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### Biogeochemistry, grain size and mineralogy of the central and southern Adriatic Sea sediments: a review

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## Biogeochemistry, grain size and mineralogy of the central and southern Adriatic Sea sediments: a review

Federico Spagnoli<sup>a\*</sup>, Antonio Dell'Anno<sup>b</sup>, Antonio De Marco<sup>c</sup>, Enrico Dinelli<sup>d</sup>, Mauro Fabiano<sup>e</sup>, Marta Velia Gadaleta<sup>f</sup>, Carmela Ianni<sup>g</sup>, Francesco Loiacono<sup>c</sup>, Elena Manini<sup>a</sup>, Mauro Marini<sup>a</sup>, Giovanni Mongelli<sup>h</sup>, Giancarlo Rampazzo<sup>i</sup>, Paola Rivaro<sup>g</sup> and Luigi Vezzulli<sup>j</sup>

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This review aims to present the current status of studies on geochemical (major minor and trace elements), biochemical (total organic carbon, total nitrogen, isotopic carbon composition, Bacteria, Archaea, phytopigments, proteins, carbohydrates, lipids, humic and fulvic acids), mineralogical (light and heavy minerals, clay minerals) and pollutant (trace metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, pesticides, organic stannic compounds) parameters, grain-size composition and sediment–water interactions (early diagenesis and benthic fluxes) for the bottom sediments of the central and southern Adriatic Sea. The review highlighted gaps in or completeness of the parameters needed for research, of areas in which the parameters were investigated, as well as the interdisciplinary nature of the studies. In general, biogeochemical, mineralogical, grain-size and pollutant studies in the central and southern Adriatic Sea are restricted to limited areas, consider only single parameters without an interdisciplinary approach and, except for some more recent projects, are predominately out of date. On the whole, there is a lack of an organised study concerning the various parameters for the entire central and southern Adriatic Sea and their evolution over time.

**Keywords:** biogeochemistry; mineralogy; grain size; pollutants; superficial sediment; Adriatic Sea

### 1. Introduction

The scope of this review is to present the current status of research on the biogeochemistry, mineralogy, grain size and pollution in superficial sediments of the central and southern Adriatic Sea. For an exhaustive review of studies carried out in the past it was useful to consider both

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data collected from the literature and data relating to research projects conducted in recent years and provided by the participants in the research. Furthermore, to enable clear presentation and discussion of the material, Supplementary Tables S1a and S1b (online only) group the data into different subjects, specifying the area investigated, the parameters analysed and the period of study; a short review of the most recent projects is given in the main text.

Coastal and geophysical studies are not considered here because the specificity and extensiveness of such research deserve to be treated separately. The results of such research are recalled only when needed to explain the data discussed in the text.

The review presents data on the central and southern Adriatic Sea, from the Mid-Adriatic Depression at the Otranto Strait [1,2] (Figure 1(a)).

## 2. Recent research projects

In the recent past (2000 to present), only two research projects have been entirely dedicated to studying the biogeochemical, mineralogical and grain-size characteristics, and contamination of the superficial sediments of the central and southern Adriatic Sea: the INTERREG II Italy–Albania Project and the PITAGEM Project. Other projects (ASCOP, PRISMA 1, INTERREG II Italy–Greece, Technological and Scientific Cooperation Agreement between Italy and Albania)

