.	12	13-33	18.8	1.3	12	105-178	142	1.2
1989.	12	21-33	27.1	1.1	12	176-340	264	1.3
1990.	8	9-18	13.5	1.3				
1990. (Me-Hg)	8	2.2-6	3.4	1.4				
<b>Split area</b>								
1983.	4	300-730	532.0	1.5	4	75-280	114	1.8
1984.	8	20-240	149.0	2.3	8	10-140	65	2.3
1985.	12	10-93	39.6	2.6	12	40-240	87	1.6
1986.	9	12-84	35.3	2.1	9	5-85	28	2.8
1987.	15	19-152	48.9	1.9	15	60-160	90	1.3
1988.	9	19-395	53.7	3.4	9	50-90	63	1.2
1989.	9	19-152	59.2	2.2	9	42-92	66	1.3
1990.	9	11-88	32.9	2.0	9	38-86	60	1.3
1991.	4	15-58	28.8	1.8	4	12-92	43	2.4
<b>Klek-Neum area</b>								
1988.	3	25-30	27.7	1.1	3	30-40	35	1.2
1989.	3	10-17	13.9	1.3	3	4.6-6.4	5	1.2
1990.	3	28-35	31.0	1.1	3	6.8-7.4	7	1.0
1991.	1	20	-	-	1	12	-	-
<b>Dubrovnik area</b>								
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
1987.	5	12-22	16.2	1.3	5	96-195	133	1.3
1988.	4	15-24	20.1	1.2	4	90-166	126	1.3
1989.	4	20-27	22.3	1.2	4	211-325	258	1.2
<b>Montenegrin coastal area</b>								
1987.	-	-	-	-	4	345-540	421	1.2
1988.	-	-	-	-	4	180-380	267	1.4
1989.	-	-	-	-	1	514	-	-

**Table 3.2.4.2.** Mean statistical data (N-number of samples, range, GM-geometric mean, GSD-geometric standard deviation) for heavy metal (HM-Hg, Cd, Pb, Cu, Zn) mass fraction ( $w$ ) in different marine organisms (fresh weight) from different areas.

Metal	Sampling area	Year	$w_w(\text{HM}) \cdot 10^9$			
			N	Range	GM	GSD
<i>Mytilus galloprovincialis</i>						
Pb	Rijeka area	1991.	8	240-990	536	1.6
Cu	Montenegrin coastal area	1989.	1	1840	-	-
Pb	"	"	1	38400	-	-
Zn	"	"	1	14800	-	-
<i>Ostrea edulis</i>						
Hg	Dubrovnik area	1984.	2	17-22	19	1.2
		1985.	3	22-47	37	1.5
		1986.	2	31-55	41	1.5
		1987.	1	28	-	-
		1989.	1	39	-	-
Cd	"	1984.	2	457-672	554	1.3
		1985.	3	525-1140	766	1.5
		1986.	2	690-810	748	1.1
		1987.	1	885	-	-
		1989.	1	590	-	-
Cu	"	1989.	1	19500	-	-
Pb	"	"	1	110	-	-
Zn	"	"	1	149000	-	-
<i>Pagellus erythrinus</i>						
Hg	Slovenian coastal area	1983.	2	420-618	509	1.3
		1984.	5	338-1413	782	1.8
		1985.	7	390-827	437	1.6
		1986.	4	47-410	134	2.7
		1987.	7	268-843	581	1.5
		1988.	5	204-319	252	1.2
Cd	"	1984.	5	3.3-5.1	4	1.2
		1985.	7	1.9-5.5	3	1.6
		1986.	4	20.7-3.4	2	2.0
		1987.	7	<2.8-36.3	11	2.6
		1988.	5	2.0-2.4	2	1.5

**Table 3.2.4.3.** Mean year statistical data (N-number of samples, range, GM-geometric mean, GSD-geometric standard deviation) for heavy metal (HM-Hg, Cd, Pb, Cu, Zn) mass fraction ( $w$ ) in plankton from different areas.

Metal	Sampling area	Year	$w(\text{HM}) \cdot 10^9$			
			N	Range	GM	GSD
Hg	Rovinj area - zooplankton (fresh weight)	1985.	6	3-9	5.1	1.6
		1988.	2	5-7	6.0	1.2
	Dubrovnik area - plankton (dry weight)	1984.	5	20-70	33.0	1.6
		1985.	10	10-36	13.5	1.8
		1986.	9	10-94	38.1	2.4
		1987.	4	32-113	51.2	1.7
		1989.	4	14-44	29.2	1.7
	Dubrovnik area - plankton (dry weight)	1984.	5	276-683	395	1.5
		1985.	10	95-1460	383	2.6
		1986.	9	747-3570	1750	1.7
		1987.	5	958-2950	1663	1.5
		1989.	4	53-1920	555	5.3
Cd	Rovinj area - zooplankton (fresh weight)	1985.	6	62-180	97.0	1.4
		1988.	2	7-11	8.6	1.4
Cu	Dubrovnik area - plankton (dry weight)	1989.	4	3.5-124	12.3	5.2
		1989.	4	1.5-25	6.4	3.2
Zn	"	1989.	4	11-625	145.8	6.3

@ In general, from the viewpoint of mussel consumption suitability, it should be emphasized that maximum Hg mass fraction (measured in mussels during the last four years) did not exceed the allowed limit of  $500 \cdot 10^{-9}$  (fresh weight) proposed by the WHO (UNEP/FAO/WHO, 1987).

The mean Cd mass fraction in *Mytilus galloprovincialis* from the various investigated areas differed more significantly than the Hg mean values. The lowest GM value was calculated for Klek-Neum Bay ( $5.3 \cdot 10^{-9}$ ) and the highest for the Montenegrin coastal area ( $514 \cdot 10^{-9}$ ).

The mass fractions of Cd, Cu, and particularly Zn in *Ostrea edulis* from the Dubrovnik area (Table 3.2.4.2) were higher than the values for mussels from unpolluted areas (Table 3.2.4.4). However, this was not observed for Hg and Pb. Significantly higher Cd, Pb, and Zn mass fractions were measured in mussels from the Montenegrin coastal area, and for Pb in samples from the Rijeka area.

The Hg mass fraction in *Pagellus erythrinus* from the Slovenian coastal area varied significantly during the investigated period (Table 3.2.4.2; Fig. 3.2.4.6), and a decrease of the GM mass fraction from  $782 \cdot 10^{-9}$  (in 1984) to  $252 \cdot 10^{-9}$  (in 1988) was observed. However, the human consumption of this fish should still be under control, because the allowed Hg mass fraction limit is  $500 \cdot 10^{-9}$  (UNEP/FAO/WHO, 1987). In contrast, the Cd content of this species was very low (Table 3.2.4.2).

An intercalibration of sampling techniques should be carried out to assess if the differences observed for the Hg and Cd mass fractions in zooplankton between the Rovinj and Dubrovnik area were realistic (Table 3.2.4.3).

**Table 3.2.4.4.** Value range for different heavy metals (HM-Hg, Cd, Pb, Cu, Zn) mass fractions ( $w$ ) in *Mytilus galloprovincialis* (fresh weight) from unpolluted areas along the Eastern Adriatic coast ("probably background concentration", Martinèæ et al, 1987a).

Metal	Hg	Cd	$w_w(\text{HM}) \cdot 10^9$		
			Pb	Cu	Zn
Range	19-34	130-190	210-380	700-1200	18100-19200

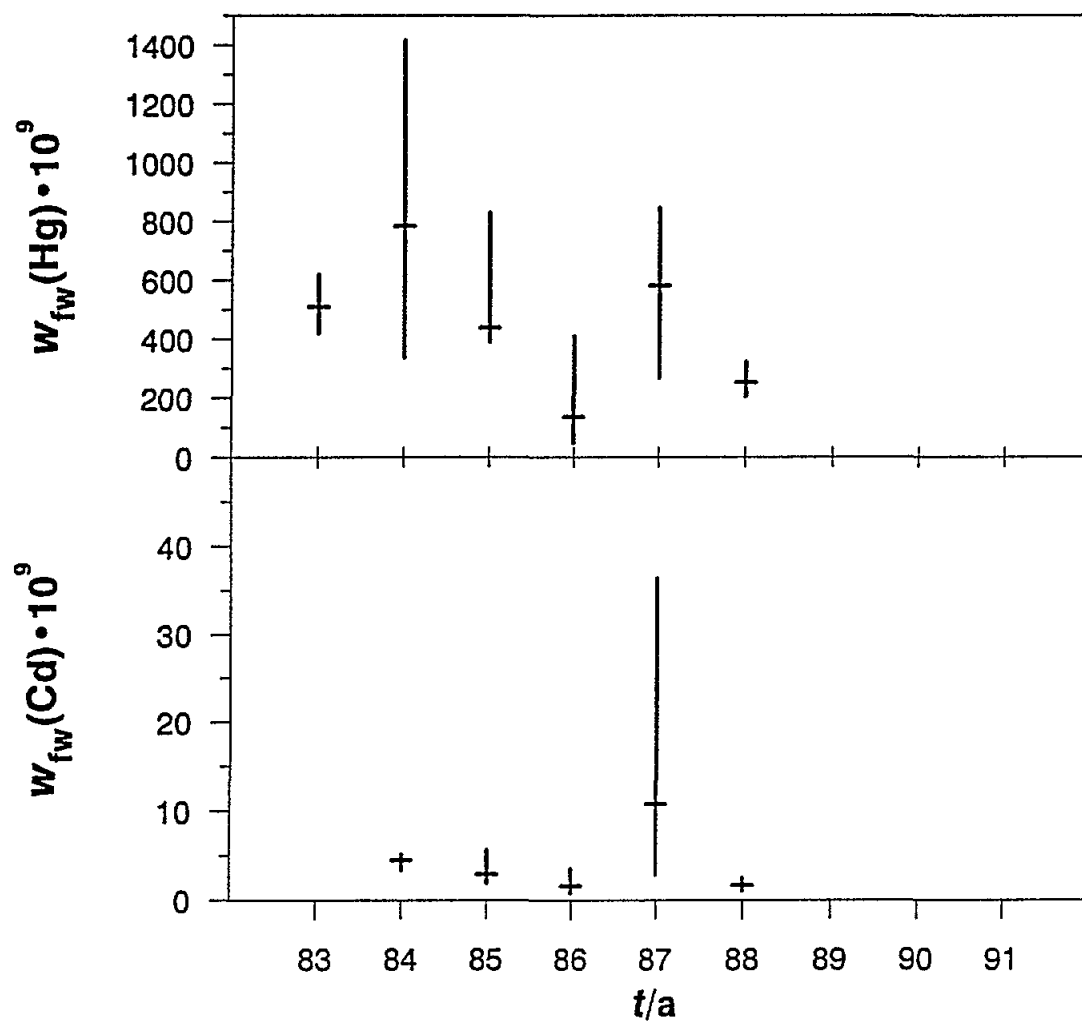


Fig. 3.2.4.6. Hg and Cd mass fractions ( $w$ , GM with ranges) for different years ( $t$ ) in *Pagellus erythrinus* (fresh weight) from the Slovenian coastal area.

### 3.3. Organic pollutants

Various groups of organic pollutants were determined in the framework of this programme in effluents, seawater, marine sediments, and organisms (chlorinated and petroleum hydrocarbons, phenols, anionic detergents). Basic statistical parameters were elaborated with the collected data. Averages, median, geometric means (as measures of the central tendency of the data), standard deviations, minima and maxima (which describe the data spreading) were calculated. Furthermore, skewness coefficient was used to estimate the degree of the data distribution asymmetry. The concentration or mass fraction data for all pollutant groups had positive values of skewness. Kurtosis coefficients describe the relative flatness or steepness of the data distribution in respect to a Gaussian, normal distribution. While for a normal distribution the kurtosis coefficient is 3.0, higher values were calculated from the data for all pollutant analysed. This means that the distribution curves were steep at the centre or had relatively long tails. Standardized skewness and kurtosis coefficients were also used to test if the actual data distribution significantly deviated from a normal distribution. For a relatively large sample, these standardized coefficient should approximate the value of 1.0 for normal data distribution. In contrast, when the values are outside the range of -2.0 to +2.0, it is accepted that the tested data distribution deviates significantly from a normal distribution.

Consequently, medians and geometric means should be more appropriate measures of the central tendency of organic pollutant data than arithmetic means (averages). In fact, the medians did not differ significantly from the geometric mean, while the arithmetic means were several times or up to two orders of magnitude higher (eg for phenols in effluents; Table 3.3.1.2). However, averages were used in this report when Adriatic data were compared with data from other marine regions, because, unfortunately, they were the most usual statistical parameters reported in the literature.

Due to non-normal distributions of the elaborated data, it was necessary to use logarithmic values. These values approximated well a normal distribution, which is a prerequisite to use parametric statistics (Phillips and Rainbow, 1988). Thus, the yearly means of the natural logarithmic values and their standard errors were compared to study levels and changes of the organic pollutant concentrations or mass fractions within or among the various investigated areas.

One way analysis of variance (ANOVA) was applied to test if the variability of organic pollutant concentrations or mass fractions (natural logarithmic values) was statistically significant between the investigated areas, or sampling periods, seasons, and effluent types (urban or industrial). The data variability in relation to the sampling period, season, or effluent type was also tested for each of the investigated area. It was assumed that significant differences occurred at probability levels  $<0.05$  (95% confidence intervals).



### 3.3.1. Chlorinated hydrocarbons

Residues of synthetic chlorinated pesticides and industrial chlorinated hydrocarbons are widespread throughout the terrestrial and oceanic environments, because of their resistance to degradation. Toxicological and other harmful effects of these compounds on ecosystems have been well documented (eg Moore and Ramamoorthy, 1984; Tanabe *et al.*, 1987). Accumulation of chlorinated compound residues, contributed through the atmosphere, may have occurred in the Adriatic Sea, for which water renewal time is for less than 10 years. Moreover, additional quantities of these pollutants were added to the sea through various local sources (mainly sewage and industrial wastewater disposal, port activities, agriculture drainage), located on the coast, including semi-enclosed embayments (Picer M. *et al.*, 1978b; Picer N., 1989).

The measurements in the Adriatic were focused on DDT<sub>total</sub> (the insecticide DDT and its analogues DDE and TDE), and on PCBs, which belong to the group of the most persistent organic pollutants. Effluents, discharged along the coast, and various matrices of the marine environments were investigated.

#### 3.3.1.1. Chlorinated hydrocarbons in effluents

Only a few data were available in the literature on chlorinated hydrocarbon concentrations in wastewaters, discharged in the Adriatic and other Mediterranean areas. In slaughter wastewaters of Alexandria the concentration of some chlorinated hydrocarbon pesticides ranged from 0.19 (BHC) to 0.95  $\mu\text{g dm}^{-3}$  (p,p' DDE; UNEP/FAO/WHO/IAEA, 1990). In wastewater samples from the Rijeka area, collected in the period 1976-1987, the concentration varied from <0.26-57.2  $\text{ng dm}^{-3}$  for DDT<sub>total</sub>, and from <0.3-9115.5  $\text{ng dm}^{-3}$  for PCBs. DDT and PCB concentrations in various wastewater types were summarized in Table 3.3.1.1. The value ranges were extremely large: eg for DDT from "non detected" (depending on the analytical method) up to 130,000  $\mu\text{g dm}^{-3}$ .

Chlorinated hydrocarbon concentrations in Zadar effluents, measured in the period 1988-1990, were higher than in Rijeka area wastewaters (period 1976-1987; Table 3.3.1.2). The one way ANOVA confirmed a statistically significant concentration difference between areas (Table 3.3.1.3). Significant differences were also noticed considering all data for DDT<sub>total</sub> in dependence on sampling period, but not for PCBs. No differences were observed in relation to the sampling season and effluent types.

Several ECD peaks were evident in the "pesticide" fraction of the analysed eluates, obtained after purification and separation steps of the extracted lipophilic materials from wastewater samples. These peaks could not be ascribed to DDT and derivatives. It is recommended to carry out the identification of these substances in a future monitoring, because, owing to their chromatographic characteristics, they may be highly lipophilic and potentially dangerous to the marine environment.

**Table 3.3.1.1.** Average, minimum and maximum concentration (c) of chlorinated hydrocarbons in wastewaters and sewage sludge.

Location and year	Compound(s)	c/ $\mu\text{g dm}^{-3}$			References
		Average	Min.	Max.	
Great Britain, sewage Holden & Marsden, 1966	DDT	36		130	
effluents	Dieldrin	200		300	
Great Britain, sewage Lowden <i>et al.</i> , 1969	DDT	130.9(21)		800	
effluents	BHC	92.5(21)		390	
	Dieldrin	145.0(21)		1900	
Canada, Southern Ontario Lawrence & Tosine, 1977	PCB	2.0(8)	0.6	4.4	
raw sewage (5 cities)					
Hamilton (raw sewage)	PCB	10.8(38)	1.5	27.3	Portman, 1979
Sewage	DDT		36000	130000	
"	Dieldrin		100000	300000	
Sewage sludge	PCB <sup>a</sup>		40	5000	
"	DDT <sup>a</sup>		10000	500000	
"	Dieldrin <sup>a</sup>		1000	2500000	
Los Angeles County tertiary 1979					Baird <i>et al.</i> ,
treatment system, 1978					
Influent	BHC	0.056	0.025	0.080	
"	Dieldrin	0.010	0.005	0.030	
Effluent	BHC	0.044	0.005	0.080	
"	Dieldrin	0.009	0.005		
"	DDT <sub>total</sub>		ND		
Tokyo treatment plants Terada, 1980 (four plants)	PCB		ND		
Great Britain, sewage Anon., 1984b	BHC	0.19(5)	0.02	0.32	
effluents	Dieldrin	0.17(5)	0.12	0.21	
Ispra standard sewage Tarradellas <i>et al.</i> , 1985	PCB	2600(4)	1150	4900	
sludge					
Aluminium smelt wastewater from sedimentation basin	Decachlorobi- phenyl	54			Vogelgesang, 1986
	Hexachlorobenzene	470			
Cortiu, France (Urban sewage-outlet point, 1984)	PCB 1988	0.057(1)			Marchand <i>et al.</i> ,
Rijeka town waste Picer N. & waters, 1986	DDT <sub>total</sub>	0.008(12)	ND	0.027	
	Picer M., 1992				
	PCB	0.069(12)	ND	0.223	

ND - Not detected (under sensitivity limit)

<sup>a</sup> values were presented as mass fraction ( $\times 10^9$ ) of compound(s) in sewage sludge

**Table 3.3.1.2.** Basic statistical data of chlorinated hydrocarbons, phenols, detergents and petroleum hydrocarbons concentrations (c) in wastewater samples.

Investigation area Stat. parameter/Pollutant	c/ng dm <sup>-3</sup>		c/μg dm <sup>-3</sup>		
	DDT <sub>total</sub>	PCB	Phenols	Detergents	Petr.hydr.
<b>All data<sup>a</sup></b>					
Number of samples	46	46	683	869	274
Average	107	124	700	3622	3673
Median	17	50	16	2040	800
Geometric mean	18	49	15	1292	706
Skewness	6.2	5.6	23.6	4.0	4.6
Standardized skewness	17.1	15.5	252.2	47.7	30.8
Kurtosis	40.1	33.2	583.0	23.5	22.9
Standardized kurtosis	55.5	45.9	3109.9	141.2	77.4
<b>Slovenian coastal area</b>					
Number of samples				130	
Average				1078	
Median				445	
Geometric mean				297	
<b>Pula area</b>					
Number of samples			112	112	
Average			52.3	1701	
Median			17.5	800	
Geometric mean			13.8	344	
<b>Rijeka area</b>					
Number of samples	12	12	332	382	62
Average	8	69	1339	4798	3459
Median	6	48	26	2730	573
Geometric mean	3	24	20	2104	618
<b>Zadar area</b>					
Number of samples	32	32	45	45	
Average	148	151	305	6978	
Median	22	50	25	3400	
Geometric mean	34	69	31	2016	
<b>Split area</b>					
Number of samples			194	196	196
Average			72	3416	3858
Median			8	2900	850
Geometric mean			9	2708	716

<sup>a</sup> include additional samples for Slovenian coastal and Šibenik area

**Table 3.3.1.3.** Significance level for mean difference of one way ANOVA for  $\ln$  values of chlorinated hydrocarbons, phenols (Phe), detergents (Det) and petroleum hydrocarbons (PH) concentration (c) in wastewater samples depending upon sampling area, period, season, and water type.

<b>Investigation area</b>					
Response variable	Number of samples	Significance level for mean difference			
		Area	Period	Season	Type
<b>All data</b>					
$\ln c(\text{DDT}_{\text{total}})/\text{ng dm}^{-3}$	46	0.0000	0.0003	0.5469	0.4519
<sup>a</sup> $\ln c(\text{PCB})/\text{ng dm}^{-3}$	46	0.0452	0.0898	0.2302	0.5495
$\ln c(\text{Phe})/\mu\text{g dm}^{-3}$	683	0.0000	0.0000	0.0528	0.0000
$\ln c(\text{Det})/\mu\text{g dm}^{-3}$	869	0.0000	0.9465	0.6298	0.0000
$\ln c(\text{PH})/\mu\text{g dm}^{-3}$	274	0.8108	0.0000	0.9615	0.9466
<b>Slovenian coastal area</b>					
$\ln c(\text{Det})/\mu\text{g dm}^{-3}$	130		0.0995	0.3418	0.0000
<b>Pula area</b>					
$\ln c(\text{Phe})/\mu\text{g dm}^{-3}$	112		0.6479	0.6550	0.0000
$\ln c(\text{Det})/\mu\text{g dm}^{-3}$	112		0.7748	0.6051	0.0000
<b>Rijeka area</b>					
$\ln c(\text{DDT}_{\text{total}})/\text{ng dm}^{-3}$	12			0.9070	0.0000
$\ln c(\text{PCB})/\text{ng dm}^{-3}$	12			0.5837	0.0000
$\ln c(\text{Phe})/\mu\text{g dm}^{-3}$	332		0.0000	0.0329	0.0025
$\ln c(\text{Det})/\mu\text{g dm}^{-3}$	382		0.0006	0.7035	0.0000
$\ln c(\text{PH})/\mu\text{g dm}^{-3}$	62		0.0000	0.4838	0.5623
<b>Zadar area</b>					
$\ln c(\text{DDT}_{\text{total}})/\text{ng dm}^{-3}$	32		0.5998	0.9616	0.4285
$\ln c(\text{Phe})/\mu\text{g dm}^{-3}$	45		0.5214	0.8627	0.3127
$\ln c(\text{Det})/\mu\text{g dm}^{-3}$	45		0.7605	0.7269	0.2430
<b>Šibenik area</b>					
$\ln c(\text{PH})/\mu\text{g dm}^{-3}$	11		0.9669	0.186	
<b>Split area</b>					
$\ln c(\text{Phe})/\mu\text{g dm}^{-3}$	194		0.0004	0.4925	
$\ln c(\text{Det})/\mu\text{g dm}^{-3}$	196		0.0000	0.7613	
$\ln c(\text{PH})/\mu\text{g dm}^{-3}$	196		0.0000	0.5386	

<sup>a</sup> included data from Zadar area

### 3.3.1.2. Chlorinated hydrocarbons in sediments

Many pollutant species, particularly if persistent, accumulate significantly in sediment. Thus, a long term sediment monitoring can provide useful information on pollution processes (Larsen and Jensen, 1989).

In the framework of this programme chlorinated hydrocarbons were determined in sediment surface samples (upper 0.5-1 cm), from various eastern Adriatic areas, to assess the present pollution level and detect changes in the pollutant fluxes. Averages and ranges, calculated from these results and other data obtained in the open and eastern Adriatic (Table 3.3.1.4), were compared with sediment data obtained in other Mediterranean areas (Table 3.3.1.5). In six of these areas (II, III, VI, VIII, IX and X; Fig. 3.3.1.1) DDT<sub>total</sub> mass fractions in sediment were higher than for the Adriatic. In five areas (I, II, IV, VI and VIII) the PCBs values were higher compared to the Adriatic.

Higher DDT<sub>total</sub> geometric mean (GM) mass fractions were calculated for sediments from the Zadar, Šibenik, and Dubrovnik areas with respect to the other investigated areas, and particularly to the open northern and central Adriatic sediments (Table 3.3.1.4; Figs 3.3.1.2-3). Higher PCB GM mass fractions were measured in sediments of the Istrian, Zadar and Dubrovnik areas. Statistically significant differences were obtained between areas and sampling periods for all DDT<sub>total</sub> and PCB data (Table 3.3.1.6). A significant variability of DDT<sub>total</sub> and PCB mass fractions was also evidenced in dependence on the sampling period for samples collected in the eastern Adriatic during 1976-1990 (Picer M. and Picer N., 1991b). However, this was not the case for some of the investigated areas, when analysed separately (Table 3.3.1.6). Remarkably, in the first part of the 1970s, when this programme was started, much higher values were observed in the Dubrovnik area, compared with other investigated areas (Figs 3.3.1.2-3). However, in the next period much lower values were measured, similar to other areas. This was rather due to some analytical difficulties than to real changes in pollution loads.

The natural logarithm of the PCB/DDT<sub>total</sub> ratios in sediments of the Rovinj and Dubrovnik areas varied mostly between one and two during the investigated period (Fig. 3.3.1.4). In contrast, this ratio was higher for the Šibenik area. Data for the other areas were available for a few years only.

Mean DDT<sub>total</sub> and PCB mass fractions, and PCB/DDT<sub>total</sub> ratios (natural logarithms), measured in sediments from the open northern Adriatic, varied significantly in the period 1979-1990 (Fig. 3.3.1.5). This was also confirmed by one way ANOVA in dependence on sampling period (Table 3.3.1.7). However, no defined trends were observed.

Marked differences were noticed between sediments from the western, central and eastern parts of the northern Adriatic. The highest values for chlorinated hydrocarbons, as well as for sediment organic content and silt fraction contribution, were measured in the western part. The value decreased gradually going towards the east (Fig. 3.3.1.6). However, while a statistically significant variability of the sediment chlorinated hydrocarbon mass fractions was obtained

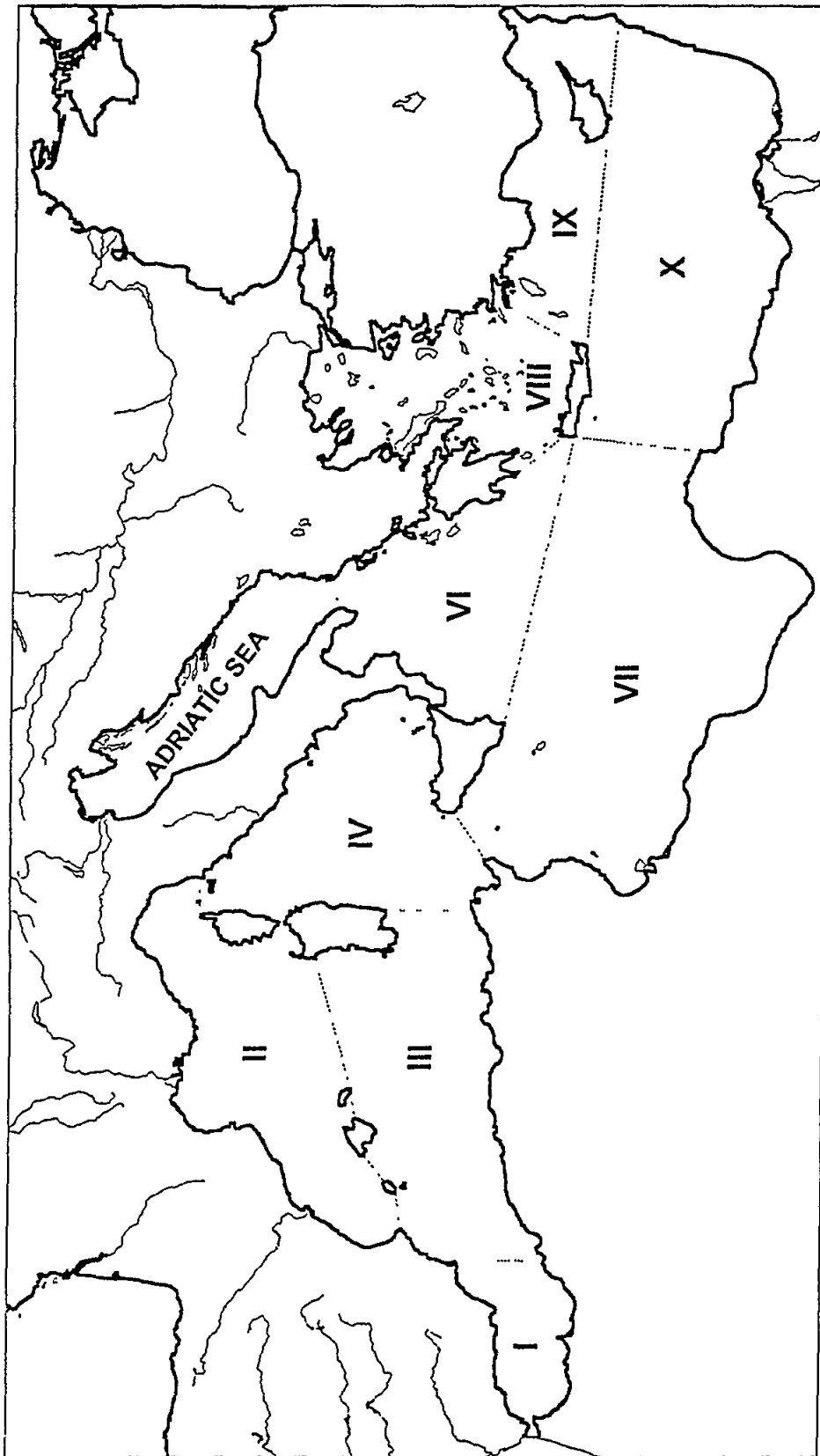


Fig. 3.3.1.1. MED POL areas.

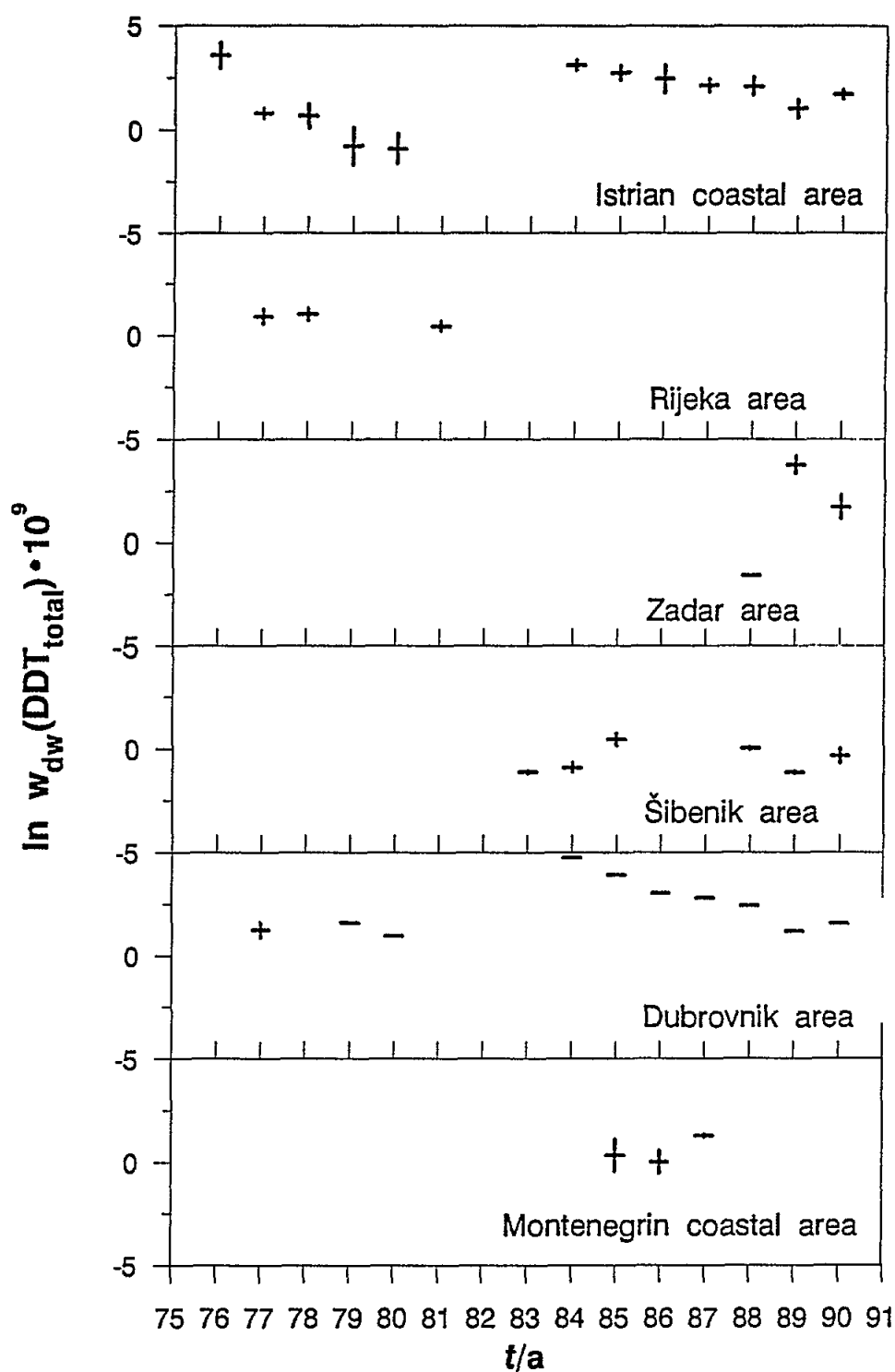


Fig. 3.3.1.2. Natural logarithm of means and their standard errors of mass fraction ( $w$ ) of  $\text{DDT}_{\text{total}}$  in sediment (dry weight) from different investigated areas in the period ( $t$ ) 1976-1990.

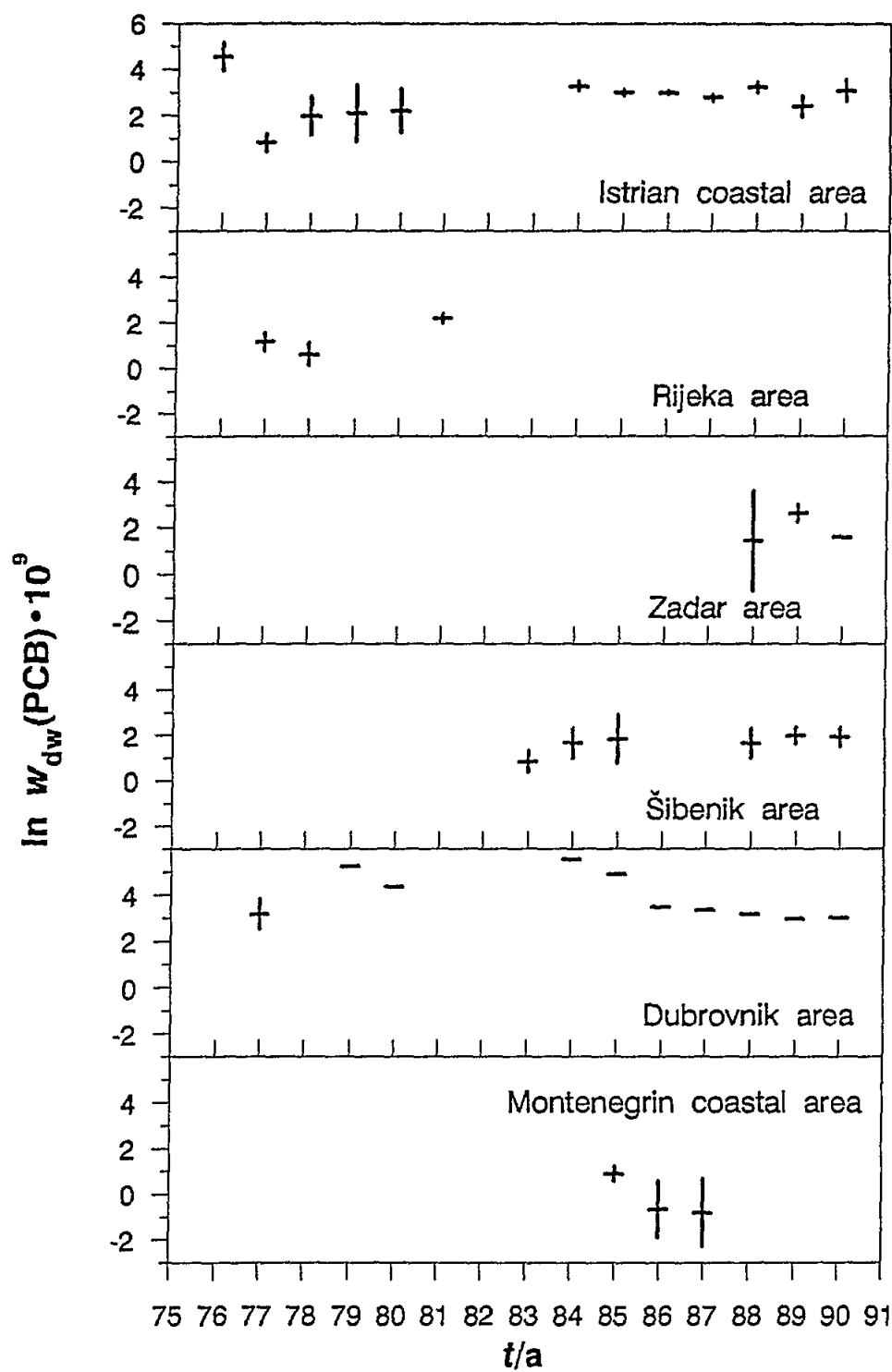


Fig. 3.3.1.3. Natural logarithm of means and their standard errors of mass fraction ( $w$ ) of PCB in sediment (dry weight) from different investigated areas in the period ( $t$ ) 1976-1990.



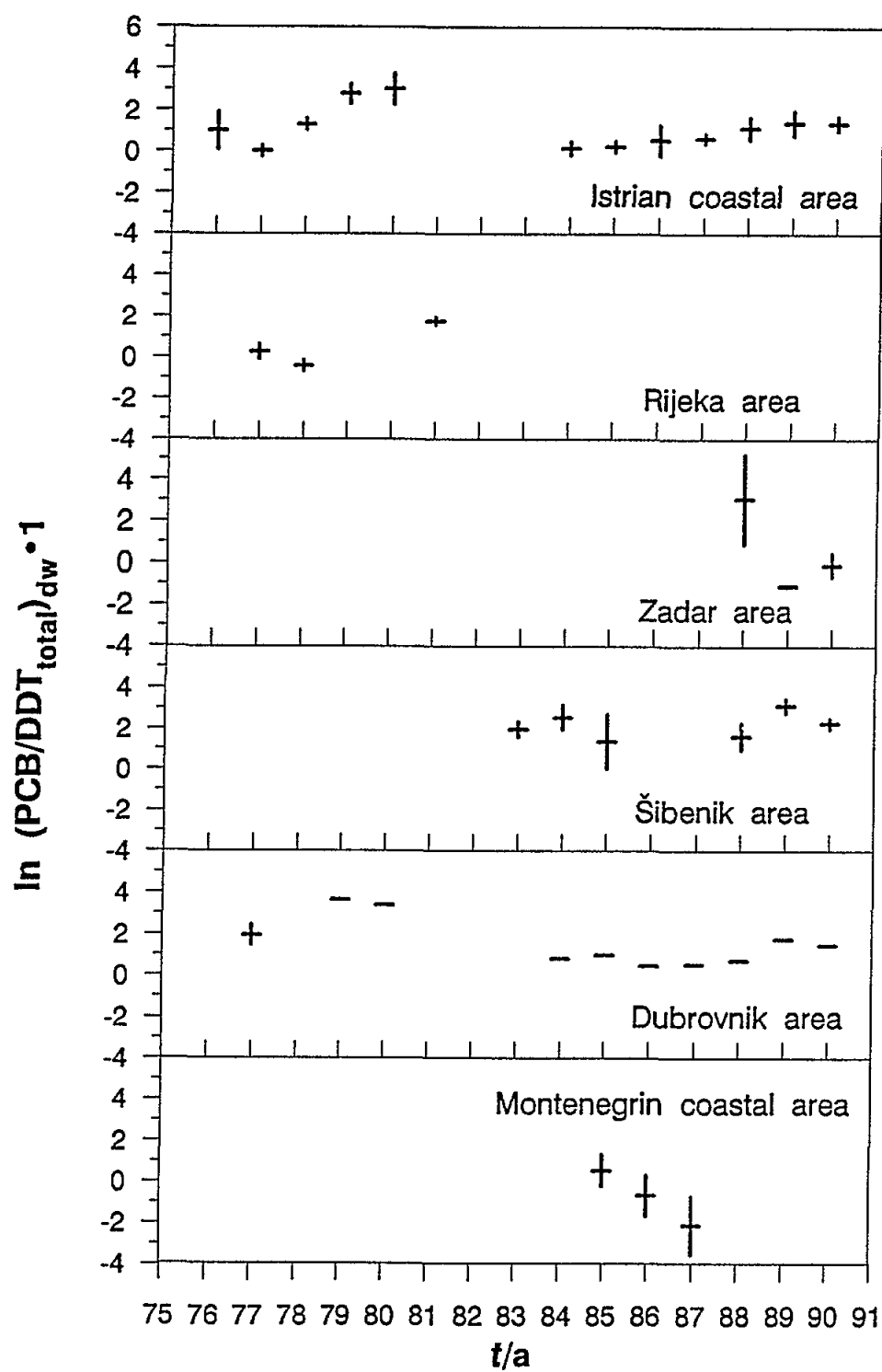


Fig. 3.3.1.4. Natural logarithm of means and their standard errors of PCB/DDT<sub>total</sub> ratio in sediment from different investigated areas in the period (t) 1976-1990.

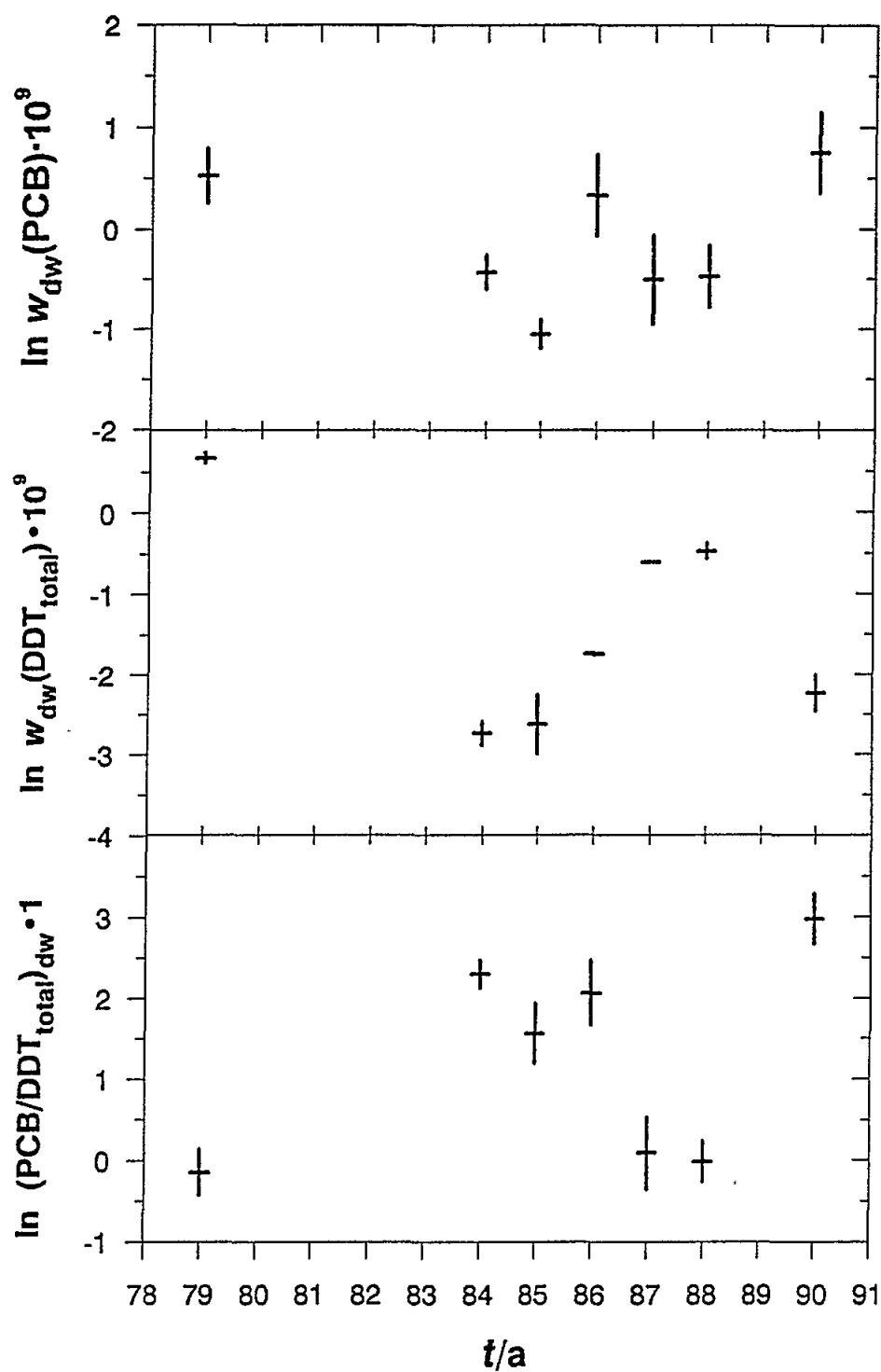


Fig. 3.3.1.5. Natural logarithm of means and their standard errors of mass fraction ( $w$ ) of  $\text{DDT}_{\text{total}}$ , PCB and  $\text{PCB}/\text{DDT}_{\text{total}}$  ratio in sediment (dry weight) from the northern Adriatic in the period ( $t$ ) 1979-1990.