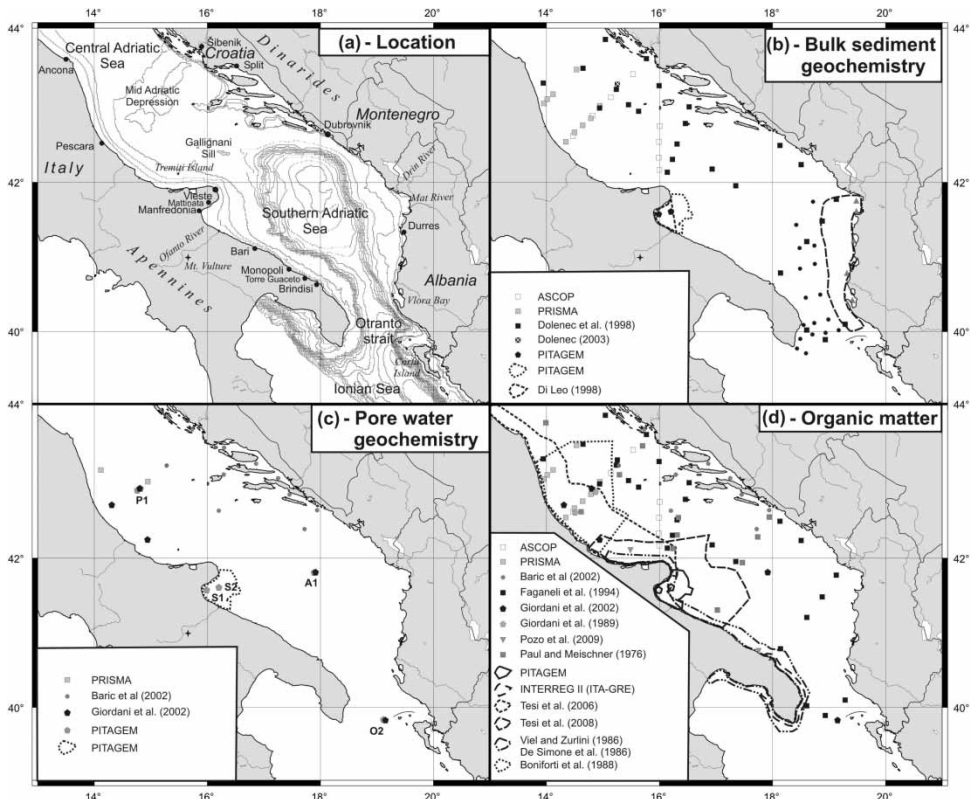


Figure 1. (a) The central and southern Adriatic Sea indicating the main sites named in the text and the study areas for the projects and articles reviewed. In each map, the sampling sites or areas are drawn for each parameter investigated. (b) Bulk sediment geochemistry, (c) pore water geochemistry, (d) organic matter, (e) mineralogy, (f) trace elements, (g) organic contaminants, (h) grain-size.

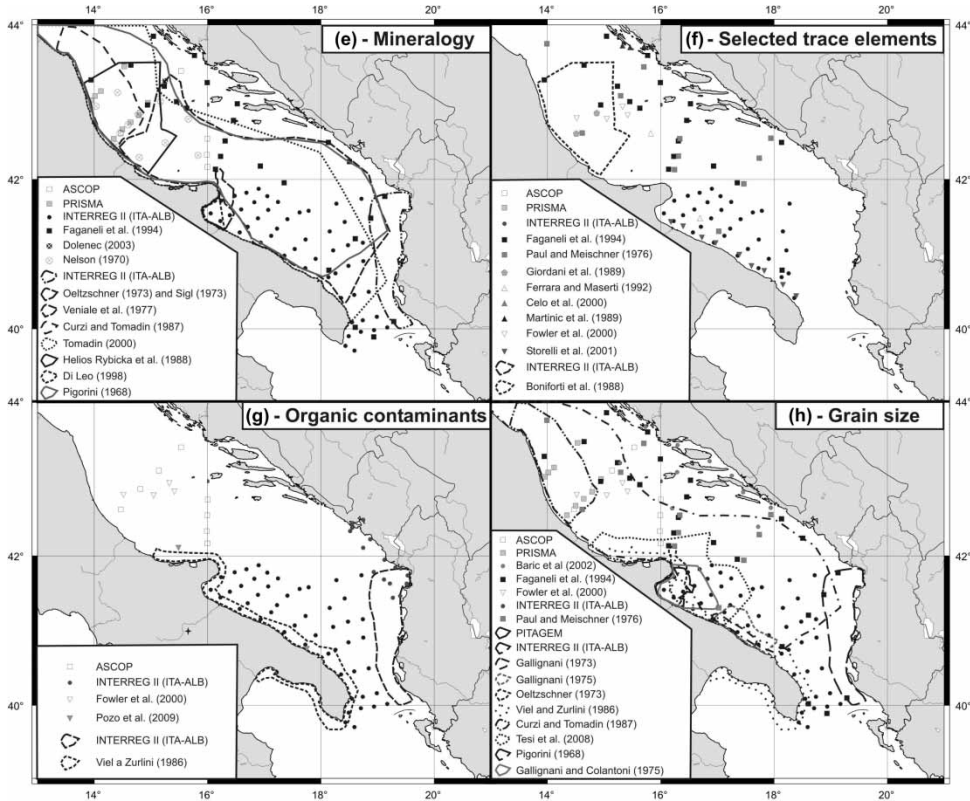


Figure 1. Continued.

have considered only part of the central and southern Adriatic Sea or examined only one or a few parameters.

The Adriatic Scientific Cooperation Program (ASCOP) Project [3] is the oldest of all the considered projects; lasting from 1977 to 1990, it was a multidisciplinary research project carried out within the framework of the Italian–Yugoslavian Multidisciplinary Program for the Protection of the Adriatic Sea and Coastal Regions from Pollution. In the context of this multidisciplinary project, several parameters (Supplementary Table S1a – online only) were investigated in the superficial sediments of the central and southern Adriatic Sea (Figure 1(b),(d)–(h)).

The PRISMA 1 Project [4] lasted from 1994 to 1998 and its main goal was to study physical, physico-chemical, geochemical and biological processes involving nutrients in the northern and central Adriatic Sea. Within this context, the subtheme ‘Fluxes from and towards bottom’ studied the biogeochemical, mineralogical and sedimentological properties and processes (Supplementary Table S1a – online only) of the superficial sediments (Figure 1(b)–(f), (h)) [5].

The INTERREG II Italy–Greece programme lasted from 1997 to 1999. It had several aims, mainly related to management issues. One of these aims related to the marine environment, namely reducing marine pollution and promoting and protecting areas of particular natural beauty. In this context, some biochemical investigations (Supplementary Table S1a – online only) were carried out in the Apulia offshore (Figure 1(d)–(h)) [6].

The project INTERREG II Italy–Albania (axis 3 ‘Environment’, 2000–2002) [7] lasted from January 1999 to December 2001, and its aim was to monitor the southern Adriatic Sea from the Apulian coast (Manfredonia Gulf–Otranto Strait) to the Albanian coast (Drin Gulf–Corfù Isle)

(Figure 1(d)–(h)) making detailed biogeochemical, mineralogical, sedimentological and pollution analyses (Supplementary Table S1a – online only) of the water and superficial bottom sediments.

The PITAGEM Project lasted from February 2001 to December 2004. It had several objectives including setting up new oceanographic instruments, a new coastal marine-monitoring integrated network in the Gulf of Manfredonia, in the Gulf of Taranto and along the coasts of Sicily, the realisation of a marine coastal satellite data elaboration method and database to estimate biological and physical parameters and, finally, a multidisciplinary study of the trophic and biogeochemical processes in the water column of the Gulf of Manfredonia and their relationships with the bottom sediments [8]. The last objective involved studying biogeochemical and sedimentological characteristics (Supplementary Table S1a – online only) of the Gulf of Manfredonia (Figure 1(b), (d)–(h)) and early diagenesis processes and benthic fluxes (Supplementary Table S1a – online only) of the Gulf of Manfredonia and the central and southern Adriatic Sea (Figure 1(c)) [9–11].

The project ‘Environmental impact evaluation of the old Porto Romano (Durres) factory site’, was the most recent study of superficial sediment pollution to be carried out in the southern Adriatic Sea [12]. It was performed within the context of the International Scientific and Technological agreement between Italy and Albania from 2006 to 2007 and aimed to evaluate the distribution of Lindane (Supplementary Table S1a – online only) in the coastal sediments in front of the highly polluted industrial area of Durres (Albania) (Figure 1(g)).

### 3. Geochemistry of superficial sediments

Among studies that dealt with the distribution of major and trace elements from a chronological point of view, it is important to mention the ASCOP Project [3], the PRISMA Project [4,5], the work of Donelec and colleagues [13,14] and finally the PITAGEM Project [9].

The ASCOP Project looked at the superficial sediment geochemistry of the central and southern Adriatic Sea (Figure 1(b)). The project analysed major and trace elements and, as ancillary data, the calcite and dolomite content, the percentage of sand, silt and clay, and the polycyclic aromatic hydrocarbon (PAH), polychlorinated biphenyl (PCB), dichlorodiphenyltrichloroethane (DDT) and organic matter content (Supplementary Table S1a – online only) of superficial sediments along the transects Pescara–Sibenik and Vieste–Split (Figure 1(b)). In this project, De Lazzari et al. [3] processed the data using a mathematical–statistical calculation of principal components (factors) which established relationships among the components. Areal distribution of the statistical factors showed that the fine grain-size fraction, with oxides and hydroxides, is the main means of sediment transport and the principal link between chemical, physical and granulometric elements in the Adriatic Sea, adsorbing most of the metals considered and some organic contaminants. Other components are organic matter, mainly humic materials, which concentrate organic micropollutants such as PCBs and PAHs, detrital minerals such as quartz and calcite, with no toxic metals associated, and the dolomite component. The main problems with this study are the low-density sampling sites, their distribution (along only two transects) and the sampling date (19 years ago; Supplementary Table S1a – online only), however, on a positive note, the authors tried to give interdisciplinary interpretations of the data.

The PRISMA 1 Project, in the central Adriatic Sea (Figure 1(b)), studied the geochemical composition of superficial sediments in correlation with biochemical, mineralogical and grain-size parameters (Supplementary Table S1a – online only) using statistical analysis to elaborate thematic maps. These maps describe the sedimentological processes, the physiography and the biogeochemical characteristics of the sediments. In practice, areal distribution maps for geochemical elements, single minerals, grain-size fractions, total organic carbon (TOC), total nitrogen (TN), biogenic Si, total phosphate (TP), inorganic phosphate (IP), water content and pH and Eh values

have been drafted; these maps, together with previous bibliographic data, enabled the development of: (1) a summary thematic map characterising, in the central Adriatic, the sandy coastal zone, the active silico-clastic sedimentation zone, the slope zone with different grain sizes, and the basin zone with predominately clay sedimentation [15] (Figure 2(a)); and (2) a map of sediment reactivity [weak (zone D) and very weak (zone E) diagenetic processes in the central Adriatic area] [16] (Figure 2(b)). It is important to note the good interdisciplinary approach used in this project, however, the research area covered only the Mid-Adriatic Depression and the central–western shelf.

Donelec et al. [13] investigated the concentrations and distributions of major, minor and trace elements in superficial sediments (Supplementary Table S1b – online only) for the whole central and southern Adriatic Sea, however, they used a low-density sampling net (35 stations on the whole Adriatic; Figure 1(b)). Donelec et al. [13] found that the distribution of these elements is influenced by catchment geology, the structural type of the sediment, the predominant currents and, to a lesser extent, morphological characteristics of the sea bottom, anthropogenic inputs and local hydrological and chemical conditions. They also found the highest trace element concentrations