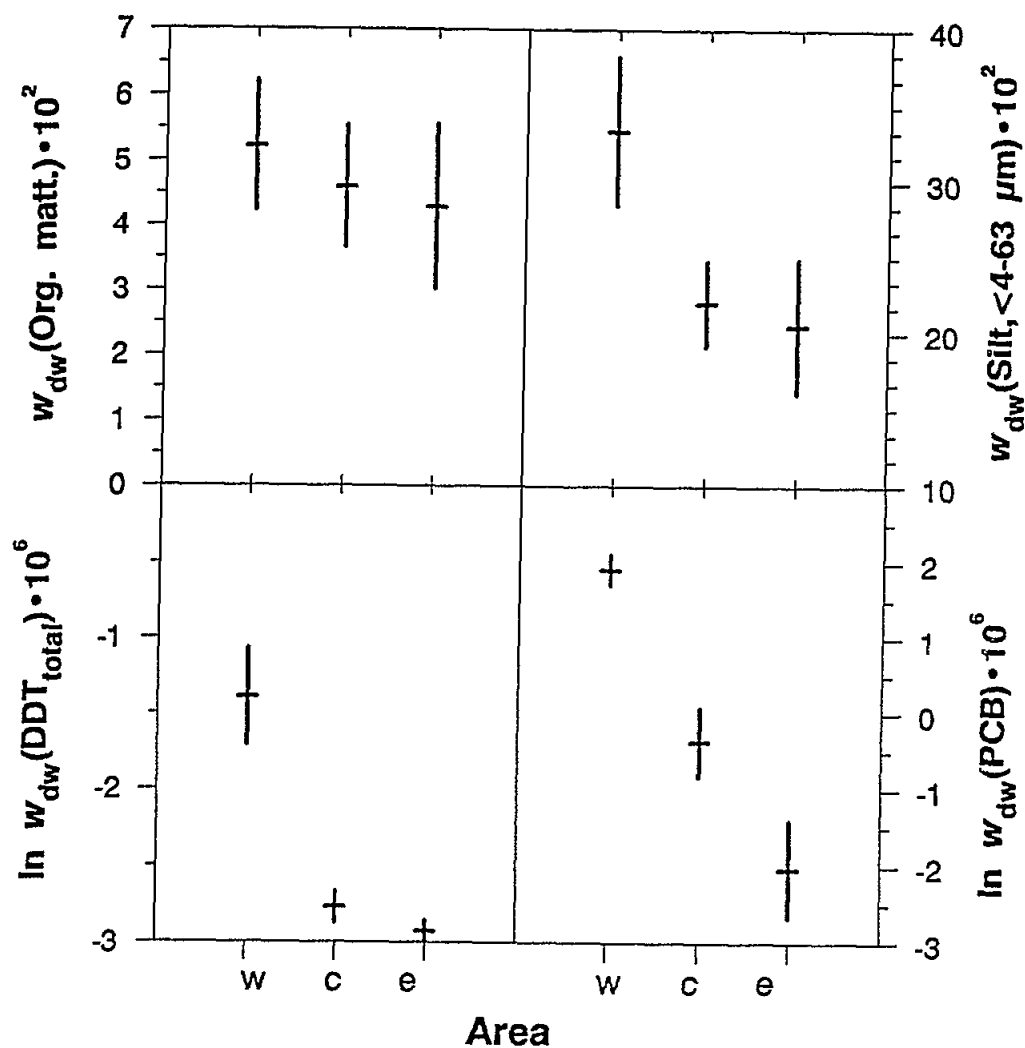


Fig. 3.3.1.6. Natural logarithm of means and their standard errors of chlorinated hydrocarbons, organic matter, and silt ( $4-63 \mu\text{m}$ ) mass fraction ( $w$ ) in sediment from the northern and central Adriatic for three areas (west-w, central-c and east-e).

**Table 3.3.1.4.** Basic statistical data of mass fraction ( $w$ ) of chlorinated hydrocarbons (CH) in sediments (dry weight) and mussels (wet weight) in the Adriatic sea.

Matrix	Investigation	Number of	$w(\text{CH}) \cdot 10^9$		
Pollutant (CH)	area	samples	Average	Median	Geo. m.
<b>Sediment</b>					
DDT <sub>total</sub>	Adriatic coast	238	7.1	1.9	1.9
	Istrian coast	93	9.1	3.7	3.2
	Rijeka area	51	4.3	1.7	1.9
	Zadar area	8	28.4	15.5	6.7
	Šibenik area	30	12.9	5.0	5.5
	Dubrovnik area	14	17.8	6.0	7.5
	Montenegrin coast	19	5.3	1.4	1.4
	Northern Adriatic	60	0.3	0.1	0.1
	Central Adriatic	12	0.1	0.1	0.
					1
PCB	Adriatic coast	239	24.2	7.5	6.
	Istrian coast	93	28.9	19.1	8.
					3
	Pula area	50	12.4	5.4	5.9
	Rijeka area	50	12.4	5.4	5.9
	Zadar area	8	14.4	7.5	8.
					1
	Šibenik area	30	12.9	4.9	5.5
	Dubrovnik area	14	68.8	37.1	40.2
	Montenegrin coast	19	12.3	1.3	1.2
	Northern Adriatic	60	2.5	1.0	1.0
	Central Adriatic	12	1.2	0.4	0.3
<b>Mussels</b>					
DDT <sub>total</sub>	Adriatic coast	466	23.4	4.5	4.9
	Istrian coast	118	21.9	4.3	6.2
	Pula area	68	20.8	5.1	3.8
	Rijeka area	79	58.4	3.5	7.1
	Zadar area	39	28.9	10.5	14.6
	Šibenik area	23	1.9	1.3	1.5
	Split area	64	7.9	3.6	3.7
	Dubrovnik area	74	8.2	4.6	2.9
PCB	Adriatic coast	465	74.2	21.2	21.7
	Istrian coast	118	51.1	7.7	10.0
	Pula area	68	74.8	24.6	32.0
	Rijeka area	79	82.3	20.2	18.3
	Zadar area	39	123.8	31.3	28.1
	Šibenik area	23	20.0	17.3	11.7
	Split area	64	80.1	66.2	57.5
	Dubrovnik area	74	87.3	19.0	28.8

**Table 3.3.1.5.** Mass fraction (*w*) of chlorinated hydrocarbons (CH) in sediments (dry weight) from the Mediterranean sea.

Area*	Pollutant (CH)	Average	$w(\text{CH})_{\text{dw}} \cdot 10^9$ Minimum	Maximum	References
I	DDT <sub>total</sub>	2.7	0.4	11.0	Cousteau, 1978; Elder <i>et al.</i> , 1976; Villeneuve & Burns, 1982
	BHC <sub>total</sub>	0.3	0.2	0.3	
	PCB	34.6	0.3	323	
II	DDT <sub>total</sub>	8.2	0.4	200	Arnoux <i>et al.</i> , 1980a; Arnoux <i>et al.</i> , 1980b; Arnoux <i>et al.</i> , 1980c; Badia & Garcia, 1978; Burns & Villeneuve, 1983; Burns <i>et al.</i> , 1985; Cousteau, 1978; Chabert & Vincente, 1980; Marchand <i>et al.</i> , 1976; Marchand <i>et al.</i> , 1985; Monod & Arnoux, 1978
	BHC <sub>total</sub>	225	0.1	1880	
	PCB	85.5	0.2	15850	
	Hexachlorobenzene	5.6	ND	32	
III	DDT <sub>total</sub>	11.0	1.2	40.0	Cousteau, 1978; Elder <i>et al.</i> , 1976; Villeneuve & Burns, 1982
	BHC <sub>total</sub>	1.6	0.9	2.1	
	PCB	7.4	0.1	14	
IV	DDT <sub>total</sub>	4.3	0.2	27	Amico <i>et al.</i> , 1982; Baldi <i>et al.</i> , 1983; Cousteau, 1978; Elder <i>et al.</i> , 1976; Monod & Arnoux, 1978; Pucetti & Leoni, 1980; Villeneuve & Burns, 1982
	BHC <sub>total</sub>	1.8	0.1	27	
	PCB	102	0.6	3200	
VI	DDT <sub>total</sub>	10.3	0.1	35.5	Amico <i>et al.</i> , 1982; Cousteau, 1978; Villeneuve & Burns, 1982; Villeneuve <i>et al.</i> , 1980
	BHC <sub>total</sub>	0.7	0.1	2.6	
	PCB	38.1	0.8	347	
VII	DDT <sub>total</sub>	0.2	0.1	0.4	Cousteau, 1978; Villeneuve & Burns, 1982
	BHC <sub>total</sub>	1.1	0.2	2.2	
	PCB	0.8	0.1	1.1	

**Table 3.3.1.5. - continued**

Area *	Pollutant (CH)	Average	$w(\text{CH})_{\text{dw}} \cdot 10^9$ Minimum	Maximum	References
VIII	DDT <sub>total</sub>	128	0.3	1893	Cousteau, 1978; Dexter & Pavlou, 1973; Villeneuve <i>et al.</i> , 1980; Villeneuve & Burns, 1982
	BHC <sub>total</sub>	0.6	0.4	0.8	
	PCB	155	0.6	775	
IX	DDT <sub>total</sub>	12.0	0.4	29.0	Balkas <i>et al.</i> , 1978; Bastyrk <i>et al.</i> , 1980; Cousteau, 1978; Villeneuve <i>et al.</i> , 1980; Villeneuve & Burns, 1982
	BHC <sub>total</sub>	0.2	0.2	0.3	
	PCB	1.5	ND	3.0	
X	DDT <sub>total</sub>	390	1	780	Cousteau, 1978; Villeneuve & Burns, 1982); Villeneuve <i>et al.</i> , 1980
	BHC <sub>total</sub>	0.7	-	-	
	PCB	2.2	0.6	5.1	
The iatic Sea	DDT <sub>total</sub>	6.8	ND	47.8Adr	Cousteau, 1978; Donazzolo <i>et al.</i> , 1982; Fossato, 1982; Picer, M. & Picer, N., 1982; Picer, M. <i>et al.</i> , 1985; Picer, N. & Picer, M., 1978; Picer, M. <i>et al.</i> , 1981b; Picer, M. & Picer, N., 1991b; Picer, M. & Picer, N., 1993b; Vilièæet <i>et al.</i> , 1978
	BHC <sub>total</sub>	1.1	0.1	4.6	
	PCB	24.1	ND	332	
	Hexachlorobenzene	7.2	-	-	
	Dieldrin	0.1	ND	0.7	

ND Not detected (under sensitivity limit)

- No available data

\* See Fig. 3.3.1.1.

**Table 3.3.1.6.** One way ANOVA of mass fraction ( $w$ ) of chlorinated hydrocarbons (natural logarithmic values) in sediment (dry weight) and mussels (wet weight) depending upon sampling area and period.

Matrix	Response variable	Number of samples	Significance level for mean difference	
Investigation area			Area	Period
<b>Sediment</b>				
All data	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	228	0.0000	0.0020
	$\ln c(\text{PCB}) \cdot 10^9$	228	0.0000	0.0510
Istrian coast	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	81		0.0000
	$\ln c(\text{PCB}) \cdot 10^9$	81		0.0068
Rijeka area	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	48		0.3828
	$\ln c(\text{PCB}) \cdot 10^9$	48		0.0105
Zadar area	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	5		0.0010
	$\ln c(\text{PCB}) \cdot 10^9$	5		0.5962
Šibenik area	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	24		0.0015
	$\ln c(\text{PCB}) \cdot 10^9$	24		0.9661
Dubrovnik area	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	4		0.1510
	$\ln c(\text{PCB}) \cdot 10^9$	4		0.7749
Montenegrin coast	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	16		0.7638
	$\ln c(\text{PCB}) \cdot 10^9$	16		0.2422
<b>Mussels</b>				
All data	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	464	0.0000	0.0000
	$\ln c(\text{PCB}) \cdot 10^9$	464	0.0000	0.1934
Istrian coast	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	102		0.0000
	$\ln c(\text{PCB}) \cdot 10^9$	102		0.0023
Pula area	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	57		0.0000
	$\ln c(\text{PCB}) \cdot 10^9$	57		0.0000
Rijeka area	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	69		0.0000
	$\ln c(\text{PCB}) \cdot 10^9$	69		0.0031
Zadar area	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	34		0.0000
	$\ln c(\text{PCB}) \cdot 10^9$	34		0.5386
Šibenik area	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	19		0.4310
	$\ln c(\text{PCB}) \cdot 10^9$	19		0.8290
Split area	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	54		0.0000
	$\ln c(\text{PCB}) \cdot 10^9$	54		0.0002
Dubrovnik area	$\ln c(\text{DDT}_{\text{total}}) \cdot 10^9$	64		0.0341
	$\ln c(\text{PCB}) \cdot 10^9$	64		0.0561

**Table 3.3.1.7.** One way ANOVA of some sediment characteristics and mass fraction ( $w$ ) of chlorinated hydrocarbons (natural logarithmic values) in sediment from the northern Adriatic open waters depending upon sampling area and period.

Response variable	Number of samples	Significance level for mean difference	
		Area	Period
Specific surface area $S_A/m^2g^{-1}$	17	0.0468	
Organic matter content $w_{dw}(\text{Org.matt.}) \cdot 10^2$	17	0.1503	
Sediment fraction			
$w_{dw}(>100 \mu m) \cdot 10^2$	17	0.1266	
$w_{dw}(16-100 \mu m) \cdot 10^2$	17	0.6569	
Silt, $w_{dw}(4-63 \mu m) \cdot 10^2$	17	0.2663	
$w_{dw}(4-16 \mu m) \cdot 10^2$	17	0.0961	
Clay, $w_{dw}(<4 \mu m) \cdot 10^2$	17	0.0527	
Pollutant fraction			
$w_{dw}(\text{DDT}_{\text{total}}) \cdot 10^9$	55	0.0003	0.0000
$w_{dw}(\text{PCB}) \cdot 10^9$	53	0.0101	0.0254
PCB/DDT <sub>total</sub>	53	0.0000	0.0000

in dependence on sampling area, this did not result for some sedimentological and physico-chemical parameters, except sediment specific surface area (Table 3.3.1.7).

Mass fractions of DDT<sub>total</sub> and PCBs in sediments were compared by means of linear regression analysis (Table 3.3.1.8. and Fig. 3.3.1.7). The linear correlation coefficients for all data, as well as for data from the western Istria (including Pula), Rijeka, Šibenik, and Dubrovnik areas, were statistically significant at very high confidence intervals (97-99.9%). These results suggested that pollution with both DDT<sub>total</sub> and PCBs in the mentioned areas originated from the same source, but this was probably not the case for the Zadar and Split areas.

Statistically significant correlations were observed between DDT<sub>total</sub> and PCB mass fractions, chlorinated hydrocarbons and petroleum hydrocarbons, and chlorinated hydrocarbons and the clay fraction in sediments from the open northern and central Adriatic (Table 3.3.1.10). Interestingly, no correlation was generally found between chlorinated hydrocarbons and the sediment organic matter.



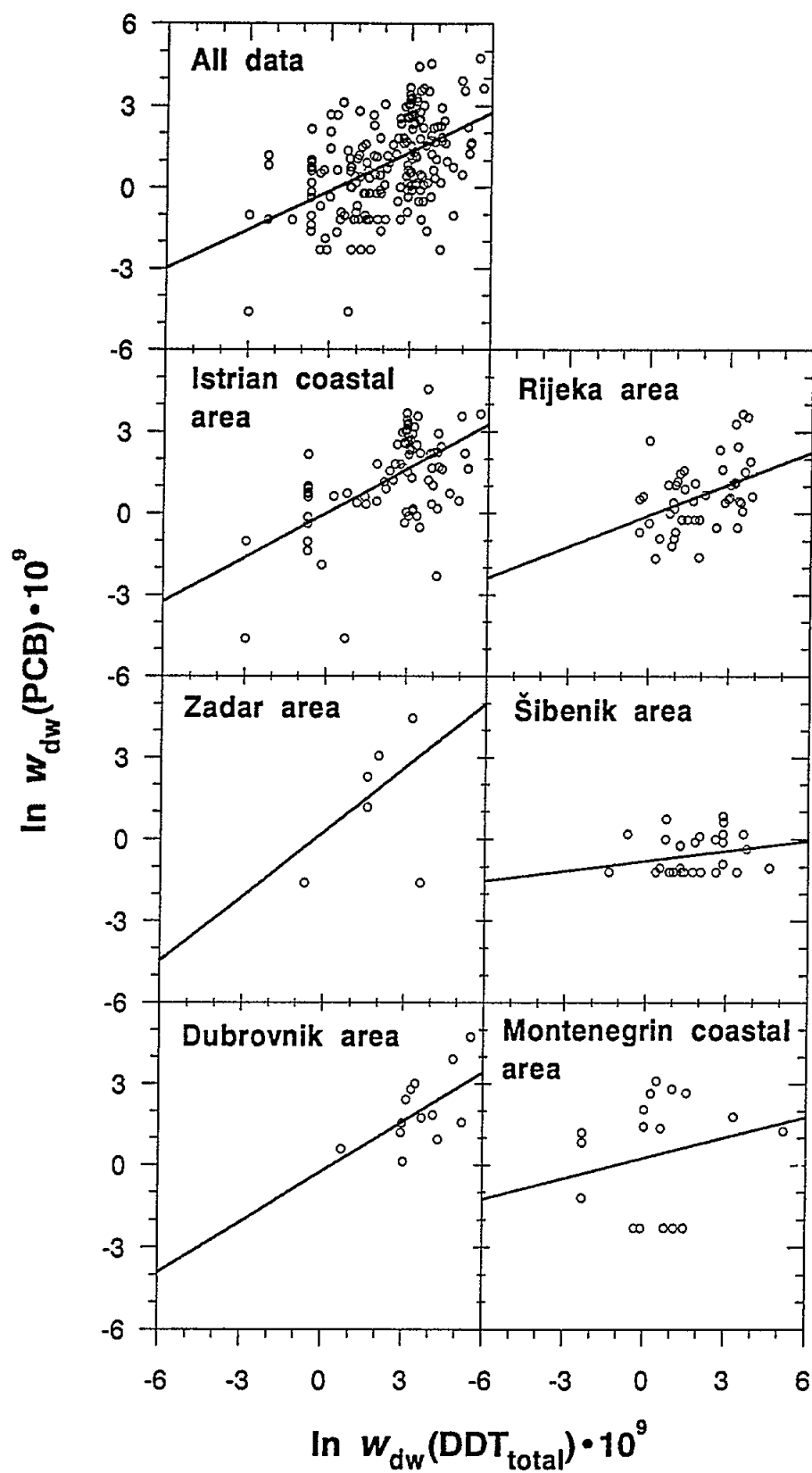


Fig. 3.3.1.7. Linear regression analysis of natural logarithmic values of  $\text{DDT}_{\text{total}}$  and PCB mass fractions ( $w$ ) in sediment.

**Table 3.3.1.8.** Results of the linear regression analyses of pollutant (phenols-Phe, detergents-Det, etc) concentrations (c) and mass fractions (w) in wastewater, sediment, mussels and with extractable organic matter (EOM - wet weight) of mussels.

Matrix Area	Dependent variable	Independent variable	Number of pairs	Correlat. coef.	Signific. level
<b>Waste water</b>					
Pula	$c(\text{Det})/\mu\text{g dm}^{-3}$	$c(\text{Phe})/\mu\text{g dm}^{-3}$	111	<0.1	>0.1
Pula	$\ln c(\text{Phe})/\mu\text{g dm}^{-3}$	$\ln c(\text{Det})/\mu\text{g dm}^{-3}$	111	0.71	0.000
Rijeka	$c(\text{Det})/\mu\text{g dm}^{-3}$	$c(\text{Phe})/\mu\text{g dm}^{-3}$	325	<0.1	>0.1
Rijeka	$\ln c(\text{Phe})/\mu\text{g dm}^{-3}$	$\ln c(\text{Det})/\mu\text{g dm}^{-3}$	324	0.14	0.01
Zadar	"	"	34	0.43	0.01
Split	"	"	193	0.12	0.08
<b>Sediment</b>					
All data	$\ln w(\text{DDT}_{\text{total}}) \cdot 10^9$	$\ln w(\text{PCB}) \cdot 10^9$	223	0.51	0.000
Rijeka	"	"	48	0.43	0.002
Zadar	"	"	6	0.45	>0.1
Šibenik	"	"	28	0.25	>0.1
Dubrovnik	"	"	12	0.58	0.03
Mont. coast	"	"	17	0.25	>0.1
<b>Mussels</b>					
All data	$\ln w(\text{PCB}) \cdot 10^9$	$\ln w(\text{DDT}_{\text{total}}) \cdot 10^9$	464	0.24	0.000
Istrian	"	"	116	0.31	0.001
Pula	"	"	66	0.48	0.000
Rijeka	"	"	77	0.24	0.030
Zadar	"	"	37	<0.1	>0.1
Šibenik	"	"	21	0.54	0.008
Split	"	"	62	0.36	>0.1
Dubrovnik	"	"	72	0.39	0.001
<b>Between pollutants and EOM</b>					
All data	$\ln w(\text{DDT}_{\text{total}}) \cdot 10^9$	$w(\text{EOM}) \cdot 10^2$	365	0.19	0.000
	$\ln w(\text{PCB}) \cdot 10^9$	"	364	0.14	0.009
Istrian	$\ln w(\text{DDT}_{\text{total}}) \cdot 10^9$	"	116	<0.1	>0.1
	$\ln w(\text{PCB}) \cdot 10^9$	"	116	<0.1	>0.1
Pula	$\ln w(\text{DDT}_{\text{total}}) \cdot 10^9$	"	47	0.34	0.016
	$\ln w(\text{PCB}) \cdot 10^9$	"	47	<0.1	>0.1
Rijeka	$\ln w(\text{DDT}_{\text{total}}) \cdot 10^9$	"	77	0.25	0.027
	$\ln w(\text{PCB}) \cdot 10^9$	"	77	0.28	0.012
Zadar	$\ln w(\text{DDT}_{\text{total}}) \cdot 10^9$	"	12	0.29	>0.1
	$\ln w(\text{PCB}) \cdot 10^9$	"	12	-0.31	>0.1
Šibenik	$\ln w(\text{DDT}_{\text{total}}) \cdot 10^9$	"	21	0.58	0.004
	$\ln w(\text{PCB}) \cdot 10^9$	"	21	0.38	0.076
Split	$\ln w(\text{DDT}_{\text{total}}) \cdot 10^9$	"	29	0.63	0.000
	$\ln w(\text{PCB}) \cdot 10^9$	"	29	0.34	0.064
Dubrovnik	$\ln w(\text{DDT}_{\text{total}}) \cdot 10^9$	"	50	0.38	0.004
	$\ln w(\text{PCB}) \cdot 10^9$	"	50	0.23	0.100
<b>Between matrixes</b>					
	Sediment	Water			
Šibenik	$w(\text{Kuw.oil}) \cdot 10^6$	$c(\text{Kuw.oil})/\mu\text{g dm}^{-3}$	28	<0.1	>0.1
	$w(\text{Chr.}) \cdot 10^6$	$c(\text{Chr.})/\mu\text{g dm}^{-3}$	28	-0.12	>0.1
	$\ln w(\text{Kuw.oil}) \cdot 10^6$	$\ln c(\text{Kuw.oil})/\mu\text{g dm}^{-3}$	28	0.31	0.097
Split	$w(\text{Chr.}) \cdot 10^6$	$c(\text{Chr.})/\mu\text{g dm}^{-3}$	18	<0.1	>0.1
	$\ln w(\text{Chr.}) \cdot 10^6$	$\ln c(\text{Chr.})/\mu\text{g dm}^{-3}$	18	<0.1	>0.1

**Table 3.3.1.9.** Mass fraction (*w*) of chlorinated hydrocarbons in mussels (fresh weight) from the Mediterranean Sea.

AREA <sup>a</sup>	Period	$w_w(\text{DDT}_{\text{total}}) \cdot 10^9$		$w_w(\text{BHC}_{\text{total}}) \cdot 10^9$		$w_w(\text{PCB}) \cdot 10^9$		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 <i>et al.</i> , 1972; Marchand <i>et al.</i> , 1976; Risebrough <i>et al.</i> , 1976; Soler, 1972
II	1976/79	25.9(15)	1.5-46.0	0.90(11)	0.02-1.87	126.1(15)	10.9-233.0	Arnoux <i>et al.</i> , 1980d; Bolognari <i>et al.</i> , 1978; Contardi <i>et al.</i> , 1979; Contardi <i>et al.</i> , 1980; Ferro <i>et al.</i> , 1979; Monod and Arnoux, 1978
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 <i>et al.</i> , 1982; Marchand, 1985
IV	1978/81	34.7	9.0-57.3	-	2.30-4.29	96.4	20.0-172.7	Bolognari <i>et al.</i> , 1978; Focardi <i>et al.</i> , 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 <i>et al.</i> , 1979; Bolognari <i>et al.</i> , 1978
VIII	1975/79	23.9(96)	-	1.74(56)	-	383.4(96)	-	Kilikidis <i>et al.</i> , 1980
Adr.	1973	34363(7)	-	6160(7)	-	-	-	Štirn <i>et al.</i> , 1974
"	1973/74	98.7(67)	ND-506.9	-	-	153.9(67)	ND-390.1	Picer, M. <i>et al.</i> , 1978a; Picer, M. <i>et al.</i> , 1985; Nasci & Fossato, 1982
"	1976/80	12.9(140)	ND-301.1	1.67	0.40-3.05	82.5(77)	ND-1586	Bolognari <i>et al.</i> , 1978; Dujmov <i>et al.</i> , 1978; Fossato & Craboledda, 1980; Picer, M. & Picer, N., 1982; Picer M. <i>et al.</i> , 1981b; Nazansky <i>et al.</i> , 1978; Viličič <i>et al.</i> , 1978; Picer, M. <i>et al.</i> , 1985; Picer, N. & Picer, M., 1990; Picer, M. & Picer, N., 1991a
"	1983/86	8.7(108)	ND-41.0	-	-	21.2(107)	ND-68.0	Anon., 1987

ND Not detected (under sensitivity limit); Number of samples in brackets; Adr. - Adriatic

<sup>a</sup> See Fig. 3.3.1.1.

**Table 3.3.1.10.** Results of the linear regression analyses of pollutant concentrations (*c*) and mass fraction (*w*) and some sediment characteristics in water and sediment from the northern and central Adriatic open waters.

Area	Dependent variable	Independent variable	Number of pairs	Correlat. coef.	Signific. level
<b>Matrix</b>			<b>N</b>	<b>r</b>	<b>p</b>
<b>Northern and central Adriatic Sediment</b>					
	$\ln w(\text{DDT}_{\text{total}}) \cdot 10^9$	Clay, $w_{dw}(<4 \mu\text{m}) \cdot 10^2$	30	0.160	>0.100
	$\ln w(\text{Kuw.oil}) \cdot 10^6$	Sp. surf., $S_A/m^2g^{-1}$	31	0.320	0.090
	"	$w(\text{Org.matt.}) \cdot 10^2$	31	0.400	0.030
	"	$w_{dw}(>100 \mu\text{m}) \cdot 10^2$	31	0.580	0.001
	$\ln w(\text{Chr.}) \cdot 10^6$	Silt, $w_{dw}(4-63 \mu\text{m}) \cdot 10^2$	31	0.510	0.004
	$\ln w(\text{Kuw.oil}) \cdot 10^6$	"	30	0.620	0.000
	$\ln w(\text{Chr.}) \cdot 10^6$	$w_{dw}(4-16 \mu\text{m}) \cdot 10^2$	31	0.514	0.004
	$\ln w(\text{Kuw.oil}) \cdot 10^6$	"	31	0.652	0.000
	"	Clay, $w_{dw}(<4 \mu\text{m}) \cdot 10^2$	30	0.445	0.014
	$\ln w(\text{DDT}_{\text{total}}) \cdot 10^9$	$\ln w(\text{PCB}) \cdot 10^9$	31	0.649	0.000
	"	$w(\text{Kuw.oil}) \cdot 10^6$	31	0.729	0.000
	$\ln w(\text{PCB}) \cdot 10^9$	"	31	0.497	0.003
	$\ln w(\text{Chr.}) \cdot 10^6$	"	31	0.893	0.000
<b>Northern Adriatic Sediment</b>					
	$w(\text{DDT}_{\text{total}}) \cdot 10^9$	$w(\text{PCB}) \cdot 10^9$	20	0.933	<0.010
	$\ln w(\text{DDT}_{\text{total}}) \cdot 10^9$	$w(\text{Kuw.oil}) \cdot 10^6$	19	0.898	0.000
	$w(\text{PCB}) \cdot 10^9$	"	19	0.728	0.000
	$w(\text{DDT}_{\text{total}}) \cdot 10^9$	$w(\text{Org.matt.}) \cdot 10^2$	17	0.615	<0.010
	$\ln w(\text{DDT}_{\text{total}}) \cdot 10^9$	"	16	0.303	>0.100
	"	$\ln w(\text{Org.matt.}) \cdot 10^2$	16	<0.100	>0.100
	$w(\text{PCB}) \cdot 10^9$	"	16	<0.100	>0.100
	$w(\text{DDT}_{\text{total}}) \cdot 10^9$	Clay, $w_{dw}(<4 \mu\text{m}) \cdot 10^2$	17	0.603	<0.010
	$w(\text{PCB}) \cdot 10^9$	"	17	0.495	0.05>p>0.01
	Chrysene.	$w(\text{Kuw.oil}) \cdot 10^6$	20	0.859	<0.010
	$w(\text{Kuw.oil}) \cdot 10^6$	$w(\text{Org.matt.}) \cdot 10^2$	17	0.819	<0.010
	"	Sp. surf., $S_A/m^2g^{-1}$	17	0.622	<0.010
	"	$w_{dw}(>100 \mu\text{m}) \cdot 10^2$	-	0.608	<0.010
	"	Silt, $w_{dw}(4-63 \mu\text{m}) \cdot 10^2$	17	0.566	0.05>p>0.01
	"	Clay, $w_{dw}(<4 \mu\text{m}) \cdot 10^2$	17	0.851	<0.010
<b>Water</b>					
	$c(\text{Chr. ext})/\mu\text{g dm}^{-3}$	$c(\text{Chr. part})/\mu\text{g dm}^{-3}$	62	0.536	0.000
	$\ln c(\text{Chr. ext})/\mu\text{g dm}^{-3}$	$\ln c(\text{Chr. part})/\mu\text{g dm}^{-3}$	62	0.464	0.000
	$c(\text{Kuw.oil ext})/\mu\text{g dm}^{-3}$	$c(\text{Kuw.oil prt})/\mu\text{g dm}^{-3}$	62	0.457	0. 0 0 0
	$\ln c(\text{Kuw.oil ext})/\mu\text{g dm}^{-3}$	$\ln c(\text{Kuw.oil prt})/\mu\text{g dm}^{-3}$	62	0.462	0.000

### 3.3.1.3 Chlorinated hydrocarbons in organisms

In the framework of baseline studies, chlorinated hydrocarbons were measured in various species of the principal marine organism groups: plankton, benthos, nekton, birds and mammals. However, among them, mussel, which is widespread around the world ocean, was considered as one of the best indicator organism, and has been analysed more frequently than other species (Picer M., 1986b). However, the results of long-term monitoring of chlorinated hydrocarbons in mussels were reported only in few publications (eg Goldberg *et al.*, 1978; Fossato and Craboleda, 1980; Picer N. and Picer M., 1990, Picer M. and Picer N., 1991a).

The chlorinated hydrocarbon mass fractions determined in mussels from the eastern Adriatic coastal areas after 1976 were significantly lower than in various areas of the Mediterranean Sea (Table 3.3.1.9). The lowest averages were calculated for the data obtained in the framework of this programme from 1983-1986: about 50% for DDTs and four times for PCBs, compared with the 1976-1980 Adriatic values (Table 3.3.1.9).

The highest DDT<sub>total</sub> GM mass fraction in the period 1976-1990 was obtained for mussels from the Zadar area, and the lowest in samples from the Šibenik area (Table 3.3.1.4). Higher values for PCBs were calculated for the Pula, Zadar, Dubrovnik areas, and particularly the Split area, compared to the rest of the investigated region. Differences among areas were also confirmed by the one way ANOVA of the mass fraction data in dependence on sampling area (Table 3.3.1.8). A statistically significant variability was also obtained in relation to the sampling period. However, no temporal trends were noticed in most of the areas, even when earlier data were included in the analysis (since 1976; Figs 3.3.1.8-9). Only in the Pula area had the DDT level decreased evidently during the 1980s, particularly in respect of the early 1970s.

The PCB/DDT<sub>total</sub> mass fraction ratios did not change significantly during the monitoring period in the most part of the investigated eastern Adriatic areas (Fig. 3.3.1.10). Only recently (since 1990) this ratio has increased in the Pula area in respect of the earlier monitoring periods. The variations of the PCB/DDT<sub>total</sub> ratio in the Šibenik area could be rather ascribed to changes of sampling location during the monitoring period.

Long-term chlorinated hydrocarbon analyses in mussels from the western Istrian coastal area led to the conclusion that concentrations of DDT and its metabolites DDE and DDD decreased following an exponential function, rather than linearly. Such a nonlinear model was used to calculate the relationship between chlorinated hydrocarbon concentration in mussels and sampling time. A higher negative correlation coefficient was calculated from the logarithmic values of total DDT concentrations than from the raw data. A higher positive correlation coefficient was obtained after the logarithmic transformation of PCB concentration data, but it was still not statistically significant (Picer M. and Picer N., 1991a).

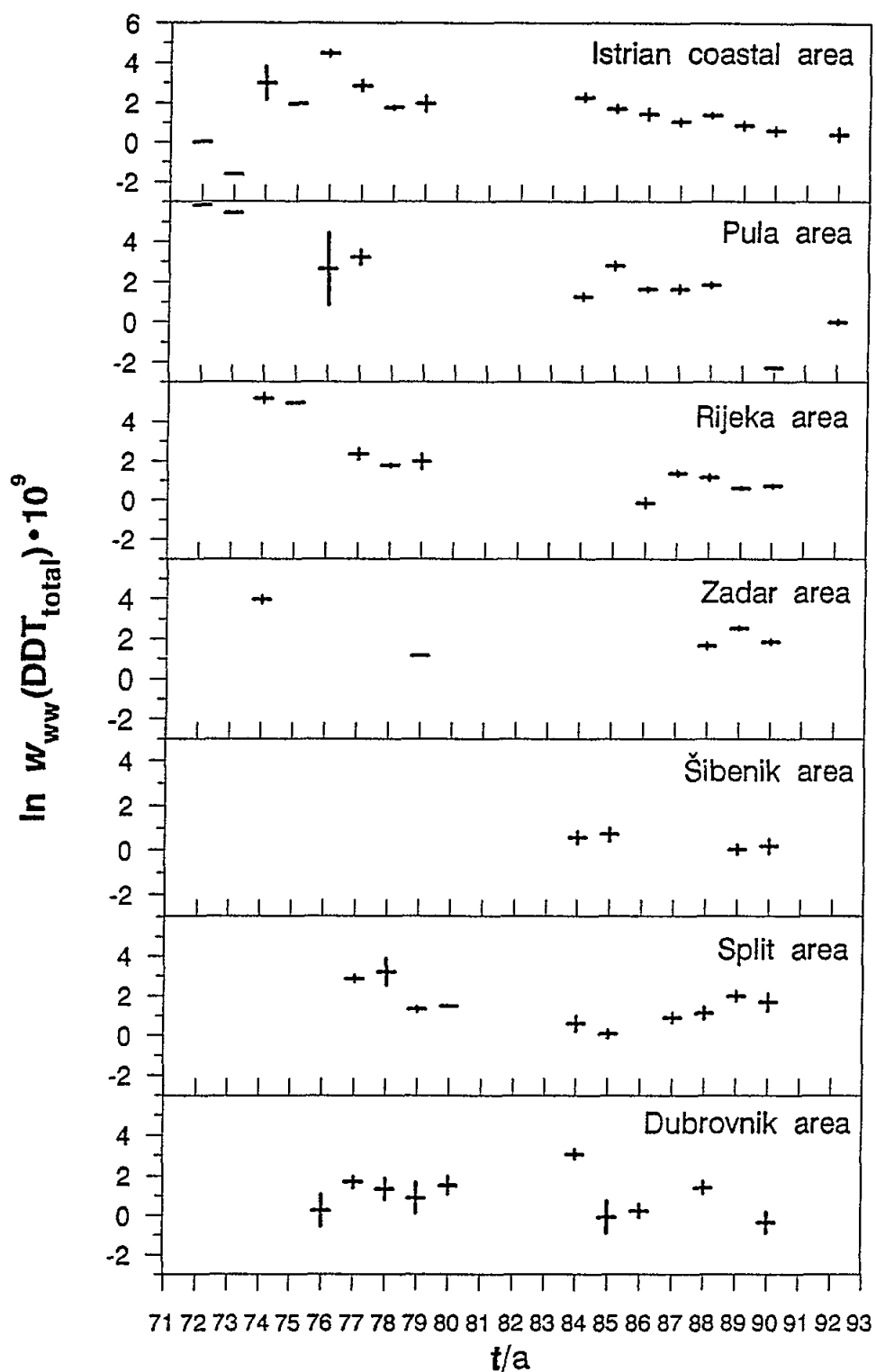


Fig. 3.3.1.8. Natural logarithm of means and their standard errors of mass fraction ( $w$ ) of  $\text{DDT}_{\text{total}}$  in mussels (wet weight) from different investigated areas in the period ( $t$ ) 1972-1992.

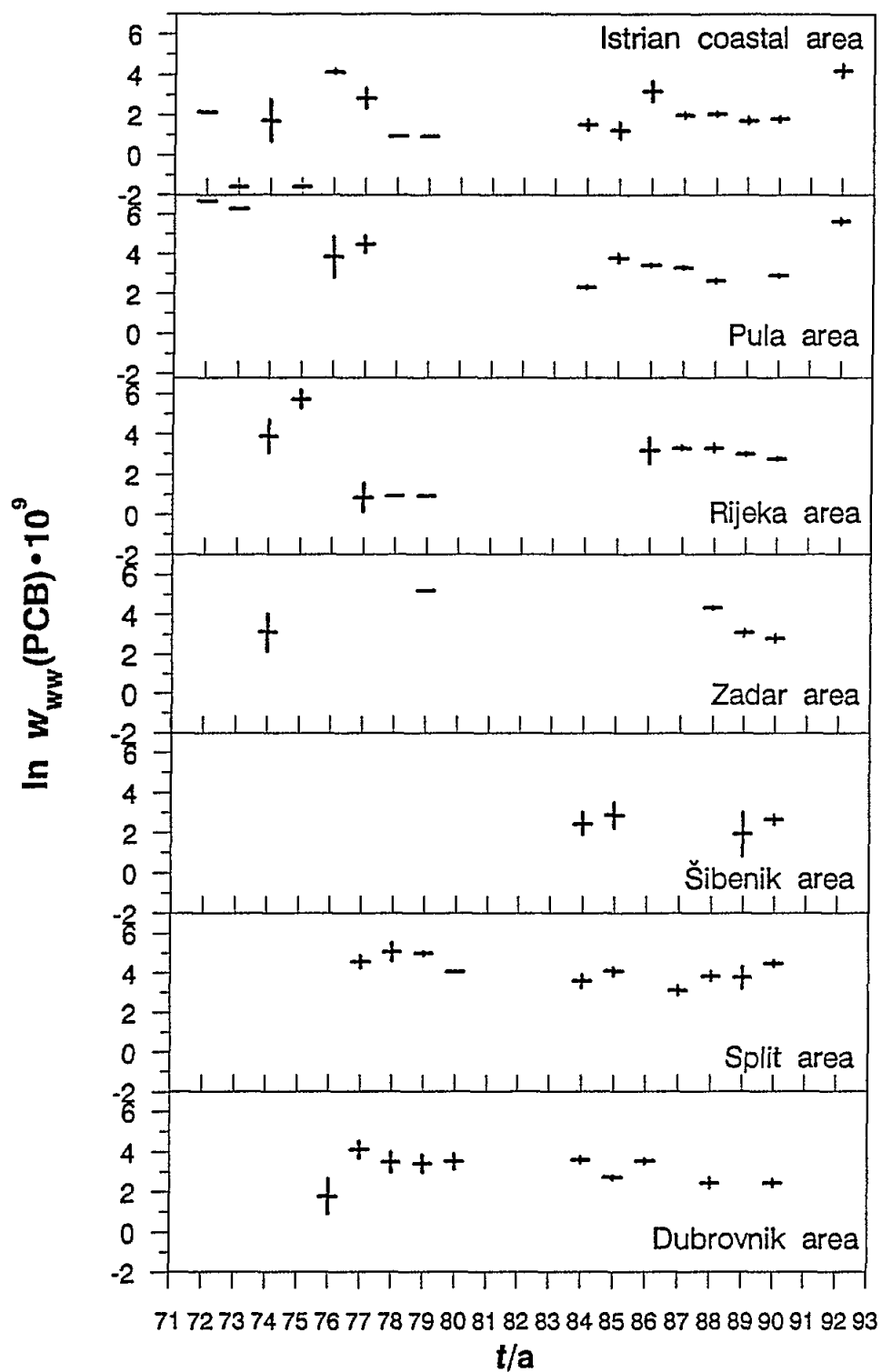


Fig. 3.3.1.9. Natural logarithm of means and their standard errors of mass fraction ( $w$ ) of PCB in mussels (wet weight) from different investigated areas in the period ( $t$ ) 1972-1992.

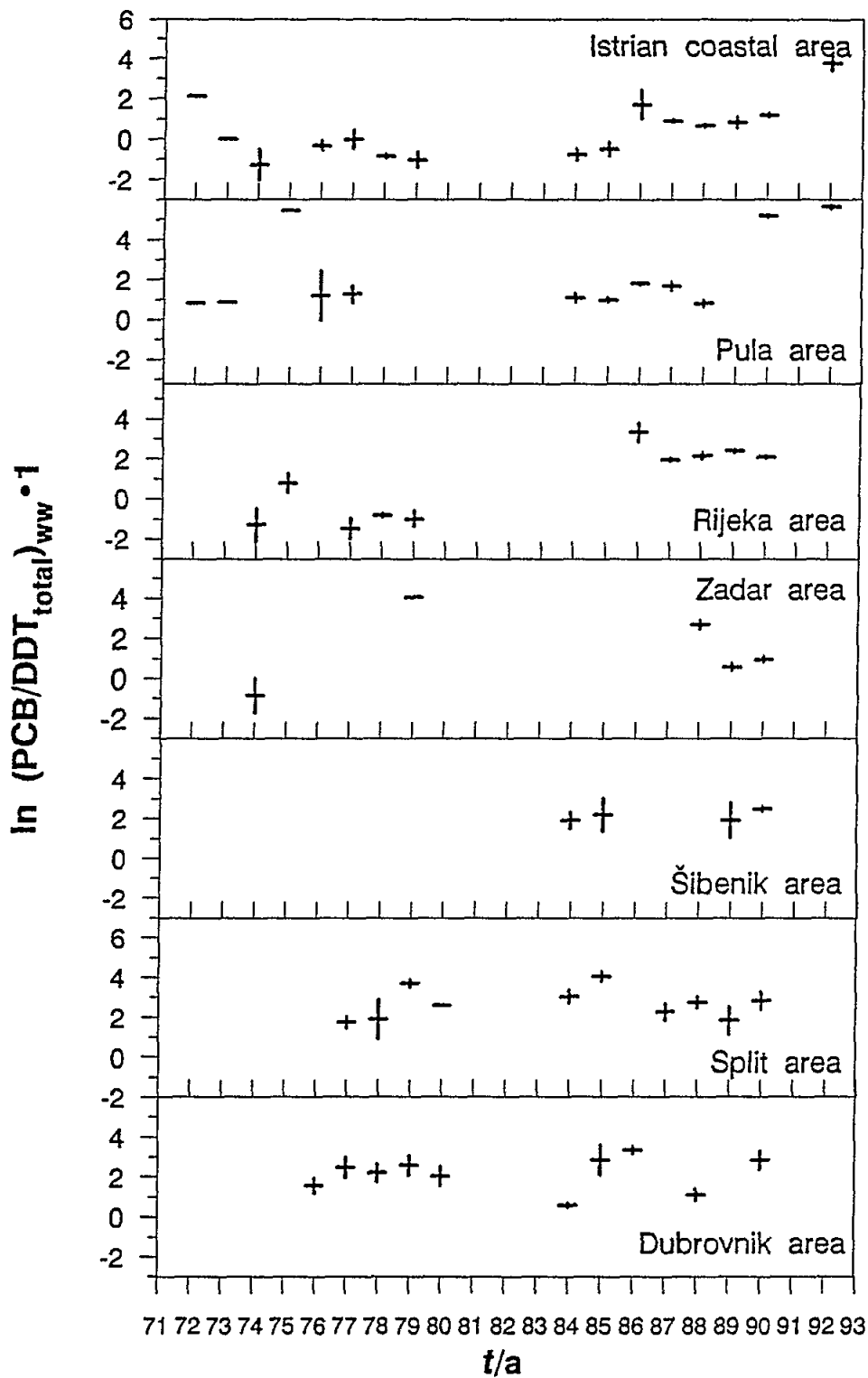


Fig 3.3.1.10. Natural logarithm of means and their standard errors of  $\text{PCB/DDT}_{\text{total}}$  ratios in mussels (wet weight) from different investigated areas in the period (t) 1972-1992.



Significant linear correlation coefficients were obtained between  $\text{DDT}_{\text{total}}$  and PCB mass fractions in mussels (natural logarithmic values) for all data and for the most of the investigated areas, except the Zadar and Split areas (Table 3.3.1.10; Fig. 3.3.1.11).

Chlorinated hydrocarbon mass fractions in mussels were correlated with the extractable organic matter (EOM) percentage (on wet mussel mass; Figs 3.3.1.12. and 3.3.1.13.). Significant correlation coefficients were obtained at 95-99% confidence intervals for all data and most of the investigated areas, except western Istria and the Zadar area (Table 3.3.1.8). Statistically significant correlations between chlorinated hydrocarbon concentrations and EOM were reported only in few publications (eg UNEP/FAO/WHO/IAEA, 1990; Picer N., 1989).

The bioaccumulation potential of three highly toxic coplanar PCB isomers ( $\text{T}_4\text{CB}$  and  $\text{H}_6\text{CB}$ ) was investigated during a transplantation experiment at two locations in Hong Kong waters, using green-lipped mussels (*Perna viridis* L.) as a bioindicator. In contrast to the relatively rapid uptake and release of many other PCB isomers, the non-ortho chlorine substituted coplanar PCB congeners exhibited a slow uptake rate and clearance. Coplanar PCB bioaccumulation is probably not specific for mussels only, but may occur in other aquatic organisms and be enhanced throughout the food chain, up to higher consumers (including humans), with possible toxic effects (Kannan *et al.*, 1989).