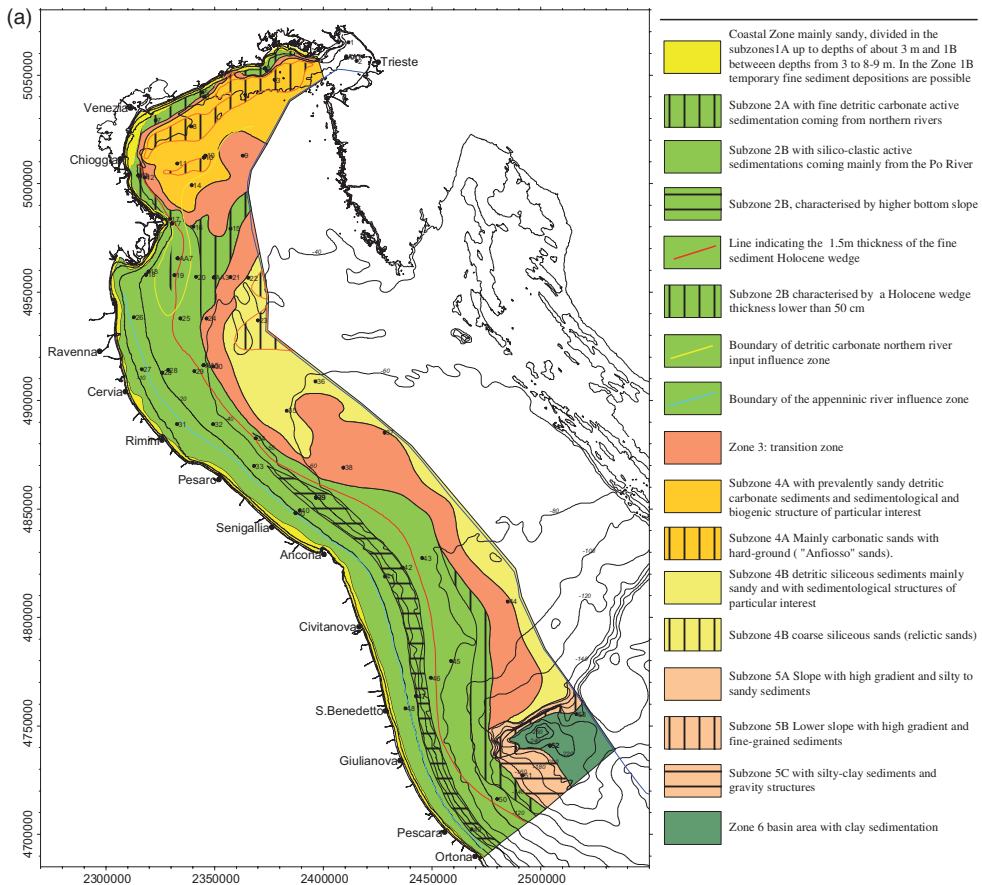


Figure 2. (a) Thematic map of the central and northern Adriatic Sea (PRISMA 1 Project). In the central Adriatic it is possible to see: zone 1, coastal area, predominantly sandy; zone 2, pelitic Holocene wedge, divided into several subzones (i) silico-clastic Holocene fine-grained sediment wedge with input mainly from the Po River, (ii) very thin silico-clastic Holocene fine sediment wedge ( $<50$  cm), and (iii) Holocene wedge with higher bottom sea slope; subzone 5C, Mid-Adriatic slope with variable grain-size composition of clayey silty and sand, and with gravity structures; zone 6, Mid-Adriatic basin area with clay sedimentation. Redrawn from Frascari et al. [16]. (b) Reactivity map of the central and northern Adriatic Sea (PRISMA 1 Project). In the central Adriatic Sea it is possible to note areas with slight, low and middle reactivity. Redrawn from Matteucci et al. [17].

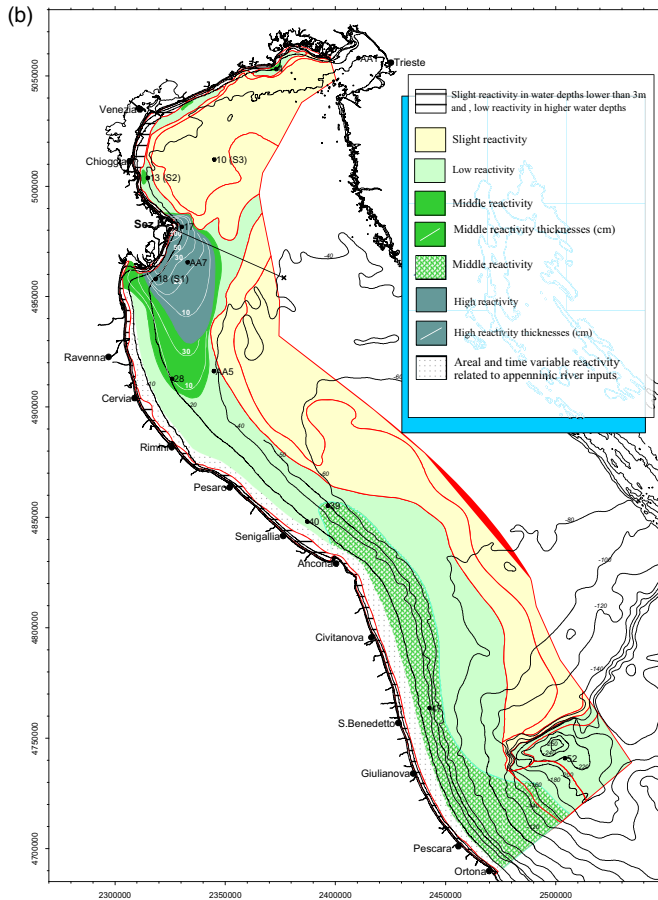


Figure 2. Continued.

in the southern Adriatic Sea and along the Italian coastal area in direct correlation with clay mineral content, iron phase concentrations and heavy mineral fractions, whereas the role of organic matter was unimportant. Furthermore, they found that in the southern Adriatic Sea, the trace element distribution pattern reflects the mafic–ultramafic rocks occurring in Albania and man-made influences, whereas in the central Adriatic, trace elements are introduced from the southern and northern Adriatic and from the land. The main problems with the Donelec et al. study [13] are the low-density sampling net, analyses restricted to the geochemistry only and the age of the research data (1975; Supplementary Table S1b – online only).