### 3.3.2. Phenols

#### 3.3.2.1. Phenols in effluents

Effluents containing phenolic compounds can originate from various sources: livestock dips, wood distillation, rotting vegetation, domestic sewage and chemical manufacturing operations. These compounds are also released from energy-related operations such as coal distillation to produce coke, coal gasification and petroleum refining. In experimental coal conversion technologies currently developed, such as underground coal gasification and coal liquefaction, wastewaters with moderate to high levels of phenolic compounds are produced (DeGreave *et al.*, 1980; Picer, M., 1984). Phenolic material, found in almost all surface waters, impair the organoleptic properties of chlorinated water. Consequently, extremely low concentration ( $1\text{-}2\text{ ng dm}^{-3}$ ) has been adopted as a standard limit for water supply. Higher phenol concentrations can be toxic for aquatic organisms (Polisois *et al.*, 1975).

Phenols were determined in effluents from the Pula, Rijeka and Split areas in the period 1984-1990 and the Zadar area from 1988 to 1990. The average concentrations for these effluents were lower than those calculated for various industrial wastewaters around the world (eg paper mill, oil refinery, coke plant; Table 3.3.2.1). Generally, the phenol concentrations are lower in sewages than in industrial wastewaters. The measured values in the effluents from the investigated areas were in similar ranges as for sewages from other world areas (Table 3.3.2.1).

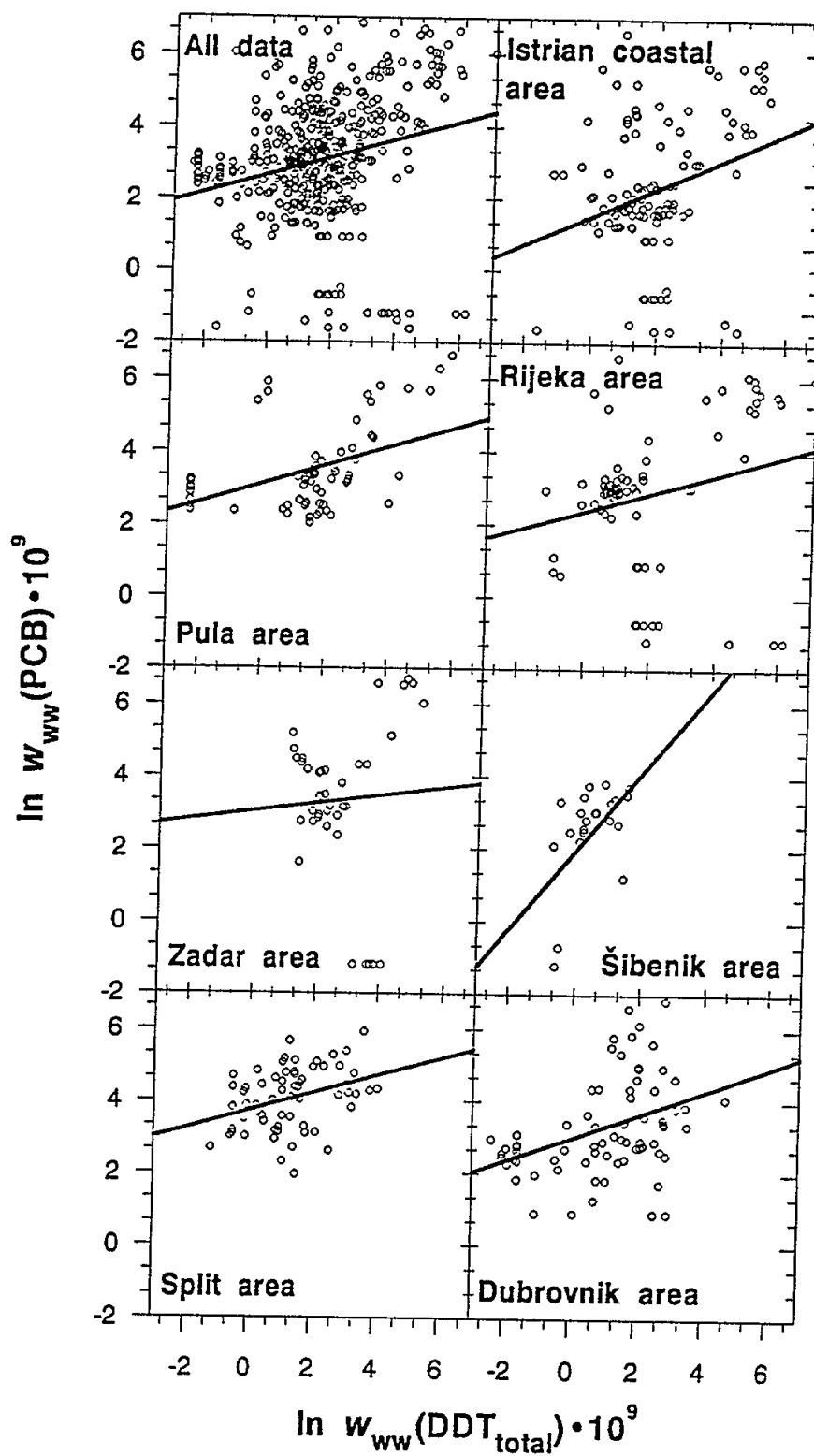


Fig 3.3.1.11. Linear regression analysis of natural logarithmic values of  $\text{DDT}_{\text{total}}$  and PCB mass fractions ( $w$ ) in mussels (wet weight).

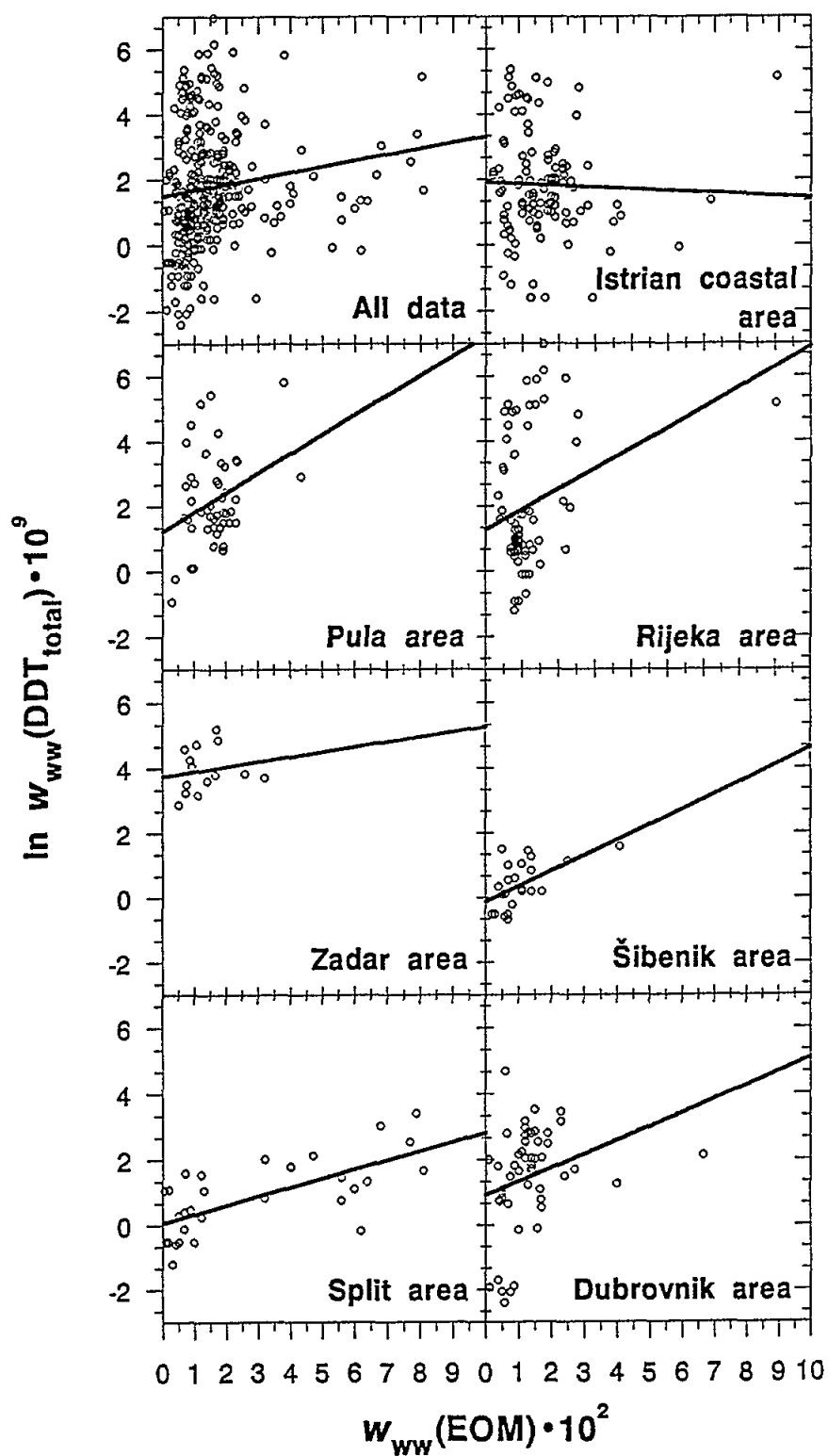


Fig 3.3.1.12. Linear regression analysis of natural logarithmic values of  $\text{DDT}_{\text{total}}$  mass fractions in mussels (wet weight) with their mass fraction of extractable organic matter (EOM, wet weight).

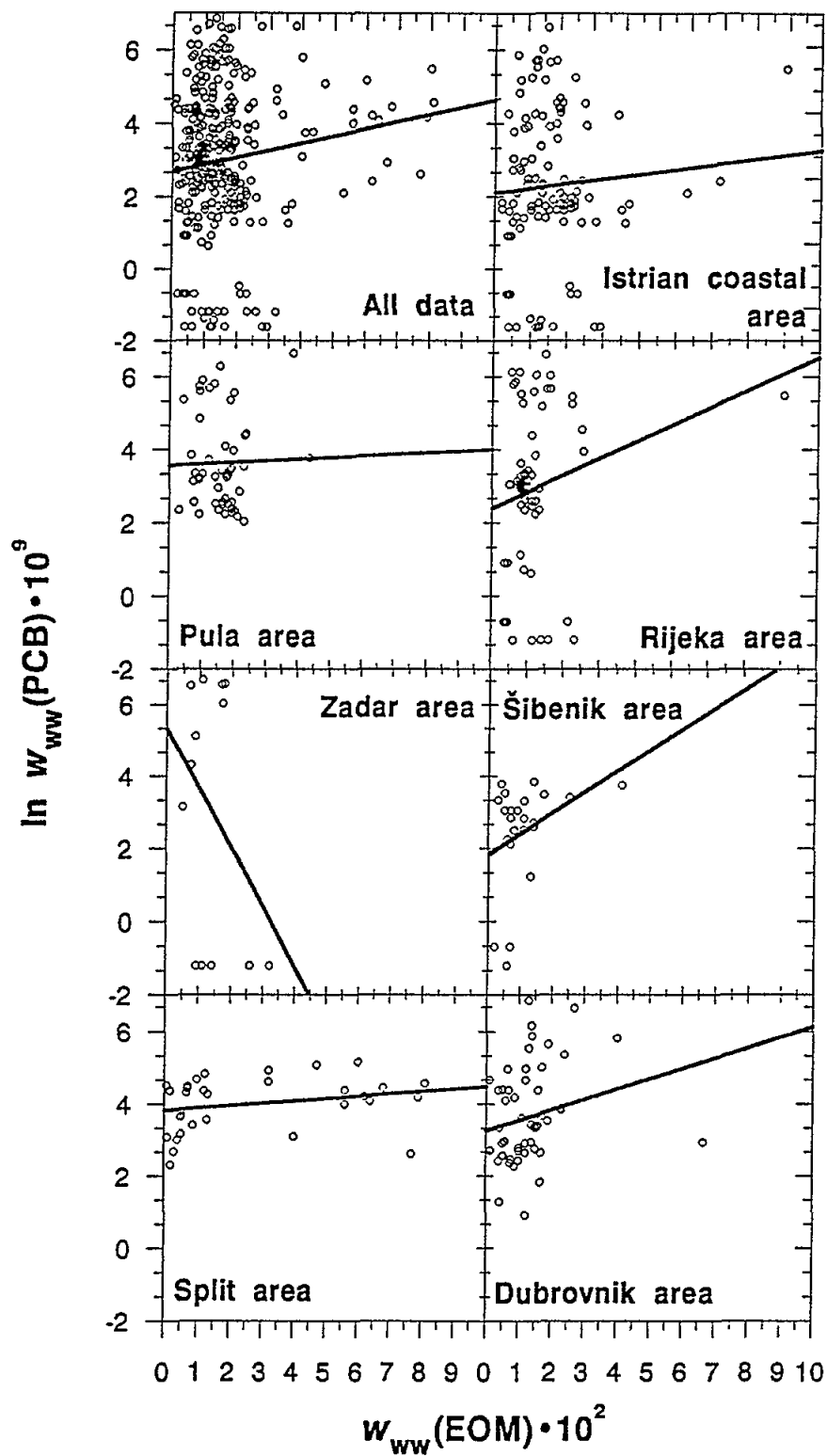


Fig 3.3.1.13. Linear regression analysis of natural logarithmic values of PCB mass fractions in mussels (wet weight) with their mass fraction of extractable organic matter (EOM, wet weight).

**Table 3.3.2.1.** Phenol concentration (c) in waste water.

Waste	Phenolics (Phe)	Method of analysis	c(Phe)/mg dm <sup>-3</sup>	References
Paper mill (raw waste)	Phenols	?	10-2000	Nebel <i>et al.</i> , 1976
Wood preserving plant (Settling point)	o-cresol m-cresol	GC-MS GC-MS	1.4 2.5	Webb, 1973
Petroleum refinery (8 hrs 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 <i>et al.</i> , 1976
Integrated oil refinery (Raw effluent)	phenol	?	120	Volesky <i>et al.</i> , 1974
Petrochemicals (5 day lagoon effluent)	phenol	GC-MC	0.06	Webb, 1973
Coke plant waste	tot. phenol	?	410-2400	Rubin & 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, 1976
Raw Pittsburg sewage	total phenolics	4-AAP	0.072	Hoak, 1957
Eastern Adriatic town wastewaters	phenols	4-AAP	ND-16.5	Anon., 1987

ND = Not detected (under sensitivity limit)

The highest geometric mean (GM) concentration was calculated for the Split effluent and the lowest for the Rijeka (Table 3.3.1.2; Fig. 3.3.2.1). The concentrations varied significantly between the investigated areas because of different effluent types. In fact, a significant variability of phenol concentrations in dependence of both the sampling area and effluent type was obtained by one way ANOVA (Table 3.3.1.3). This variability was mainly due to differences between effluent samples from the Rijeka and Split areas. High significance levels were also calculated in dependence on sampling period and season for all data and for the Rijeka and Split (period only) effluents, but not for the other investigated areas. Moreover, only the phenol concentration in the Rijeka effluents was higher during the high season (summer months) compared to the low season (Fig. 3.3.2.2). Despite this variability, no defined temporal trends were observed in the period 1983-1990 in most of the investigated areas (Fig. 3.3.2.1). The phenol concentration decrease observed recently (1989-1990) in the Rijeka effluent should be confirmed with additional measurements.

### 3.3.2.2. Phenols in coastal waters

Volatile phenols in seawater were monitored in the Montenegrin coastal area (Anon., 1987). The concentrations varied in the range from  $<1 - 42 \mu\text{g dm}^{-3}$ , with an average of  $14 \mu\text{g dm}^{-3}$ . However, the 4-aminoantipyrine method used for these analyses may be not suitable for determinations in seawater (Picer, M., 1984, 1985b). Thus, these results should be interpreted with caution.

### 3.3.3. Anionic detergents

#### 3.3.3.1. Anionic detergents in wastewaters

Owing to their detergent and emulsifying properties, surface active agents are increasingly used in many sectors of human activity. Consequently, increasing amounts of such substances are discharged in surface waters or directly into the sea, causing significant pollution. As an example, in interstitial waters of surface sediments in several zones of the Mediterranean continental platform, the anionic surfactants concentration is generally about  $30 \mu\text{g dm}^{-3}$ , but can increase up to  $2000 \mu\text{g dm}^{-3}$  in wastewater outfall discharge areas or in estuaries of polluted rivers (Alfano *et al.*, 1982). Anionic detergents are typical pollutants in sewages and generally occur in much higher concentrations than other organic compound (Picer M., 1983b).

Anionic detergent concentrations were determined in effluents from the Slovenian, Pula, Rijeka and Split areas in the period 1984-1990, and the Zadar area from 1988 to 1990. Detergent concentration can vary considerably, depending upon wastewater types (Table 3.3.3.1). The average value for the eastern Adriatic raw effluents is about three times lower than for some USA sewages, and even lower than in treated effluents (eg at Haifa, Israel; Table 3.3.3.1).

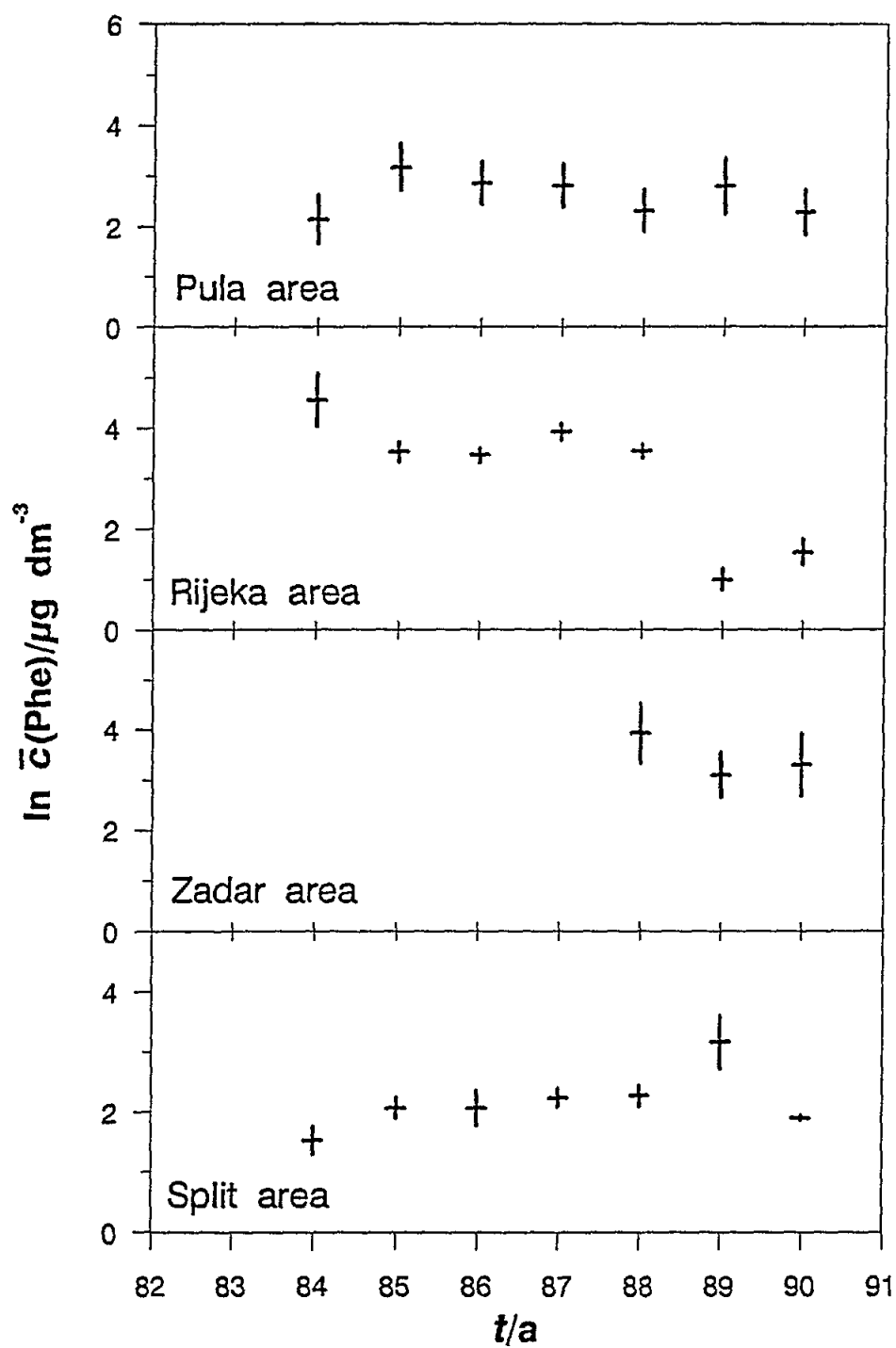


Fig. 3.3.2.1. Natural logarithm of means and their standard errors of phenols (Phe) concentrations ( $\bar{c}$ ) in wastewaters from different investigated areas in the period ( $t$ ) 1983-1990.

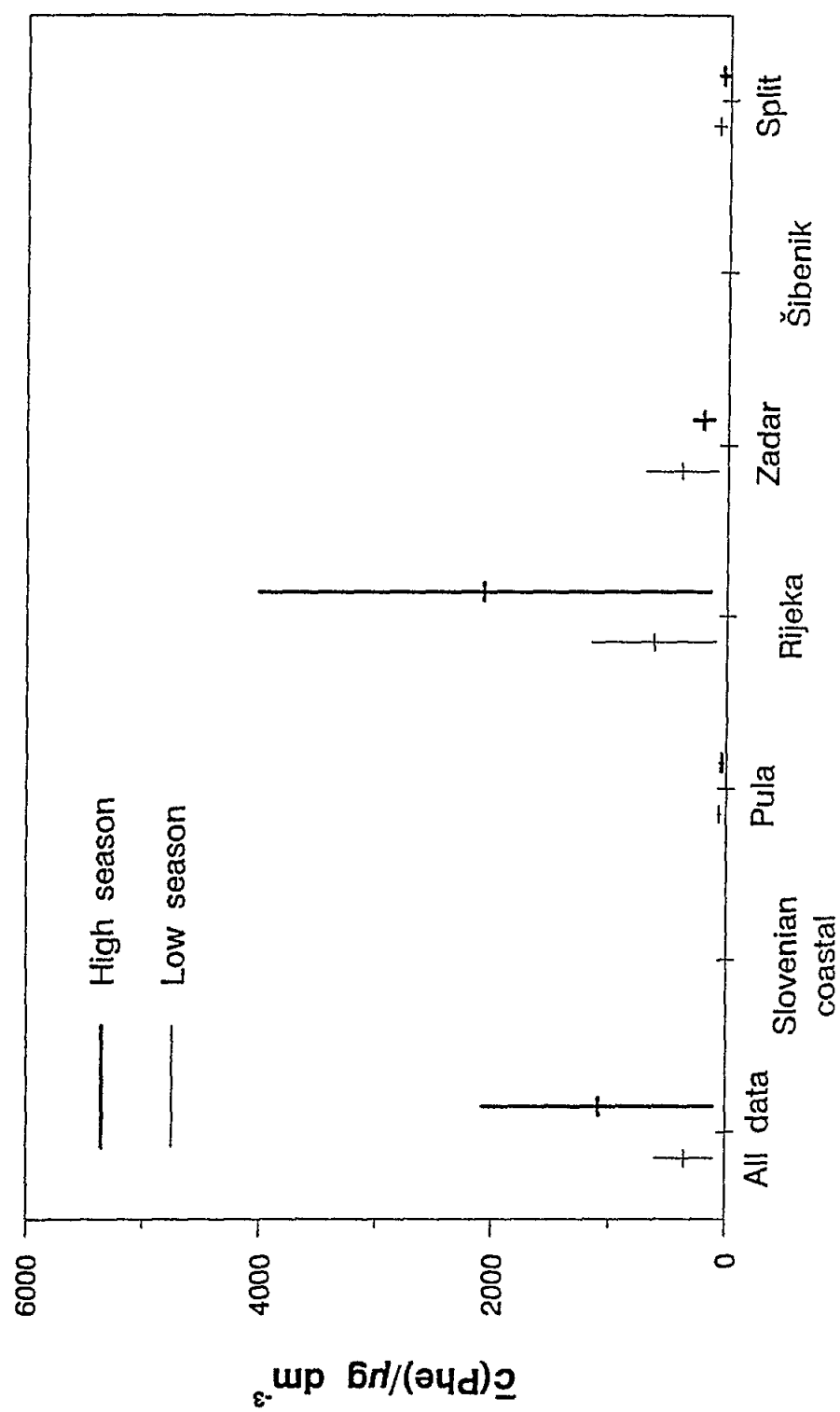


Fig. 3.3.2.2. Means and their standard errors of phenols (Phe) concentrations ( $\bar{c}$ ) in wastewaters during low and high season period of the year for different investigated areas.



**Table 3.3.3.1.** Anionic detergents concentration (c) in wastewaters.

Location and year	Compound(s) (Det)	c(Det)/ $\mu\text{g dm}^{-3}$		References
		Average	Range	
Sewage from individual home, USA	Detergent	6200(154)		Watson <i>et al.</i> , 1967
Effluents after primary and secondary treatment, UK	Manoxol OT	580(3)	750-2500	Eden & Truesdale, 1967
Raw wastewater, South Nevada, USA	MBAS	7000	-	Culp & Culp, 1971
Primary effluent Windhoek, South Africa	ABS	16200	-	Stander & Vuuren, 1970
Nassau County, N.Y. USA, 1965 Raw water nonfiletred	Detergent	770	-	Stevens & Peters, 1966
Tertiary effluent nonfiletred	Detergent	<20	-	
Haifa, Israel, waste water treatmant plant. Oxidation pond	Anionic det.	8500	-	Manka & Rebhun, 1982
Lime clarifier	Anionic det.	6500	-	
Textile fabrics, Croatia, 1980	Anionic det. (TBS)	6200	70-14280	Vojvodiet <i>et al.</i> , 1981
Plastic industry, Croatia, 1979/80	Anionic. det. (NaLS)	36720(17)	95-246000	Vojvodiet <i>et al.</i> , 1981
Laundry effluent, Croatia	Anionic. det.		12000-70000	Kozarac <i>et al.</i> , 1976
Eastern Adriatic town wastewaters 1984-86	Anionic. det.	2100(325)	20-16300	Anon., 1987

Number of samples in brackets.

In the effluents from the Rijeka, Zadar, and Split areas the detergent geometric mean (GM) concentrations were higher than in the Slovenian and Pula effluents (Table 3.3.1.2). A significant variability by area and effluent type was observed for all data, elaborated by one way ANOVA (Table 3.3.1.3). Differences between effluent types occurred in most of the investigated areas, except the Zadar area.

However, a statistically nonsignificant variability was observed in dependence on sampling period and season, considering all data (Table 3.3.1.3). In contrast, high statistical significance levels were obtained for the Rijeka and Split data in relation to the sampling period. The detergent concentrations (yearly means of natural logarithms) in the effluents of the investigated areas did not change markedly during the investigated period (1984-1990; Fig. 3.3.3.1). Moreover, these concentrations also did not differ significantly between the low and high seasons (Fig. 3.3.3.2), even though some differences may be expected due to influence of an additional touristic population.

### 3.3.3.2. Anionic detergents in coastal and estuarine waters

In 1985 and 1986 detergents were determined in the Montenegrin coastal waters (Anon., 1987). The average and range of these values were higher than those calculated from concentration data for the Krka River estuary and Šibenik coastal area, but still similar to other Mediterranean areas. This discrepancy might result from different extraction and analytical methods used in the Šibenik and other Mediterranean areas, respectively.

### 3.3.4. Petroleum hydrocarbons

#### 3.3.4.1. Petroleum hydrocarbons in effluents

Petroleum hydrocarbon concentrations were determined in effluents from the Rijeka and Split areas in the period 1984-1990 and the Šibenik area from 1984 to 1987 (Table 3.3.1.2; Fig. 3.3.4.1). The averages of the obtained values were lower than those for wastewaters from some international urban centres (Table 3.3.4.1). However, some variability can also arise from different analytical methodologies applied in the analysis of these pollutants. Therefore, it is necessary to state the methodology used and the reference oil type or hydrocarbon compound to which the analysis result is referred.

IR spectrophotometry was used to analyse most of the wastewater samples, collected in the framework of this programme. Some of the samples from the Rijeka and Šibenik areas were analysed with UV spectrofluorometry (in 1986), while UV spectrophotometry was applied in the Split area from 1984-1986. Remarkably, average petroleum hydrocarbon concentrations measured in Rijeka industrial wastewaters with IR spectrophotometry and UV spectrofluorometry were not significantly different. An apparent discrepancy occurred between values for sewages mixed with industrial wastewaters, but it was not statistically significant. The UV spectrofluorometrical method has some advantages in respect to IR spectrophotometry, because additional data on the nature of wastewater petroleum

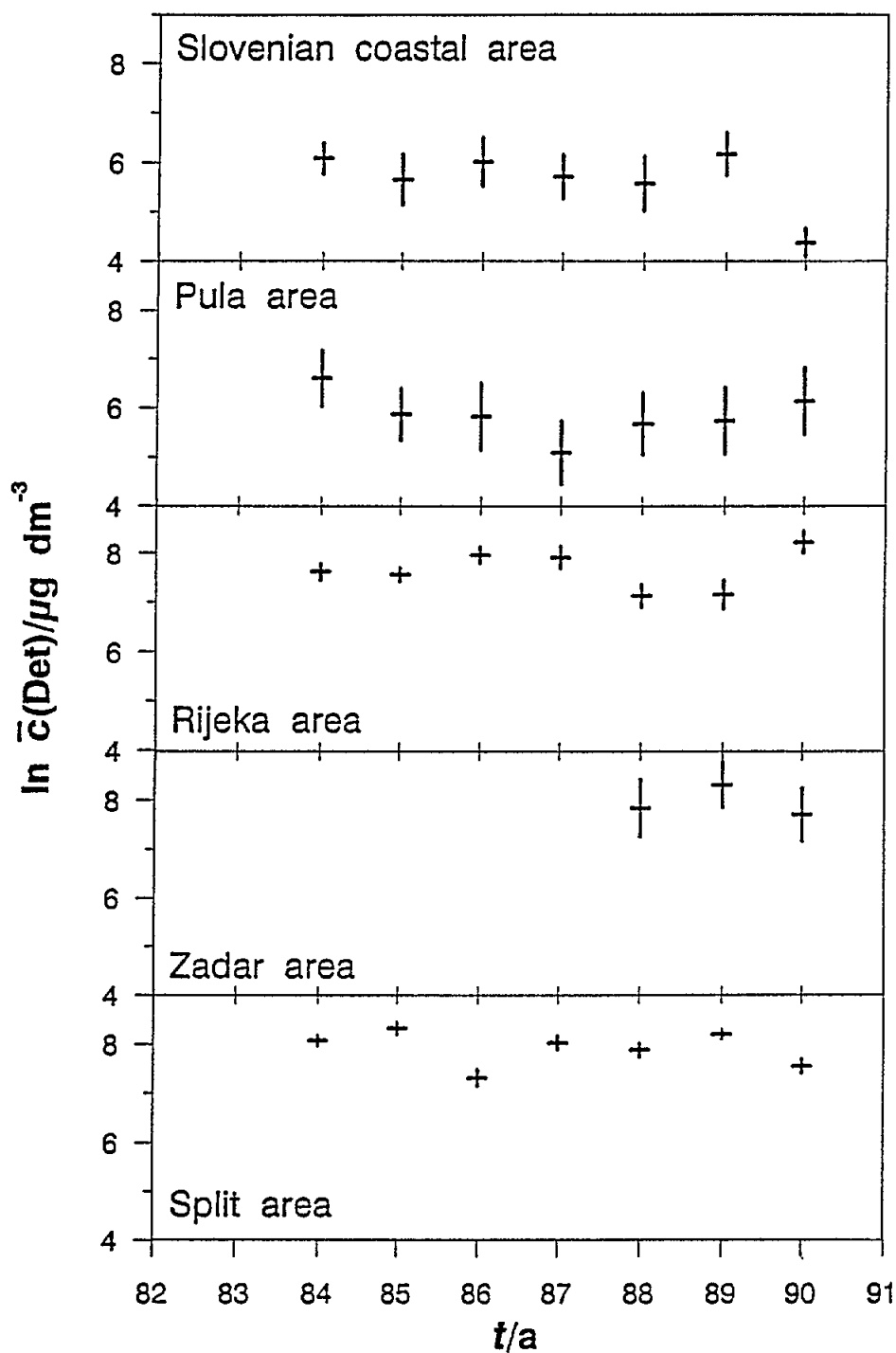


Fig. 3.3.3.1. Natural logarithm of means and their standard errors of detergents (Det) concentrations ( $\bar{c}$ ) in wastewaters from different investigated areas in the period ( $t$ ) 1983-1990.

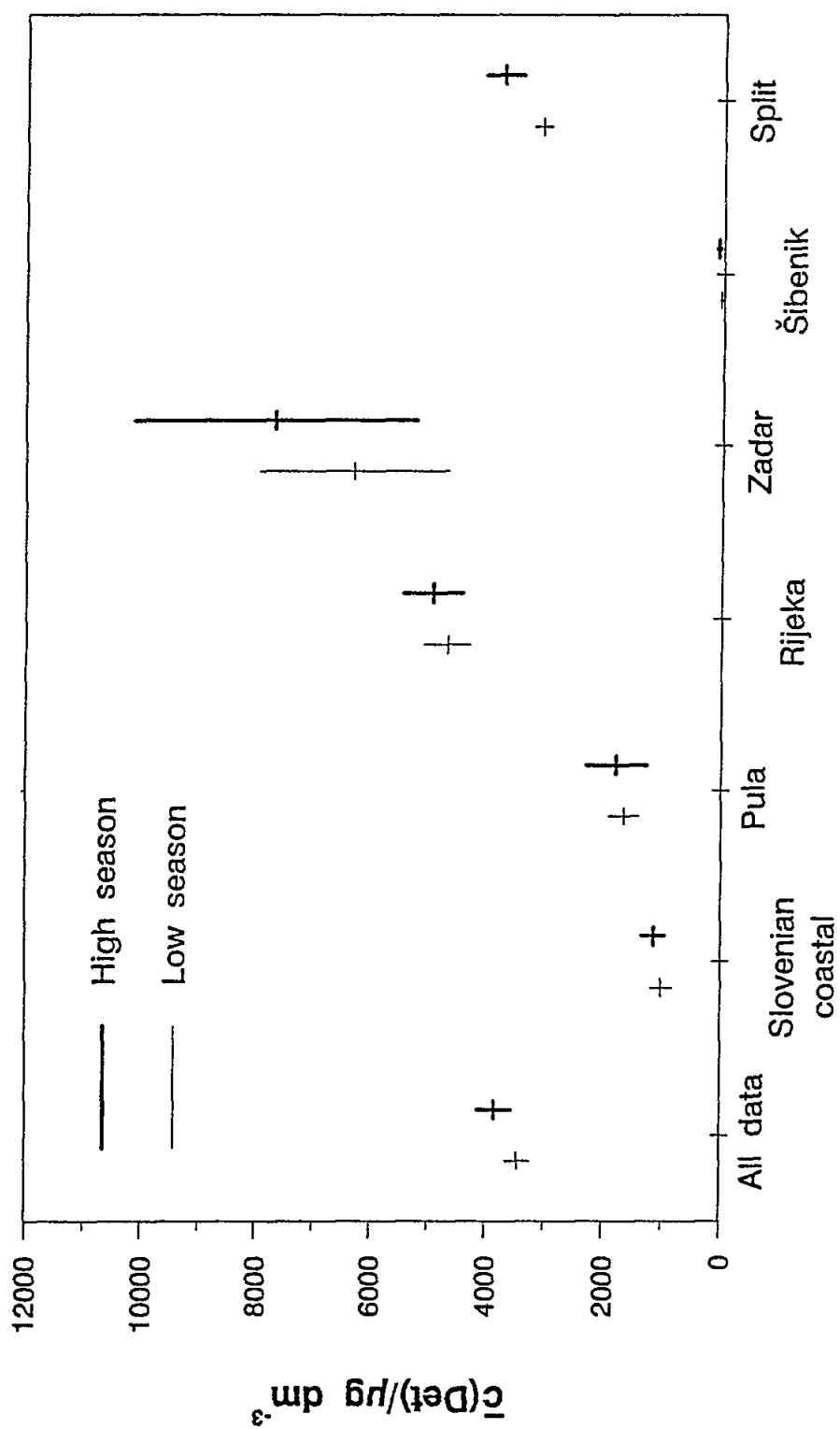


Fig. 3.3.3.2. Means and their standard errors of detergents (Det) concentrations ( $\bar{c}$ ) in wastewaters during low and high season period of the year for different investigated areas.

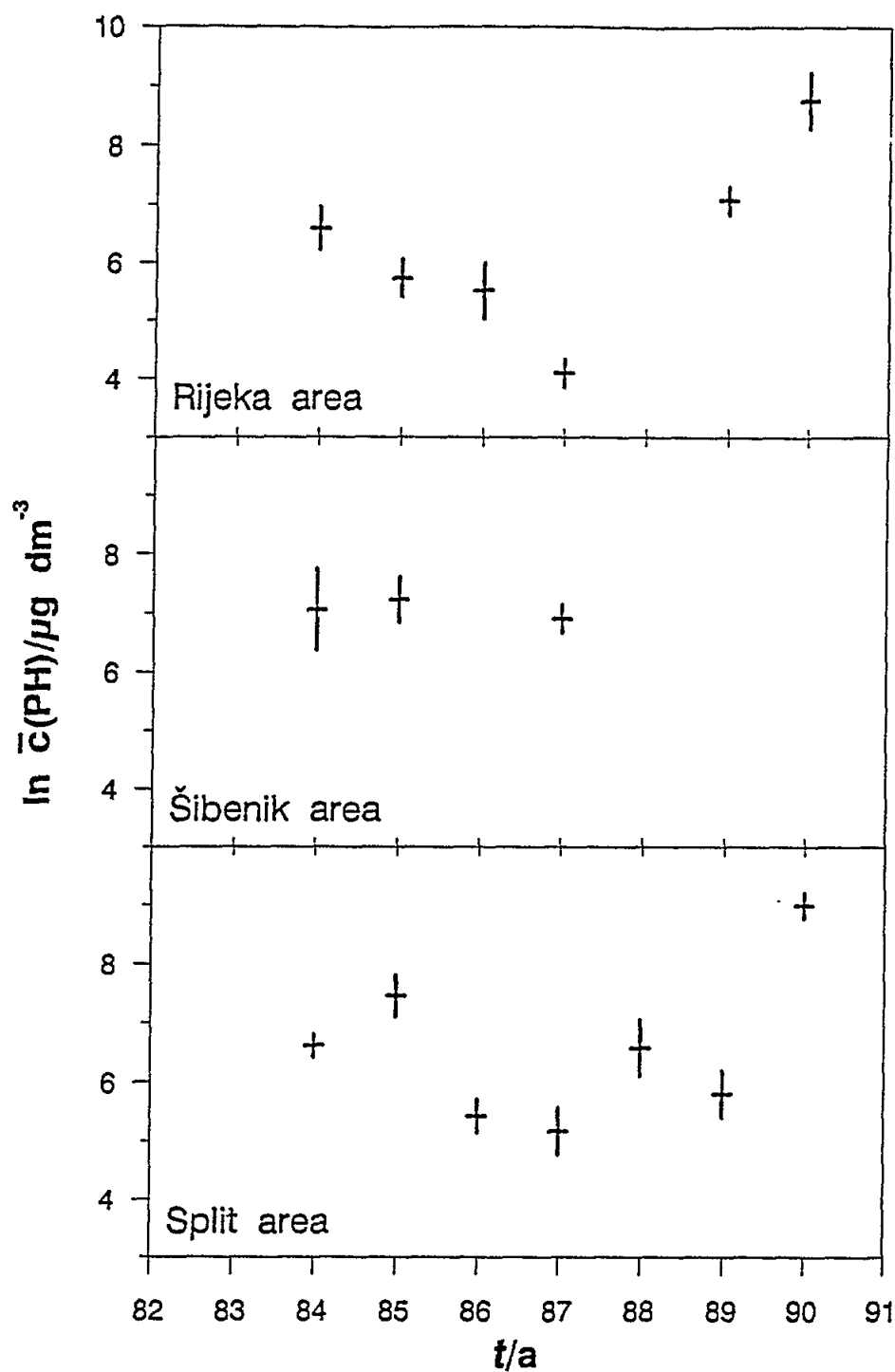


Fig. 3.3.4.1. Natural logarithm of means and their standard errors of petroleum hydrocarbons (PH) concentrations ( $\bar{c}$ ) in wastewaters from different investigated areas in the period ( $t$ ) 1983-1990.

**Table 3.3.4.1.** Petroleum and polyaromatic hydrocarbon concentrations (c) in waste waters.

Location and Year	Method of Analysis	Compound(s) (PH)	$c(\text{PH})/\mu\text{g dm}^{-3}$		Reference
			Average	Range	
North Providence secondary & Quinn, 1973 wastewater treatment plants (3 cities) effluents, USA	GC	Hydrocarbons	7000(9)	<500-16200	Farrington
Domestic wastewater	Hunter & Jen	Aromatic hydrocarb.	1300	-	kelekian, 1965
		Aliphatic hydrocarb.	4000	-	
Petroleum refining industry; 12 refineries McKinney, 1967		Oil total	57000	-	
Sewage sludge (Germany)	GC	Benzo(a)pyrene <sup>a</sup> Polyaromatics <sup>a</sup>	1700 26820	-	Grimmer <i>et al.</i> , 1978
Southern California municipal wastewaters (5 effluents); 1979 Unfiltered samples Filtered "	TLC grav.	Total hydrocar.	60700(27)	5100-397000	Egenhouse & Kaplan, 1982
	GC-MS	Polyaromatic	3650(25)	1200-17600 13-1250	
Gdansk sewage, Poland	GC	Polyaromatics		30800-161640	Grzybowski <i>et al.</i> , 1983
Petroleum refin. indust.	IR analyser	Total oil	37312	11200-53900	Ibievele, 1986
Louisiana oil refinery Influent water Effluent water	"	Polyaromatics	607	441-837	Stubblefield & Maki, 1986
		Polyaromatics	<10		
Eastern Adriatic town wastewaters	IR analysis UV floures.	Total oil Chrysene	1100(113) 352(27)	10-8600 3-3310	Anon., 1987

<sup>a</sup> Values were presented as mass fraction ( $w_{\text{dw}} \cdot 10^9$ ) of dry weight of sewage sludge  
Number in brackets represent the number of samples

hydrocarbons can be provided. Moreover, the concentration of the polyaromatic fraction in the determined total hydrocarbons can be estimated. The results have shown that the polyaromatic fraction in industrial wastewaters (expressed as chrysene equivalents) can account for about 13% of the total hydrocarbons. In urban wastewaters the polyaromatic fraction was around 16% of total hydrocarbons. In a Šibenik sewer the concentration and percentage of the polyaromatic fraction was higher than in industrial and urban wastewaters of the Rijeka area (Anon., 1987).

The geometric means of the petroleum hydrocarbon concentrations in the Rijeka and Split effluents did not differ significantly (Table 3.3.1.2). This was also confirmed by one way ANOVA of the data in dependence on the investigated area and effluent type (Table 3.3.1.3). Marked fluctuations were observed between the year means (natural logarithms) during the investigated period (1984-1990), but without any defined trend (Fig 3.3.4.1). In fact, statistically significant differences were evidenced for all and Rijeka data in relation to sampling period, but not to season (Table 3.3.1.3). The means (natural logarithms) for the low and high seasons were not significantly different in most of the investigated areas, except the Šibenik area (Fig. 3.3.4.2).

#### 3.3.4.2. Petroleum hydrocarbons in coastal and estuarine water

Oil slicks and other floating pollutants were monitored in the period 1985-90 in the Rijeka Bay (Table 3.3.4.2). Oil slicks or other floating material were recorded in 26% of about thousand observations. In 13% of the cases when pollution occurred, floating material had a continuous cover. In the most of the cases of pollution (59%) the sea surface coverage was minimal (1/8). In 6.4% of the cases a maximum coverage was observed (8/8).

The concentrations of petroleum hydrocarbons in seawater from the eastern Adriatic coastal areas were similar to those measured in other Mediterranean areas (Tables 3.3.4.3-4). The values obtained in the open Adriatic waters were even significantly lower than in coastal areas. Petroleum hydrocarbon pollution of the Mediterranean waters had already been documented in the 1970s: the concentration of aromatic hydrocarbons (expressed as phenanthrene equivalents) at the depth of 1 m was five times higher than in the north-west Atlantic, but accounted for only 60% of the average concentrations for the Baltic Sea (see Gabrielides *et al.*, 1984 for review).

The concentrations of petroleum hydrocarbons in the seawater of the Šibenik and Split areas (means of natural logarithms and their standard errors) were similar and did not change significantly during most of the investigation period (1983-1990; Fig. 3.3.4.3). Statistically significant differences were evidenced by one way ANOVA between the investigated areas (Table 3.3.4.5). Unexpected high values were measured in the Šibenik area in 1983 only (Fig. 3.3.4.3). Probably for this reason significant differences in relation to sampling period was obtained for all and Šibenik data, but not for the data from the other investigated areas (Table 3.3.4.5). Moreover, no significant variability occurred in dependence on sampling season.

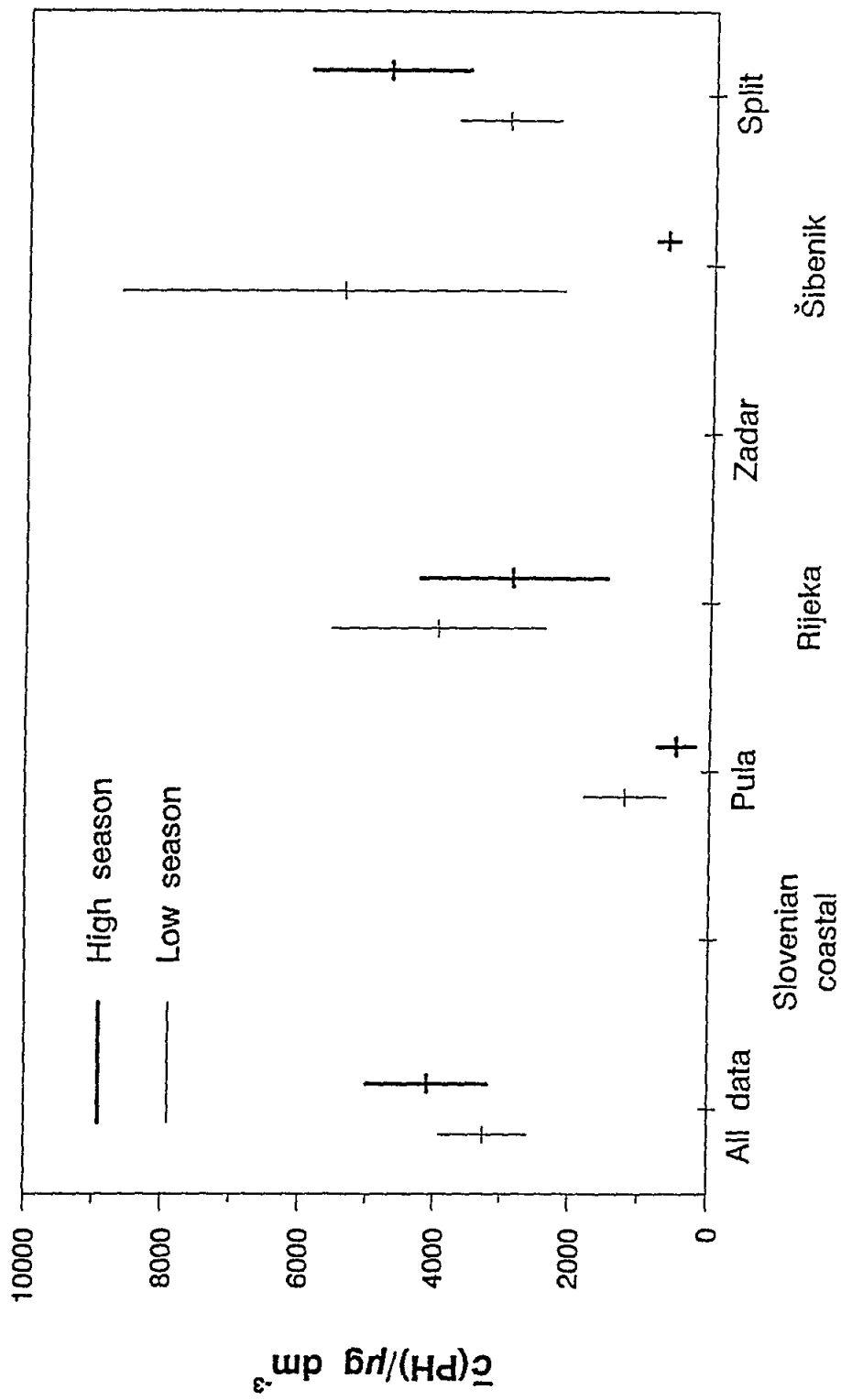


Fig. 3.3.4.2. Means and their standard errors of petroleum hydrocarbons (PH) concentrations ( $\bar{c}$ ) in wastewaters during low and high season period of year for different investigated areas.



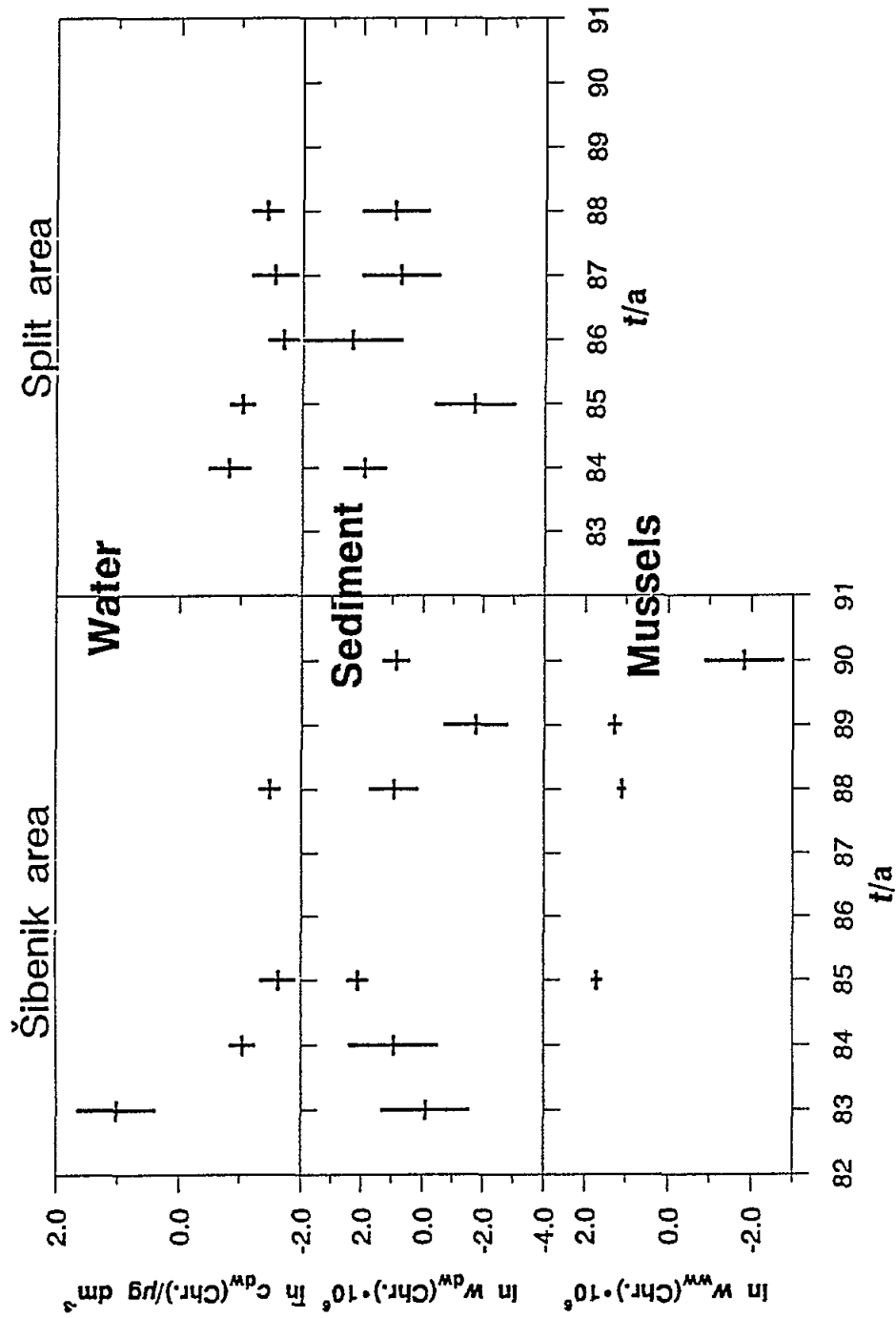


Fig. 3.3.4.3. Natural logarithm of means and their standard errors of petroleum hydrocarbons (Chrysene equivalents - Chr.) concentrations (c) in sea water and mass fractions (w) in sediment and mussels from Šibenik and Split areas in the period (t) 1983-1990.

**Table 3.3.4.2.** Oil slicks and other floating pollutants in the Rijeka area 1985-1990.

A) Status of observation	0	1				
Number of observations	719	259				
Frequency (%)	74	26				
B) Types of pollutants	1	4	1/4			
Frequency (%)	21	37	42			
C) Type of coverage	1	2	3	4		
Frequency (%)	12.7	76.3	5	6		
D) Coverage	1	2	3	4	6	8
Frequency (%)	59	15.2	8.7	7.2	3.5	6.4

Explanation of codes:

- (A) 0 = Sea surface observed but no pollutants to report  
1 = 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) Values reported in eighths (e.g., 1=1/8)

**Table 3.3.4.3.** Polyaromatic hydrocarbon concentration (c) in seawater from the Mediterranean Sea.

Area <sup>a</sup>	Location	Year	Method of analysis	Compound(s) or oil	c/μg dm <sup>-3</sup>		References
					Average	Range	
I II II Garrigues <i>et al.</i> , 1990 III IV VI VII VIII <i>et al.</i> , 1984 IX	Coastal and open waters	1976	UV-Fluores.	Kuwait crude oil equival.	7.9(23)	4.3-14.6	Faraco & Ros, 1978
	Coastal and open waters	1975-77	UV-Fluores.	Kuwait crude oil equival.	4.3(26)	1.8-18.2	Faraco & Ros, 1978
	Coastal and open waters	1987	HPLC-UV Fluores.	Total of 12 PAHs unsubstituted	4.3(?)	-	
	Coastal and open waters	1975-77	UV-Fluores.	Kuwait crude oil equival.	17(31)	1.0-123.5	Faraco & Ros, 1978
	Coastal and open waters	1975-77	UV-Fluores.	Kuwait crude oil equival.	9.3(41)	1.9-20.5	Faraco & Ros, 1978
	Coastal and open waters	1977-82	UV-Fluores.	Chrysene equiv.	5.1(90)	1.1-38.2	Mimicos, 1980
	Coastal and open waters	1980	UV-Fluores.	No data	3.7(60)	0.2-20	Gerges & Durgham, 1983
	Coastal Open waters	1980-82 1980-81	UV-Fluores. "	Chrysene equiv. Kuwait crude oil equival.	1.9(28) 4.4(23)	0.5-11.5 1.6-13.7	Scoullou <i>et al.</i> , 1982 G a b r i e l i d e s
	Coast.waters <i>al.</i> , 1982 Open waters	1980-82 "	UV-Fluores. "	Chrysene equiv. "	1.5	0.5-3.5 2.0-6.0	S u n a y e t

**Table 3.3.4.3.** - continued

Area <sup>a</sup>	Location	Year	Method of analysis	Compound(s) or oil	c/μg dm <sup>-3</sup>		References
					Average	Range	
IX	Coast. waters	1983	UV-Fluores.	Chrysene equiv.	1.5(9)	0.1-5.6	Saydam <i>et al.</i> , 1984
	Open waters	1983	"	"	1.9(6)	0.8-3.8	
X	Coast. waters	1979-80	UV-Fluores.	Chrysene equiv.	6.4(23)	0.7-41.4	Wahby & El Deeb, 1980
	Coast. waters	1981-82	"	"	3.0(39)	0.5-13.0	
	Coast. waters	1978-79	"	Iranian crude oil equiv.	7.4(138)	1.1-35.2	Aboul Dahab & Halim, 1980a
	1 m deep	"	"	"	5.5(12)	0.6-9.1	
	9.3 m deep	"	"	"	3.7(12)	2.2-4.5	Aboul Dahab & Halim, 1980b
	18.6 m deep	"	"	"	3.7(32)	0.7-35.2	
A D R I A T I C	Open waters	1983-84	UV-Fluores.	Chrysene equiv.	0.2(38)	-	Serrazanetti & Viviani, 1989
	Open waters	"	"	Kuwait crude oil equiv.	0.9(38)	-	
	Open waters	1984-85	"	Chrysene equiv.	0.7(25)	0.1-2.0	Picer M. <i>et al.</i> , 1985
	Open waters	"	"	Kuwait crude oil equiv.	2.9(25)	0.5-7.0	
	Open waters	1983-86	UV-Fluores.	Chrysene equiv.	0.1(17)	ND-0.5	Anon., 1987
	Coastal and estuarine	"	"	"	0.8(83)	ND-25.0	
	Open waters	"	"	Kuwait oil	0.8(14)	ND-3	Anon., 1987
	Coastal	"	"	"	5.2(62)	ND-510	

ND - Not Detected (under sensitivity limit); Number of samples in brackets.

<sup>a</sup> - See Fig. 3.3.1.1.

**Table 3.3.4.4.** Basic statistical data of petroleum hydrocarbon concentration (c) in sea water samples and their mass fraction (w) in sediment (dry weight), mussels and some benthic organisms (fresh weight).

Matrix	Investigation area	Number of samples	Average	Median	Geom. mean	
Petr.hydr.equiv.						
Sea water						
c(Chr.)/μg dm <sup>-3</sup>	Adriat.coast	228	1.1	0.3	0.3	
	Šibenik area	79	2.1	0.4	0.4	
	Split area	72	0.5	0.2	0.3	
	Mont. coast	64	0.8	0.5	0.5	
c(Kuw.oil)/μg dm <sup>-3</sup>	North. Adriat.	153	2	1	1	
Sediment						
w <sub>dw</sub> (Chr.)·10 <sup>6</sup>	Adriat.coast	55	11.6	2.9	3.5	
	Šibenik area	30	6.3	3.5	2.2	
	Split area	20	21.9	2.1	2.4	
	Mont. coast	5	1.7	1.9	0.5	
w <sub>dw</sub> (Kuw.oil)·10 <sup>6</sup>	North. Adriat.	81	3.9	2.4	2.5	
	Central Adriatic	12	5.7	4.0	4.4	
Mussels						
w <sub>w</sub> (Kuw.oil)·10 <sup>6</sup>	Adriat. coast	29	29.7	22.2	14.2	
	Šibenik area	23	25.8	22.2	14.6	
	Mont. coast	6	44.7	35.4	12.8	
Benthic organisms						
w <sub>w</sub> (Kuw.oil)·10 <sup>6</sup>						
	Asteroidea	North Adriatic	21	6.5	3.5	3.5
	Holothuria	"	22	12.9	7.9	7.4
	Bivalvia	"	17	9.1	4.7	5.8

Chr. - Chrysene; Kuw. oil - Kuwait oil

**Table 3.3.4.5.** One way ANOVA of petroleum hydrocarbon concentrations (*c*) in water and mass fractions (*w*) in sediment and mussels samples depending upon sampling area, period, and season.

Matrix Area	Response variable	Number of samples	Significance level for mean difference		
			Area	Period	Season
<b>Water</b>					
All data	c(Chr.)/μg dm <sup>-3</sup>	227	0.0010	0.0001	0.1664
Šibenik		79		0.0085	0.4204
Kornati		12		0.5828	0.5339
Split		72		0.1280	0.5673
Mont. coast.		64		0.7916	0.6004
<b>Sediment</b>					
All data	w <sub>d</sub> w(Chr.)·10 <sup>6</sup>	50	0.4120	0.1536	0.0969
Šibenik		30		0.0122	0.0073
Split		20		0.2037	
<b>Mussels</b>					
All data <sup>a</sup>	w <sub>w</sub> (Kuw.oil)·10 <sup>6</sup>	29	0.8112	0.0095	0.8594
Šibenik		23		0.0001	0.8752

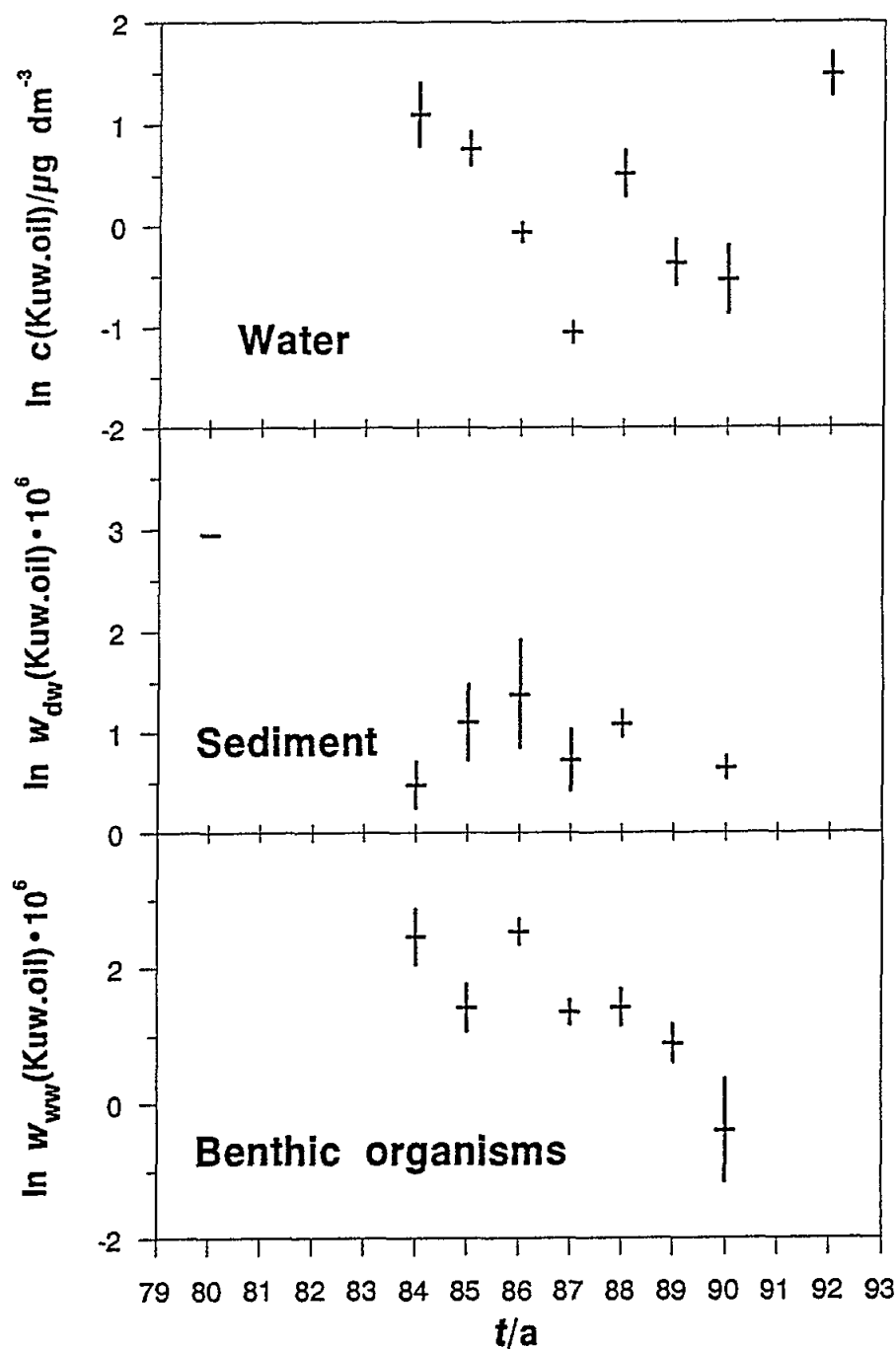
Chr. - Chrysene; Kuw. oil - Kuwait oil

<sup>a</sup> included Montenegrin coastal area data

Also, in the open northern Adriatic waters the petroleum hydrocarbon concentration (Kuwait oil equivalents) did not change significantly in the period 1979-1990 (Fig. 3.3.4.4), although a significant variability of data in dependence on sampling period was evidenced (Table 3.3.4.6). Statistically significant concentration differences occurred between the western, central and eastern northern Adriatic areas (Fig. 3.3.4.5), which agreed with the significant variability observed in dependence on the sampling area (Table 3.3.4.6). The lowest values were measured in the central area.

### 3.3.4.3. Petroleum hydrocarbons in sediments

The sources of polyaromatic hydrocarbons (PAH) in coastal sediments are mainly anthropogenic. These compounds originate from combustion processes (industry, cars), and enter the marine environment with rain flushing of urban areas, as well as with wastewater and polluted river discharges. Significant gradients can be established off the pollution source. As an example, some industrialized and urbanized area of the French Mediterranean coast (near Toulon or Monaco) were highly contaminated (total PAH mass fraction about  $10 \cdot 10^{-6}$ ; Garrigues *et al.*, 1990). In others areas (eg Cannes) a moderate PAH pollution occurred (about  $0.5 \cdot 10^{-6}$ ), compared with other clean French coastal areas (eg the southwestern Atlantic coast).



**Fig 3.3.4.4.** Natural logarithm of means and their standard errors of petroleum hydrocarbons (Kuwait oil equivalents - Kuw. oil) concentrations in sea water and mass fractions ( $w$ ) in sediment and benthic organisms from the northern Adriatic in the period ( $t$ ) 1984-1992.

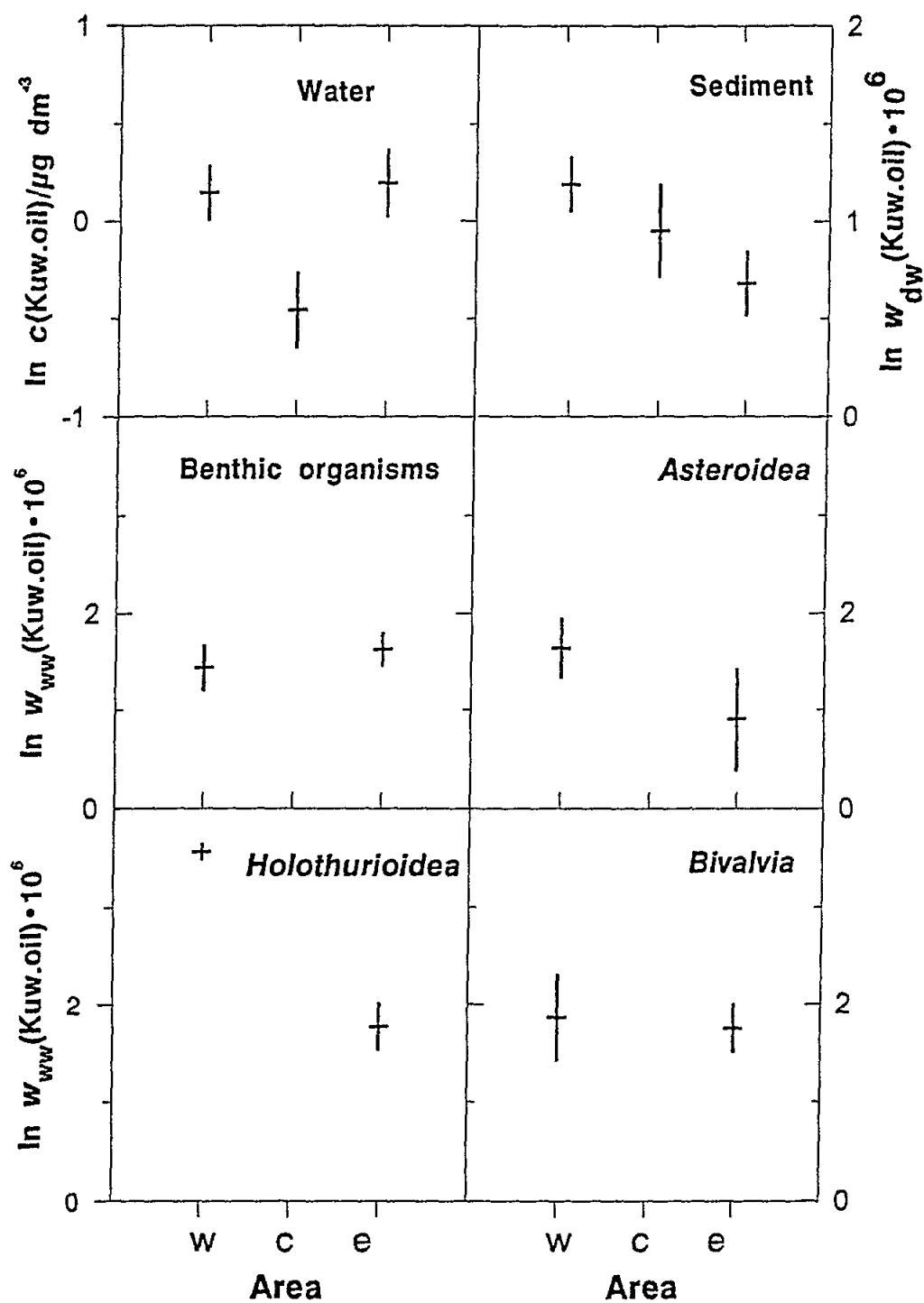


Fig. 3.3.4.5. Natural logarithm of means and their standard errors of petroleum hydrocarbons (Kuwait oil equivalents - Kuw. oil) concentrations ( $c$ ) in sea water and mass fractions ( $w$ ) in sediment and benthic organisms from the northern Adriatic for three areas (west-w, central-c and east-e).



**Table 3.3.4.6.** One way ANOVA of petroleum hydrocarbon concentration (c) in water and mass fraction (w) in sediment and organisms from the northern Adriatic open waters depending upon sampling area and period.

Matrix	Response variable	Number of samples	Significance level for mean difference	
			Area	Period
<b>Water</b>	c(Kuw.oil)/ $\mu\text{g dm}^{-3}$	153	0.0000	0.0482
<b>Sediment</b>	$w_{\text{dw}}(\text{Kuw.oil}) \cdot 10^6$	81	0.0003	0.0352
<b>Organisms</b>				
All organs	$w_{\text{w}}(\text{Kuw.oil}) \cdot 10^6$	96	0.0000	0.6204
Astroidea		16	0.0014	0.2446
Holothuria		17	0.0001	0.0202
Bivalvia		13	0.0016	0.8439

Petroleum (polyaromatic) hydrocarbons were analysed in the Adriatic sediments with UV spectrofluorometry. The mass fractions (chrysene equivalents) in these sediments were in similar ranges or even higher than in other Mediterranean areas (Tables 3.3.4.4. and 3.3.4.7). In contrast, mass fractions of benzo(a)pyrene in the Adriatic were significantly lower compared with the northwestern Mediterranean (zone II, Fig. 3.3.1.1).

The mass fractions of polyaromatic hydrocarbons in sediments of Šibenik and Split areas (natural logarithm of means and their standard errors) varied significantly in the period 1983-1990, but without defined trends (Fig. 3.3.4.3). The geometric mean mass fractions for these two areas were very close, but they were higher than the value for the Montenegrin coastal area (Table 3.3.4.4). One way ANOVA has shown that no statistically significant difference occurred between the polyaromatic hydrocarbon content of the Šibenik and Split sediments (Table 3.3.4.5). Significant variability was obtained in dependence on sampling period and season for the Šibenik data only.

Petroleum hydrocarbons mass fractions in open northern Adriatic sediments samples varied significantly in the period 1984-1990, but defined trends were not evidenced (Fig. 3.3.4.4). One way ANOVA has shown a statistically significant variability of the mass fraction data in relation to the sampling period (Table 3.3.4.6). The significance was even higher for the sampling area. In fact, a significant difference of the petroleum hydrocarbons mass fractions occurred between the western, central and eastern parts of the northern Adriatic (Fig. 3.3.4.5). The values increased gradually from east to west. A similar distribution was also observed for data obtained in the northern and central Adriatic (Fig. 3.3.4.6).

Statistically significant correlations were observed between petroleum hydrocarbon and chlorinated hydrocarbon mass fractions and between petroleum hydrocarbons and some characteristics (organic content, specific surface area, various textural fractions) of sediments from the open northern and central Adriatic (Table 3.3.1.10; Figs. 3.3.4.7-8).

#### 3.3.4.4. Petroleum hydrocarbons in organisms

Many organic pollutants occur in marine waters at concentrations of  $\text{ng dm}^{-3}$  or lower. Sufficiently sensitive methods for a direct determination of such a low concentration have been developed, but they require too much time and material expenses to be suitable for routine monitoring work. In contrast, many field studies, laboratory experiments and monitoring results have shown that analyses of mussels and some other bivalves can provide valuable information on the sources and distribution of petroleum hydrocarbons in coastal environment, particularly the most toxic polyaromatic hydrocarbons (PAH). From mussel contents it is possible to estimate roughly the concentrations in the surrounding water. However, it should be considered that organisms can partially metabolize PAH. Thus, for a more reliable control of organisms that are used for food some PAH metabolites should also be monitored (Farrington *et al.*, 1988).

Uptake and release of petroleum hydrocarbons by mussels are relatively fast processes (in order of days). Thus, repeated measures on samples from a local population is useful to assess if contamination in an area originated from an accident or chronic pollution. To reduce the data variability, it is useful to recalculate the hydrocarbon content on a lipid weight basis and collect mussels of similar size and physiological state. Generally, hydrocarbon content in mussels varies more significantly in areas in which pollutant discharge is not continuous (Fossato *et al.*, 1979; Burns and Smith, 1981).

Petroleum hydrocarbons in mussels, collected in the framework of this programme (in the Šibenik and Montenegrin areas) and other studies in the Adriatic, were analysed with UV spectrofluorometry. These values were higher than in other Mediterranean areas, in which the same method was used (Tables 3.3.4.4. and 3.3.4.8). In contrast, the mass fractions of some polyaromatic compounds (benzo(a)pyrene-BaP, perylene-Pe) in the Adriatic were significantly lower than in other world regions. While the accumulation and release dynamics of petroleum hydrocarbons by bivalve molluscs have been extensively studied, only a few experiments were performed using BaP or other polyaromatic compounds. Mussel BaP and Pe contents can change markedly during the year. The concentration range of BaP and Pe in mussels from the Venice Lagoon did not differ significantly compared with similar environments around the world and probably these compounds do not represent a serious risk in mussels human consumption (Fossato *et al.*, 1979).

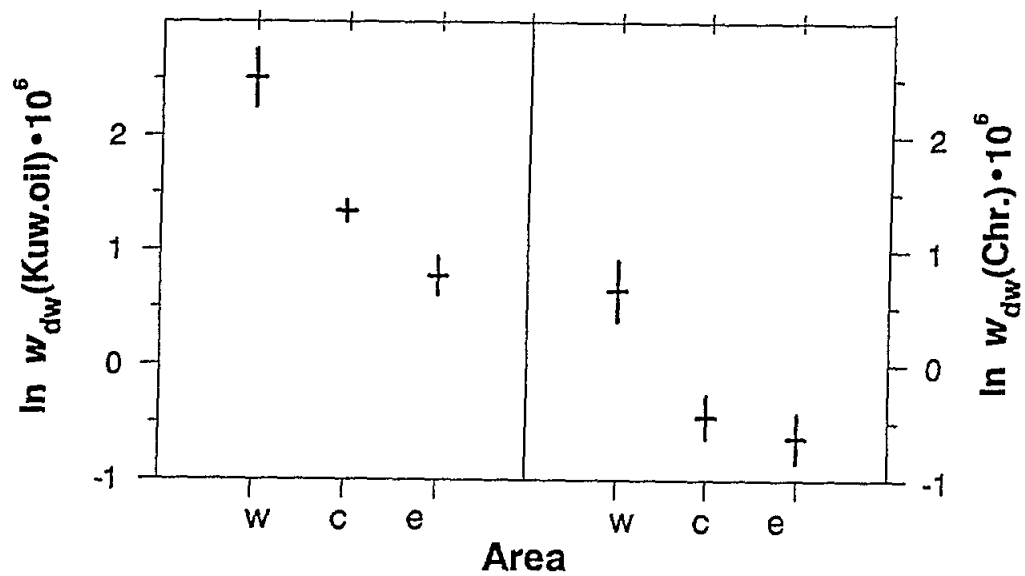


Fig. 3.3.4.6. Natural logarithm of means and their standard errors of petroleum hydrocarbons (Kuwait oil-Kuw.oil and Chrysene-Chr. equivalents) mass fraction ( $w$ ) in sediment from northern and central Adriatic for three areas (west-w, central-c and east-e).

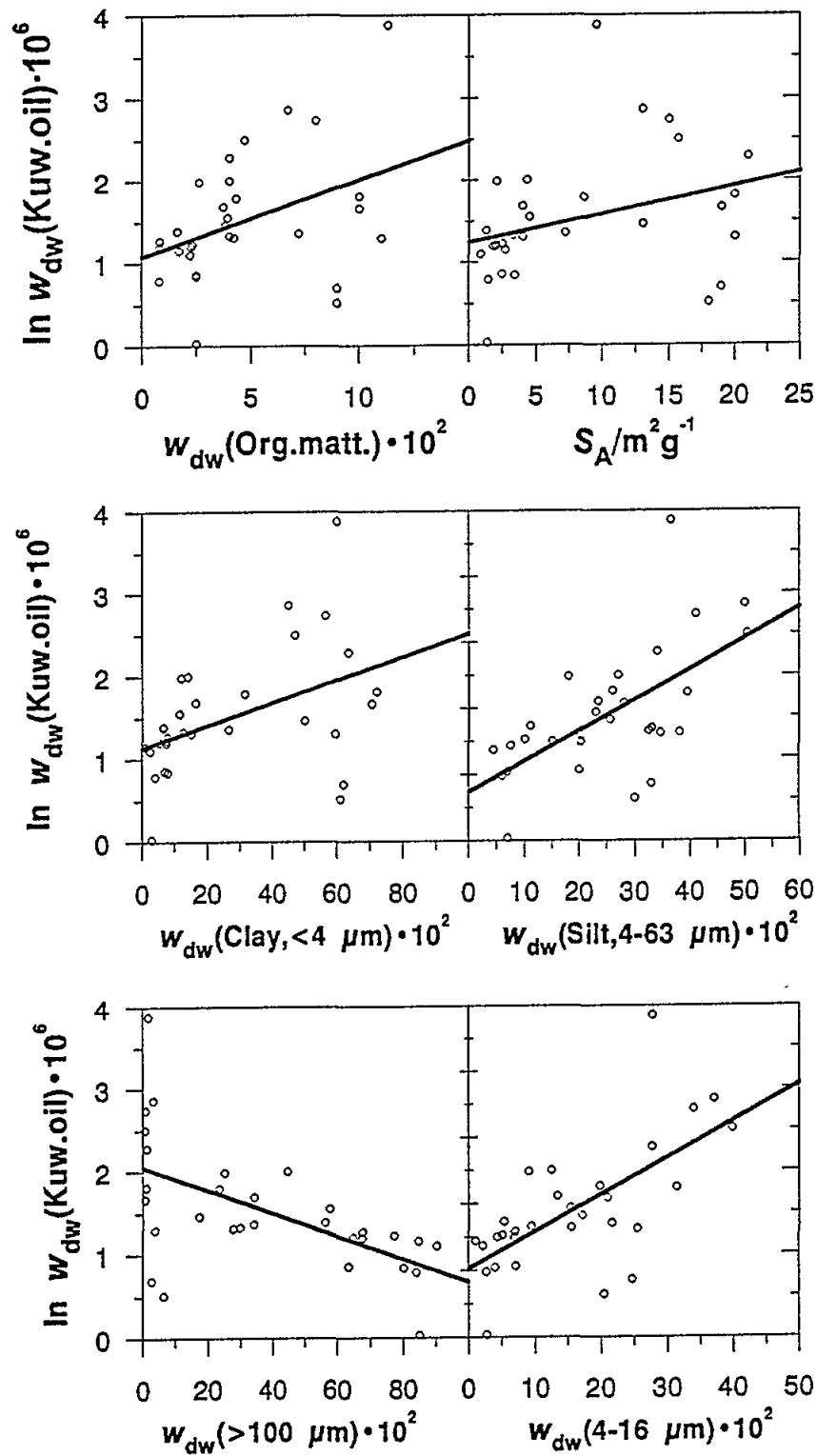


Fig. 3.3.4.7. Linear regression analysis of natural logarithmic values of the petroleum hydrocarbons (Kuwait oil-Kuw. oil equivalents) mass fractions ( $w$ ) in sediment and sediment characteristics (organic matter and different sediment fraction mass fractions, and specific active surface) for northern and central Adriatic.

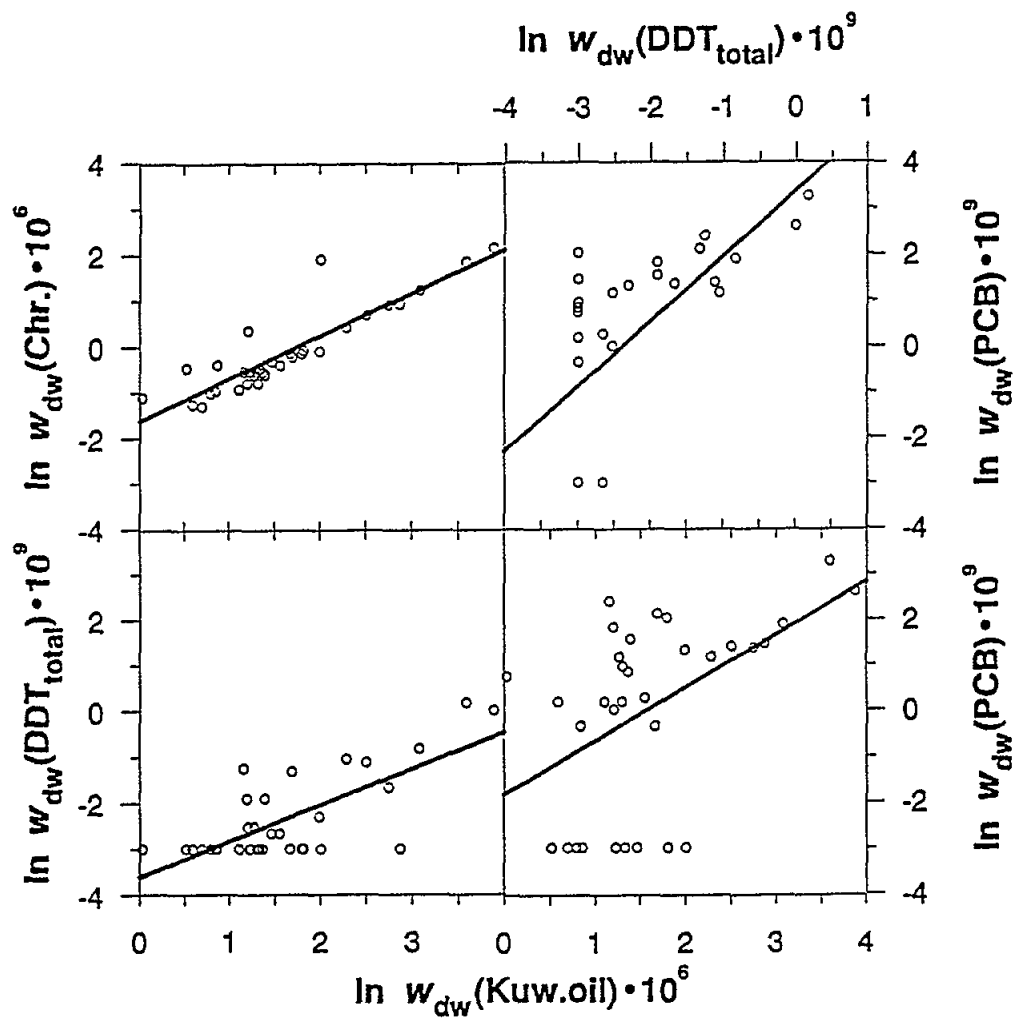


Fig. 3.3.4.8. Linear regression analysis of natural logarithmic values of the pollutants ( $\text{DDT}_{total}$ , PCB, Kuwait oil and chrysene equivalents) mass fractions in sediment from the northern and central Adriatic.

**Table 3.3.4.7.** Mass fraction (*w*) of polyaromatic hydrocarbons in sediment (dry weight) from the Mediterranean Sea.

Area <sup>a</sup>	Water Depth (m)	Year	Method or Analysis	Compound(s) or oil	$w_{dw}(PH) \cdot 10^9$		References
					Average	Range	
II	10-1000 "	1980 "	GC "	Polyaromatics Benzo(a)pyrene	10400(20) 10(20)	500-40000 ND-64	Albaiges <i>et al.</i> , 1982
II	10-225 "	1983 "	GC-MS "	Polyaromatics Benzo(a)pyrene	851(18) 60(18)	195-2685 7-168	Grimalt <i>et al.</i> , 1984
II	250 "	1981 "	GC-MS "	Tot. Polyaromat. Chrysene	726(4) 95(4)	599-847 63-121	Burns & Villeneuve, 1983
II	Coastal waters	?	UV-Floures.	Tot. Polyaromat.	60600(12)	3700-402000	Mille <i>et al.</i> , 1982
II & III	Coastal and open waters "	?	GC-MS	Chrysene	5.2(17)	ND-14	Arnoux <i>et al.</i> , 1982
			"	Benzo(a)pyrene	3.2(17)	ND-9	
II	Coastal waters	1987	HPLC-UV- Floures.	Total of 12 PAHs unsubstituted	1165(?)		Garrigues <i>et al.</i> , 1990
VIII	15-28	1980	UV-Floures.	Chrysene equiv.	9300(9) <sup>b</sup>	ND-23600	Scoullos <i>et al.</i> , 1982
IX	30-90	1980-82	UV-Floures. & GC-MS	Chrysene equiv.	240(16)	40-680	Sunay <i>et al.</i> , 1982
X	19	1981-82	UV-Floures.	Chrysene equiv.	980(8)	100-3000	El Samra <i>et al.</i> , 1982

**Table 3.3.4.7.** - continued

Area <sup>a</sup>	Water Depth (m)	Year	Method or Analysis	Compound(s) or oil	$w_{dw}(PH) \cdot 10^9$		References
					Average	Range	
The Adria- tic Sea	38-69	1967-68	UV-Floures.	Benzo(a)pyrene	25.9(15)	3.3-55.1	Olmo & Molinas, 1969
	12-351	1965-66	UV-Floures.	Benzo(a)pyrene	22.1(5)	11.4-35.0	Piccinetti, 1968
	40-50	1984-85	UV-Floures.	Chrysene equiv.	800(17)	150-3040	Picer M. <i>et al.</i> , 1985 Picer M. <i>et al.</i> , 1986b
	40-50	1984-85	UV-Floures.	Kuwait crude oil	3900(17)	740-18020	Picer M. <i>et al.</i> , 1986b
	Various	1984-86	UV-Floures.	Chrysene Kuwait oil	19,600(24) 476,000(16)	ND-193,700 ND- 2,270,000	Anon., 1987

ND - Non detected (under sensitivity limit); Number in brackets represent the number of samples

<sup>a</sup> - See Fig. 3.3.1.1.

<sup>b</sup> - Values were presented as mass fraction ( $w_{fw} \cdot 10^9$ ) of sediment fresh weight

**Table 3.3.4.8.** Mass fraction (w) of polyaromatic hydrocarbons in bivalves (fresh weight).

Location and Year	Organisms	Method of Analysis	Compound(s)	$w_w(\text{PH}) \cdot 10^6$		References
				Average	Range	
Vancouver harbour, Canada, 1975	<i>M. edulis</i>	UV-Floures.	Benzo(a)pyrene	0.045(6)	0.005 (S.E.M)	Dunn & Stih, 1976
Southern Calif. Bight, USA, 1974-75	<i>M. edulis</i>	UV-Floures.	Benzo(a)pyrene	0.003(4)	0.0004-0.008	Dunn & Young, 1976
	<i>M. californ.</i>	"	"	0.0004(22)	<0.0001-0.0023	
Coast of Norway 1978/79	<i>Modiolus mod.</i>	Gas chrom.	Total poliarom.	<0.100	100-2.650	Knutzen & Sortland, 1982
	<i>M. edulis</i>	"	"	0.660(9)		
Northern Baltic 1982	<i>M. edulis</i>	UV-Floures.	Total poliarom.	0.006(19)	0.003-0.012	Broman & Ganning, 1985
	<i>Macoma balt.</i>	"	"	0.021(5)	0.018-0.028	
Mediterranean Sea	1965-66	<i>Ostrea edulis</i>	UV-Floures.	0.004(4)	0.001-0.033	Piccinetti, 1968
		<i>Chlamys varia</i>	"	0.002(3)	0.002-0.016	
	1965-66	<i>Ostrea edulis</i>	UV-Floures.	0.003		Scaccini & Scaccini-Cicatelli, 1969
	1975-76	<i>M. galloprov.</i>	UV-Floures.	0.006	0.001(S.D.)	
		"	"	0.001	0.0001(S.D.)	Fossato <i>et al.</i> , 1979
		"	Perylene			
	1985	<i>M. galloprov.</i>	Gas chrom.	0.110(57)		Iosifidou <i>et al.</i> , 1982
		"	Total poliarom.			
		"	Chrysene equiv.	0.900(5)	0.210-1.690	Anon., 1987
		"	Kuw. oil equiv.	8.880(5)	1.700-19.500	
1988	<i>M. edulis</i>	HPLC	Total poliarom.	0.295		Amodio-Cocchieri <i>et al.</i> , 1990
	<i>Cardium edule</i>	"	"	0.198		
	<i>Ensis siliqua</i>	"	"	0.199		

Number in brackets represent the number of samples; S.D. - Standard deviation; S.E.M. = Standard error of mean



In 1990 the polyaromatic hydrocarbon (PAH) mass fraction in mussels from the Šibenik area was lower than in the preceding period (1985-1989; Fig. 3.3.4.3). However, more measurements should be carried out to confirm a possible trend. Results of one way ANOVA has shown a significant variability of PAH mass fraction in dependence on sampling period, but not on season (Table 3.3.4.5). No significant variability was noticed in relation to sampling area (Šibenik and Montenegrin coastal areas).

The petroleum hydrocarbons mass fractions of various benthic organisms samples (*Asteroidea*, *Holothurioidea* and *Bivalvia* species) from the open northern Adriatic did not change significantly in the period 1984-1989, but a lower value was calculated for 1990 (Fig. 3.3.4.4). A statistically significant variability in dependence on the sampling period were obtained for the petroleum hydrocarbon content in *Holothurioidea* only (Table 3.3.4.6). However, significant differences were noticed in all organism groups in dependence on the sampling area. Comparing the means of natural logarithms and their standard errors for the western and eastern parts of the open northern Adriatic, significant differences were observed again for *Holothurioidea* only (Fig. 3.3.4.5).

### 3.4. Faecal coliforms

Over six million residents live along the Adriatic coast, of which about 1.3 million occupy the coastal area of the former Yugoslavia. During summer, the afflux of tourists can significantly raise this number. Thus, in the touristic centres the total population can increase several times with respect to the winter. Most of the urban effluents are still inadequately discharged into the sea, also near recreational areas, in which sometimes high faecal coliform levels can be detected.

#### 3.4.1. Faecal coliforms in effluents and discharge areas

A significant part of the urban, agricultural and industrial wastewaters from the Slovenian coastal area is disposed in the Rižana Stream, which discharges into Koper Bay (Lenarčič 1981, Turk *et al.*, 1983). In this stream (mean yearly discharge rate of  $150 \times 10^3 \text{ m}^3 \text{ a}^{-1}$ ) high faecal coliform concentrations were measured (up to  $10^5 \text{ dm}^{-3}$ ). However, the Rižana Stream represents a significant faecal pollution source for a restricted estuary area only (stations 13 and 14; Fig. 2.3.3; Table 3.4.2.1).

**Table 3.4.2.1.** Distribution of faecal coliforms concentration (C) and evaluation of sanitary quality according to WHO/UNEP interim criteria (1983c) in the Slovenian coastal area from 1983-1991.