Donelec [14] investigated the presence of ferromanganese crusts and coatings on shells and other biogenic detritus (Supplementary Table S1b – online only) exposed to seawater in the Mid-Adriatic Depression (Figure 1(b)). He studied the composition of these crusts and hypothesised the genesis as hydrogenous precipitation at the sediment–water interface in an oxygenated environment. Obviously, the main problem with this study is that it concentrated on only one matrix and was localised at one site for one time.

In the PITAGEM Project, major and trace elements (Supplementary Table S1a – online only) were analysed in the superficial sediments of the Gulf of Manfredonia (Figure 1(b)) together with TOC, TC, TN and grain size [9]. The sediments were collected according to a grid covering the entire gulf for a total of 73 samples (Figure 1). In the study by Spagnoli et al. [9], the origins and main transport and deposition processes of particulates and the presence of biogenic sediments are

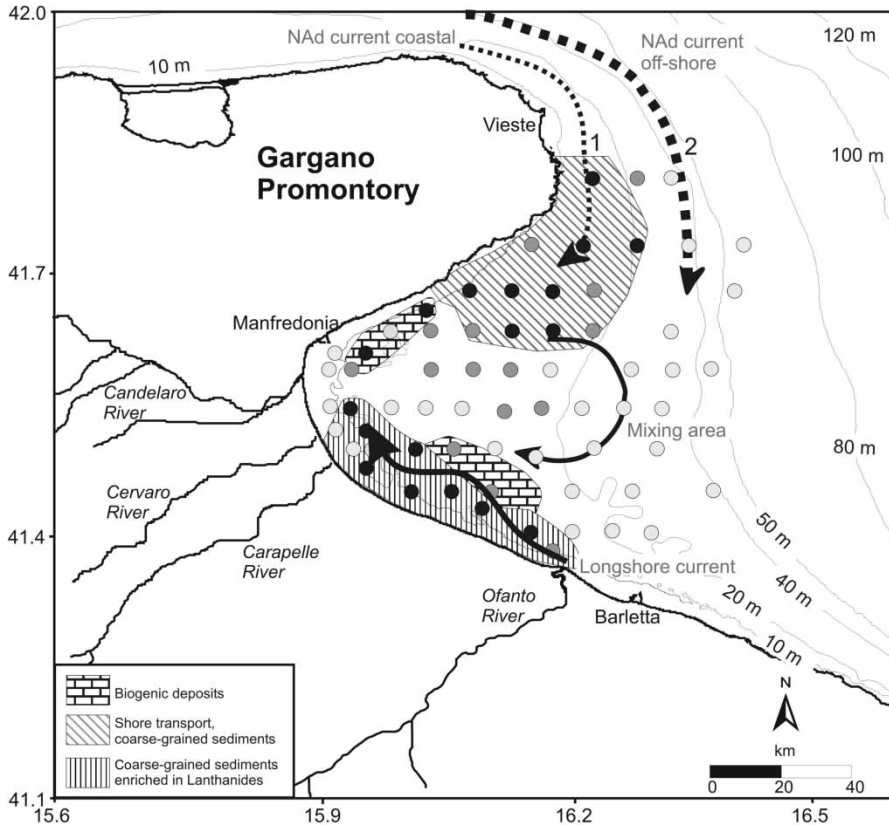


Figure 3. Thematic map of superficial sediments from the Gulf of Manfredonia (Spagnoli et al. [9]). Dots indicate the collection stations. Biogeochemical and grain-size data allowed the separation of areas with different sediment inputs, namely: Ofanto River inputs, characterized by coarse grain size and high lactanide content; coarse-grained north Adriatic sediment inputs, caused by coastal southward current transport (arrow 1); fine-grained north Adriatic sediment inputs, caused by offshore southward current transport (arrow 2); and biogenic intrabacinal deposits. The main dispersion patterns caused by bottom currents (dotted and continuous lines) are also shown.

inferred from the distribution of the biogeochemical properties (Figure 3). The distributions were drawn by drafting superficial distribution maps of single parameters and the ratios between certain elements and then using statistical analyses to form a synthetic map from which the following were identified:

- (1) an area located in the north-east of the gulf (Figure 3) containing sediments transported and deposited by the western Adriatic current flowing southward. These sediments are coarser (sand fraction > 10%) near the coast (because of the higher hydrodynamic energy of the nearshore currents) and finer (clay fraction > 20%) in offshore (related to the lower hydrodynamic energy);
- (2) an area located in the south-west of the gulf, characterised by sediments from the Ofanto River which are distributed north-westward by the nearshore drift;
- (3) two areas in the north-west and south-west characterised by biogenic carbonatic formations; and
- (4) an anticyclonic gyre which distributes the coarser sediments of the Ofanto River north and north-westward and the fine-grained sediments of the Ofanto River in the centre of the gulf with partial mixing with fine sediments coming from the north.