Station	Number of samples		Samples (%) exceeding the limits of C(FC)/dm <sup>-3</sup>				Sanitary* quality during bathing season
			1000		10000		
	Total	Bathing season	Total	Bathing season	Total	Bathing season	
Zone I	570	268	27.0	14.6	1.2	0.0	S
Zone II	374	175	14.2	5.1	1.1	0.0	S
Zone III	967	449	9.3	4.2	0.3	0.0	S
Zone IV	741	337	32.8	22.8	4.7	1.5	S
13-14	190	84	99.5	98.8	87.4	79.8	NS
34-36	253	117	1.6	1.7	0.0	0.0	S
K	83	37	14.5	8.1	0.0	0.0	S
MA	97	45	1.0	2.2	0.0	0.0	S

\* S - satisfactory; NS - not satisfactory

Zone I - stations 1-5, 17

Zone II - stations 21-24

Zone III - stations 25-33, 37

Zone IV - stations 8, 10-12, 15-16, 18, 20

Raw wastewaters from the town centre, including those from a fish processing plant and a tobacco factory, are still discharged into the Rovinj harbours, significantly affecting the hygienic quality of neighbouring beaches. In some industrial effluent samples the faecal coliform concentration varied from  $200 \times 10^6$  -  $300 \times 10^6$   $\text{dm}^{-3}$ .

About  $20 \times 10^3$   $\text{m}^3$   $\text{a}^{-1}$  of urban and industrial wastewaters are discharged yearly into the Pula harbour from 14 outfalls of various dimensions. Faecal coliform concentrations up to  $340 \times 10^{18}$   $\text{dm}^{-3}$  were measured in these wastewaters.

In the monitored effluents from the Rijeka area the faecal coliform concentration changed in the range from  $30 \times 10^3$  -  $11 \times 10^{12}$   $\text{dm}^{-3}$ . These effluents influenced the sanitary quality of some recreational areas.

The area close to the Zadar town centre is still affected by industrial and urban wastewaters, in which faecal coliform concentrations ranged from 0 -  $140 \times 10^6$   $\text{dm}^{-3}$ . The absence of faecal coliforms in some industrial effluents might be due to the inhibitory effects of toxic compounds (eg chromium).

The wastewaters discharged in the Split main harbour and in the eastern part of Kaštela Bay (Vranjic) contained  $270 \times 10^3$  -  $11 \times 10^{21}$   $\text{dm}^{-3}$  faecal coliforms.

#### 3.4.2. Faecal coliforms in sea water

The WHO/UNEP (1983c) interim criteria were used to assess the seawater sanitary quality of beaches and other coastal zones. These criteria fixed the frequency with which the concentrations of faecal coliforms (FC) and faecal streptococci (FS), as main indicators of faecal pollution, should be below the next limits:

$$\begin{aligned} C_{50}(\text{FC}) &= 1000 \text{ dm}^{-3} & C_{90}(\text{FC}) &= 10000 \text{ dm}^{-3} \\ C_{50}(\text{FS}) &= 1000 \text{ dm}^{-3} \\ C_{90}(\text{FS}) &= 10000 \text{ dm}^{-3} \end{aligned}$$

In 1988 the Government of the Republic of Croatia issued new regulations concerning the sanitary quality of bathing and recreational marine areas. The Croatian criteria for FC and FS concentrations were based on CEC recommendations, and are more restrictive than the WHO/UNEP criteria. In addition, a limit for the total coliform (TC) concentration was also prescribed:

$$\begin{aligned} C(\text{TC}) &= 5000 \text{ dm}^{-3} \\ C_{80}(\text{FC}) &= 1000 \text{ dm}^{-3} \\ C_{80}(\text{FS}) &= 1000 \text{ dm}^{-3} \end{aligned}$$

Several sewage treatment and disposal facilities (with long submarine outfalls) are under construction along the eastern Adriatic coast, many of which are already operating, at least partially. Thus, the hygienic quality of some areas was improved, but in others, including some recreational areas, the levels of faecal coliforms bacteria may be still critical.

In general, bacterial pollution is marked at the discharge site of untreated effluent, but decreases significantly with distance. Morphological and oceanographic conditions (steep bottom, vertical and horizontal mixing, due to wind and sea currents), which are favourable for effluent dilution and dispersion, prevail in most of the eastern Adriatic coastal region.

The faecal coliform concentration data, collected since 1983, were summarized for each investigated region, and the sanitary quality of subareas was evaluated using the WHO/UNEP interim criteria.

Along the Slovenian and the bordering northernmost Croatian coast, from Kanegra up to Cape Savudrija (Fig. 2.3.3), seawater samples were collected in all public beaches, mainly during the bathing season. In most of the investigated area the sanitary quality of the beaches was satisfactory (Table 3.4.2.1). As an example, in 85-98% of samples collected during the bathing season the faecal coliform concentration was lower than  $1,000 \text{ dm}^{-3}$ . In contrast, in zone IV, ie in the area under influence of the polluted Rižana Stream, this condition was satisfied only in 67% of the samples. However, for this zone the WHO/UNEP interim criteria were respected. This was not true for the Rižana mouth (stations 13 and 14), where the faecal coliform concentration was higher than  $10,000 \text{ dm}^{-3}$  in most of the samples. Polluted estuary waters are transported in various directions, depending on hydrometeorological and oceanographic conditions (wind, tides, currents), but most often towards the middle of Koper Bay (Turk and Faganeli, 1990). Nevertheless, with increasing distance from the Rižana mouth the bacteria concentration decreases substantially. Thus, the sanitary conditions at station K were found satisfactory.

While the sanitary quality was locally improved after reconstruction of sewage disposal systems, no significant changes of average faecal coliform concentration were observed in the investigated period, considering the Slovenian coastal area as a whole (Fig. 3.4.2.1).

The sanitary quality was satisfactory in the entire Rovinj coastal area, and particularly good on the principal public beaches (Table 3.4.2.2). Remarkably, the WHO/UNEP criteria were also satisfied in the restricted area (stations 6-8), which is under a direct influence of the main Rovinj harbour waters, even if the more restrictive limits were not respected (in up to 33% of samples the faecal coliform concentration was higher than  $1000 \text{ dm}^{-3}$ ).

The situation in the Rovinj area has improved since 1988 (Fig. 3.4.2.1), due to a reduction of the effluent discharge in the town harbours (Fuks *et al.*, 1989; Fuks and Devescovi, 1990). In fact, part of the urban waters were diverted in a new sewerage system, provisionally provided by a 800 m long submarine outfall. When this system is completed, including two 2-3 km long submarine outfalls, the faecal pollution should be eliminated from this area.

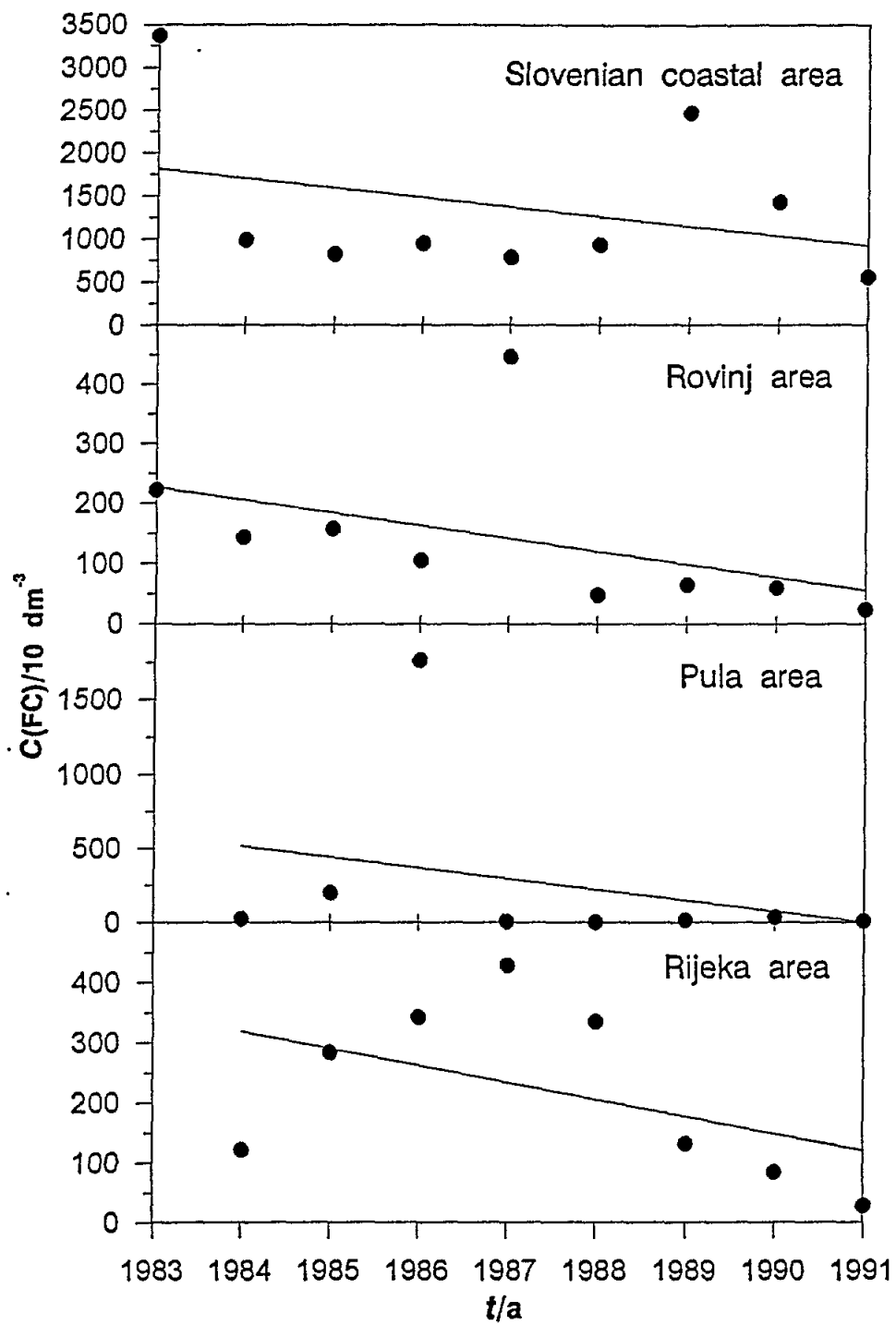


Fig. 3.4.2.1. Average faecal coliform concentration ( $C$ ) for different years ( $t$ ) in seawater samples from different areas in northern Adriatic.

**Table 3.4.2.2.** Distribution of faecal coliforms concentration (C) and evaluation of sanitary quality according to WHO/UNEP interim criteria (1983c) in the Rovinj area from 1983-1991.

Station	Number of samples		Samples (%) exceeding the limits of C(FC)/dm <sup>-3</sup>				Sanitary* quality during bathing season
	Total	Bathing season	1000		10000		
			Total	Bathing season	Total	Bathing season	
03	135	84	11.9	17.9	3	4.8	S
04	135	84	3	3.6	0	0	S
05	135	84	8.9	9.5	0	0	S
06	135	84	28.1	28.6	3.7	4.8	S
07	135	84	24.4	21.4	7.4	7.1	S
08	135	84	36.3	33.3	6.7	7.1	S
09	135	84	0.7	1.2	0	0	S

\* S - satisfactory; NS - not satisfactory

Until 1988 the Pula Town sewages and industrial wastewaters were disposed in the Pula harbour, threatening the ecological equilibrium of the area and causing "red tide" events, with shellfish killing (Maretiæet al., 1978). Afterwards, actions were undertaken to realize a more adequate wastewaters disposal from the Pula urban area and major neighbouring tourist resorts. A part of the urban wastewaters was diverted into the open sea through a 1,254 m long submarine outfall, provided by a mechanical sewage pretreatment plant. Several smaller treatment plants for industrial effluents were also put into operation. Individual tourist resorts were also provided with submarine outfalls. Thus, the sanitary quality of the investigated area as a whole was improved, particularly in the principal public beaches (Fig. 3.4.2.1). In most of the monitored beaches from Peroj to Raša Bay, even the more restrictive sanitary criteria were respected (Table 3.4.2.3). Only in two locations (stations 9 and 11) were the WHO/UNEP limits slightly exceeded.

The sanitary quality of the nearby coastal waters in the Rijeka area as a whole, including the Liburnian Riviera (stations 1-6), the city area (stations 7-12), the northern coast of Krk Island (stations 13-15), and the Vinodolski Kanal (station 16), has been improved since 1987 (Fig. 3.4.2.1).

When the reconstruction of the sewer system along the Liburnian Riviera has been completed, the sanitary quality at stations 3-5 should be further improved. At present at these stations the faecal pollution is near or even above the allowed limits. In contrast, the beaches in the eastern part of the Riviera were not significantly affected by faecal wastewaters (Table 3.4.2.4).

**Table 3.4.2.3.** Distribution of faecal coliforms concentration (C) and evaluation of sanitary quality according to WHO/UNEP interim criteria (1983c) in the Pula area from 1984-1991.

Station	Number of samples		Samples (%) exceeding the limits of C(FC)/dm <sup>-3</sup>				Sanitary* quality during bathing season
	Total	Bathing season	1000		10000		
			Total	Bathing season	Total	Bathing season	
01	87	69	8	8.7	0	0	S
02	87	69	2.3	1.4	0	0	S
03	87	69	5.7	7.2	1.1	1.4	S
04	86	69	1.2	1.4	0	0	S
05	88	70	9.1	11.4	0	0	S
06	87	69	6.9	8.7	1.1	1.4	S
07	86	69	0	0	0	0	S
08	87	69	0	0	0	0	S
09	87	69	18.4	23.2	10.3	13	NS
10	87	69	16.1	20.3	3.4	4.3	S
11	87	69	20.7	26.1	9.2	11.6	NS
12	86	66	0	0	0	0	S
13	86	65	4.7	1.5	0	0	S

\* S - satisfactory; NS - not satisfactory

**Table 3.4.2.4.** Distribution of faecal coliforms concentration (C) and evaluation of sanitary quality according to WHO/UNEP interim criteria (1983c) in the Rijeka area from 1984-1991.

Station	Number of samples		Samples (%) exceeding the limits of C(FC)/dm <sup>-3</sup>				Sanitary* quality during bathing season
	Total	Bathing season	1000		10000		
			Total	Bathing season	Total	Bathing season	
01	87	70	5.7	5.7	0	0	S
02	87	70	4.6	4.3	1.1	1.4	S
03	87	70	50.6	50	19.5	18.6	NS
04	87	70	50.6	50	10.3	10	S
05	87	70	35.6	28.6	5.7	4.3	S
06	87	70	21.8	14.3	0	0	S
07	86	69	17.4	18.8	5.8	5.8	S
08	87	70	29.9	25.7	3.4	4.3	S
09	87	70	36.8	34.3	2.3	1.4	S
10	87	70	5.7	2.9	0	0	S
11	87	70	21.8	21.4	6.9	7.1	S
12	87	70	2.3	2.9	0	0	S
13	85	68	1.2	1.5	0	0	S
14	86	69	1.2	1.4	0	0	S
15	86	69	3.5	1.4	1.2	0	S
16	87	70	2.3	2.9	0	0	S

\* S - satisfactory; NS - not satisfactory



Faecal pollution was significant in the coastal zones bordering with Zadar harbour (stations 4-6, and 7), because of an inadequate disposal of urban and industrial effluents (Table 3.4.2.5). Apparently, the pollution level was increased (Fig. 3.4.2.2), but this should be confirmed by an additional monitoring, because, in the past, measurements were carried out over a five year period only. In contrast, in recreational areas, at higher distances from the town (stations 1-3, 8, 10 and 11), the WHO/UNEP interim criteria were fulfilled.

**Table 3.4.2.5.** Distribution of faecal coliforms concentration (C) and evaluation of sanitary quality according to WHO/UNEP interim criteria (1983c) in the Zadar area from 1988-1991.

Station	Number of samples		Samples (%) exceeding the limits of C(FC)/dm <sup>-3</sup>				Sanitary quality during bathing season
			1000		10000		
	Total	Bathing season	Total	Bathing season	Total	Bathing season	
01	47.0	33.0	8.5	6.1	0.0	0.0	S
02	45.0	33.0	8.9	9.1	0.0	0.0	S
03	46.0	33.0	21.7	18.2	0.0	0.0	S
04	46.0	33.0	71.7	66.7	28.3	30.3	NS
05	46.0	33.0	89.1	93.9	60.9	60.6	NS
06	46.0	33.0	89.1	90.9	71.7	72.7	NS
07	46.0	33.0	58.7	51.5	19.6	18.2	NS
08	46.0	33.0	23.9	6.1	0.0	0.0	S
09	46.0	33.0	50.0	33.3	34.8	21.2	NS
10	46.0	33.0	19.6	9.1	4.3	6.1	S
11	46.0	33.0	17.4	12.1	0.0	0.0	S

\* S - satisfactory; NS - not satisfactory

A part of the sewage from the southeastern Zadar urban area is discharged into the Zadar Channel by a 1,500 m long submarine outfall, off Kolovare. However, water column stratification is not significant at the discharge point, not even in summer. Consequently wastewaters rise to the sea surface, causing faecal contamination at station 9.

In the River Krka estuary and Šibenik urban and neighbouring areas the water sanitary quality was not satisfactory only at station E2, near Skradin (Table 3.4.2.6). At the other stations, including that off the Šibenik harbour, the WHO/UNEP criteria were respected. At most of these stations (except at the Krka River mouth) even the more restrictive criteria have been fulfilled. No significant changes of the mean faecal coliform concentrations were observed during the monitoring period in the area as a whole (Fig. 3.4.2.2).

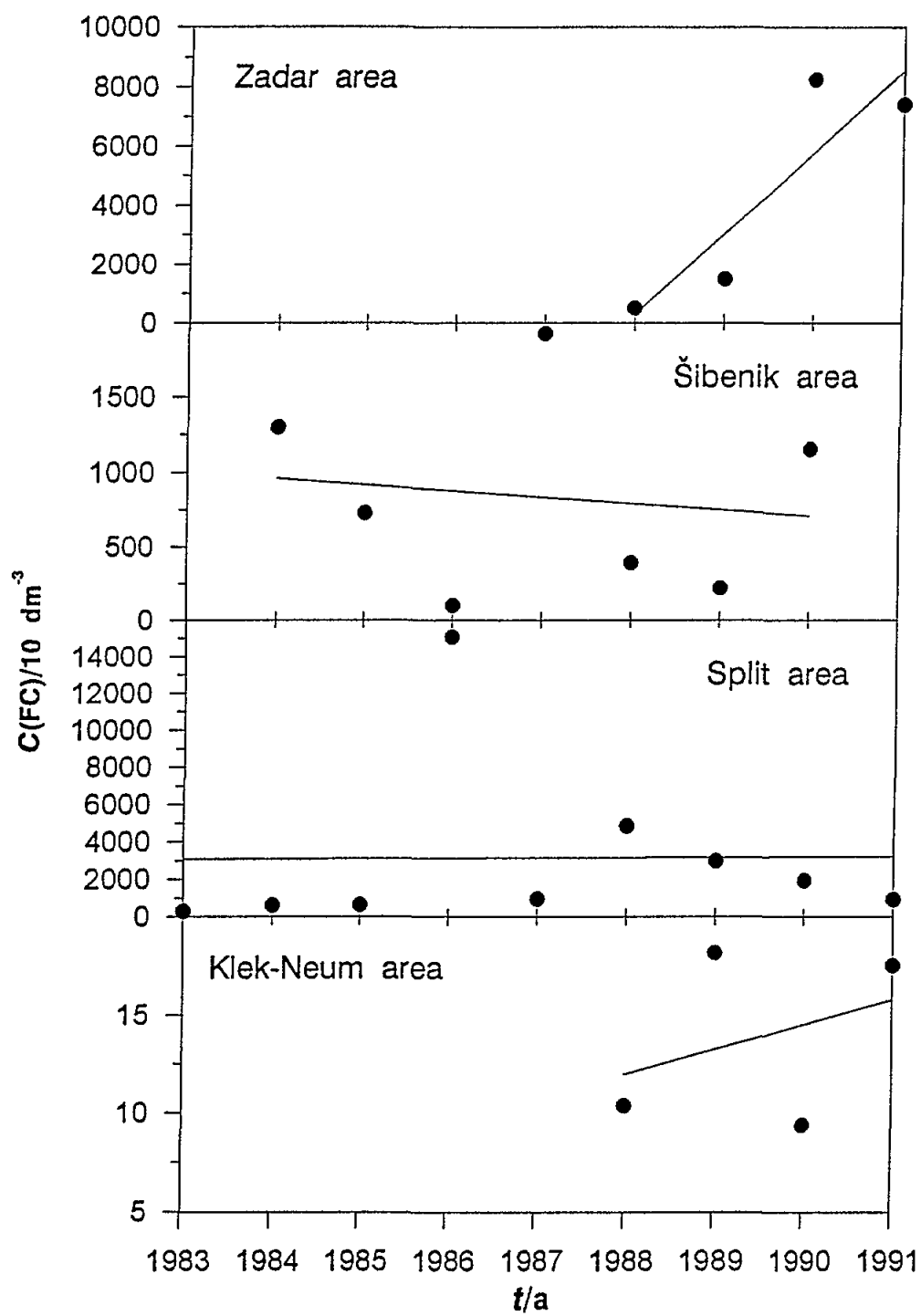


Fig. 3.4.2.2. Average faecal coliform concentration ( $C$ ) for different years ( $t$ ) in seawater samples from different areas in central Adriatic.

**Table 3.4.2.6.** Distribution of faecal coliforms concentration (C) and evaluation of sanitary quality according to WHO/UNEP interim criteria (1983c) in the Šibenik area from 1984-1990.

Station	Number of samples		Samples (%) exceeding the limits of C(FC)/dm <sup>-3</sup>				Sanitary* quality during bathing season
	Total	Bathing season	1000		10000		
			Total	Bathing season	Total	Bathing season	
C1,2	56	56	3.6	3.6	0	0	S
C3	58	58	8.6	8.6	6.9	6.9	S
E1	67	67	47.8	47.8	4.5	4.5	S
E2	70	70	65.7	65.7	22.9	22.9	NS
E3	20	20	0	0	0	0	S
E4	53	53	17	17	1.9	1.9	S
E5	51	51	5.9	5.9	2	2	S

\* S - satisfactory; NS - not satisfactory

In the Split area considerable quantities of sewage and industrial wastewater are discharged into the nearby coastal waters (Šobot, 1981; Krstulović and Šobot, 1982; Krstulović 1986; Krstulović and Šoljić 1990), particularly in the Vranjic (station 1) and main city harbour (station 5) areas. The WHO/UNEP criteria were satisfied only in three (stations 3, 7, and 8) of the eight beaches monitored (Table 3.4.2.7). Moreover, no significant changes of the water sanitary quality in the area as a whole was observed during the monitoring period (Fig. 3.4.2.2). However, lower faecal coliform values measured in some localities in 1991 should be ascribed to the absence of tourists, because the existing wastewater disposal systems were not improved in the meantime.

The water sanitary quality monitoring in the Klek-Neum Bay started only in 1988. Preliminary results suggested that high water quality prevailed in this bay (Table 3.4.2.7. and Fig. 3.4.2.2), but additional measurements should be performed before drawing a reliable qualification.

**Table 3.4.2.7.** Distribution of faecal coliforms concentration (C) and evaluation of sanitary quality according to WHO/UNEP interim criteria (1983c) in the Split area from 1983-1991 and in the Klek-Neum area from 1988-1991.

Station	Number of samples		Samples (%) exceeding the limits of C(FC)/dm <sup>-3</sup>				Sanitary* quality during bathing season
	Total	Bathing season	1000		10000		
			Total	Bathing season	Total	Bathing season	
Split area							
01	97	77	90.7	94.8	73.2	77.9	NS
02	97	77	30.9	28.6	15.5	14.3	NS
03	97	77	22.7	23.4	6.2	7.8	S
04	97	77	52.6	58.4	11.3	11.7	NS
05	97	77	81.4	87	78.4	84.4	NS
06	97	77	42.3	44.2	12.4	11.7	NS
07	97	77	36.1	40.3	9.3	9.1	S
08	79	67	27.8	28.4	7.6	9	S
09	79	67	49.4	52.2	12.7	13.4	NS
10	78	66	20.5	21.2	9	10.6	NS
Klek-Neum area							
01	12	11	0	0	0	0	S
02	9	8	11.1	12.5	0	0	S
03	12	11	0	0	0	0	S
04	12	11	8.3	9.1	0	0	S

\* S - satisfactory; NS - not satisfactory

At the station near Igalo, in the Boka Kotorska area, the water sanitary quality was not satisfactory (Table 3.4.2.8). At the other stations the WHO/UNEP criteria were fulfilled, except for the more restrictive criteria. An increasing pollution trend resulted from the data (Fig. 3.4.2.3), but they should be confirmed by future monitoring. Probably, the sanitary quality of the bay waters can be only significantly improved by sewage disposal into the open sea.

In the Montenegrin coastal area high water quality was observed (Table 3.4.2.8. and Fig. 3.4.2.3), except near the Bojana River mouth (station 10), but even at this station, as well as at all other stations, the WHO/UNEP criteria was respected.

**Table 3.4.2.8.** Distribution of faecal coliforms concentration (C) and evaluation of sanitary quality according to WHO/UNEP interim criteria (1983c) in the Boka Kotorska and Montenegrin coastal areas from 1985-1991.

Station	Number of samples		Samples (%) exceeding the limits of C(FC)/dm <sup>-3</sup>				Sanitary* quality during bathing season
	Total	Bathing season	1000		10000		
			Total	Bathing season	Total	Bathing season	
Boka Kotorska area							
01	56	30	64.3	80	14.3	16.7	NS
02	58	31	24.1	25.8	3.4	3.2	S
03	55	29	10.9	20.7	1.8	3.4	S
04	58	32	34.5	37.5	0	0	S
Montenegrin coastal area							
05	60	32	13.3	6.3	0	0	S
06	50	27	0	0	0	0	S
07	57	31	21.1	25.8	1.8	0	S
08	60	32	8.3	12.5	0	0	S
09	58	32	1.7	3.1	0	0	S
10	58	31	56.9	64.5	5.2	6.5	S

\* S - satisfactory; NS - not satisfactory

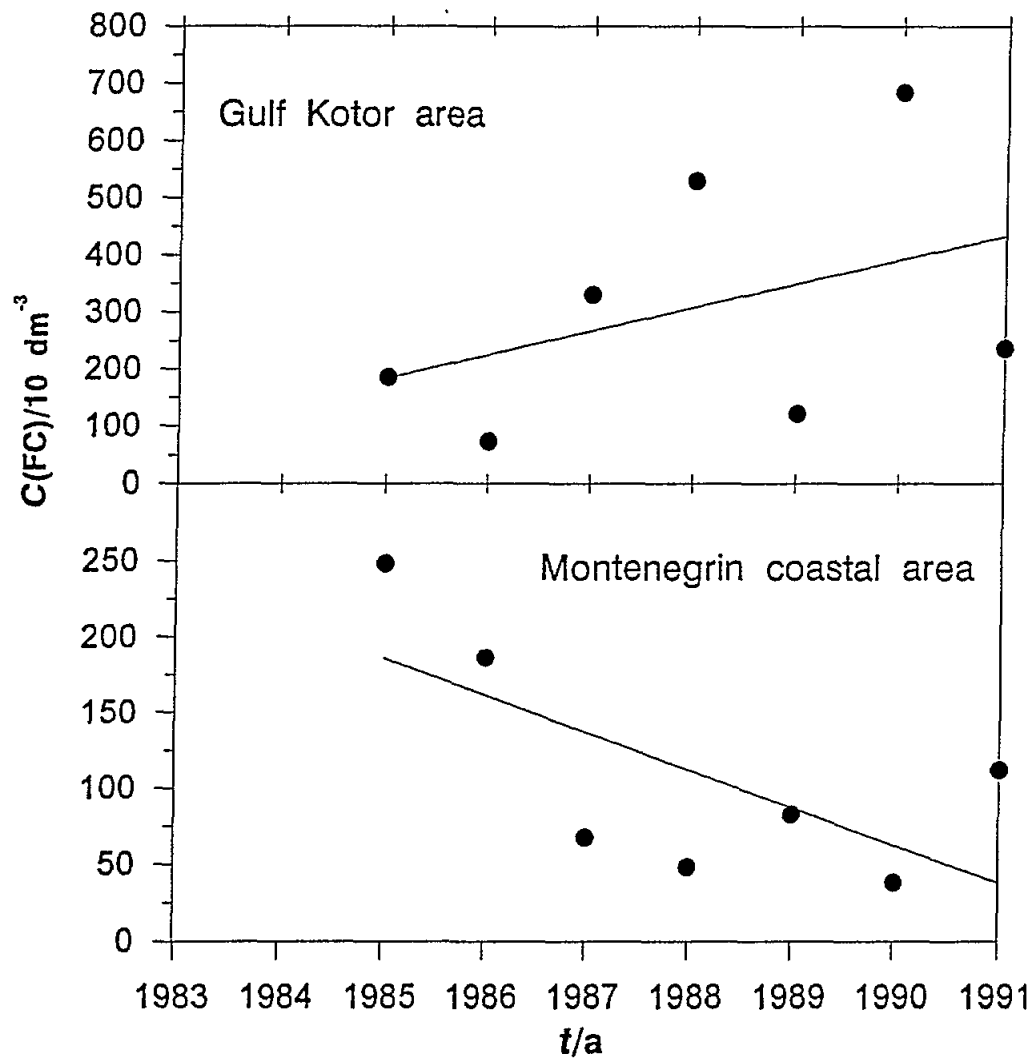


Fig. 3.4.2.3. Average faecal coliform concentration ( $C$ ) for different years ( $t$ ) in seawater samples from different areas in southern Adriatic.

### 3.4.3. Sanitary quality of shellfishes

To assess the hygienic safety of shellfish (mussels), WHO/UNEP (1983c) criteria were used, which fixed the following limits for the faecal coliform level:

$< 2 \text{ g}^{-1}$	- sale allowed
$3-10 \text{ g}^{-1}$	- sale temporarily forbidden
$>10 \text{ g}^{-1}$	- sale forbidden

Shellfish samples were collected in mariculture areas and in their natural breeding plots, ie both in clean and polluted waters.

The mussels collected at the two stations in the Slovenian coastal area did not meet the WHO/UNEP criteria (Fig. 3.4.3.1). Thus, the shellfish cultivated in the Strunjan Bay must be purified before sale.

Analysed mussels from the Limski Kanal (station 1 is inside the mariculture area) mainly fulfilled the sanitary criteria. Occasional deviations from the criteria suggest that a permanent and more systematic monitoring of commercial shellfish should be carried out in this area (Fig. 3.4.3.1). Moreover, the sanitary control should be enlarged to pathogens, because hepatitis A virus was found in seawater, mussels and sediment, and Echovirus in mussels at both stations in the Limski Kanal (Ežek *et al.*, 1992).

The sanitary quality of shellfish from the Pula mariculture areas (stations 12 and 13) was satisfactory, except station 12 in 1985 (Fig. 3.4.3.2).

Shellfish samples were collected in their natural habitat at two monitoring sites in Rijeka Bay (Fig. 3.4.3.2). High concentration of faecal coliforms was often measured in samples from station 4. This was not surprising, because a considerable faecal pollution load originates in this zone.

The unsatisfactory mussel sanitary quality observed in the Zadar area (stations 6 and 11) resulted from a significant faecal pollution in seawater (Fig. 3.4.3.3). In fact, both stations, and particularly the station 6, are located in a zone with a high faecal pollution load.

High faecal coliform levels were also measured in mussels from the Split area (stations 1, 2a, 4 and 9), as a consequence of faecal pollution at the sampling points (Fig. 3.4.3.3).

Despite some opinions that faecal pollution level in the Klek-Neum waters is not significant, the measured faecal coliform contents indicated that local shellfish were not suitable for human consumption (Fig. 3.4.3.4).

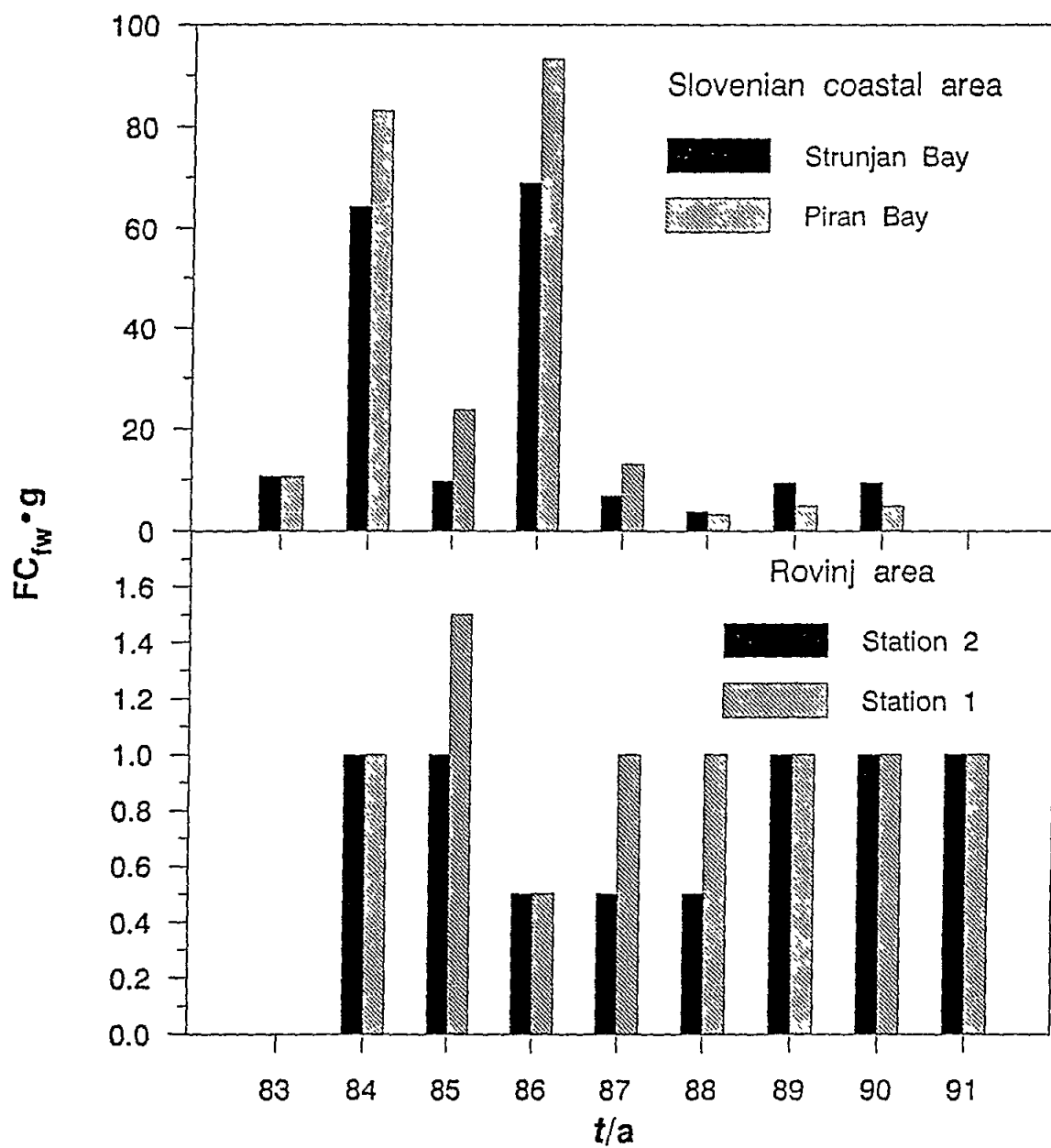


Fig. 3.4.3.1. Average faecal coliform content for different years ( $t$ ) in shellfish (fresh weight) samples from Slovenian coastal and Rovinj areas.



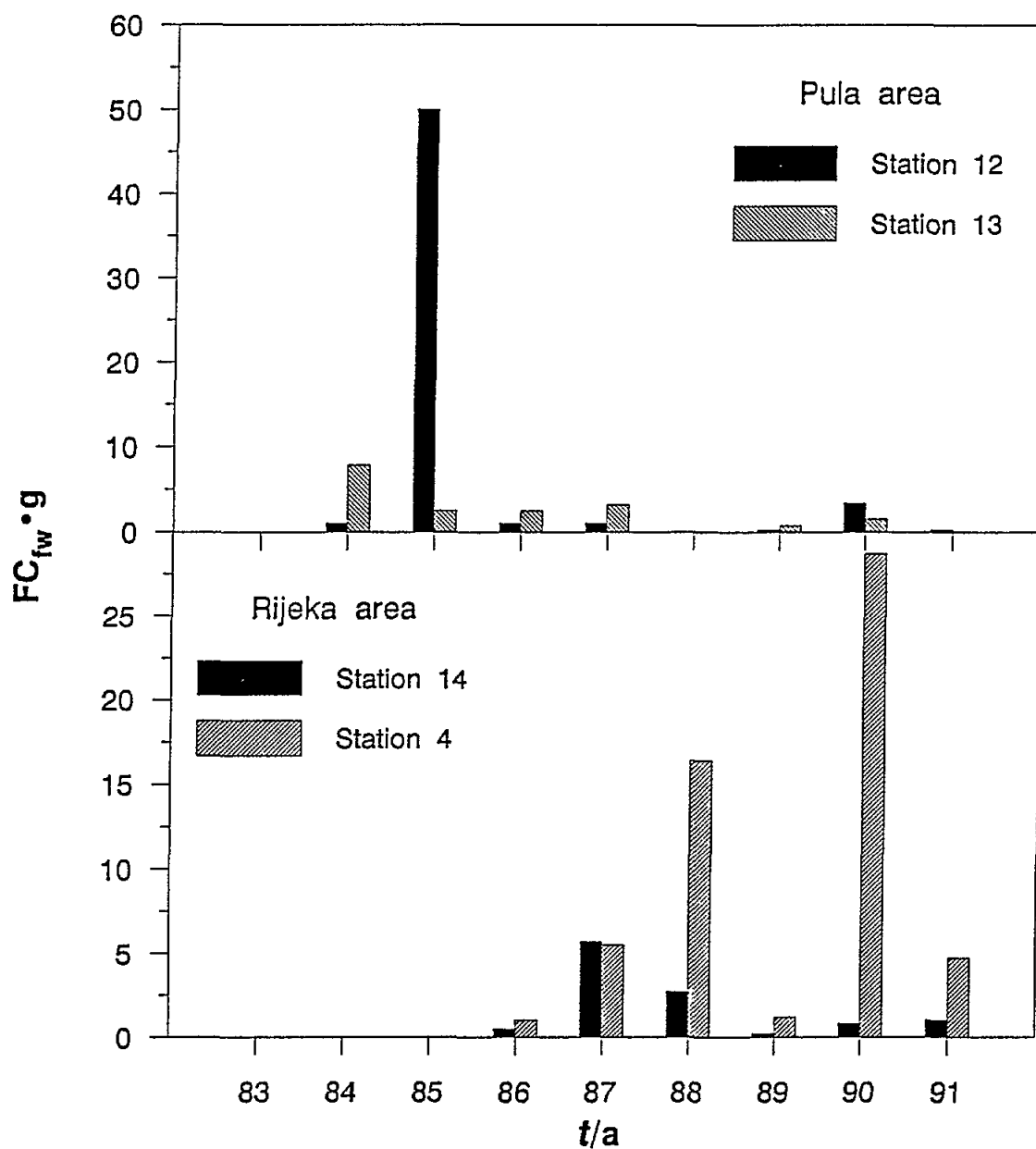
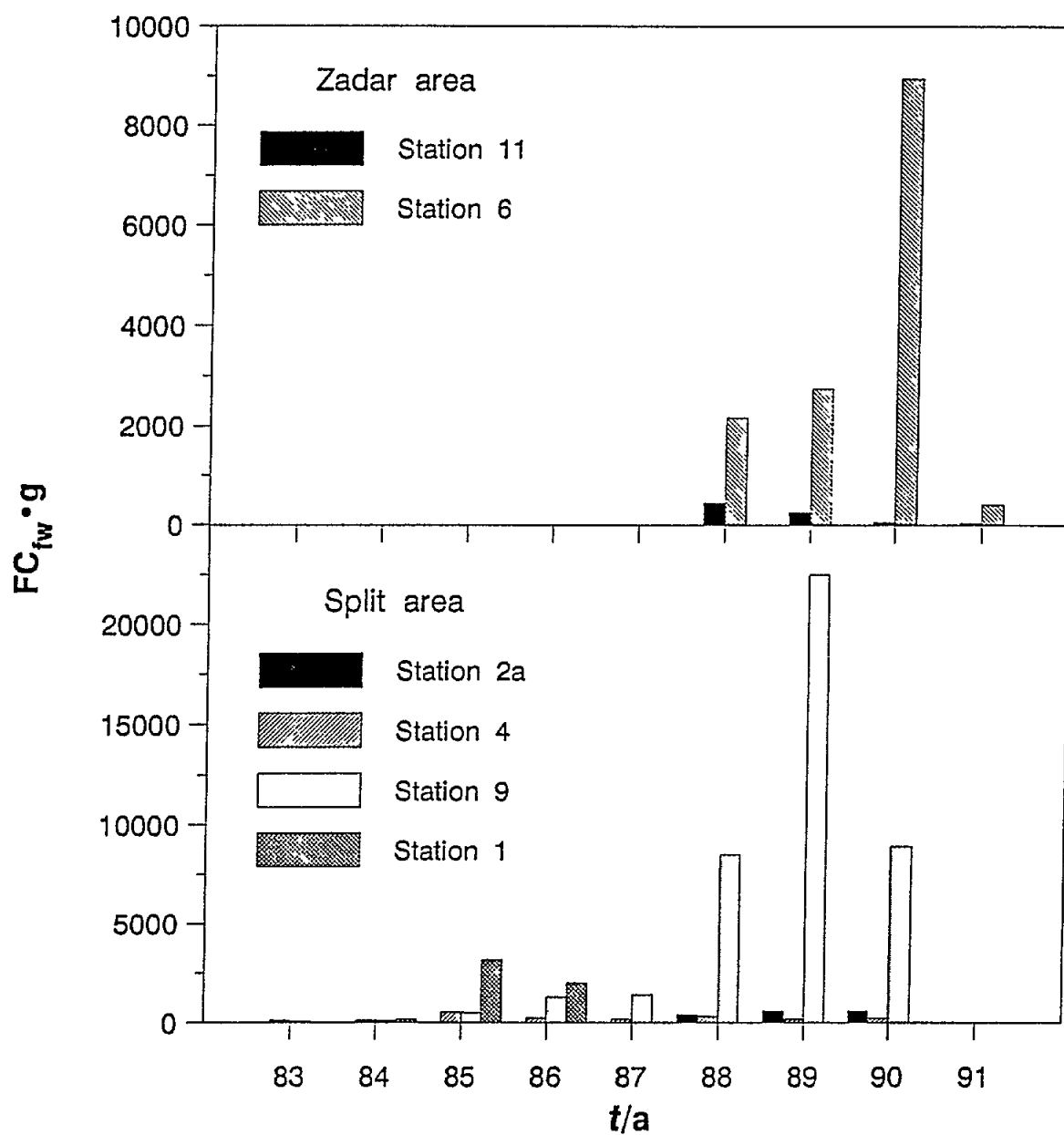


Fig. 3.4.3.2. Average faecal coliform content for different years ( $t$ ) in shellfish (fresh weight) samples from Pula and Rijeka areas.



**Fig. 3.4.3.3.** Average faecal coliform content for different years ( $t$ ) in shellfish (fresh weight) samples from Zadar and Split areas.

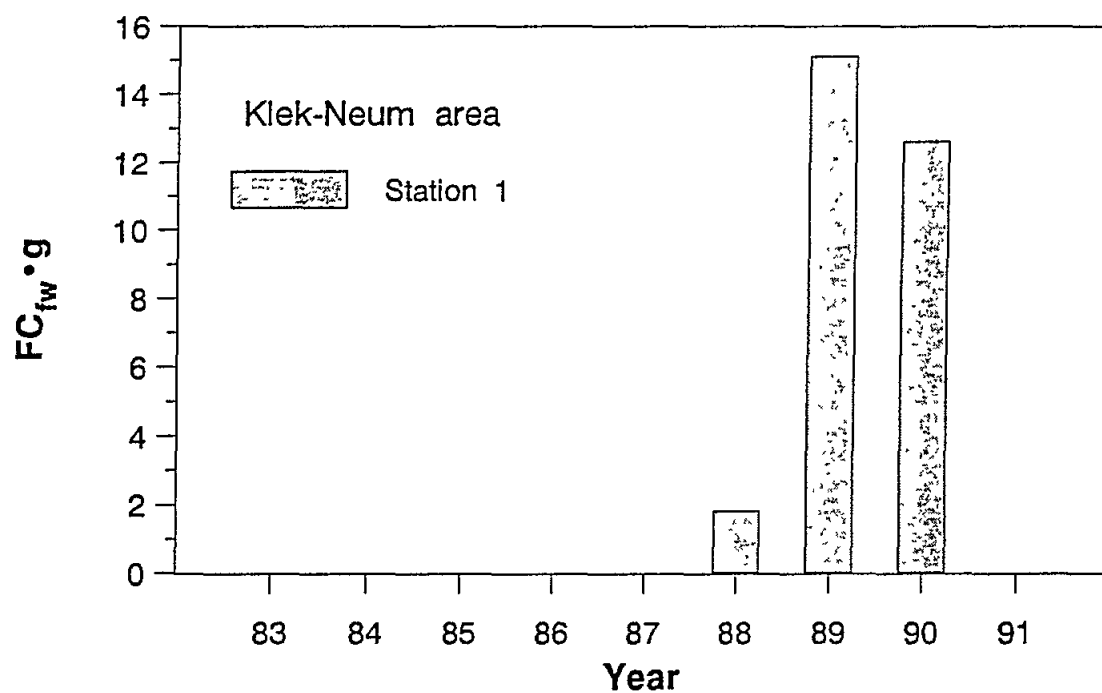


Fig. 3.4.3.4. Average faecal coliform content for different years (*t*) in shellfish (fresh weight) samples from Klek-Neum area.

## 4. GENERAL DISCUSSION

### 4.1. State of pollution

Eutrophication and pollution problems in the eastern Adriatic coastal sea are less marked than, for instance, along the western (Italian) coast.

Firstly, the eastern coast is much less densely populated (Tab. 4.1.1). Along the coast there are only 10 cities with populations exceeding 10,000, including two (Rijeka and Split) exceeding 200,000 inhabitants. Freshwater discharge rate into the eastern Adriatic (mainly due to diffused karstic groundwater sources) is several times lower than along the western coast.

**Table 4.1.1.** Data about anthropogenic eutrophication and pollution along the eastern and western Adriatic coasts.

PARAMETER	EASTERN ADRIATIC	WESTERN ADRIATIC
Shoreline length, including islands (km)	6,116	1,259
Resident population	1,400,000	4,100,000
Inhabitants per km shoreline	228	3,257
Tourist overnights	70,000,000	120,000,000
Freshwater discharge (km <sup>3</sup> a <sup>-1</sup> )	22	73

Modified from Sekuliac (1985) and Cavazzoni Galverni (1972).

Secondly, although several times higher than in seawater, orthophosphate concentrations in karstic waters is generally much lower than in polluted alpine rivers on the western Adriatic coast (Tab. 3.1.1 in the previous report, UNEP, 1988; Degobbis, 1988). The very high N/P ratio of karstic waters is unfavourable for phytoplankton growth. Unfortunately, no extended data sets are available for pollutants in these waters, with the exception of some heavy metals in the Krka River mouth area. In this area metal levels were in typical ranges for unpolluted rivers (Elbaz-Poulichet *et al.*, 1991).

Thirdly, the eastern coast is steeper than the western coastal sea, so that the depth increases to 100 m within a few hundreds metres from the shore. The water dynamics is significant, particularly in the channels between the shore and islands (Zore-Armanda, 1979). Thus, dispersion of introduced nutrients and pollutants is favoured and their impact on the marine ecosystem reduced.

However, in some semi-enclosed areas: harbours of the major urban centres, or within bays, like the Šibenik and Kaštela bays, but still in limited nearly coastal zones, pollutant accumulation in the sediments and negative consequences of anthropogenic eutrophication were observed (increasing frequency of phytoplankton blooms, non-toxic "red tides", near anoxic conditions in the bottom layer with benthic organism and fish kills).

#### 4.1.1. Eutrophication degree of the investigated regions

##### *Criteria*

The evaluation of eutrophication level in marine coastal area is more difficult than in lakes, and must be based on an exhaustive knowledge of the basic eutrophication mechanisms, typical for each region. Unfortunately, this is not the case for all the investigated areas. Thus, the classification of these areas according to their eutrophication degree given below should be considered only tentatively.

Yamada *et al.* (1980) elaborated complex criteria to classify coastal regions, based on several oceanographic, chemical and biological parameters, including lists of phytoplankton species, which typically occur at the various eutrophication degrees, ranges of viable bacteria concentrations, BOD<sub>5</sub> and COD. Chiaudani *et al.* (1982) proposed some ranges for chlorophyll *a* and total phosphorus concentrations to classify the western (Italian) coastal Adriatic waters. These criteria (some examples in Tab. 4.1.2) were applied to the studied Adriatic regions, considering mean values and standard deviations of relevant parameters (Fig. 4.1.1), and other results described in the sections 3.1.3 and 3.1.4, primarily concerning phytoplankton concentration and species composition. Only surface nutrient concentrations were used (Fig. 4.1.1), which should be more directly correlated to external inputs. Other processes (sedimentation, regeneration, desorption from the sediment, etc.) can be more important to control nutrient concentration levels and changes in deeper layers. Bottom oxygen saturation was not considered, because unusual physical conditions, rather than eutrophication forcing, have played a major role in near-anoxia or anoxia events observed in bottom layers (eg at station 5R during the late 1980s and in Prokljan Lake in 1988; section 3.1.4 of this report). Total phosphorus values were not available for the Split stations. Thus, orthophosphate concentrations were compared with the values for the other investigated zones, in which both parameters were measured.

##### *Proposed eutrophication degrees*

The "reference" areas - the Kornati Islands (stations R-1 and R-2) and Vis Island waters (station 11) - can be classified as typical **oligotrophic** regions.

Parameter values from the eastern part of the northern Adriatic (station 5R) varied over ranges for **oligotrophic** and **mesotrophic** regions. "Eutrophic" phytoplankton species occurred, but usually in concentrations ranges typical for oligotrophic regions. Only exceptionally, as in June 1977, chlorophyll *a* concentration in this region was higher than 5 µg dm<sup>-3</sup>, due to an unusually marked freshwater intrusion (Degobbis *et al.*, 1979). Based on available parameters (no chlorophyll *a* and

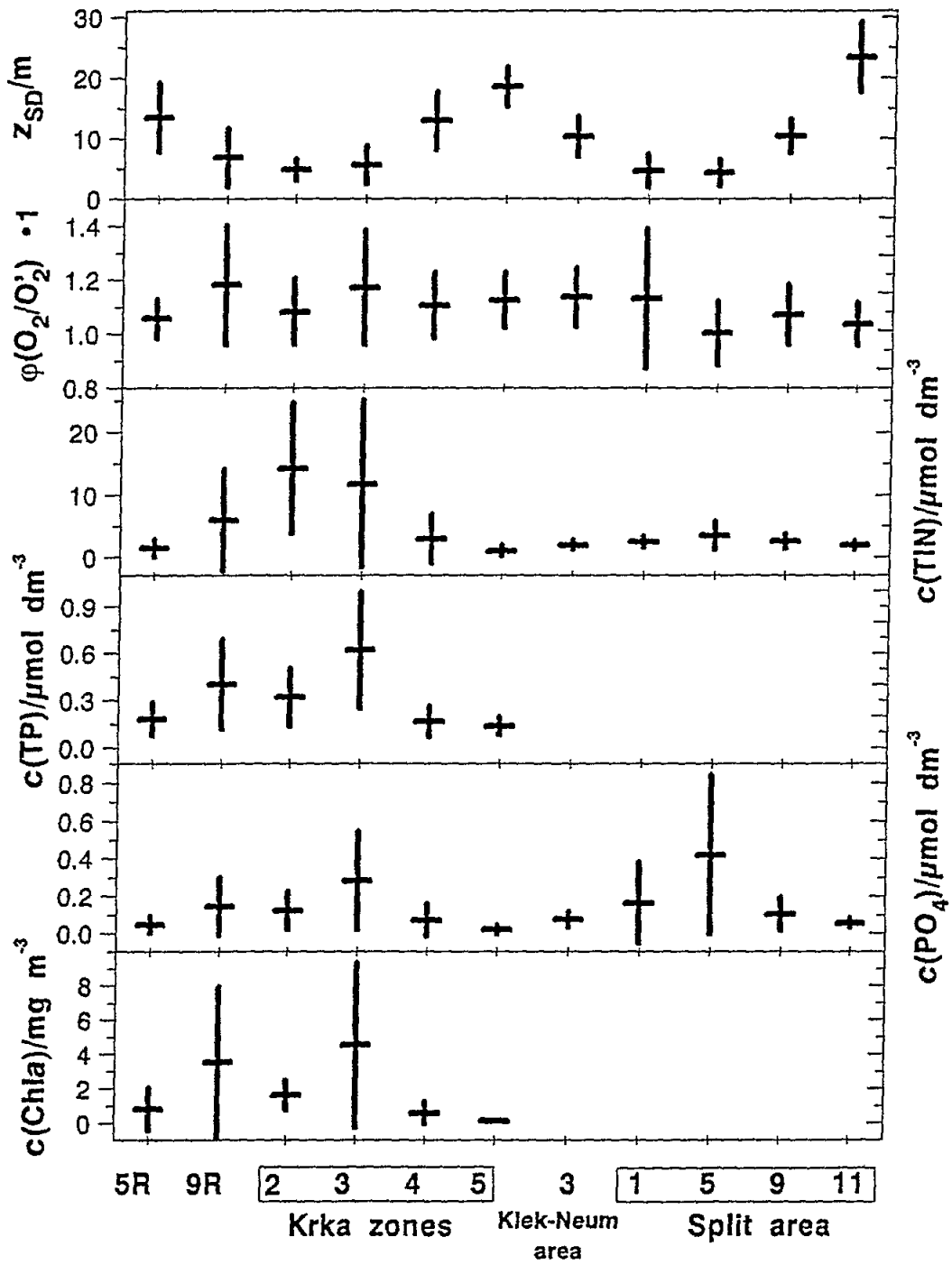


Fig. 4.1.1. Means and standard deviations of surface values for parameters relevant to estimate the eutrophication degree of the investigated areas ( $z_{SD}$  - Secchi depth;  $\phi(O_2/O'_2)$  - oxygen saturation ratio; TP - total phosphorus; Chla - Chlorophyll a).

phytoplankton count data were available), such eutrophication degree could also be ascribed to the coastal area in front of the Krka estuary mouth (stations C-1 and C-2), Klek - Neum Bay (station 3) and the Žrnovica Estuary (Split area, station 9).

**Table 4.1.2.** Classification of eutrophic levels

Parameter <sup>a</sup>	Eutrophication levels <sup>b</sup>				
	O	ME	E	EE	S
Transparency	>10	3-10		<3	<3
Coloration	Rare	Occasional		Usual	Usual
DO/% - surface	80-100	80-100		100-200	0-30
- bottom		30-80		0-30	
TIN/ $\mu\text{mol dm}^{-3}$	<2	2-10		10-100	>100
TP/ $\mu\text{mol dm}^{-3}$	<0.3	0.3-0.6	0.6-1.3	>1.3	
Chlorophyll a/ $\mu\text{g dm}^{-3}$	<1	1-5	5-10	>10	
Microphytoplankton concentration/ $\text{dm}^{-3}$	<10 <sup>3</sup>	10 <sup>3</sup> -10 <sup>6</sup>		10 <sup>6</sup> -10 <sup>8</sup>	>10 <sup>6</sup>

<sup>a</sup> TIN-total inorganic nitrogen; TP-total phosphorus

<sup>b</sup> O-oligotrophic, ME-mesotrophic, E-eutrophic, EE-extremely eutrophic, S-saprobic levels; modified from Chiaudani et al. (1982) and Yamada et al. (1980).

According to the values for total phosphorus and chlorophyll *a* concentrations the upper Krka River estuary (Skradin area and Prokljan Lake) should be classified as a **mesotrophic region**, although some parameters (eg Secchi disk and TIN) may indicate a higher eutrophication degree. However, an increased turbidity is probably due to land drainage, and high nitrate levels did not have a corresponding impact on the phytoplankton growth, which is mainly P-limited.

In the western part of the northern Adriatic, 25 km off the Po delta (station 9R), mainly **mesotrophic** and **eutrophic** characteristics prevail. In the coastal area of the delta, extremely eutrophic conditions are dominating (Chiaudani *et al.*, 1982). Once in a while, but more frequently in the last five years, when high freshwater discharge rate was combined with calm weather, a stable water column, and favourable current patterns, Po plumes reached the station 9R area. In these plumes intense blooms of *Skeletonema costatum* (but also of other diatoms species) occurred, in concentrations typical for extremely eutrophic conditions ( $>8 \cdot 10^6 \text{ dm}^{-3}$ ; Yamada *et al.*, 1980). As an example, concentrations up to  $17 \cdot 10^6 \text{ dm}^{-3}$  of *Chaetoceros socialis* (or *C. radians*; Degobbis, 1989; Filipiæ 1990) were measured in July 1988, or up to  $30 \cdot 10^6 \text{ dm}^{-3}$  of *S. costatum* in February 1991 (Anon., 1993). Similar considerations may be done for the Vranjic area (station 1) and the station 5 area, which is under the direct influence of waters from the Split main harbour. For both areas most of the parameter values are in ranges assumed for mesotrophic and eutrophic regions. However, during "red tide" events in the Vranjic area, phytoplankton concentration can increase up to values characteristic for extremely

eutrophic area. At station 5 orthophosphate is on average very high, in ranges typical for extremely eutrophied regions. However, it appeared from the other parameters that at this station the orthophosphate impact was lower than expected and probably prevented by a significant water exchange with clean Brač Channel waters.

Finally, Šibenik Bay, at least in its eastern part, near the urban centre, should be considered as a typical **eutrophic** region, not only because of the highest variability of most of the parameters, compared with other studied areas, but particularly because of the significant anthropogenic phosphorus impact on phytoplankton.

#### 4.1.2. Heavy metal levels

##### *Effluents*

Heavy metal concentrations in effluents from various investigated areas did not generally differ substantially, neither between sewage effluents nor industrial wastewaters. Significantly higher concentrations were only measured for Cr in the Zadar tannery wastewaters, compared with other regions. However, budget calculations indicated that the Split effluents represented the most significant Hg and Cd pollution sources in respect of effluents from the other investigated areas.

##### *Suspended matter*

Hg (GM annual values  $3.9-13.2 \cdot 10^{-6}$ ) and Cd ( $2.6-26 \cdot 10^{-6}$ ) mass fractions in suspended particles from the Slovenian coastal area were within ranges reported for coastal waters under a moderate anthropogenic influence. Based on 1989 and 1990 determinations, one can hypothesize that this area may be also overloaded with other heavy metals (Mn, Cr, Zn and Cu), particularly in the bottom layer.

##### *Sediment*

The Hg GM mass fraction in the Slovenian coastal sediment has increased during the investigated period (up to  $372 \cdot 10^{-9}$ ). However, the values were in similar ranges reported for the open northern Adriatic sediments and much lower than in the northern (Italian) part of the Gulf of Trieste during the late 1970s, which is under the influence of the Soča (Isonzo) River (Donazzolo *et al.*, 1983). The watershed area of this river is rich in Hg, which was extracted for several decades from a mine near Idrija.

The relatively high Hg GM mass fractions in the Rovinj sediments (up to  $745 \cdot 10^{-9}$ ) were primarily due to values measured in the Rovinj harbour, close to a town sewage outfall. In fact, a significantly lower Hg content should be representative for this area.



The highest Hg GM mass fractions were calculated for the Šibenik (up to  $620 \cdot 10^{-9}$ ) and Split (up to  $2839 \cdot 10^{-9}$ ) sediments. The relatively high means in the Šibenik area were due to values measured at a station, which was under the influence of the main harbour ( $1095\text{--}2295 \cdot 10^{-9}$ ). In contrast, the values from the others stations in the Krka estuary and near Zlarin Island varied within the range for the reference station ( $210\text{--}350 \cdot 10^{-9}$ ). Extremely high values in the Split area were primarily measured in Kaštela Bay, in the location where a chloro-alkali plant was operating. In 1990 the plant was closed and the emission of elementary mercury interrupted. However, the reserves accumulated in the sediment will probably represent a significant Hg source for the water column and organisms for a longer period.

The Cd mass fractions were also higher in the Šibenik and Split sediments, compared to other investigated areas. Preliminary measurements indicated that the sediment Pb, Cu and Zn contents in the Split area were higher than in the Slovenian and Montenegrin coastal areas.

Concluding, results have strongly indicated that heavy metal levels in the sediments of most of the eastern Adriatic area were typical for unpolluted coastal sediments. In contrast, these levels can be up to one order of magnitude higher in restricted areas, which are under a significant anthropogenic influence (city harbours, industrial zones). However, a more precise evaluation of the anthropogenic contribution should be based on specific research of the interactions (physico-chemical and mineralogical processes) between metals and sediments in relation to their basic characteristics (organic content, textural composition, etc).

### *Organisms*

Geometric mean mass fractions of total Hg in mussels (*Mytilus galloprovincialis*) did not differ greatly among the investigated areas, with values generally ranging from  $17\text{--}47 \cdot 10^{-9}$  (related to fresh weight). In fact, in most of these areas the values were always lower than  $150 \cdot 10^{-9}$  (or even  $<60 \cdot 10^{-9}$  in Slovenian, Rovinj, Klek-Neum, and Dubrovnik mussels). Values about  $400 \cdot 10^{-9}$  were occasionally measured in the Zadar (1990-1991) and Split (1988) areas. Even higher values were obtained in 1983-1984 in Šibenik and Split samples, but one cannot exclude that they were due to contamination during sampling or analytical procedures. Thus, it is probably justifiable to assert that the Hg content in mussels from all investigated areas was significantly lower than the limit of  $500 \cdot 10^{-9}$ , recommended by WHO for human consumption (UNEP/FAO/WHO, 1987).

The mean mass fractions for Cd in mussels from the various areas differed more significantly than for Hg. The lowest values were measured in mussels from Klek-Neum Bay, while significantly higher values were recorded in the Montenegrin and Slovenian coastal areas.

High mass fractions of Cd, Cu, and particularly Zn, were determined in *Ostrea edulis* samples from the Dubrovnik area. Significantly, high mass fractions of Cd, Pb and Zn were also observed in mussels from the Montenegrin coastal area, and for Pb in the Rijeka samples.

High Hg mass fractions were measured in *Pagellus erythrinus* from the Slovenian coastal area (GM up to  $782 \cdot 10^{-9}$  in 1984). Even if more recently the values were lower (down to  $252 \cdot 10^{-9}$  in 1988), the use of this fish for food should still be under control.

#### 4.1.3. Organic pollutants

##### Chlorinated hydrocarbons

###### *Effluents*

DDT<sub>total</sub> (the insecticide DDT and its analogues DDE and TDE) and PCB concentrations (medians  $0.017$  and  $0.050 \mu\text{g dm}^{-3}$ , respectively) in the analysed effluents from the Rijeka and Zadar areas were significantly lower than in other areas of the world. In Rijeka and Zadar sewage effluents the PCB concentrations were about three times higher than DDT<sub>total</sub> concentrations. The levels for both groups of chlorinated hydrocarbons were higher than in the Rijeka industrial wastewaters. This difference was statistically significant, according to one way analysis of variance of concentrations in dependence on the effluent type.

###### *Sediment*

The DDT<sub>total</sub> and PCB mass fractions in the eastern Adriatic sediments were generally lower than in other Mediterranean areas. Only a few extremely high values were measured in some Adriatic samples, especially for DDT<sub>total</sub> ( $>30 \cdot 10^{-9}$ , related to dry weight). However, it is not excluded that these values were due to contamination during the analytical procedure.

A higher DDT<sub>total</sub> content was measured in the Zadar, Šibenik, and Dubrovnik sediments, compared to the other investigated areas, and particularly to the open northern and central Adriatic sediments. Higher PCB mass fractions were measured in sediments of the Istrian, Zadar and Dubrovnik areas.

In the western part of the northern and central open Adriatic ( $>12$  Nm from the coast) the sediment chlorinated hydrocarbon levels were higher than in the central and eastern parts. However, the accumulation degree of these pollutants can differ greatly relative to physico-chemical and mineralogical characteristics of the sediment. Metal accumulation processes should be investigated in more detail to evaluate more accurately the contribution of local sources.

###### *Organisms*

Similarly as in sediments, the chlorinated hydrocarbon levels in mussels from the eastern Adriatic were lower than in various Mediterranean areas. Moreover, the values obtained in the Adriatic mussels since 1983 were even lower than those for the period 1976-1980 (about 50% for DDT<sub>total</sub> and four times for PCBs).

Among the eastern Adriatic investigated areas, the highest DDT<sub>total</sub> content was observed in Zadar mussels, and the lowest in Šibenik samples. The highest PCB levels were measured in the Split area.

## Phenols

### *Effluents*

Phenol concentrations, as expected, were much higher in industrial wastewaters from the Pula and Rijeka areas (up to  $16.5 \text{ mg dm}^{-3}$ ) than in sewage effluents. However, this difference was not significant in the Zadar effluents. Remarkably, the phenol levels in the eastern Adriatic sewage effluents (median  $0.016 \text{ mg dm}^{-3}$ ) were generally lower than in other world regions.

Statistical analyses have shown that the phenol content in the eastern Adriatic wastewaters also varied seasonally, except in the Zadar effluents. This was particularly evident when the concentrations measured in the Rijeka effluents in the high tourist season (higher values) and low season were compared.

## Anionic detergents

### *Effluents*

The average detergent concentrations in the eastern Adriatic effluents were several times lower than in some USA sewage effluents or even in effluents from the Haifa treatment plant (Israel).

Differences of the detergent content were evident between sewage effluents and industrial wastewaters of most of the investigated eastern Adriatic areas, except the Zadar area. The concentrations did not vary significantly between the high and low seasons.

## Petroleum hydrocarbons

### *Effluents*

Petroleum hydrocarbon concentrations were higher in some industrial wastewaters ( $>15 \text{ mg dm}^{-3}$ ) than in sewages or mixed sewage effluents and industrial wastewaters (median for all samples  $0.8 \text{ mg dm}^{-3}$ ). However, due to the extreme variability of the values this difference was not statistically significant. Probably for the same reason, no significant differences of the wastewater petroleum hydrocarbon content were evident between the investigated areas or seasons. Despite this variability, the petroleum concentration in sewage effluents from the eastern Adriatic was evidently lower than in various world areas.

### *Coastal and estuarine waters*

Oil slicks and other floating pollutants were noticed in the Rijeka Bay in 26% of about one thousand observations. In 13% of the positive observations oil slick was continuous, and in 6.4% the sea surface coverage was at a maximum.

The petroleum hydrocarbons concentrations in the eastern Adriatic coastal waters did not differ significantly from values measured in various Mediterranean areas. The values obtained in the open northern Adriatic were lower than in the coastal area, particularly in relation to the central part.

### *Sediment*

The polyaromatic hydrocarbon (PAH) content in eastern Adriatic sediments (analysed by UV fluorescence) was within the range measured in other Mediterranean areas. The values increased gradually in the open northern and central Adriatic going towards the west coast.

### *Organisms*

The polyaromatic hydrocarbon levels in mussels from the eastern Adriatic (determined by UV fluorescence) were higher than in other Mediterranean areas. Statistical analysis has shown that seasonal changes of these levels were not significant.

The PAH content in *Holothurioidea* from the eastern part of the northern Adriatic was lower than in the western part. However, this was not noticed for other benthic organism groups (*Asteroidea* and *Bivalvia*).

Polyaromatic hydrocarbon monitoring in edible marine organisms from the eastern Adriatic should be essential in relation to human health protection. Moreover, research should be carried out to indicate if additional monitoring of some PAH metabolites would be necessary.

#### 4.1.4. Faecal coliforms

### *Coastal and estuarine waters*

A significant faecal pollution was recorded in some of the controlled locations of the monitored areas.

According to the WHO/UNEP *interim* criteria, the sanitary quality of seawater at most of the stations in the Slovenian coastal area was satisfactory, particularly along the major beaches. This was not the case for the Rižana Estuary and the adjacent Koper Bay waters.

While the water quality assessment for most of the monitored beaches showed that they were suitable for bathing, the water quality of some zones, next to the Rovinj harbours, was often unsatisfactory. However, since 1988 the situation in these zones has improved, after some technical measures were applied (see Section 4.2).

In the eastern part of Rijeka Bay, including the Krk Island coast, a high water quality was recorded. To the contrary, some locations in the northwestern coastal area were probably not suitable for recreational use.

Also in four of the eleven stations in the Zadar area, particularly those next to the harbour, the bacteriological levels were higher than the recommended limits, due to the influence of an inadequate sewage disposal. This was probably also the reason for an unsatisfactory water quality near Skradin, while the other monitored zones of the Krka Estuary and Šibenik coastal area were suitable for recreational purposes.

Only in three of the eight controlled beaches of the Split area were the recommended sanitary criteria respected. In the others the influence of polluted waters from the Split urban centre, as well from minor settlements in the Vranjic, northern Marjan Cape, and Žrnovica Estuary areas can be detected.

The highest water quality among the investigated areas was observed in Klek-Neum Bay, also in zones next to urban settlements and touristic resorts.

Near Igalo in the Boka Kotorska area the water sanitary quality was not satisfactory. In the other investigated zones of the Montenegrin coastal area the recommended criteria were respected, but the microbial levels were often near the allowed limits.

### *Shellfish*

The hygienic quality of shellfish samples collected in natural habitats along the Slovenian, Rijeka, Zadar and Split areas was not satisfactory. In those from the Pula area the criteria were respected only occasionally.

The very restrictive criteria for seawater that can be used for shellfish culture were met in the Limski kanal, in some zones of the Pula area, and near Omišalj (Krk Island).

A continuous sanitary control of shellfish should be recommended also in zones that apparently are not under the influence of sewage effluents. In fact, due to the karstic nature of the eastern Adriatic coast, unexpected contamination can occur through underground water discharges from sources located away from the coast.

## 4.2. Trends

### 4.2.1. Eutrophication

The evaluation of eutrophication trends must be done carefully, particularly if available scientific data are not sufficient to evidence the causes and relationships between the causes and consequences, which is the case for many marine coastal areas. Natural successions of species in the phytoplankton community, or changes in water exchange rate, which can significantly influence the oxygen budget in bottom layers, can produce similar modifications in the ecosystem as an increase of the anthropogenic nutrient input. As an example, different authors did not agree that increased frequency of anoxia events in the deeper layers of the Baltic proper, observed since 1929, was due to changes of the water exchange mechanism with the Atlantic Ocean or to anthropogenic eutrophication (see Kullenberg, 1983 for review). This latter is often invoked in the literature related to the Adriatic, but often without evidence based on reliable data.

Unfortunately, much shorter historical data series are available for the studied Adriatic areas, compared to the Baltic Sea. Thus, only some hypotheses concerning eutrophication trends can be elaborated, which may help to design future research and monitoring activity.

#### Open northern Adriatic

Relevant data to eutrophication study were collected with a fixed sampling and analytical protocol (Gilmartin *et al.*, 1972 *et seq.*) at three (since 1966) to six (since 1972) stations (including stations 5R and 9R), distributed along a marked eutrophication gradient, from the Rovinj coastal waters up to the border of Italian territorial waters, off the Po delta. Unfortunately, the measurement frequency varied greatly in various periods, ranging from a few up to twenty in a year. Due to this inhomogeneity, the reliability of conclusions related to long-term changes of some parameter values was decreased.

Temporal series for several parameters were analysed and compared to establish eventual modifications in the marine ecosystem during the last two decades. Total phosphorus and total nitrogen concentrations in low salinity surface layer should be considered the best indicator of nutrient input changes. No significant trends were observed for these parameters in the surface layer of the northern Adriatic in any seasonal period over the last two decades (see examples for stations 5R and 9R in Fig. 4.2.1.1). Relationships between salinity and nutrient concentrations for the 1970s and the 1980s for the station 25 km off the Po Delta did not differ significantly (CMR-R, unpublished results). This indicates that the nutrient concentrations in the diluted water, which has been spread from the Po Delta coastal zone to the open area, have not changed significantly in the last two decades.

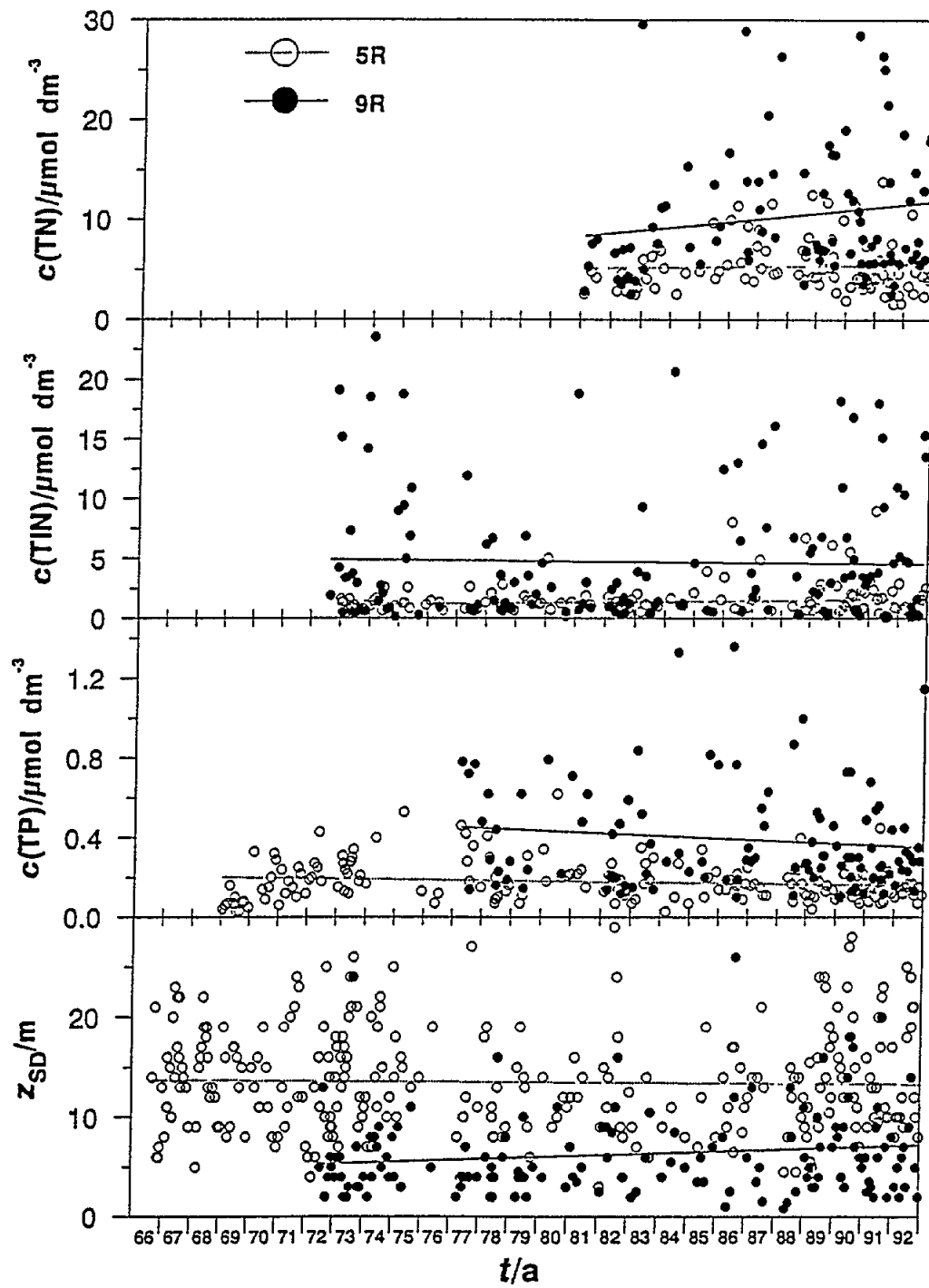


Fig. 4.2.1.1. Temporal ( $t$ ) series of total nitrogen (TN), total inorganic nitrogen (TIN), and total phosphorus (TP) concentrations ( $c$ ), and water transparency ( $z_{SD}$ ) in the surface layer of the stations 5R (○) and 9R (●) in the open northern Adriatic.

Remarkably, contrasting information on anthropogenic influence was reported. While Marchetti *et al.* (1985, 1989) reported that the inorganic nitrogen and orthophosphate concentrations (and loads) in the Po River, 70 km from the delta, at least doubled in the first part of the 1980s compared to the 1970s, the anthropogenic phosphorus (inorganic and organic) load in northern Italy did not apparently change (Bressan, 1986). Furthermore, Tartari *et al.* (1991) reported that orthophosphate (but not inorganic nitrogen) concentration in the Po River has been reduced since the middle of the 1980s, probably because of polyphosphate reduction in commercial detergents. However, it should be also considered the possibility of systematic errors among data sets collected by different authors in different time intervals, and with different methods, from which time series (1968-1990) of nutrient concentrations in this river were "reconstructed". Anyhow, changes in the river loads do not necessarily imply some corresponding changes in the open sea. Additional river nutrients may have been mostly recycled in the coastal area, which can work as a "treatment plant", moderating the river eutrophication influence on the open northern Adriatic ecosystem (eg Smolaka and Degobbis, 1987).

Contrary to the nutrient loads, a significant increase of the diatom concentration was observed during the 1980s in respect to the 1970s, particularly evident in the eastern, more oligotrophic regions. Related to this may be a slight decrease of orthosilicate in surface layer, and a corresponding increase in the bottom layer, observed recently. Mean chlorophyll *a* concentrations, as a measure of total phytoplankton standing crop, did not change significantly. Concurrently, the episodes of higher dinoflagellate concentration were reduced, which partly compensate the diatom increase. Besides, a shift towards smaller diatom species also contributed to maintain the average total phytoplankton standing crop at the same level, despite the increased diatom contribution.

Data on phytoplankton composition also indicate that some changes occurred in the northern Adriatic ecosystem. In the 1970s *Skeletonema costatum*, *Nitzschia seriata*, and *Prorocentrum micans* were prominent bloom constituents in the northern Adriatic under the influence of the Po River discharge (Voltolina, 1971; Revelante and Gilmartin, 1977, 1985; Montresor *et al.*, 1982; Socal *et al.*, 1982). In contrast, during the 1980s other species (*Nitzschia delicatissima* complex and *Chaetoceros socialis* or *radians*) played such a role (Filipiaë 1990; Degobbis *et al.*, 1991b; Revelante and Gilmartin, 1992; CMR-R, unpublished results).

Even if nutrient concentrations and phytoplankton standing crop did not change significantly, changes in the oxygen cycle might have occurred in the bottom layer during the summer and the beginning of the autumn. Near-anoxia (and anoxia) events in bottom layers were apparently more frequent during the 1980s than during the 1970s, particularly in the eastern, more oligotrophic regions of the northern Adriatic. As an example, an analysis of the available data has shown that the bottom oxygen saturation at station 5R was exceptionally as low as 65-70% in the period August-November 1955-1976 (Degobbis *et al.*, 1979). In contrast, undersaturation between 35-60% was measured almost each year after 1977, and even values near zero in November 1989 (CMR-R, unpublished results).



Concluding, the results apparently support the hypothesis that climatic changes, which occurred during the 1980s, may have modified hydrological regimes and oceanographic conditions (eg when related to density structure and flushing characteristics of the region). In these conditions, the actual nutrient input might have a different impact on the northern Adriatic ecosystem, resulting in unusual (and often undesirable) events.

Long-term changes in the ecosystem of the open northern Adriatic will be described in more detail in the final report of the project YUG/86-H "Eutrophication Trends in the Northern Adriatic Sea", which is in preparation.

#### The Krka River estuary, the Šibenik coastal area and the Kornati Islands region

The Krka River estuary is threatened by anthropogenic eutrophication due to various, often conflicting human activities and inadequate sewage disposal. Although only a few studies were carried out in periods prior to 1983 (Buljan, 1969; Vilièæ and Stojanoski, 1987; Buljan *et al.*, 1980; Vilièæ 1989), there were strong indications that significant changes have occurred in the Krka Estuary ecosystem, particularly in Šibenik Bay.

Nutrient measurements evidenced a significant increase in orthophosphate (but not in nitrate and orthosilicate) concentrations from 1949 (0.0-0.25 mmol m<sup>-3</sup>, Buljan, 1969) to present (0.0-1.7; this programme). Already by 1973/74, the average orthophosphate concentration in Šibenik Bay was 0.2 mmol m<sup>-3</sup> (Buljan *et al.*, 1980), ie approximately at the level measured in the period 1983-1991 in the framework of this programme. Moreover, this 1983-1991 data set did not reveal significant changes in nutrient concentrations (Fig. 4.2.1.2) and other relevant parameters (oxygen saturation, transparency, chlorophyll *a* concentration), indicating that nutrient loads had not changed significantly during the last decade. A decrease of the total inorganic nitrogen (mainly nitrate) concentration, shown in the figure, is well correlated with a salinity increase, perhaps due to a reduced freshwater inflow during the 1980s.

However, a significant shift was observed in the period 1983-1985 in the relative dominance of diatoms to dinoflagellates in Šibenik Bay (lower estuary; Marasoviæ 1986), compared with the middle 1970s. While in that period only diatom typical for the Adriatic eutrophic regions (*Nitzschia seriata*, *N. delicatissima*, *Skeletonema costatum*, *Thalassionema nitzschioides*, *Leptocylindrus* spp., and others) were involved in the summer blooms as dominant species, during the 1980s (1983-1985) dinoflagellates also occurred, particularly the potentially toxic *Prorocentrum minimum* var. *minimum* (concentration up to 3·10<sup>6</sup> dm<sup>-3</sup>, 15-30% of the total microplankton concentration). This species was not observed in the Adriatic before 1983 (Marasoviæ *et al.*, 1990). However, there was not sufficient evidence to assert if these composition changes of the phytoplankton community were due to an anthropogenic influence, or if a natural biological succession was in progress.

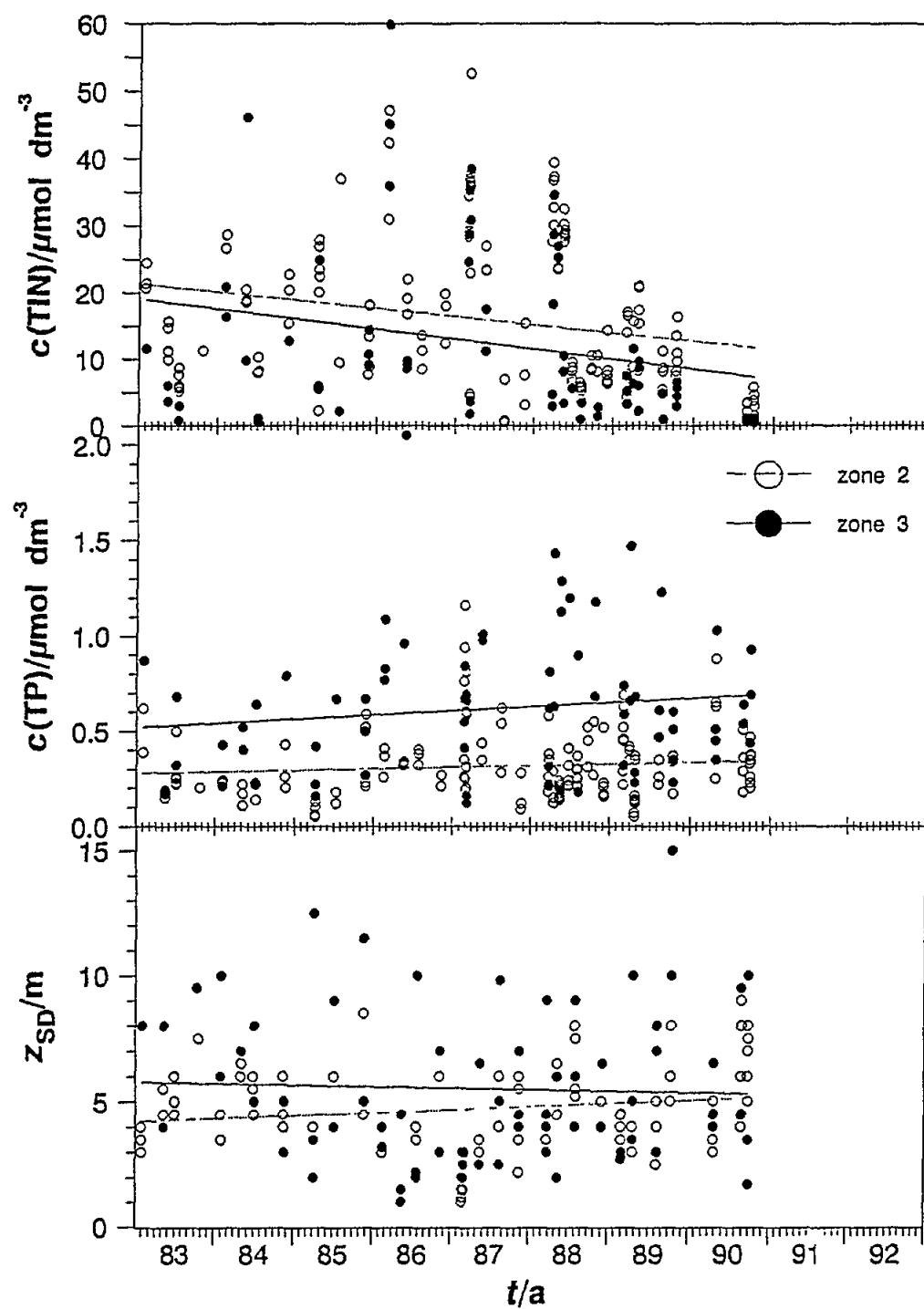


Fig. 4.2.1.2. Temporal ( $t$ ) series of total inorganic nitrogen (TIN) and total phosphorus (TP) concentrations ( $c$ ), and water transparency ( $z_{\text{SD}}$ ) in the layer above the halocline of the upper Krka estuary (zone 2,  $\circ$ ) and Šibenik Bay (zone 3,  $\bullet$ ).

### The Split coastal area

Similarly, as in the other investigated area, no significant trends can be obtained for any parameter in the Split coastal areas in the period 1984-1991, except an increase of total inorganic nitrogen concentration at station 5 (examples for nutrients in Fig. 4.2.1.3).

However, some changes that occurred in Kaštela Bay in the past were well documented. Several parameters had been monitored since the 1960s at one station in the centre of this bay. Primary production increased from about  $120 \text{ g m}^{-2} \text{ a}^{-1}$  of organic carbon in 1963 to about  $250 \text{ g m}^{-2} \text{ a}^{-1}$  in 1984, correlated with a rapid urbanization of the area (from 60,000 inhabitants in 1960 to 250,000 in 1989; Pucher-Petković *et al.*, 1988; Marasović 1989). Concurrently, average concentration of heterotrophic bacteria (CFU) increased from 300 to  $1,000 \text{ cm}^{-3}$  (Šoljan and Krstulović 1991). Orthophosphate concentration has gradually increased from a yearly mean of  $0.05 \text{ } \mu\text{mol dm}^{-3}$  in 1962 to a value of 0.08 in 1971, but has remained approximately at this level over the following 10 years (Barić 1989). In the 1950s and 1960s the mean oxygen concentration in the surface and bottom layer did not differ significantly. During the 1970s and 1980s the surface values gradually increased and bottom values decreased differing on average up to 20% during the early 1980s.

Before 1967, only characteristic temperate spring and autumn phytoplankton blooms occurred (Pucher-Petković and Marasović 1980). After this date a third summer bloom occurred with increasing intensity (chlorophyll *a* concentrations up to  $13 \text{ } \mu\text{g dm}^{-3}$ ), which was ascribed to anthropogenic influence (Marasović 1989; Pucher-Petković and Marasović 1989). This bloom was dominated by a small number of species typical for Adriatic eutrophic environments: *Nitzschia seriata*, *Skeletonema costatum*, *Leptocylindrus danicus*.

In the Vranjic area (station 1) a first "red tide" event was observed in summer 1980, and ascribed to land drainage during construction of harbour facilities (Marasović and Vukadin, 1982). However, "red tides", mainly due to dinoflagellate *Gonyaulax polyedra*, appeared again several times during the 1980s in late spring and summer, with increased intensity (concentration of cells up to  $70 \cdot 10^6 \text{ dm}^{-3}$  in 1989) and duration (from two weeks up to over the entire summer; Marasović 1990; Kušpilić *et al.*, 1990).

More marked "red tides" developed in conditions of warm and calm weather, independently on nutrient concentrations (Marasović *et al.*, 1991). Thus, these specific events may have been rather caused by changes in oceanographic and/or biological properties of the bay (due to some climatic fluctuations). Consequently, the effects of the existing anthropogenic nutrient loads may be enhanced.

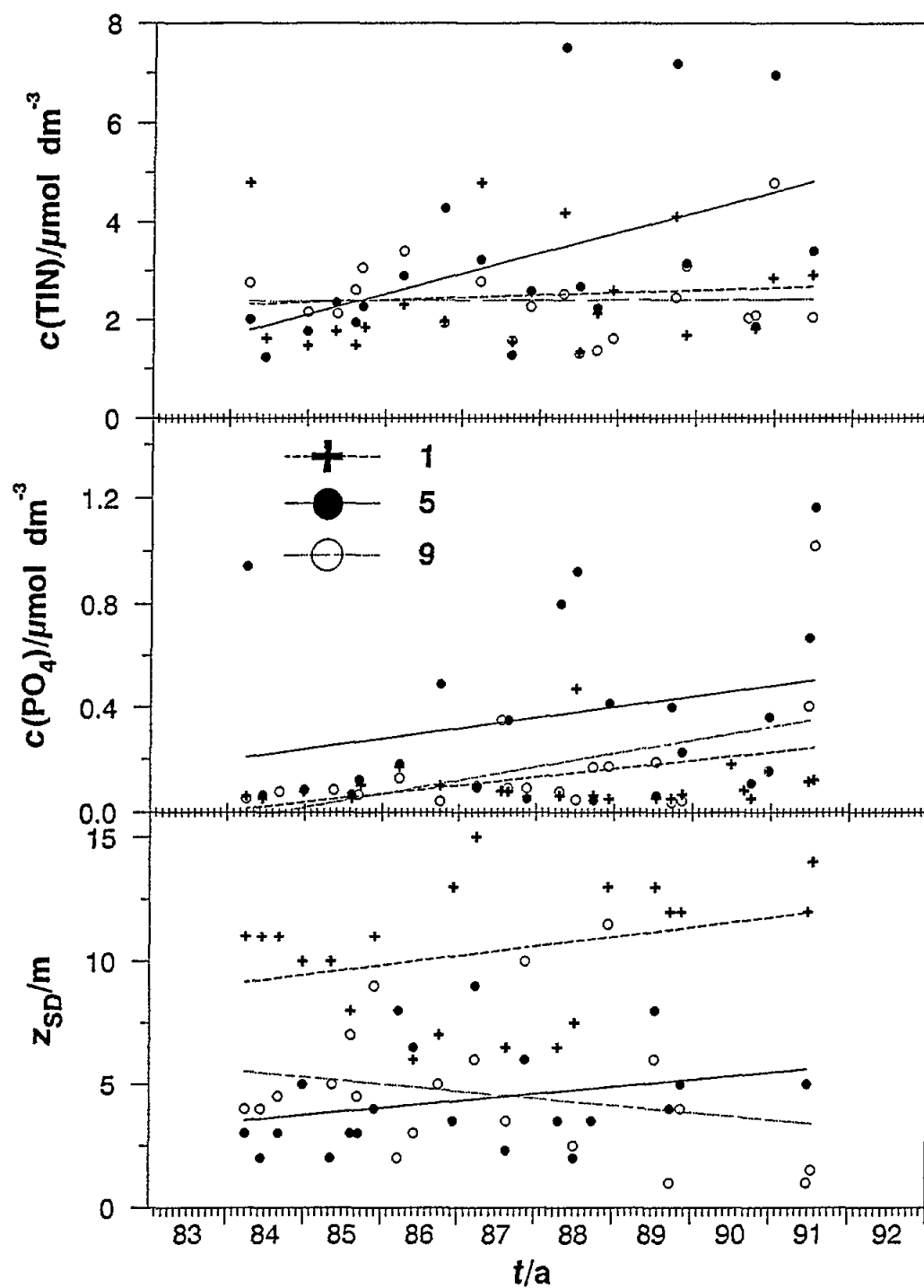


Fig. 4.2.1.3. Temporal ( $t$ ) series of total inorganic nitrogen (TIN) and orthophosphate ( $\text{PO}_4$ ) concentrations ( $c$ ), and water transparency ( $z_{\text{SD}}$ ) in the surface layer of stations 1 (Vranjic area, +), 5 (Split city harbor area, ●), and 9 (Žrnovica Estuary, ○).