Considering the available geochemical data on superficial sediments of the central and southern Adriatic Sea, it can be stated that data are widely available for the Gulf of Manfredonia [9] and along the Vieste–Split and Pescara–Sibenik transects [3,13], whereas knowledge of sediments from the Mid-Adriatic Depression [3–5,13,14] and other areas of the central and southern Adriatic Sea is only partial [13]. Moreover, the geochemical data were obtained using different analytical methods so it is difficult to compare samples and results from different studies and areas, and even samples from within the same area. In future it would be better to standardise analytical techniques so that data from different studies and different areas can be compared. Furthermore, several studies were carried out a long time ago [3,13,14] (see Supplementary Tables S1a,b – online only) and need to be repeated to evaluate changes in geochemical composition over time.

#### 4. Early diagenesis and benthic fluxes

Studies on early diagenesis processes and dissolved benthic fluxes at the sediment–water interface in the central and southern Adriatic Sea were carried out in the PRISMA 1 [5] and PITAGEM projects [11], and are reported by Baric et al. [17] and Giordani et al. [18].

In the PRISMA1 Project, early diagenesis processes and dissolved benthic flux calculations (Supplementary Table S1a – online only) in the Mid-Adriatic Depression (Figure 1(c)) were studied by analysing and modelling the concentration profiles of different parameters and chemical species in pore waters and the solid phase [5].

In this site, sediments were characterised by the presence of low-reactive organic matter that produces low nutrient concentrations in pore waters and weak nutrient and dissolved inorganic carbon (DIC) fluxes at the sediment–water interface. Moreover, sediments were characterised by an oxic environment in the first 10 cm and a sub-oxic, non-sulphidic environment in the rest of the sediment.

Baric et al. [17] dealt with nutrient benthic fluxes and sediment phosphorus concentrations (Supplementary Table S1b – online only) in the central and southern Adriatic Sea (Figure 1(c)). They found silica fluxes of  $0.16\text{--}2.67\text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , phosphate fluxes of  $0.031\text{--}0.164\text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , ammonia fluxes of  $0.51\text{--}2.03\text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  and nitrate and nitrite fluxes of  $1.32\text{--}1.62\text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ . They also observed that silica fluxes show a decreasing gradient from the coast to the open sea, ammonia was the main nitrogen species in fluxes at the estuary and bay stations, whereas nitrate and nitrite fluxes were predominant at the open sea stations. Furthermore, they observed relationships between phosphate and ammonia fluxes ( $r = 0.699$ ,  $p < 0.01$ ), as well as between phosphate and silicate fluxes ( $r = 0.529$ ,  $p < 0.01$ ).

The study by Baric et al. [17] covers a side of the Adriatic Sea for which early diagenesis processes and benthic fluxes are relatively unknown (Figure 1(c)). The main problem with this research is that the authors measured benthic fluxes but did not study the early diagenesis processes that generate these fluxes.

Giordani et al. [18] investigated the benthic response to particulate organic matter fluxes from the photic layer (Supplementary Table S1b – online only) in stations in the Mid-Adriatic Depression, the southern Adriatic basin and the Otranto Strait (Figure 1(c)). In these stations, in addition to the carbon budget at the seafloor, the sediment oxygen consumption and nutrient benthic fluxes were evaluated by *in situ* and on-deck incubations. The authors reported that in the central and southern Adriatic stations the amount of carbon burial and respired carbon is a function of depth, with particle organic carbon input to the sediments of  $15.7\text{ g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$  in the Mid-Adriatic Depression,  $4.4\text{ g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$  in the southern Adriatic basin and  $6.96\text{ g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$  in the Otranto Strait. Furthermore, in the central and southern Adriatic Sea and in a station in the Ionian Sea, carbon rain to the sediment was between 26 and 3% of primary production.

In the PITAGEM Project, as in the PRISMA 1 Project, early diagenesis processes were studied by analysing and modelling the concentration profiles of different parameters and chemical species in pore waters and in the solid phase (Supplementary Table S1a – online only) for sediment cores collected from five stations of the central and southern Adriatic Sea (Figure 1(c)) [11,19]. Only in the Gulf of Manfredonia (two sites) cores were collected in two different seasons to evaluate annual variability [11].

Pore water concentration data showed high inputs for reactive organic matter in the two shelf stations of the Gulf of Manfredonia (stations S1 and S2) [9] and minor inputs in the basin areas of the central and southern Adriatic Sea (stations A1 and P1) [19]. This is deduced from the higher penetration depth for oxygen (a few centimetres compared with a few millimetres) and the production of minor organic matter degradation products ( $\text{NH}_4^+$  and DIC) in pore waters in the basin sediments.

Furthermore, basin areas can be differentiated because the southern basin station (A1) has minimal organic matter reactivity, the mid-Adriatic station (P1) has medium reactivity and the Otranto Strait station (O2), despite its position, shows the highest reactivity.

In the Gulf of Manfredonia sites, degradation processes led to anoxic non-sulphidic organic matter degradation within the first millimetres of sediments, whereas in basin areas, the oxic layer reaches a depth of 2–10 cm. In basin stations, strong nitrification processes, supported by  $\text{NH}_4^+$  concentrations close to 0 and strong increases in  $\text{NO}_3^-$  concentrations in the first centimetres of the sediments, are also present. Moreover, in the shelf stations of the Gulf of Manfredonia, early diagenesis processes present seasonal cycles with more intense organic matter degradation processes in summer, because of higher temperatures, and little spatial variability.