#### 4.2.2. Heavy metals

##### *Effluents*

Heavy metal concentrations in effluents from the investigated eastern Adriatic areas did not change significantly during the period 1983-1991.

##### *Suspended matter*

The Cd mass fraction in suspended matter from the Slovenian coastal areas was higher in 1989-1990 than in the preceding period (1983-1988). In contrast, the Hg content has not varied significantly since 1986.

##### *Sediment*

The Hg mass fraction in the Slovenian coastal sediment gradually increased (up to one order of magnitude) during the period 1983-1989. In contrast, the data for the Zadar area indicated a decrease between 1988 and 1991. However, the trend in this area should be verified with additional measurements. In other investigated areas (Rovinj, Šibenik, and Split) the values varied considerably from year to year, but defined trends were not observed. The data available for the Klek-Neum Bay, Dubrovnik, and Montenegrin coastal areas were not sufficient to assess long-term changes of the sediment heavy metal contents.

Evidently, despite the high variability of the data, the average Cd content in the Pula, Šibenik and Split sediments did not change significantly during the investigation period. The data for the other areas were not sufficient to allow some reliable conclusions about long-term changes.

##### *Organisms*

While an increase of the Hg content was noticed in mussels (*Mytilus galloprovincialis*) from the Rijeka and Zadar areas during the investigated period, an opposite trend was evident in the Split area and probably in the Šibenik area, particularly in the two last monitoring years (1990-1991). The decrease in the Split area was clearly related to the interruption of Hg emission after the chloro-alkali plant in Kaštela Bay was closed in 1990. In contrast, no significant long-term changes were observed in the other investigated areas.

The Cd content in the Zadar area mussels was significantly increased during the investigated period (1988-1991). In contrast, long-term changes were not identified in other investigated areas. The available data were not sufficient to assess some trends in the Klek-Neum Bay and Montenegrin area mussels.

Heavy metal monitoring should be continued in eastern Adriatic areas, in which higher levels or trends were evidenced, and related to a possible anthropogenic influence.

#### 4.2.3. Organic pollutants

An extremely high variability of chlorinated and petroleum hydrocarbon, phenol and detergent levels occurred in effluents, coastal and estuarine waters, sediments and organisms of the eastern Adriatic region. Different sampling and analytical procedures were used in various investigated areas. This introduced an additional variability in the data sets.

Data elaboration with different statistical methods has shown that no significant long-term changes of the levels occurred for most of the parameters in the period 1983-1991, both in the eastern coastal areas and in the open region of the northern and central Adriatic. However, due to their variability and an inadequate sampling frequency, the collected data were very probably insufficient to draw reliable conclusions on possible trends of the pollutant levels.

Fortunately, when the results for chlorinated hydrocarbons, obtained in the framework of this programme, were elaborated together with other data collected since the early 1970s by the research group from CMR-Zagreb, some statistically significant changes became evident.

DDT<sub>total</sub> (the insecticide DDT and its analogues DDE and TDE) and PCB concentrations were determined in Rijeka wastewaters in the period 1979-1981 and in 1986 (Picer N. and Picer M., 1992). The arithmetic mean concentrations of both chlorinated hydrocarbon groups were apparently lower in 1986 than in the previous period. However, when the medians and geometric means of the two data sets were compared, this decrease was evident for DDT<sub>total</sub> only. In fact, the PCB median concentration in 1986 was even higher than in 1979-1981. The conclusions based on the arithmetic means were very probably less reliable than those drawn from the comparison of the medians and geometric means, because it was shown that the data distributions were probably not normal.

Regression analysis was used to study long-term changes of DDT<sub>total</sub> and PCB mass fractions, measured in the period 1976-1990 in eastern Adriatic coastal sediments (Fig. 4.2.3.1; Picer M. and Picer N., 1991b). A statistically significant negative correlation occurred for both nontransformed and logarithmic DDT<sub>total</sub> values (indicating a decrease of the level), but the correlation coefficient was higher for the transformed data. In the case of PCBs, the correlation was not significant even when the logarithmic values were elaborated.

Significant negative correlation coefficients were obtained by a linear regression analysis of DDT<sub>total</sub> mass fraction changes in mussels from the western Istrian coastal area and Rijeka Bay during an eighteen year period (1972-1990; Picer N. and Picer M., 1990; Picer M. and Picer N., 1991a). In contrast, for DDT<sub>total</sub> (small negative coefficient) and PCBs (small positive coefficient) the correlations were not statistically significant. The trend of the DDT<sub>total</sub> level in mussels followed an exponential-like function, which could be linearized after a logarithmic transformation of the data. In fact, higher negative correlation coefficient for DDT<sub>total</sub> was obtained from the logarithmic values than in the case when

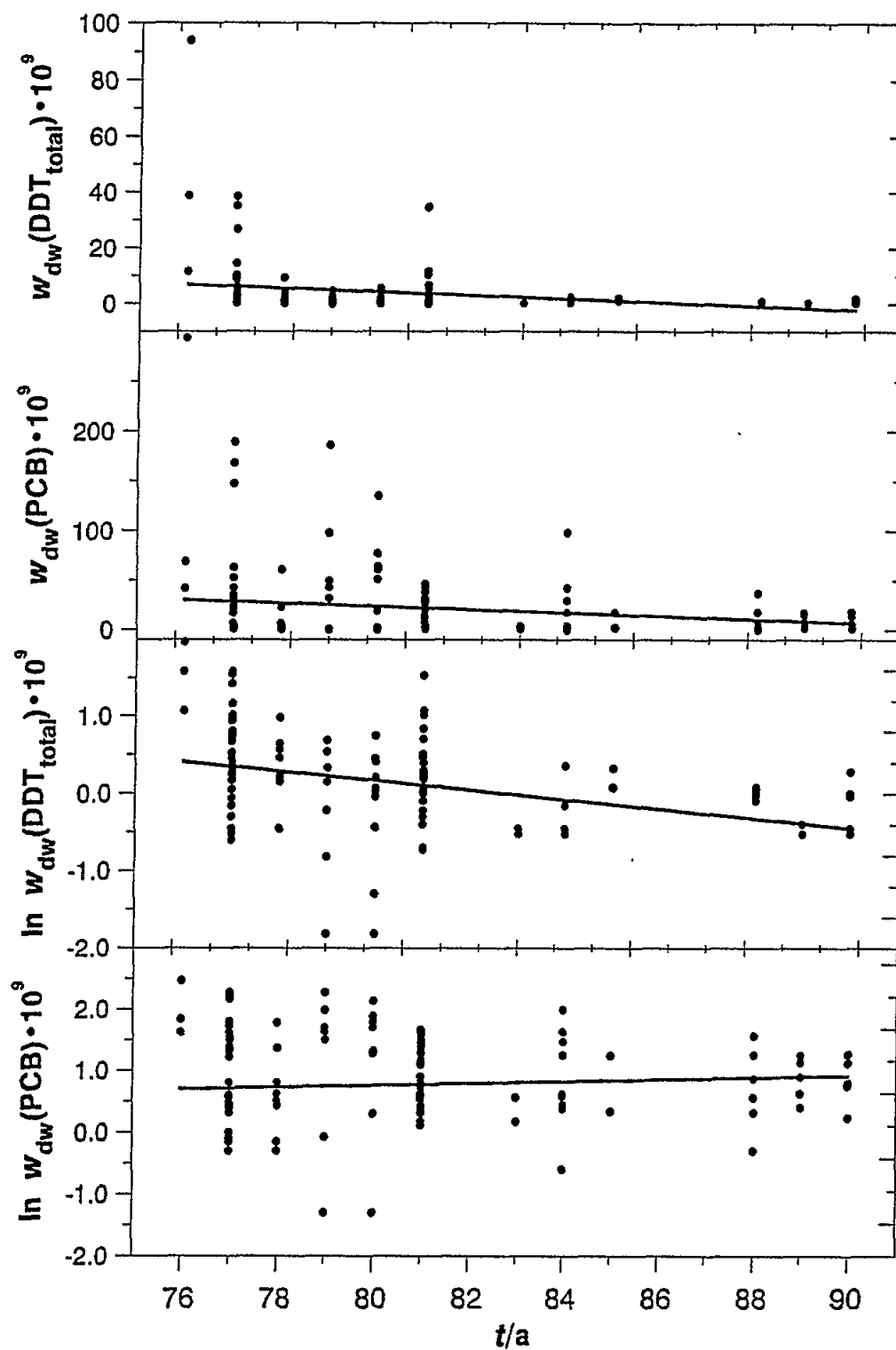


Fig. 4.2.3.1. Linear regression analysis of  $DDT_{total}$  and PCB mass fractions ( $w$ ) in sediments (dry weight) from eastern Adriatic vs time ( $t$ ) in the period 1976-1990.

nontransformed data were used (Fig. 4.2.3.2). However, the coefficient for logarithmic PCB values resulted still not statistically significant.

In Conclusion, the  $DDT_{total}$  level in the eastern Adriatic coastal environment decreased significantly during the last two decades. This was probably due to a reduction of the input from local land sources, because the levels in the open northern Adriatic sediment (probably mainly due to regional and global sources) did not apparently change.

#### 4.2.4. Faecal coliforms

The sanitary quality of beaches in some of the investigated areas were improved during the last monitoring years.

Following a period of several years (1983-1987), during which the water quality in the Rovinj recreational areas did not change significantly, an improvement was observed in the next period (1988-1991; Fig. 3.4.2.1). In this period, the WHO/UNEP criteria were respected at all sampling locations, including those in which significant coliform levels have often been previously measured. This improvement can be related to the reconstruction of the Rovinj existing sewerage and sewage disposal through a new 800 m provisional submarine outfall (Fuks and Devescovi, 1990). The drastic reduction of tourist overnights in 1991 also contributed to preserve high water quality in the Rovinj area.

The water quality of some beaches in the northern and western parts of the Rijeka Bay was higher in 1991 than in the previous years. This was probably mainly due to the reduction of tourist visits. However, in some beaches of the Zadar and Split areas, near the urban centre, the sanitary conditions were also unfavourable in 1991, despite the absence of tourists. However, when the sewerage, treatment plants and disposal systems (provided with long submarine outfalls), which are under construction in all urban and tourist centres along the eastern Adriatic coast, are in operation, a significant improvement of the sanitary quality of the coastal waters can be expected, also in areas next to the harbours, which at present are significantly affected by pollution.



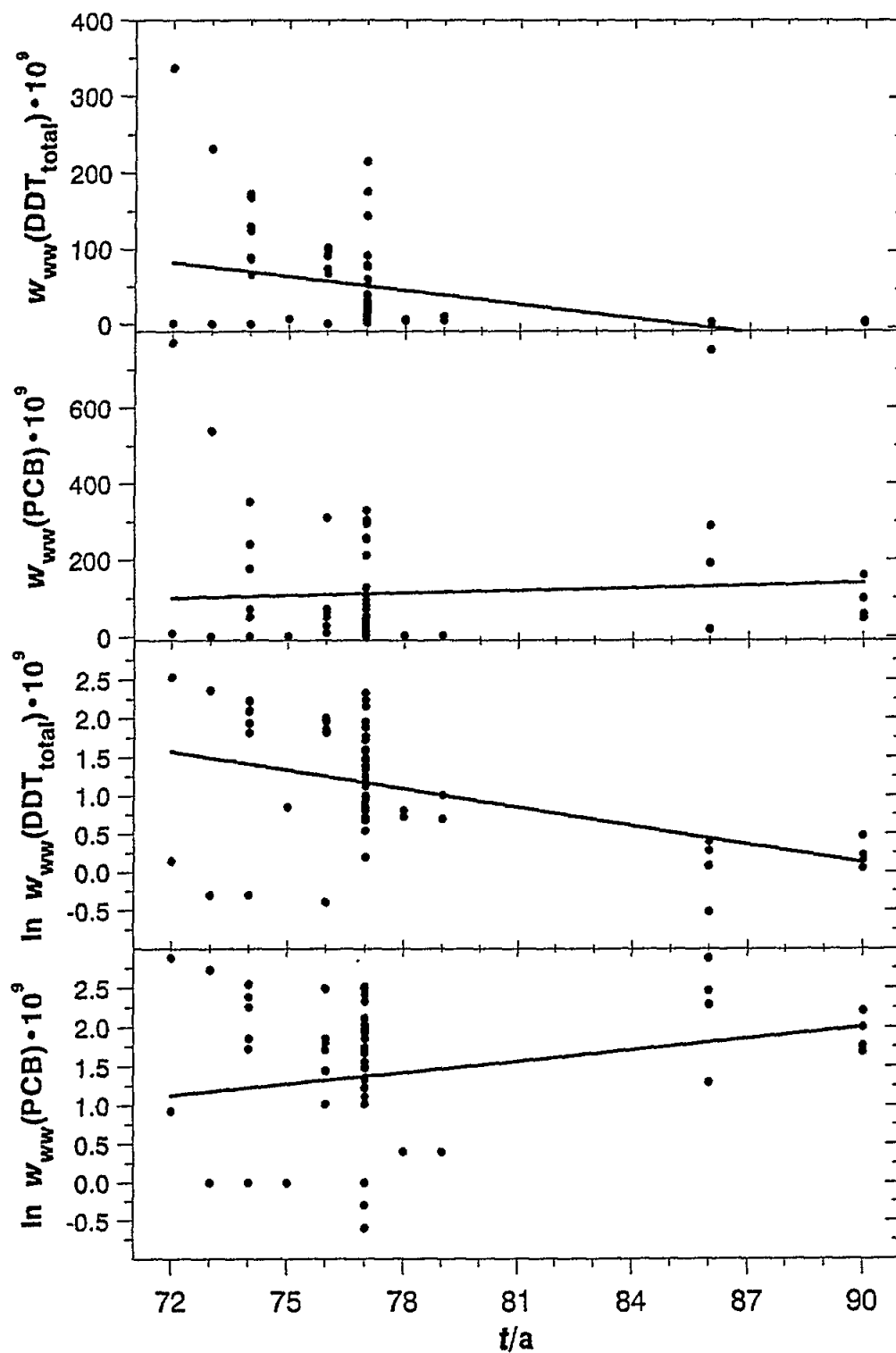


Fig. 4.2.3.2. Linear regression analysis of  $\text{DDT}_{\text{total}}$  and PCB mass fractions ( $w$ ) in mussels (wet weight) from western Istrian and Rijeka areas vs time ( $t$ ) in the period 1976-1990.

### **4.3. Evaluation of the Monitoring Programme**

Different environmental problems are actual along the highly indented eastern Adriatic coast (approximately 2,000 km long) and in the area of about one thousand islands and reefs (with additional 2,200 km of coastline). In some semienclosed embayments (eg Bakar Bay, Kaštela 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 to minimize pollution, and thus, the negative consequences on these same activities.

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

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

Naturally, even when the programme had already been in operation for a decade, some of the activities were still insufficient or inadequate, partly because of limited technical and financial means.

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) provide information on changes in pollutant loads, while the coastal water measurements identify the possible consequences of these changes, which may be different in various marine systems. The effluents on the eastern 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, are an essential and complementary activity in the framework of a monitoring programme. In addition, several processes involving nutrients and pollutants occur in the sewage effluents and at the wastewater-seawater interface, leading to a significant loss from the water phase by various physico-chemical and biological processes. A knowledge of these processes is needed to evaluate with more accuracy the quantities of pollutants actually introduced into the marine ecosystem. Great efforts are needed to monitor industrial wastewater discharge, since the concentration variability is very high, depending on the technological process.

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 concerning effluents (both wastewaters and natural freshwaters), because of the high variability of the values. Related to this, a number of streams and rivers and their estuaries were not included in the monitoring (eg the Mirna, Rječina, Neretva, and Cetina rivers). Furthermore, the number of data for some parameters varied greatly for different sampling areas, which made their comparison difficult.

Finally, the analytical techniques used were not completely standardized and intercalibrated. Sampling and sample storage techniques were also not fully standardized. In some regions some parameters were determined immediately after collection, while in other areas samples were stored frozen and analysed in the laboratories ashore.

These limitations influenced the comparison of the various investigated areas and introduced great difficulties for a quantitative evaluation of the total nutrient and pollutant loads, as well as the eutrophication degree and levels of the most of the pollutants in the eastern Adriatic coastal region. However, results have shown trends, and needs for geographic, parameter and frequency coverage for the design of a future research and monitoring programme, have been identified.

## 5. CONCLUSIONS

To obtain more comprehensive and reliable information on eutrophication and pollution degrees and trends in the eastern Adriatic Sea the data set collected in the framework of this programme was integrated with relevant results obtained during research and monitoring activities conducted since the early 1960s. These activities were primarily supported by national authorities and partly by international research agencies (eg UNEP, UNDP, Environment Protection Agency, National Science Foundation, Smithsonian Institution, Alpe-Adria Osservatorio per l'Alto Adriatico) in the framework of various national and international programmes (eg long-term research in the open northern and central Adriatic, numerous ecological studies, Dalmatian coastal monitoring "Vir-Konavle", collaboration activities with Italian institutions-ASCOP and Alpe-Adria projects).

From the analysis and discussion of this data pool the following conclusions could be drawn:

- A.** a large part of the eastern Adriatic can be considered oligotrophic and unpolluted, particularly the coastal areas distant from the major urban centres and the offshore waters;
- B.** eutrophication has manifested at a regional level in the open northern Adriatic, but the eutrophication degree has not probably change significantly in the last 25 years.

A significant increase in eutrophication of Kaštela Bay (Split area), due to local anthropogenic sources, was documented with data time series collected since the early 1960s. Eutrophication events were observed in restricted areas of the Pula, Rijeka, Šibenik, and Split harbours. Unfortunately, available data series were not sufficient to fully describe eutrophication trends in these zones. Some modification in the marine plankton communities, observed during the 1980s in eutrophied areas (eg the northern Adriatic and Šibenik and Vranjic bays), might be due primarily to climatic changes;

- C.** significant organic and inorganic pollutant contents were determined in restricted areas (harbours of major cities, industrial centres along the coast). However, the levels of most of the pollutants (except petroleum hydrocarbons) were lower than in other Mediterranean coastal areas, both in effluents and marine environment.

The most marked heavy metal pollution was measured in Kaštela Bay. However, a significant decrease of the mercury level in mussels has been noticed since 1990, after a chloro-alkali plant has been closed. In contrast, an increase of the mercury content apparently occurred in sediments of the Slovenian coastal area.

A significant decrease of the DDT (but not PCB) content was statistically evidenced in sediments and mussels from the eastern Adriatic area during the last twenty years. The data available for other organic pollutants (petroleum hydrocarbons, phenols, detergents) were not sufficient for a reliable assessment of long-term changes, because of their high variability;

- D.** faecal contamination was significant along beaches near to harbours and sewage discharge areas. A significant improvement of the water quality occurred in the Rovinj area under harbour influence after a partial diversion of sewage to a new long submarine outfall; and
- E.** local pollution has been mainly generated by inadequate disposal of untreated urban and industrial wastewaters in near coastal zone. The problem will be reduced or eliminated when wastewater disposal systems, provided with long submarine outfalls and required pretreatment of industrial wastewaters, are operating. These systems are under construction in most of the urban centres along the eastern Adriatic coast.

## 6. RECOMMENDATIONS

The achieved results are essential to plan future monitoring activities with defined strategies and goals to improve the management of the eastern Adriatic coastal area.

A. From the present experience some general lines, useful to design operative programmes producing reliable and conclusive results, can be suggested:

- @ The overall objective of the National Monitoring Programme is to provide information necessary to plan measures for marine pollution prevention and control, as well as for management of coastal zones to protect the marine ecosystems and human health.
- @ The National Monitoring Programme should be mainly oriented for managerial purposes, while the main objective of a research monitoring has to be the understanding of the complexity of an ecosystem and establishing appropriate and efficient techniques for monitoring. Particularly, efforts should be made to integrate monitoring data with the knowledge on physical dispersion and biogeochemical processes, with the aim of estimating nutrient and pollutant budgets, as well as their fate and effects in the coastal marine ecosystem.
- @ Areas of priority interest in which a serious pollution problem was identified, or which selected for preservation (primarily the national natural parks), should be listed. Accurate eutrophication and pollution source inventories would be useful for areas ranking. It is also essential to consider those areas (like the Limski kanal, the Raša and Maloston bays, and the Krka River estuary) that have unique natural characteristics, but at the same time were designed for economic exploitation, often with contrasting activities (eg tourism or port activities concurrent with mariculture). Furthermore, the monitoring of the northern Adriatic open waters, which significantly influence the western Istrian coastal area, should also have a high priority.
- @ It is advisable to carry out initial screening prior to embarking on a monitoring programme.
- @ Only parameters proven to give significant and reliable results can be considered and selected in relation to the specific environmental problem of each investigated area.
- @ Selected parameters must be monitored with frequencies adapted to their time variability in the selected areas. As an example, the measurement frequency might vary from daily to seasonal, each year or periodically with interruptions of several years.
- @ An optimal number of stations, parameters, and samplings for each area must be determined, below which the measurements should not be performed at all because they may not give significant results.

- @ Standardization and intercalibration of sampling techniques and analytical methods should be continued at various levels: from regional (primarily sponsored by UNEP) to local (among eastern Adriatic laboratories), taking care of methodology improvements and tending to a common sampling protocol. In fact, only previously intercalibrated procedures should be accepted in the monitoring programme.
- B.** The activities within the National Monitoring Programme should fall into two categories: (a) monitoring for compliance purposes, and (b) monitoring for status and trends, including changes in the ecosystem, especially in relation to biodiversity.
- (a) The following monitoring for compliance purposes would be organized:
- @ Monitoring of land-based sources of pollution to assess the inputs of contaminants into the marine environment, complying with the provisions of the LBS Protocol, the national standards for quality of waste water, and international standards.
  - @ Monitoring of sanitary quality of beaches to protect human health, complying with the national standards for quality of bathing waters.
  - @ Monitoring of impacts of fin-fish mariculture on the marine environment, complying with national standards which should be developed.
  - @ Monitoring of shellfish mariculture sites to protect human health, complying with the national standards on presence of toxic phytoplankton species, which should be developed according to international criteria and the national criteria on sanitary quality of coastal waters for shellfish mariculture.
- (b) The following objectives of monitoring status and trends are identified as:
- @ Evaluation of eutrophication trends and effects, particularly on the oxygen budget and phytoplankton, zooplankton and benthic communities (abundance and species composition).
  - @ Identification of hot spot areas to be monitored on a long-term basis in respect to priority pollutant level changes, particularly in commercial marine organisms and their possible deleterious biological effects.
  - @ Monitoring of changes in the ecosystem and biodiversity trends, including phenomena of unusual intensity (eg mucilage hypertrophy, near anoxia or anoxia events, organism invasions and appearance of undesirable species).

**C.** To make the future monitoring activities operative, the following recommendations are suggested:

- @ An organization structure able to use monitoring results, to design and carry out additional activities essential for the understanding and interpretation of pollution state and trends should be established. For instance, the Ministry of Civil Engineering and Environmental Protection could establish a Steering Committee (management group) for the National Monitoring Programme, which should consist of representatives from governmental bodies (ministries), main institutions participating in the monitoring programme and end-users of monitoring data. A number of selected international experts could be associated members of the Steering Committee. The Steering Committee could set up a series of working groups on specific topics to implement the monitoring strategy and to coordinate all programmes within the National Monitoring Programme.
- @ An information system and organization of data exchange that will enable the creation of a data base structured for fast and useful responses on pollution events on different time scales, including accidents and long-term changes, should be elaborated.
- @ Basic research of mechanisms and processes connected with eutrophication, pollution and unusual events identified during monitoring should be encouraged.
- @ New techniques of data acquisition (eg remote sensing - satellites, moored sensors) should be introduced.
- @ Development and/or participation in international projects relevant for the environmental protection of the Adriatic Sea are strongly recommended.





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## ANNEX I

### PARTICIPATING INSTITUTIONS 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 the 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 in the Centre is focused on:

- @ research of suspended organic matter of various origins;
- @ phytoplankton blooms;
- @ ecological and physiological marine organisms monitoring; and
- @ ecology and biocoenosis 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 been affiliated to the "Ruđer Bošković" Institute in Zagreb since 1969. CMR-R is involved in basic research in marine biology and oceanography of the Adriatic Sea as well as pollution monitoring and mariculture development. In particular, the following activities are being carried out at the present time:

- @ research of the processes within and between trophic levels (primary and secondary organic production, the cycle of biogenic elements);
- @ studies of water masses dynamics;
- @ flora, fauna and biocoenosis (taxonomy, ecology and biocoenosis in clean and polluted environments);
- @ ecological, physiological and genetical research of marine organisms (basic physiological and biochemical characteristics of marine organisms and effects of pollution);
- @ pollution and sanitary water quality monitoring;
- @ eutrophication studies; and

@ 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 sea water have been included in long-term investigation programmes since 1972. Such investigations, financially supported by the Ministry for Scientific Research of Croatia, other national sources and international organizations (eg 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".

**Public Health Institute of the Republic of Croatia (PHIR-C)** started operation in 1927 as the Institute of Hygiene. Today professional work is done by its five components:

1. Epidemiological Service
2. Sociomedical Service
3. Microbiological Service
4. Health Ecology Service
5. Administration

The waters and Water-Supply Control Department is a part of the Institute's Health Ecology Service and its activities include, among other, groundwater, fresh water and seawater research and monitoring. Protecting Croatia's water supply systems is another of its charges. PHIR-C also provides training in laboratory water monitoring methods.

**The Institutes of Public Health in Pula, Rijeka, Zadar, and Split (IPH-P, IPH-R, IPH-Z, IPH-S)** were founded in 1939, 1926, 1945 and 1933 respectively and are organizations whose main activities are connected to the research and development of public health. Some of them collaborate with the Faculty of Medicine and the World Health Organization. The institutes have participated in various basic and applied research concerning public health and environment protection. For example, they have participated in the programme "Jadran-III" with the aim of acquiring data on environmental pollution (sea water 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 other organization programmes.

**The Faculty of Civil Engineering Sciences of the University of Zagreb (FCES-Z)** was founded in 1919. Together with 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 post graduate levels in the area of civil engineering. The Department for Hydrotechnics of the Faculty carried out activities covering hydrotechnical 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 solving problems of wastewaters disposal into the sea. It is for these reasons that the Faculty was included in this programme and has carried out investigations of wastewater quality in the Rijeka area.

**The Faculty of Chemical Engineering and Technology of the University of Zagreb (FCET-Z)** was founded in 1919 and has a long tradition in education concerning chemical engineering and technology at graduate and postgraduate levels. Apart from education scientific and applied research in chemistry, physical chemistry, analytical chemistry, chemical engineering and technology is performed. Problems dealing with environmental protection against pollution are of great interest at several faculty departments. From 1988 FCET-Z has been included, instead of the FCES-Z, in the present programme, taking part in investigations of wastewater quality in the Rijeka area.

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

- @ research of the natural characteristics and impact on natural waters, research of physical, chemical and biological parameters and pollution monitoring at selected oceanographic stations in the Adriatic, particularly in the northern Adriatic and Šibenik areas;
- @ research of 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 of 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;
- @ ecological modelling and computerized elaboration of experimental data;
- @ research and development of aquaculture, intensive growing of fish and shellfish in

freshwater, estuaries and sea water; and

@ development, application and automatization 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, 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 other undergraduate and postgraduate studies 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; and
- @ 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 in solving pollution problems in smaller areas. IOF-S owns the research vessel "Bios".

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

**Biological Institute in Dubrovnik (BI-D)** was founded in 1948 with main activities concerning biological oceanography, terrestrial botany and ornithology. Its primary research activities are focused on systematics, ecology and biomass of zooplankton. These studies include research on the effects of some pollutants on zooplankton populations and on some zooplankton species.

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

**The Institute for Subtropical Cultures and Environment Protection at Bar (ISCEP-B)**

was founded in 1937 and is the oldest scientific institution of Montenegro. Its activities concern *inter alia* studies on chemical processes in natural waters, soil and foodstuff, in particular:

- @ determination and study of decaying processes of pesticides, polychlorinated biphenyls, heavy metals in natural and polluted waters, organisms and sediment; and
- @ studies on pollution processes by phenols, oil and oil products, and detergents in natural waters.

The ISCEP-B is affiliated to the Agricultural Institute of the "Veljko Vlahović" University in Titograd.



## **ANNEX II**

### **SAMPLING AND ANALYTICAL METHODS**

#### **1. Basic parameters, nitrogen and phosphorus**

##### **1.1. Basic parameters, nitrogen and phosphorus in effluents**

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

Appropriately diluted samples for BOD<sub>5</sub> determination were incubated at 20°C for five days, and the oxygen changes were measured with a Winkler titration technique, COD was determined refluxing samples with a mixture of dichromate, sulphuric acid and mercuric sulphate for two hours, and the back titration of dichromate with standard solution of ferrous ammonium sulphate. The results are expressed in an equivalent oxygen consumption.

The total suspended solids were determined by weighing, after filtration, the samples through Milipore HA membrane filters (0.45 µm pore size) and drying at 105°C.

Total nitrogen was analysed in the Rijeka and Split samples by a Kjeldahl-type treatment of samples by analysing 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 by 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-meter and glass electrode.

##### **1.2. Basic parameters, nitrogen and phosphorus in sea water**

Basic hydrometeorological observations were performed with standard WMO techniques (Anon., 1959; 1962). The sea temperature was measured with Richter and Wiese reversing thermometers, fixed on PVC Niskin bottles used to collect water samples for chemical analyses.



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

Salinity was measured in the laboratory on shore with a high precision Beckman RS-7 bench salinometer. 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 metres and glass electrodes.

Nutrient concentrations were determined with spectrophotometric methods commonly used in oceanography (Strickland and Parsons, 1972). Reactive phosphorus was analysed with a molybdenum blue technique with ascorbic acid as reducing reagent (Murphy and Riley, 1962). Ammonia of Krka estuary and Split region samples was analysed with a phenol hypochlorite method with sodium nitroprusside as a catalyst and citrate as a complexing reagent (Solorzano, 1969 and Head, 1971, respectively). Northern Adriatic and Limski Kanal samples were analysed using a modification of this method (Ivančić and Degobbis, 1984). Nitrite was measured as a pink azo dye obtained after reaction with sulfanilamide and N-naftil-ethylenediamine (Bendschneider 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 analysed 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 Šibenik 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 waste, estuary and sea waters**

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, filtered (1.0 µm GF/C Whatman glass filters) and the heavy metal content was determined in both solution and suspension. CMR-R determined Hg in effluents using cold vapour atomic absorption spectrophotometry (CVAAS) after digestion of the samples with a mixture of KNO<sub>3</sub> and KMnO<sub>4</sub> (Horvat *et al.*, 1986), while Cd was determined with AAS in samples digested with HNO<sub>3</sub>. IPH-P determined Cd and Hg in waste waters with AAS and CVAAS, respectively, after sample digestion with a mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. FCES-Z and FCET-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<sub>3</sub> in presence of H<sub>2</sub>O<sub>2</sub>. IPH-S determined Hg with CVAAS (Anon., 1980a) while Cd, Zn, Cr and Pb were determined by AAS.

CMR-Z and BI-D in Šibenik 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 a Perkin-Elmer model 410 (Martinèæ 1981; Martinèæ *et al.*, 1980b; Plavšič *et al.*, 1982; Martinèæ *et al.*, 1985a; Branica *et al.*, 1985). The samples were collected by diver into 1000 ml Nansen bottles (CMR-Z) or into 500 ml Nalgene bottles fixed on a fibreglass handle (BI-D). Special care was taken to avoid contamination of samples. Immediately after the sampling samples for Hg analysis were acidified with redistilled supra-pure HNO<sub>3</sub> to pH 2, while those for the determination of "ionic" Zn, Cd, Pb and Cu were analysed 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 using 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

During the 1983-1990 period heavy metals in suspended particles were measured only in the Slovenian coastal area (MBS-P). Sea water was sampled with Niskin bottles (Forstner and Wittman, 1983). Suspended particles were separated by filtration on 0.45 µm Millipore HA filters prewashed in 1% hot HNO<sub>3</sub>. The filter content was destroyed through a wet procedure in PTFE vessels according to UNEP/FAO/IAEA, 1983. For estimation of heavy metal sedimentation flux "sediment traps" were used. Cylindric jars with 4 cm aperture, height/width ratio of about five (Blomqvist and Kofoed, 1981) fixed approximately 1 m above the sea bottom to reduce resuspension. Suspended particles were collected at station F at 24 h intervals during June, August and October 1990 for the surface and the bottom layer. The total quantity of suspended particles was determined gravimetrically on Whatman GF/C 1.2 µm glass fibre filters through a modified method of Banse *et al.*, (1963). Filters were decomposed through a wet procedure (with HNO<sub>3</sub>) and metal concentrations (Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn) were measured with a Varian AAS (Model 1250 A) with hydrogen continuum lamp correction, using flame (FL), electrothermal (ETAS-CRA) and cold vapour technique (CVT).

### 2.3. 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 subsamples 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  $\text{HNO}_3$  and  $\text{HClO}_4$  (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.

In the Slovenian coastal area sediment samples were not analysed in 1990 and 1991. *In situ* heavy metal sedimentation flux (using "sediment traps") was measured instead for the assessment of heavy metal mass balance in the ecosystem in 1990 (procedure described in the chapter 2.2. of this ANNEX).

Sediment samples from the Rovinj coastal area were prepared for metal analysis with a wet sieving procedure through a 250  $\mu\text{m}$  nylon net. Hg and Cd contents were determined through the NAA method after sample and standard treatment in a neutron flux of  $2 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$  over 15-20 hours in a Triga Marck II reactor. After wet digestion and carbamate extraction  $^{115}\text{Cd}$  was separated (Dermelj et al., 1977, 1979), while  $^{197}\text{Hg}$  was separated in the gaseous phase and afterwards selectively tied to Se (Byrne and Kosta, 1974). Heavy metal mass fraction data from this area are not available for 1990 and 1991.

In the sediment from the Budava and Raša Bays Cd and Hg mass fractions were determined through the AAS method after wet digestion with a mixture of  $\text{HNO}_3/\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  and HF.

Sediment samples from the Zadar coastal area (0-2 cm layer) were collected by SCUBA divers. Cd content was determined through the flame AAS technique (Perkin-Elmer AAS model 630) after sediment destruction at  $450^\circ\text{C}$  (Gorusch, 1970). Hg content was determined through the AAS flameless technique (CVT, Pye Unicam AAS model SP-90) after wet sediment digestion with a mixture (10:1) of concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  (Price, 1972).

In the Šibenik area sediment samples were collected by SCUBA divers (Kniewald et al., 1987) using an acrylic glass tube ( $\phi = 6 \text{ cm}$ ;  $l = 15 \text{ cm}$ ). Under clean bench conditions the  $<75 \mu\text{m}$  granule fraction was separated by wet sieving using sea and brackish water. Sediment samples were dried until constant weight in a clean bench atmosphere at room temperature. The dry sample, 0.2-0.5 g in weight, was destroyed with a mixture of concentrated acids (0.5 ml  $\text{HClO}_4$ , 5-10 ml  $\text{HNO}_3$ , 5-10 ml HF) in closed Teflon containers at  $160^\circ\text{C}$ . For Hg analysis, 1-2 g of sediment were destroyed in a quartz still with cut stoppers. The stoppers were tightened to avoid the loss of Hg during digestion in a mixture (9:1) of concentrated  $\text{HNO}_3$  and  $\text{HClO}_4$  at  $200^\circ\text{C}$  for 1.5 hours. The acids were redistilled before use. Hg content was determined by flameless AAS (Perkin Elmer AAS model 410). The mineralized sediment samples were analysed for Cd content through an electrothermal AAS method (Perkin Elmer AAS model 3030 with HGA 400 and AS-1). Due to the matrix effect, for Cd and Pb analysis through AAS the L'vov procedure was adopted (Martinèiæ et al., 1985a).

In the Split, Vis and Klek-Neum areas, sediment samples (0-5 cm) were collected from the RV "Bios" using a gravity 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 recommended procedures (UNEP/FAO/IAEA, 1983). Up to 1990 total Hg and Cd contents were determined through an NAA at JSI-Lj (Zvonariæ and Stegnar, 1987) as described for the Rovinj area samples. In 1991 total Cd, Pb, Cu and Zn were determined in IOF-Split through electrothermal AAS (Perkin Elmer AAS model 1100B with HGA 700 and AS-70) method. Samples were degraded through wet procedure in a mixture (10:8:4) of concentrated HNO<sub>3</sub>, HF and HClO<sub>4</sub> (Juretiæ et al., 1992).

Sediment samples from the Dubrovnik area were collected and metal mass fractions determined as described for the Šibenik area.

Heavy metals in sediments from the Montenegrin coastal area were sampled with a grab sampler and determined through an AAS (Pye Unicam model SP 9) method after digestion, similar to the biological material analysis.

#### 2.4. 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 (1976) and UNEP/FAO/IAEA (1983) procedures. Two fish muscle tissue parts of a single specimen were analysed. Hg and Cd contents were analysed in two samples separated from the composite sample consisting of the homogenized edible part of 10 mussels. The determination of the metal mass fraction was carried out through the AAS method on a Varian CRA and CVT system.

Hg and Cd were the heavy metals which were most often determined in shellfish. Analyses were carried out in the following institutes, Marine Biological Station Piran (MBS-P), Centre for Marine Research Rovinj (CMR-R), Health Protection Institute Pula (IPH-P), Health Protection Institute Rijeka (IPH-R), Health Protection Institute of the Republic of Croatia Zagreb (IPHC-Z), Institute of Public Health Zadar (IPH-Z), Centre for Marine Research Zagreb (CMR-Z), Institute of Oceanography and Fisheries Split (IOF-S) and Institute for Marine Biology Kotor (IMB-K).

In the Rovinj coastal area, mussel samples for Hg and Cd determination were deep-frozen immediately after sampling and stored until analysis. First, biometry data were determined, and afterwards a sample of 30 mussels was prepared from the soft tissue out of which two subsamples were used for metal analysis. Up to 1990 Hg and Cd were determined through the NAA method (at JSI-Ljubljana), as described in the sediment methodology for the area. In 1991 Cd mass fraction was determined by flame AAS, subsamples being previously destroyed through dry combustion at 480 °C. Mercury content was determined by AAS (CVT), the organic matter being previously destroyed through wet procedure (Price, 1979).

In Budava and Raša Bays mussel samples were collected from commercial growing areas. Hg and Cd mass fractions were determined through the same methodology applied for the Rovinj area.

In the Rijeka Bay area, mussels were collected from two stations. In the laboratory, immediately after biometry data determination, the edible mussel part was separated and

homogenized. An aliquot of the homogenate was decomposed at 450°C for Cd content determination (UNEP/FAO/IAEA, 1983) by flameless AAS (Pye Unicam SP-1900). For Hg determination, an aliquot of the homogenate was digested with a mixture of concentrated HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. Hg was analysed through the AAS flameless technique - CVT (Anon., 1980a).

In mussel samples collected from the Zadar area Cd was analysed through the flame AAS technique after homogenate decomposition at 450°C and dissolving in 1.5 M HCl, while Hg content was determined through the flameless AAS (CVT on Pye Unicam SP-90), after homogenate digestion with a mixture (10:1) of concentrated HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (Price, 1972).

In the Šibenik area, 25 mussels (5-6 cm length) were sampled. The edible part was separated from the shell, weighed and homogenised in a mixer. A 0.5-1.0g homogenate was digested for cca 15 minutes at 120°C in closed Erlen-Meyer quartz bottles to which 2-4 ml of concentrated HNO<sub>3</sub> and 0.5 ml of concentrated HClO<sub>4</sub> were added. Hg was determined by flameless AAS (after Hg concentration on a gold wire) by Perkin-Elmer AAS model 410. Methyl Hg was, after isolation, determined through CVT (Horvat *et al.*, 1988).

In the coastal zone of the Split and Klek-Neum areas mussels were sampled manually, stored in polyethylene bags and deep-frozen until analysis. The samples were treated at JSI-LJ according to UNEP procedures (UNEP/FAO/IAEA, 1983). The Hg mass fraction was determined by CV AAS (Horvat *et al.*, 1988). Cd was analysed as described for sediment analysis in the Split area.

Mussel and plankton samples were collected in Maloston Bay, the Pelješac Channel and the Dubrovnik area. Oysters, *Ostrea edulis*, were sampled only in Mali Ston Bay. The samples 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<sub>3</sub> (4 ml) and HClO<sub>4</sub> (0.5 ml). Plankton samples were collected with a plankton net (200 µm pore size) dragged horizontally in the surface layer (0-5 m) at 2 Nm speed for 15-30 min. Aboard the samples were stored in 500 ml polyethylene bottles at 6±2°C and stored deep-frozen in laboratory until analysis. Before analysis the samples were dried until constant weight was achieved. A 200 mg sample was digested with concentrated HNO<sub>3</sub> and HClO<sub>4</sub>. In mussels, oysters and plankton Cd, Pb and Cu were analysed through an electrothermal AAS (Perkin Elmer AAS model 3030, HGA-40 and AS-1) method. Zn was analysed by FAAS using a Perkin Elmer AAS model 5000 and AS-50, while Hg, concentrated on a gold wire, was analysed by the flameless AAS technique using a Perkin Elmer AAS model 410 (Martiniæet al., 1985b).

Heavy metals in the biological material from the Montenegrin coastal area were determined through an AAS (Pye Unicam SP 9) method upon digestion of the homogenized samples in quartz bottles with a mixture (25:1) of HNO<sub>3</sub> and HClO<sub>4</sub>.

### 3. Organic pollutants

#### 3.1. Chlorinated hydrocarbons

Chlorinated insecticides and polychlorinated biphenyls were determined through 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 (Kerkkoff *et al.*, 1982).

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 analysed chlorinated hydrocarbons in biological material and sediment samples after Soxhlet extraction with n-hexane (Fossato *et al.*, 1982). 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 filtered about 2.5 liters of samples through a glass fibre, Whatman GF/C filter paper, by using a modified commercial apparatus for ultrafiltration (Picer N. *et al.*, 1986). The filtrate was twice extracted by 60+40 n-hexane (fluorescence grade), solid phase was freeze dried and extracted with n-hexane in Soxhlet apparatus for eight hours.

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

PHI-R analysed chlorinated hydrocarbons in mussels after Soxhlet extraction, H<sub>2</sub>SO<sub>4</sub> cleaning and florisil separation.

#### 3.2. Phenols

Volatile phenols in wastewater samples were determined by a standard 4-aminoantipyrine method. Quantification was performed through spectrophotometry after distillation and reduction with 4-aminoantipyrine and chloroform extraction of acidified water samples. The parameter was analysed in four laboratories. IPH-P, FCES-Z, FCET-Z and ISCEP-B used the standard USA method (Anon., 1975), while IPH-S used the method of the Yugoslav Federal Institute of Public Health (Anon., 1961).

### 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 by nitrogen stream in a Vickbold concentrator (Kozarac *et al.*, 1975). This preconcentration step also gives separation of anionic detergents from other interference materials. Other laboratories used direct chloroform extraction with certain modifications. MBS-P, IPH-P, FCES-Z, FCET-Z and ISCEP-B adopted the standard USA method (Anon., 1975), while IPH-S used the procedure for anionic detergent determination described in the German literature (Höll, 1970).

### 3.4. Petroleum hydrocarbons

Petroleum hydrocarbons were determined by three different methodological approaches.

Infrared spectrophotometry was used for petroleum hydrocarbon determination in wastewaters collected in the Rijeka area. Lipoid organics were extracted by 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 (1982; 1984). Some improvements on this method were described and applied during water sample analysis in the Šibenik and Kornati Islands areas (Picer M. and Hocenski, 1982; Picer M., 1984; Picer M. *et al.*, 1986c, Picer M. and Picer N., 1992; 1993a). 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 (1984).

#### **4. Faecal coliforms**

Sea water samples were taken with sterile glass samplers (30-50 cm below the surface of the sea) 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 analysed within six hours.

Effluent samples were taken 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 a 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 (UNEP/WHO, 1983a). The colonies produced by faecal coliforms were blue. The same procedure was adopted for samples inoculated on liquid media and shellfish meat (UNEP/WHO, 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 (UNEP/WHO, 1983b).





## **ANNEX III**

### **QUALITY ASSURANCE IN MONITORING PROGRAMMES OF THE EASTERN PART OF THE ADRIATIC SEA**

Monitoring, in the assessment and protection of the marine environment, has been defined as the repeated measurement of an activity or a contaminant or of its direct or indirect impact (Joanny, 1990).

The eastern Adriatic monitoring was carried out through the following projects:

- @ Land-based sources of pollution, and
- @ Long-term programme of Pollution Monitoring and Research in the Mediterranean sea (MED POL),

concurrently with an open water monitoring in the framework of the Adriatic Scientific Cooperation Programme (ASCOP).

The objectives common to these three projects were:

- @ collection of reliable data on the level of contaminants in the Adriatic Sea;
- @ description of spatial and temporal (seasonal and long-term) changes or trends of pollution; and
- @ data evaluation in agreement with nationally and/or internationally accepted environmental criteria.

Quality assurance (QA) is an essential part of any monitoring programme. The objective of the QA programme for analytical measurements is to reduce measurement errors to tolerable limits and to provide a mean of ensuring that the measurements generated have a high probability of being of acceptable quality (Taylor, 1981). In quality assurance two concepts are involved:

- @ quality control (the mechanism of minimizing errors) and
- @ quality assessment (the mechanism of verifying that the errors are in the state of statistical control).