Sediment–water interface fluxes, calculated by pore water concentration profile modelling and measured directly in the shallow stations of the Gulf of Manfredonia, show differences between shelf and basin stations: nutrient fluxes [ $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{Si}(\text{OH})_4$  and DIC] are much higher in the shelf stations than in basin stations. In the shelf stations, there is a summer increase in benthic fluxes for the higher temperatures and spatial variability caused by different grades of sediment irrigation. In all stations, sediments behave as a source of nutrients and of DIC.

In the PITAGEM Project, early diagenesis and benthic fluxes were investigated using a good and complete approach, in particular, regarding the combination of pore water chemistry and benthic chamber measurements. Again, the main problem is that these studies were limited at two stations in the Gulf of Manfredonia and three stations in the remaining basin areas of the central and southern Adriatic Sea.

On the whole, early diagenesis and benthic flux studies in the central and southern Adriatic Sea have been carried out only in stations in the centre of the two basins, the Mid-Adriatic Depression [5,11,17–19] and southern Adriatic Sea [11,17–19], as well as in the Strait of Otranto [18,19], in a few sites along the Croatian side [17] and in the Gulf of Manfredonia [11]. Consequently, most of the shelf areas and other parts of the central and southern Adriatic basins have not been studied. Considering their importance in understanding the role of sediments in the chemistry of the water column, studies on early diagenesis are very scarce, especially regarding the role of sinks and sources of pollutants, nutrients and carbon. Furthermore, early diagenesis has been investigated only once for most of stations (except the stations of the Gulf of Manfredonia), although it could be studied in at least two different seasons (late summer and late winter) and in different years to evaluate temporal variability.

## 5. Organic matter of superficial sediments

With regard to investigations of organic matter in superficial sediments of the central and southern Adriatic Sea, we should specify that they have been studied by investigating: the biochemical

properties of organic matter [18,20–25], organic matter as an indicator of trophic state and eutrophication assessment [6,26,27], and microbiological characteristics [11].

### 5.1. Organic matter biochemistry

Faganeli et al. [20] determined the organic matter parameters (Supplementary Table S1b – online only) in superficial sediments of the whole Adriatic Sea in order to study the origin, distribution and diagenetic transformations of the organic matter. Concerning the central and southern Adriatic (Figure 1(d)), Faganeli et al. [20] found that a higher terrestrial contribution to sedimentary organic matter is confined to the western part of the Adriatic, owing to the influence of the Po River and other Italian river inflows, and to the south-eastern part of the Adriatic, as a consequence of the local Albanian riverine inputs. Faganeli et al. wrote that this reflects the general water circulation and sedimentological properties of the Adriatic Sea. They also found that the high TOC content in the Mid-Adriatic Depression is a consequence of high productivity in this area. Furthermore, they found a correlation between TOC and  $d^{13}C$  and that variations in these values are a function of the allochthonous organic inputs, so the higher C content and lower  $d^{13}C$  value during the last post-glacial period were because of a larger terrestrial contribution from the increased river inputs. The work of Faganeli et al. [20] is a good example of interdisciplinary research, the only problems with the study being the low-density sampling net, as in Donelec et al. [13], and age of the sampling data (1975, Supplementary Table S1b – online only).

De Simone et al. [21] investigated humic substance (Supplementary Table S1b – online only) distribution along the Apulian offshore (Figure 1(d)) in the context of a multidisciplinary research aimed at identifying ecological environments in the Adriatic and Ionian Seas [22]. De Simone et al. [21] found high humic and fulvic acid concentrations around fluvial mouths with a relative abundance of fulvic acids. They also found humic substance was efficient at chelating some heavy metals, in particular Cd, Cr, Cu and Ni. The study by De Simone et al. [21] was a good complementary and first characterisation study of the main interdisciplinary research of Viel et al. [22], however, it was limited to Apulian shelf sediments.

Giordani et al. [18] investigated the sediment organic matter lability by determining labile biopolymers (Supplementary Table S1b – online only). They reported that the middle and southern Adriatic basins were characterised by a low terrestrial carbon input and the strong refractory nature of sediment organic matter (because of longer residence times in the water column).

Tesi et al. [23] investigated the origin, fate and variability of sedimentary TOC in superficial sediments of the western Adriatic shelf utilising elemental carbon and stable carbon isotopes (Supplementary Table S1b – online only). For the central and southern Adriatic Sea, they studied stations along the coastal shelf sediments from Pescara offshore to Gargano Pit offshore (Figure 1(d)). They reported that the dispersion of fine material drives the superficial TOC distribution on the western Adriatic continental shelf, the main inputs coming principally from the high *in situ* primary production and the high discharge of the Po River. Furthermore, they found that the ‘lighter’ terrigenous TOC ( $-27.1\text{‰ } \delta^{13}C$ ) is preferentially accumulated and preserved on the superficial sediment compared with ‘labile’ algal material ( $-20.4\text{‰ } \delta^{13}C$ ).