Applicability of monitoring data depends on their quality measured in terms of reliability, which depends on precision (reproducibility) and accuracy (true value; Taylor, 1987). The participating laboratory defines the precision of its own results by internal measures, ie repetitive measurements, internal test samples, control charts, interchange of operators and equipment. The accuracy of the results is evaluated applying (Taylor, 1987):

- @ analysis by as many different and independent methods, analysts and techniques as possible;
- @ control analysis with certified reference materials (CRMs) of known matrix and composition; and
- @ participation in intercomparison runs with the samples of composition similar to the environmental samples.

In the period from 1983-1991 the Quality Assurance/Quality Control Programme (QA/QC) was implemented into the ongoing monitoring programmes in the eastern part of the Adriatic Sea by means of:

- @ calibration and maintenance of the equipment;
- @ validation of the accuracy of the analyst(s) with the CRMs of disclosed content of analyte(s); and
- @ validation of the applied methodology with the CRMs or SRM (standard reference material produced by US NIST- former NBS) of undisclosed content of analyte(s), at two concentration levels. The intercalibration runs were conducted with the available and congruent certified samples, CRMs and SRMs, produced by US EPA, SAGAMI, IAEA MEL, US NIST.

### **Land-based sources of pollution - *Basic parameters of waste waters***

Since 1990 the Ministry of Agriculture and Forestry, Water Management Department of the Republic of Croatia has initiated certification of their laboratories. The laboratories that satisfy defined criteria received the license to measure basic chemical parameters and/or certain harmful and toxic substances in effluents, surface waters, ground waters and sea water. As part of the network of 45 Croatian certified laboratories, those which participate in MED POL Programme participated as well in the intercalibration exercises, which were conducted by the certified reference laboratory, Centre for Marine Research Zagreb, "Ruđer Bošković Institute (CMR-Z), in order to verify the accuracy of the applied methodology for measuring basic parameters in waste waters. In 1991 the analytical performance of the basic parameters of waste water was evaluated with the US EPA CRMs for total suspended solids (TSS), chemical oxygen demand (COD), biochemical oxygen demand (BOD<sub>5</sub>). The results were evaluated by the certified reference laboratory CMR-Z and the US EPA experts. A critical evaluation of the intercalibration results achieved during 1991 by all participant laboratories is presented in a Report (Raspor and Kozarac, 1992).

Among certified laboratories included in the intercomparison run for selected basic parameters of waste water were seven laboratories that participate in the MED POL Programme:

- @ Public Health Institute of the Republic of Croatia (IPHC-Z)
- @ Institute of Public Health, Pula (IPH-P)
- @ Institute of Public Health, Rijeka (IPH-R)
- @ Institute of Public Health, Split (IPH-S)
- @ Institute of Public Health, Zadar (IPH-Z)
- @ Faculty of Civil Engineering Sciences, University of Zagreb (FCES-Z)
- @ Reference Laboratory, Centre for Marine Research Zagreb, Ruder Boskovic Institute (CMR-Z).

The results of the intercomparison run with the US EPA CRMs are presented in Tables 1 to 3 and the acceptance of the results in Table 4.

During 1992 analytical performance has been evaluated for the additional basic parameters of waste waters, ie pH, orthophosphate and total phosphorous, ammonium, nitrates and total nitrogen, with the US EPA CRMs. A critical evaluation of those results was presented in a Report (Raspor and Kozarac, 1993).

### **Long-term Programme of Pollution Monitoring and Research in the Mediterranean sea (MED POL)**

Since 1973, the Monaco Laboratory of IAEA has organized regular intercomparison exercises on a worldwide and regional scale. In 1973, the development of intercomparison exercises on trace metal analyses in marine biota and sediments were started. Laboratories that are a part of the MED POL network were supported with the appropriate methodology, reference material, calibration standards to participate in the intercomparison run. Marine Environmental Studies Laboratory acts as a specialized coordinating Centre for the Regional Seas Programmes and is the Regional Analytical Centre for MED POL. In the report issued by IAEA MEL (Mee *et al.*, 1993) evaluation of analytical data quality for the MED POL Programme over 19 years (from 1973-1993) is presented. The success of these endeavours however, is still measured by the degree to which the participating institutions are willing to validate their data and the quality of the data eventually submitted (Mee *et al.*, 1993).

The intercomparison exercises by IAEA MEL are conducted by taking a very large single sample of an appropriate environmental matrix, freeze drying, homogenizing and distributing it among approximately 250 institutions. The initial processing of the sample is not a trivial matter since it may consist typically of about half a ton of raw material. This is generally freeze-dried commercially, ground and sieved in Monaco and then homogenized for at least 100 hours in a purpose-built stainless steel rotary homogenizer. The material is then packed and random samples are taken (usually ten) for homogeneity testing. Each of these samples is analysed ten times for each selected analyte. The resulting data set (100 analyses per analyte) are then analysed statistically in order to check the degree of homogeneity of the sample. The data reported by the participating institutions in the intercomparison run are statistically analysed. After exclusion of outliers for the data set the consensus median/mean values are defined (Mee *et al.*, 1993).

**Table 1.** Results ( $x_i$ =single value of measurement;  $\bar{x}$ =mean value;  $s$ =standard deviation) achieved during the 1991 intercomparison run in those certified Croatian laboratories that also participate in the MED POL Programme. Two different concentrations ( $c$ ) of total suspended solids (TSS) in the two US EPA CRMs (WP023) were evaluated.

		c(TSS)/mg dm <sup>-3</sup>			
		Sample 1		Sample 2	
US EPA:	True value	90.7		29.2	
WP023:	Acceptance limits*	83.1-95.6		24.0-32.4	
	Warning limits**	84.7-94.1		25.1-31.4	
Certified**** laboratory	c(TSS)/mg dm <sup>-3</sup>			Remark on the acceptance of x***	
		Sample 1	Sample 2	Sample 1	Sample 2
PHIR-C	x <sub>i</sub>	116.5; 141.2	27.8; 26.4		
	$\bar{x}$	128.9	27.1	-	+
	s	17.5	1.0		
IPH-P	x <sub>i</sub>	89.6; 90.5	28.0; 28.1		
	$\bar{x}$	90.1	28.0	+	+
	s	0.7	0.1		
IPH-R	x <sub>i</sub>	89.2; 91.2	28.2; 28.8		
	$\bar{x}$	90.2	28.5	+	+
	s	1.4	0.4		
IPH-S	x <sub>i</sub>	95.6; 94.0	29.4; 28.4		
	$\bar{x}$	94.8	28.3	(+)	+
	s	1.1	0.7		
FCES-Z	x <sub>i</sub>	90.3; 93.9	26.0; 28.0		
	$\bar{x}$	92.1	27.0	+	+
	s	2.5	1.4		
CMR-Z	x <sub>i</sub>	82.6; 89.8	26.8; 29.4		
	$\bar{x}$	86.2	28.4	+	+
	s	5.1	1.8		

Acceptance limits\* = A 99% confidence interval calculated from available performance evaluation data of US EPA and US state laboratories.

Warning limits\*\* = A 95% confidence interval produced in the same way as the acceptance limits.

Remark on the acceptance of  $x^{***}$ :

- not acceptable because  $x$  falls beyond the acceptance limits;
- + acceptable because  $x$  falls within the warning limits;
- (+) acceptable, but due to the fact that  $x$  falls outside the warning but within the acceptance limits, possible systematic error(s) should be reviewed.

**Table 2.** Results ( $x_i$ =single value of measurement;  $\bar{x}$ =mean value;  $s$ = standard deviation) achieved during the 1991 intercomparison run in those certified Croatian laboratories that also participate in the MED POL Programme. Analytical performance of chemical oxygen demand (COD) with  $K_2Cr_2O_7$  in the two US EPA CRMs (WP023) was evaluated.

		c(COD)/mg dm <sup>-3</sup>			
		Sample 1		Sample 2	
US EPA:	True value	201		26,3	
WP386:	Acceptance limits*	161-221		15.3-33.5	
	Warning limits**	168-213		17.5-31.2	
Certified laboratory	c(COD)/mg dm <sup>-3</sup>			Remark on the acceptance of x***	
	Sample 1		Sample 2	Sample 1	Sample 2
PHIR-C	x <sub>i</sub>	210.4; 205.8; 204.6	25.1; 23.5; 28.1		
	x	206.9	25.6	+	+
	s	3.1	2.3		
IPH-P	x <sub>i</sub>	187; 193; 177	35.7; 35.5; 31.4		
	x	186	34.2	+	-
	s	8	2.4		
IPH-R	x <sub>i</sub>	195; 184; 204	38.9; 42.8; 42.8		
	x	194	41.5	+	-
	s	10	2.3		
IPH-S	x <sub>i</sub>	215.6; 215.6; 215.6	58.8; 49.0; 49.0		
	x	215.6	52.2	(+)	-
	s		5.7		
FCES-Z	x <sub>i</sub>	207.3; 211.3; 215.3	27.2; 31.9; 35.2		
	x	211.3	31.4	+	(+)
	s	4.0	4.0		
CMR-Z	x <sub>i</sub>	187.0; 187.0; 191.9	19.2; 19.6; 18.2		
	x	188.7	19.0	+	+
	s	2.8	0.7		

Acceptance limits\* = A 99% confidence interval calculated from available performance evaluation data of US EPA and US state laboratories.

Warning limits\*\* = A 95% confidence interval produced in the same way as the acceptance limits.

Remark on the acceptance of  $x^{***}$ :

- not acceptable because  $x$  falls beyond the acceptance limits;
- + acceptable because  $x$  falls within the warning limits;
- (+) acceptable, but due to the fact that  $x$  falls outside the warning but within the acceptance limits, possible systematic error(s) should be reviewed.

**Table 3.** Results ( $x_i$ =single value of measurement;  $\bar{x}$ =mean value;  $s$ = standard deviation) achieved during 1991 intercomparison run in those certified Croatian laboratories that also participate in MED POL Programme. Analytical performance of biochemical oxygen demand ( $BOD_5$ ) in the two US EPA CRMs (WP386) was evaluated.

		Sample 1		Sample 2	
US EPA:	True value	127		18.0	
WP386:	Acceptance limits*	78.9-176		9.42-26.5	
	Warning limits**	91.0-164		11.5-24.4	
Certified laboratory		$c(BOD_5)/mg\ dm^{-3}$		Remark on the acceptance of $x^{***}$	
		Sample 1	Sample 2	Sample 1	Sample 2
PHIR-C	$x_i$	156.3; 147.7	20.3; 25.5		
	$\bar{x}$	152.0	22.9	+	+
	$s$	6.1	3.7		
IPH-P	$x_i$	120.8; 123.6; 131.2	28.4; 28.0; 30.8		
	$\bar{x}$	125.2	29.1	+	-
	$s$	5.4	1.5		
IPH-R	$x_i$	96; 115; 119	17.0; 18.7; 14.6		
	$\bar{x}$	110	16.8	+	+
	$s$	12	2.1		
IPH-S	$x_i$	103.0; 107.0; 99.1	19.6; 24.0; 20.9		
	$\bar{x}$	103.0	21.5	+	+
	$s$	4.0	2.3		
FCES-Z	$x_i$	130; 136; 124	16.2; 15.5; 15.1		
	$\bar{x}$	130	15.6	+	+
	$s$	6	0.6		
CMR-Z	$x_i$	138.4; 130.0; 136.0	18.7; 16.4; 16.4		
	$\bar{x}$	134.8	17.2	+	+
	$s$	4.3	1.3		

Acceptance limits\* = A 99% confidence interval calculated from available performance evaluation data of US EPA and US state laboratories.

Warning limits\*\* = A 95% confidence interval produced in the same way as the acceptance limits.

Remark on the acceptance of  $x^{***}$ :

- not acceptable because  $\bar{x}$  falls beyond the acceptance limits;
- + acceptable because  $\bar{x}$  falls within the warning limits;
- (+) acceptable, but due to the fact that  $\bar{x}$  falls outside the warning but within the acceptance limits, possible systematic error(s) should be reviewed.

**Table 4.** Acceptance of the results achieved during the 1991 intercomparison run with US EPA CRMs in those certified Croatian laboratories which also participate in the MED POL Programme. Mean value ( $\bar{x}$ ) of the measurement of selected basic parameters of waste water is acceptable (+) if it falls within the acceptance limits\*; it is not acceptable (-) if it falls beyond the acceptance limits\*

Certified Laboratory	c(TSS)/mg dm <sup>-3</sup>		c(COD)/mg dm <sup>-3</sup>		c(BOD <sub>5</sub> )/mg dm <sup>-3</sup>	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
PHIR-C	-	+	+	+	+	+
IPH-P	+	+	+	-	+	-
IPH-R	+	+	+	-	+	+
IPH-S	+	+	+	-	+	
FCES-Z	+	+	+	+	+	+
CMR-Z	+	+	+	+	+	+

Acceptance limits\* = A 99% confidence interval calculated from available performance evaluation data of US EPA and US state laboratories.

### ***Trace elements in marine biota and sediments***

The following laboratories participated in the intercomparison run for trace elements, organized and coordinated by IAEA MEL (Mee *et al.*, 1993):

- @ Institute of Public Health, Pula (IPH-P)
- @ Institute of Public Health, Rijeka (IPH-R)
- @ Physics Department, University of Rijeka, Rijeka (PhDU-R)
- @ Institute of Public Health, Split (IPH-S)
- @ Public Health Institute of the Republic of Croatia (IPHC-Z)
- @ Institute of Public Health, Zagreb (IPH-Zg)
- @ Centre for Marine Research Zagreb, Ruder Boskovic Institute (CMR-Z).
- @ Institute for Oceanography and Fisheries, Split (IOF-S)
- @ Marine Biological Station, Piran (MBS-P)
- @ Jozef Stefan Institute, Department of Nuclear Chemistry, Ljubljana (JSI-Lj).



During intercomparison exercises laboratories analysed trace metals in the following samples of marine origin:

- @ fish tissue,
- @ copepod,
- @ sea plant,
- @ mussel,
- @ shrimp, and
- @ sediment.

In the period 1976-1992, eight of the above-mentioned Croatian laboratories participated in intercomparison exercises on trace elements. This number does not reflect the regularity of participation. In the last column of Table 5 for the period 1976-1992 participation of each laboratory in the intercomparison runs is shown. The overall participation of Croatian laboratories in a single intercomparison run is illustrated in the last row of Table 5. Of the eight Croatian laboratories, four participated in every intercomparison run. The Institutes of Public Health joined the intercalibration exercises after 1985. In the period from 1976-1991 only CMR-Z regularly participated in the intercalibration exercises, overall in 10 intercomparison runs (see last column of Table 5).

**Table 5.** Participation of Croatian laboratories in intercomparison exercises on trace elements organized by IAEA MEL, Monaco for the period 1976-1992.

Laboratory	Cope-pod 1976	Sea plant 1977	Cope-pod 1977	Fish 1978	Sedi- ment 1985	Mussel 1985	Shrimp 1987	Fish 1988	Tuna fish 1989	Sedi- ment 1991	Sedi- ment 1992	No. of part.
IPH-P	-	-	-	-	-	-	-	-	-	X	-	1
IPH-R	-	-	-	-	-	-	X	X	X	X	X	5
PhDU-R	X	X	X	-	X	-	X	-	-	-	-	5
IPH-S	-	-	-	-	-	-	X	X	X	-	-	3
PHIR-C	-	-	-	-	-	X	-	-	-	-	-	1
IPH-Zg	-	-	-	-	-	-	-	-	X	-	-	1
CMR-Z	X	X	X	X	X	X	X	X	X	X	-	10
IOF-S	-	-	-	-	-	-	-	-	-	-	X	1
Overall=8	2	2	2	1	2	2	4	3	4	3	2	/

The participation of two Slovenian laboratories in the intercomparison run is illustrated in Table 6. In the period from 1976-1992 the two Slovenian laboratories participated regularly in the intercomparison run for trace element analysis in marine biota and sediment samples. Both Slovenian laboratories participated in all 11 intercomparison runs (last column of Table 6) in the period 1976-1992 of intercomparison exercises conducted by IAEA MEL.

**Table 6.** Participation of Slovenian laboratories in intercomparison exercises on trace elements organized by IAEA MEL, Monaco for the period 1976-1992.

Laboratory	Copepod 1976	Sea plant 1977	Copepod 1977	Fish 1978	Sediment 1985	Mussel 1985	Shrimp 1987	Fish 1988	Tuna fish 1989	Sediment 1991	Sediment 1992	No. of part.
MBS-P	X	X	X	X	X	X	X	X	X	X	X	11
JSIXLj	X	X	X	X	X	X	X	X	X	X	X	11
Overall=2	2	2	2	2	2	2	2	2	2	2	2	/

Based on the frequency of participation and the quality of reported data IAEA MEL has issued the list of selected laboratories around the Mediterranean for trace metal analysis (Mee *et al.*, 1993). Around the Mediterranean, 14 laboratories were selected for excellent analytical performance, among them three participants of the programme, namely:

- @ Centre for Marine Research Zagreb, "Ruder Boskovic" Institute, Zagreb (CMR-Z)
- @ Marine Biological Station, Piran (MBS-P)
- @ Jozef Stefan Institute, Department of Nuclear Chemistry, Ljubljana (JSI-Lj)

For this overview, data quality of cadmium and mercury analysis in the samples of marine biota and sediments is illustrated in Fig. 1 and Fig. 2 (Fig. 13 and 15 respectively) (from the report Mee *et al.*, 1993; CMR-Z). Cadmium and mercury were chosen for illustration of analytical performance because they belong to the toxic and persistent elements on the list of toxic substances of Land-Based Sources Protocol, and are priority contaminants in the MED POL Monitoring Programme.

### ***Trace organic contaminants in marine biota and sediments***

The following laboratories participated in the MED POL Programme of the eastern part of the Adriatic Sea and in the intercomparison run for trace organics organized and coordinated by IAEA MEL (Mee *et al.*, 1993):

- @ Institute of Public Health, Pula (IPH-P)
- @ Institute of Public Health, Rijeka (IPH-R)
- @ Institute of Public Health, Split (IPH-S)
- @ Centre for Marine Research Zagreb, "Ruder Boskovic" Institute (CMR-Z).
- @ Institute for Oceanography and Fisheries, Split (IOF-S)
- @ Centre for Marine Research Rovinj, Ruder Boskovic Institute (CMR-R)
- @ Agricultural Institute of Slovenia, Ljubljana (AIS-Lj)
- @ Marine Biological Station, Piran (MBS-P)

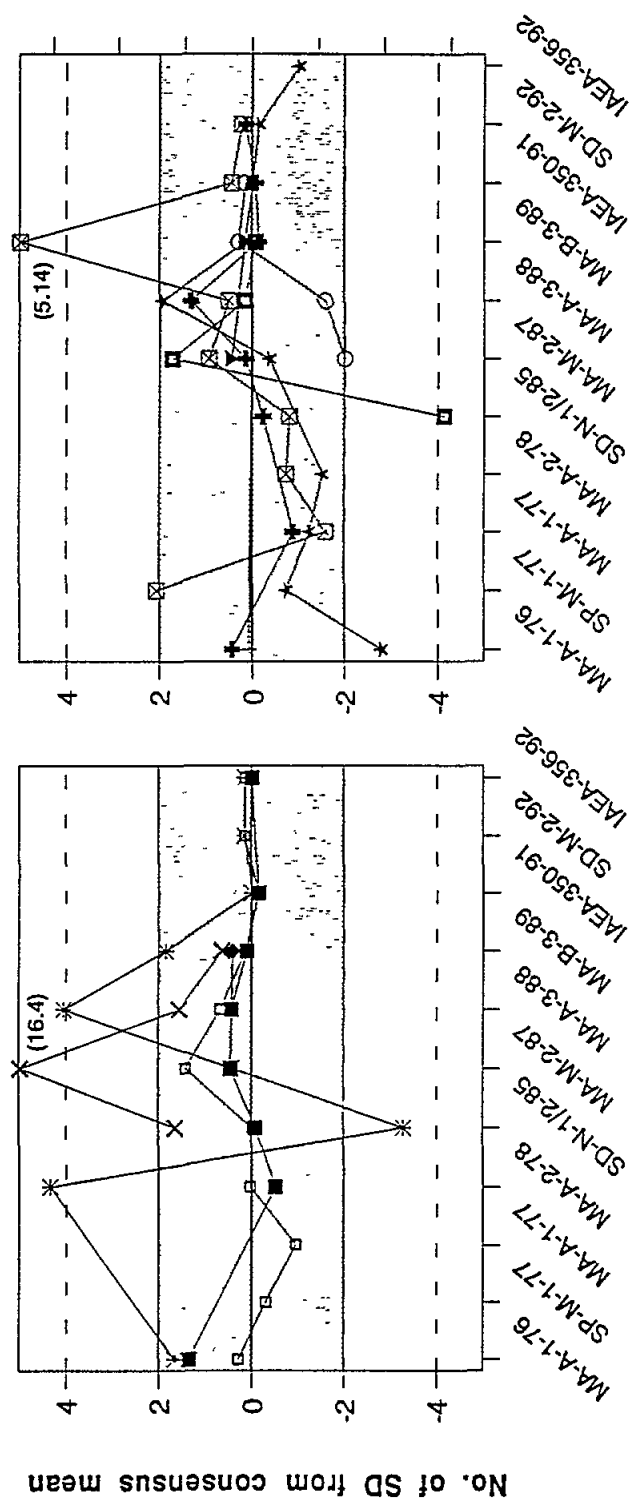


Fig. 1. Development of data quality for Cadmium content in samples of marine organisms and sediment in selected MED POL labs (taken from Mee *et al.*, 1993)  $\pm$  stay for CMR-Z. SD represent standard deviation based on the results of the world-wide intercomparison exercise. Shaded area indicates data within the control limits.

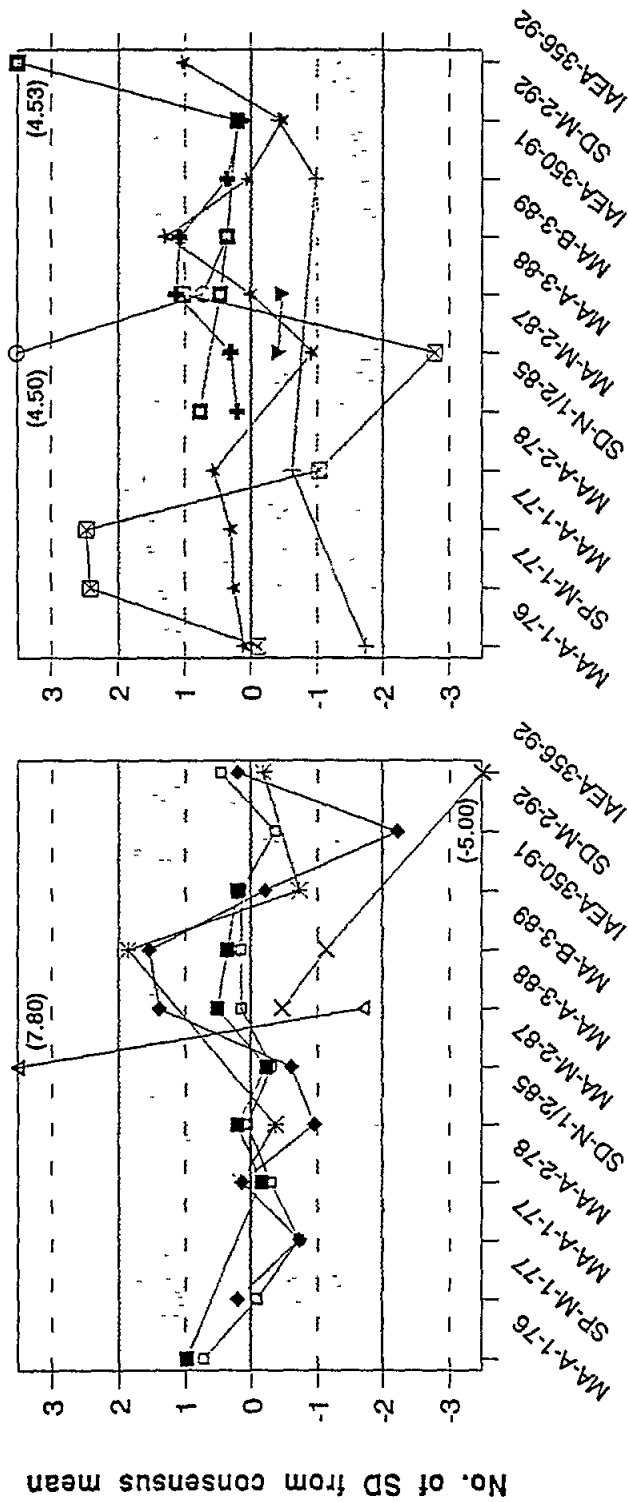


Fig. 2. Development of data quality for Mercury content in samples of marine organisms and sediment in selected MED POL labs (taken from Mee *et al.*, 1993).  $\pm$  stay for CMR-Z. SD represent standard deviation based on the results of the world-wide intercomparison exercise. Shaded area indicates data within the control limits.

Laboratories which participate in intercomparison exercises analysed traces of organic contaminants in the next samples of marine origin:

- @ fish tissue,
- @ copepod,
- @ sea plant,
- @ bivalve,
- @ shrimp, and
- @ sediment.

In the period 1976-1992, seven of the abovementioned Croatian laboratories participated in intercomparison exercises on organic contaminants. This number does not reflect the regularity of participation. In the last column of Table 7, for the period from 1976-1989, the participation of each laboratory is shown. In the last row of Table 7 the overall participation of Croatian laboratories in single intercomparison run is presented. The respective Institutes of Public Health joint the intercalibration exercises not earlier than 1988. In the period from 1976-1988 the laboratory of CMR-Z was the only Croatian laboratory which regularly participated in the intercalibration exercises for trace organochlorine compounds, overall in 9 intercomparison runs (see last column of Table 7).

**Table 7.** Participation of Croatian laboratories in intercomparison exercises on trace organochlorine compounds organized by IAEA MEL, Monaco during the period 1976-1989.

Laboratory	XAD II 1976	Sea plant 1976	Fish 1982	Cope- pod 1982	Oyster 1982	Sedi- ment 1986	Mussel 1986	Fish 1988	Shrimp 1988	Sedi- ment 1989	Tuna fish 1989	No. of part.
IPH-P	-	-	-	-	-	-	-	X	X	X	-	3
IPH-R	-	-	-	-	-	-	-	X	X	-	-	2
IPH-S	-	-	-	-	-	-	-	-	-	-	X	1
PHIR-C	-	-	-	-	-	-	-	-	-	X	X	2
CMR-Z	X	X	X	X	X	X	X	X	X	-	-	9
IOF-S	-	-	-	-	-	-	-	-	-	-	-	-
CMR-R	-	-	-	-	-	-	-	X	X	-	X	3
Overall=7	1	1	1	1	1	1	1	4	4	2	3	/

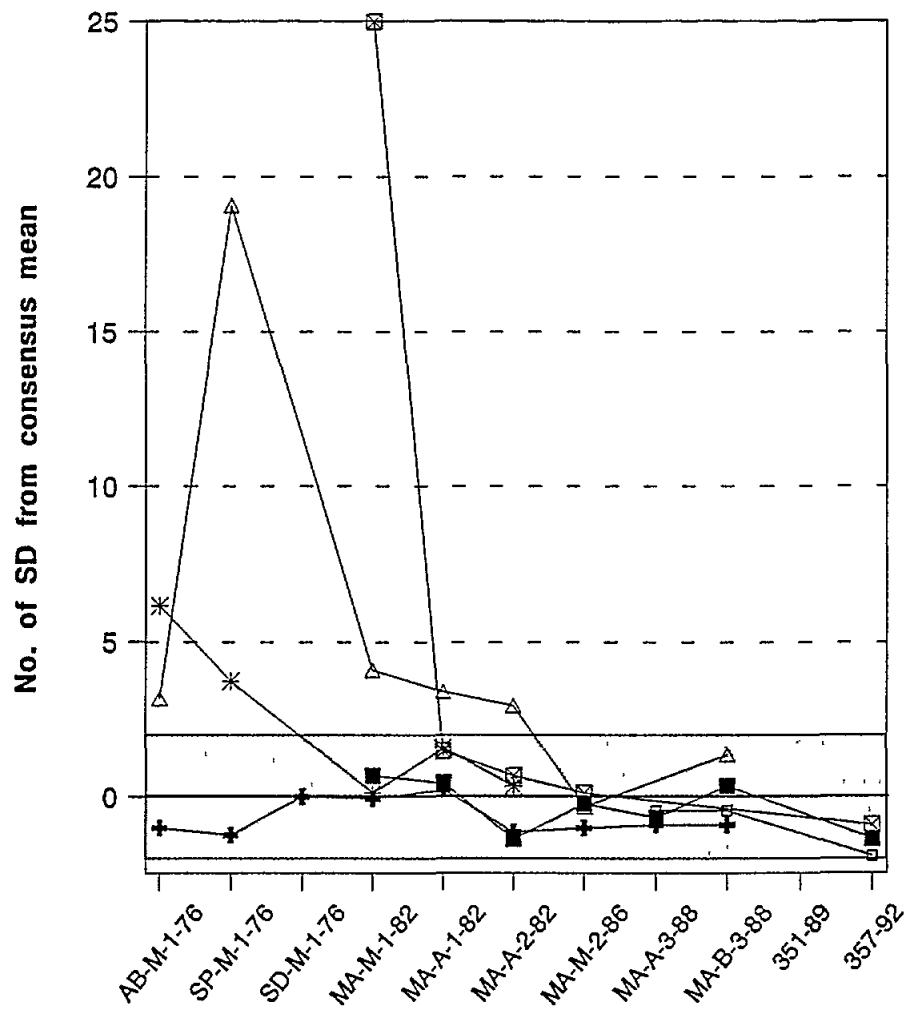
Contrary to the regular participation of Slovenian laboratories in trace metal exercises, the participation for organochlorine compounds was very irregular (Table 8). In fact, in the period 1988-1989 neither of the Slovenian laboratories participated.

**Table 8.** Participation of Slovenian laboratories in intercomparison exercises on trace organochlorine compounds organized by IAEA MEL, Monaco for the period 1976-1989.

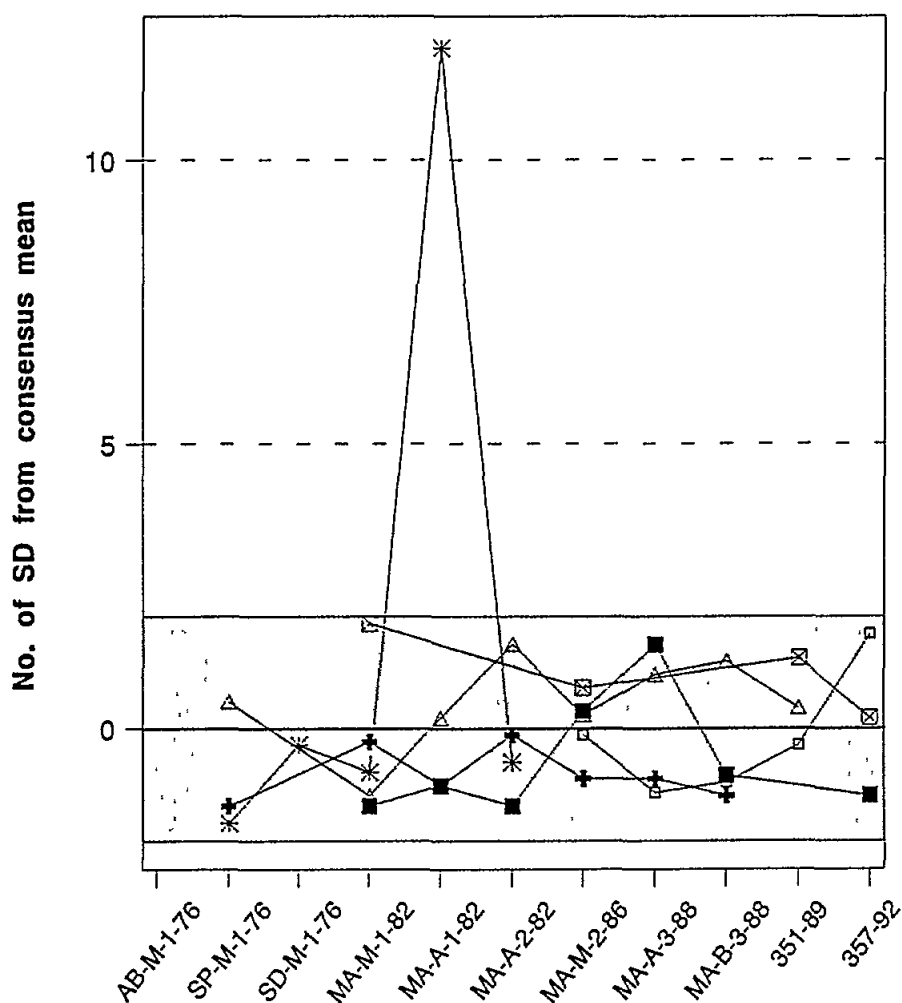
Laboratory	XAD II 1976	Sea plant 1976	Fish 1982	Cope- pod 1982	Oyster 1982	Sedi- ment 1986	Musse I 1986	Fish 1988	Shrimp 1988	Sedi- ment 1989	Tuna fish 1989	No. of part.
AIS-Lj	X	X	-	-	-	X	-	-	-	-	-	3
MBS-P	-	-	X	-	X	-	-	-	-	-	-	2
Overall=2	1	1	1	-	1	1	-	-	-	-	-	/

Based on the frequency of participation and the quality of data reported, IAEA MEL has issued the list of selected laboratories around the Mediterranean for trace organochlorine compounds analysis (Mee *et al.*, 1993). Around the Mediterranean, six laboratories were selected for excellent analytical performance, among them only the Centre for Marine Research Zagreb relate to the eastern Adriatic Sea area.

For the purpose of this overview, data quality of trace organochlorine compounds (Aroclor 1254 and pp'DDE) in the samples of marine biota and sediments is illustrated in Figs. 3 and 4 respectively, (Figs. 18 and 19 from the Report of Mee *et al.*, 1993). Specific organochlorine compounds have been chosen for the illustration of analytical performance because they belong to the toxic compounds from the list of toxic substances of Land-based Sources Protocol, and are priority contaminants in the MED POL Monitoring Programme.



**Fig. 3.** Development of data quality for Aroclor 1254 content in samples of marine organisms and sediment in selected MED POL laboratories (taken from Mee *et al.*, 1993). SD represents standard deviation based on the results of the world-wide intercomparison exercise. Shaded area indicates data within the control limits (+ means CMR-Z).



**Fig. 4.** Development of data quality for pp'DDE content in samples of marine organisms and sediment in selected MED POL labs (taken from Mee *et al.*, 1993). SD represents standard deviation based on the results of the world-wide intercomparison exercise. Shaded area indicates data within the control limits (+ means CMR-Z).



## **Adriatic Scientific Cooperation Programme (ASCOP)**

The QA Programme in the framework of the ASCOP monitoring activities started in 1979 (Accerboni, 1982). In November 1979, a field intercalibration was performed on samples from various depths, collected at a station 20 Nm off the Po River Delta using two research vessels. Subsamples were exchanged and analysed by CMR-R and two Italian laboratories (from Trieste and Venice). The results for nutrients and chlorophyll *a* concentrations were generally satisfactory, although some discrepancies (ammonium and nitrate) arose, probably generated from different sample storage and analytical techniques applied by the different laboratories.

This QA Programme has been implemented since 1986 with the purpose of identifying possible sources of errors in single laboratories and to reduce the discrepancy among results for the same parameters measured by different laboratories. The coordinating unit was the Centre for Marine Research at Zagreb (CMR-Z). The QA/QC Programme proceeded in three steps:

- @ calibration of instruments and instrumental response;
- @ validation of analytical performance with CRMs; and
- @ field intercalibration (evaluation of sampling, sample preservation and sample pretreatment).

The realization of the QA/QC Programme started in 1986 (Raspor, 1987) and 1987 (Raspor, 1988) with the ultimate step, ie with the field intercalibration. The results indicated discrepancies which have to be resolved during laboratory intercalibration applying the first two steps (Raspor, 1989; 1990). The results of the intercomparison runs were presented in progress reports (Raspor, 1987; 1988; 1989; 1990), as well as in the summary report for the period 1979-1992 (Raspor, 1992; Anon., 1993). For the purpose of this overview only results achieved during the laboratory intercalibration will be discussed (Raspor, 1989; 1990).

### ***Calibration of the instrumental response***

#### ***Chlorophyll *a****

In the framework of ASCOP the institutions responsible for measuring chlorophyll *a*, namely CMR-R and IOF-S, performed calibration of fluorometer (Raspor, 1990). Instrumental performance has been proved with the US EPA Quality Control sample that contains pure chlorophyll *a* in 90% aqueous acetone. From the defined concentration of the original sample (UNESCO, 1966) several dilutions representative of those concentrations of chlorophyll *a* in sea water were prepared and the fluorescence measured by fluorometer. The conversion factors at certain sensitivity level were determined. In both institutions the calculated conversion factors were higher compared to the previous calibration. The increase of the conversion factor of the fluorometer is the consequence of ageing of the photomultiplier and the source of UV-light. Both institutions recognized the necessity of a more frequent calibration of the instruments.

## Nutrients

The participating laboratory of CMR-R, responsible for measuring nutrients in sea water in the frame of ASCOP, checked the analyst's accuracy and precision (Raspor, 1989) with the US EPA nutrient Quality Control sample. The ampoule contained inorganic nitrogen and phosphorous and was analysed for ammonia, nitrate and orthophosphate. The concentrated solution has been preserved to avoid the changes of the defined nutrient content. This QC sample is not representative of sea water but of low salinity water type, and therefore the given statistics were not applicable. The concentrated sample containing  $14300 \mu\text{mol dm}^{-3}$  of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  and  $1600 \mu\text{mol dm}^{-3}$   $\text{PO}_4^{3-}$ , was diluted with sea water. The prepared dilutions contained concentration of nutrient elements close to the level usually found in sea water (several  $\mu\text{mol dm}^{-3}$ , see Table 9). Orthophosphate, nitrate and ammonium concentration were determined with the methods usually applied by CMR-R in the analysis of nutrients in sea water (Zavodnik, 1982; Ivancic and Degobbis, 1984). In Table 9 the mean values ( $\bar{x}$ ), standard deviations ( $\sigma$ ) and the range of concentrations of orthophosphate, nitrate and ammonia at three dilutions are presented. The bias of the mean values with respect to true values is expressed as the difference in percentages. Small systematic errors could be ascribed to the different methods of analysis and different solution media, ie high salinity instead of low salinity media.

**Table 9.** Validation of analysts' accuracy and precision with the US EPA nutrient Quality Control sample.

Nutrient	$c(\text{nutrient})/\mu\text{mol dm}^{-3}$			True value	Difference %
	$\bar{x}$	$\sigma$	Range		
$\text{PO}_4$	0.077	0.003	0.075-0.080	0.081	-4.9
	0.393	0.002	0.392-0.397	0.403	-2.5
	0.784	0.003	0.782-0.787	0.806	-2.7
$\text{NO}_3$	0.80	0.09	0.66-0.90	0.71	+12.7
	3.90	0.26	3.53-4.13	3.57	+9.2
	7.86	0.38	7.46-8.29	7.14	+10.1
$\text{NH}_4$	0.69	0.02	0.67-0.72	0.71	-2.8
	3.68	0.18	3.50-3.88	3.57	+3.1
	7.32	0.20	7.10-7.50	7.14	+2.5

## ***Validation of methodology with CRMs***

### *Nutrients*

The reliability of the applied analytical method for nutrients was evaluated with the Sagami reference material at different concentration levels of nutrients in model sea water. The marine laboratories along the eastern coast of the Adriatic Sea, which also participate in the MED POL programme, were supplied with the standard solutions of nutrients in model sea water (orthophosphate, nitrite, nitrate and orthosilicate; Raspor, 1990). The standard solutions of nutrients were prepared for spectrophotometric analysis by Wako under the supervision of the Sagami Chemical Research Centre of Japan (Cantillo, 1986).

The standard Sagami solutions were distributed to the following marine laboratories:

- @ Marine Biological Station, Piran (MBS-P)
- @ Centre for Marine Research Rovinj, "Ruder Boskovic" Institute, Zagreb (CMR-R)
- @ Institute of Oceanography and Fisheries, Split (IOF-S)
- @ Biological Institute, Dubrovnik (BI-D)
- @ Institute of Marine Biology, Kotor (IMB-K).

Among the abovementioned marine laboratories two of them (CMR-R and IOF-S) were appointed to monitor nutrients in the international waters of northern and central Adriatic Sea in the framework of ASCOP.

The results on nutrient concentrations in sea water were submitted by four institutions (MBS-P, CMR-R, BI-D and IMB-K). The IOF-S has not submitted the results of measurements. Intercomparison run with the standard Sagami solutions was performed in two different ways.

- @ MBS-P and CMR-R worked with the Sagami samples of disclosed concentrations, so that they reported on the proportionality factors  $F$  used for calculating the concentration of nutrients. The results are presented in Tables 10 and 11, respectively; and
- @ IOF-S, BI-D and IMB-K worked with the Sagami samples of undisclosed concentrations. The results of measurements are presented in Table 12.

**Table 10.** Proportionality factor F reported by MBS-P in the Sagami standard solutions for nutrient elements

Nutrient	Wave length	Optical pathlength	Factor**		True value $\mu\text{mol l}^{-1}$	Remark on the acceptance of results
	nm	cm	F	F <sub>c</sub>		
NO <sub>2</sub>	543	5	4.17	2.09	0.25	+
NO <sub>3</sub> *	543	1	23.57	2.36	15.0	+
PO <sub>4</sub> *	690	5	14.42	7.21	0.50	+
SiO <sub>4</sub>	640	5	51.71	25.86	5.00	+
SiO <sub>4</sub>	640	5	51.71	25.86	25.0	+

\* Laboratory has neither disposed with the samples of 1.00 and 5.00  $\mu\text{mol dm}^{-3}$  for NO<sub>3</sub> nor with 2.00  $\mu\text{mol dm}^{-3}$  for PO<sub>4</sub>.

\*\* F = concentration/extinction

F<sub>c</sub> = proportionality factor corrected to the optical pathlength of 10 cm.

With respect to Table 11, an additional explanation is that the unknown concentrations of nutrients in natural sea water are determined by CMR-R using the following proportionality factors F:

- @ for nitrite 2.1
- @ for nitrate 2.2-2.4
- @ for orthophosphate 4.8-5.0.

**Table 11.** Proportionality factor F reported by CMR-R in the Sagami standard solutions for nutrient elements.

Nutrient	Wave length	Optical pathlength	Extinction	Factor*		True value $\mu\text{mol dm}^{-3}$	Remark on acceptance of results
	nm	cm		F	F <sub>c</sub>		
NO <sub>2</sub>	540	10	0.118	2.12	-	0.25	+
NO <sub>3</sub>	540	10	0.46	2.10	-	1.00	+
NO <sub>3</sub>	540	1	22.84	0.219	0.022**	5.00	-
NO <sub>3</sub>	540	10	8.58	1.75***	-	15.00	-
PO <sub>4</sub>	885	10	0.099	5.05	-	0.50	+

F = concentration/extinction

F<sub>c</sub> = proportionality factor corrected to the optical pathlength of 10 cm

\*\* F<sub>c</sub> corresponds to 100 times higher concentration of NO<sub>3</sub>-N than declared

\*\*\* F is lower than expected due to cracked bottle and the probable partial loss of water.

In Table 12 the results reported by BI-D and IMB-K on the measurements of Sagami standard solutions for nutrient elements are presented. As previously indicated, the true concentrations of nutrients were undisclosed to these participant laboratories.

**Table 12.** Results reported by BI-D and IMB-K on undisclosed concentrations of nutrients in Sagami standard solutions.

Laboratory or source	c(nutrient)/ $\mu\text{mol dm}^{-3}$				Remarks on acceptance of results			
	NO <sub>2</sub>	NO <sub>3</sub>	PO <sub>4</sub>	SiO <sub>4</sub>	NO <sub>2</sub>	NO <sub>3</sub>	PO <sub>4</sub>	SiO <sub>4</sub>
Sagami	0.25	1.00	0.50	5.00				
		5.0	0.00	25.0				
		15.0						
BI-D	0.25	0.99	0.50	4.99	+	+	+	+
		5.03	2.02	25.05		+	+	+
		15.07				+		
IMB-K	0.18	ND	0.30	0.40	-	ND	-	-
		ND	1.68	1.61		ND	-	-
		ND				ND		

ND = not determined

### *Heavy metals in sediments*

Validation of the applied analytical method for measuring trace metals in sediment samples has been evaluated with the standard reference material (SRM 1646) of US NIST (former NBS; Raspor, 1989). The results were reported by CMR-Z which was the only Croatian laboratory responsible for measuring trace heavy metals in marine samples in the framework of ASCOP. Certified values of SRM 1646 were undisclosed to the analysts. In Table 13 the results on weight partition of lead, copper and zinc in the dry sediment are presented. Sediment SRM of estuarine origin (Chesapeake Bay) was divided into subsamples of different weight, dried under the clean-bench method and decomposed as described in the relevant methodology (Zavodnik, 1982). The content of lead and copper was analysed with the GFAAS technique, and the zinc content with the flame technique. Comparing the mean values for lead, copper and zinc reported by CMR-Z with the certified values by US NIST (last row of Table 13), a very good performance of the applied methodology can be determined.

**Table 13.** Weight partition of lead, copper and zinc in the US NIST SRM 1646 of estuarine sediment reported by CMR-Z responsible for trace metal analysis in the framework of ASCOP.

Sample number	Weight of sample mg	Weight partition of trace heavy metals		
		$w(\text{Pb})_{\text{DW}} \times 10^6$	$w(\text{Cu})_{\text{DW}} \times 10^6$	$w(\text{Zn})_{\text{DW}} \times 10^6$
1	250	24.1	14.55	135
2	250	31.3	12.69	127
3	500	25.9	14.17	127
4	500	25.5	14.50	128
5	750	24.2	15.40	123
6	750	25.1	15.10	133
Mean $\pm$ $\sigma$		26.0 $\pm$ 2.7	14.40 $\pm$ 0.95	129 $\pm$ 4
Relative error		10.4 %	6.6 %	3 %
US NIST X SRM 1646		28.2 $\pm$ 1.8	18 $\pm$ 3	138 $\pm$ 6
Relative error		6.4 %	16.7 %	4 %

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