Tesi et al. [24], in the context of a more general study on the origin, composition and dispersion of organic matter in the western Adriatic Sea, investigated the biogeochemistry (Supplementary Table S1b – online only) of superficial sediments from the central–western Adriatic Sea shelf (Figure 1(d)). They found three biogeochemical partitions, the central–western sites fall in the Adriatic mud-wedge area. Furthermore, the superficial sediments are strongly influenced by terrigenous humified soil-derived organic matter.

Moreover, Tesi et al. [25] reported a similar study (Supplementary Table S1b – online only) in superficial sediments along a shore-normal transect from the shelf to slope on the Bari offshore (Figure 1(d)). They found different sediment composition between shelf and slope stations, with shelf stations characterised by higher levels of TOC, TN, lignin phenols and *p*-hydroxy-benzene, higher TOC/TN ratios, depleted  $\delta^{13}\text{C}$  compositions and lower levels of fatty, dicarboxylic and benzoic acids.

The studies by Tesi et al. are a good example of innovative research within a multidisciplinary study. The hope is that this approach may be extended to the rest of the Adriatic Sea, in particular the little known eastern side.

## 5.2. Benthic trophic state and eutrophication assessment

To assess the trophic status of the benthic ecosystems, a biochemical approach, based on analysis of the quality and quantity of sedimentary organic matter, was utilised within both the INTERREG II Italy–Greece and Italy–Albania programmes [6,26,27]. The variables investigated included analyses of superficial sediments with regard to water content, porosity, total organic matter, phytopigment, protein, lipid and carbohydrate concentrations (Supplementary Table S1a – online only). Within the INTERREG II Italy–Greece programme, these variables were investigated in March and September 2000 at 24 stations, belonging to 8 transects (Figure 1(d)). The sampling strategy included transects along putative pollution gradients or from anthropogenically impacted areas (i.e. areas facing the Brindisi harbour and the power plant of Mattarelle-Lendinuso), whereas the remaining transects, without any evident anthropogenic impact (including the marine protected area of Torre Guaceto), were utilised as a ‘control’. All the investigated variables displayed significant changes among stations and transects (ANOVA,  $p < 0.01$ ). Significant temporal changes (March vs. September) were observed for chlorophyll-a, phaeopigment, protein, carbohydrate and biopolymeric carbon concentrations (all variables:  $p < 0.01$ ). In both sampling periods, most variables displayed a clear decreasing pattern moving southward. In March 2000, phaeopigment, total organic matter, protein, carbohydrate and lipid concentrations increased with water depth, whereas no clear depth-related trends were observed in September 2000. Synoptic analyses of water column and benthic variables provided different indications and classifications for the trophic state of the investigated coastal marine systems [6]. Meso-oligotrophic conditions emerged from the analyses of inorganic nutrient concentrations and phytoplankton biomass in the water column, whereas eutrophic and even ipertrophic benthic conditions, based on the analyses of quantity and biochemical composition of organic matter in the sediment, were identified (i.e. in coastal areas facing the power plant at Mattarelle-Lendinuso and Brindisi harbour). In particular, the phytopigment content of the sediments changed in response to different sources of anthropogenic impact and resulted in a useful descriptor of trophic state and environmental quality. The highest sediment chlorophyll-a concentrations (up to  $38 \mu\text{g}\cdot\text{g}^{-1}$ ), indicating increasing eutrophication, were found in areas impacted by the discharge of heated waters from a power plant. Moreover, the contribution of the autotrophic biomass to the biopolymeric carbon pool appeared to be a good descriptor of decreasing environmental quality [6,27]. Independent of the sampling period or pollution source, the contribution of the autotrophic biomass was significantly lower in transects subjected to anthropogenic impact than in control areas. Finally, major changes in the trophic state of the benthic systems were clearly identified on the basis of sediment protein content. Benthic systems with protein concentrations of  $1.5\text{--}4 \text{ mg}\cdot\text{g}^{-1}$  are classified as eutrophic, whereas systems with a protein content  $< 1.5 \text{ mg}\cdot\text{g}^{-1}$  are defined as meso-oligotrophic [6].

Analyses of the biochemical composition of sediments collected within the INTERREG II Project pinpoint higher concentrations of phytopigment and biopolymeric carbon (BPC) in sediments from the Italian coast (BPC mean  $1.2 \pm 0.7 \text{ mgC}\cdot\text{g}^{-1}$ ) compared with the Albanian coast,

as well as an increase in protein and a decrease in the contribution of carbohydrate to total biopolymeric carbon (mean  $1.0 \pm 0.4 \text{ mgC}\cdot\text{g}^{-1}$ ). Using a benthic approach to evaluate the trophic status, shallow Italian sediments (0–50 m) were mainly classified as eutrophic (based on the protein content and protein-to-carbohydrate ratio) and were subjected to stronger anthropogenic disturbance. This was particularly evident in areas in front of city harbours (i.e. Brindisi and Barletta) which were classified as hypertrophic and displayed the highest biopolymeric carbon concentrations and protein-to-carbohydrate ratio ( $>1$ ). By contrast, Albanian sediments and deeper Italian stations ( $>50$  m) were characterised mainly by meso-oligotrophic conditions (i.e. lower biopolymeric carbon content and protein-to-carbohydrate ratio) [27].

Sediment data on organic matter, prokaryotes, microphytobenthos and meiofauna collected in a wide sector of the southern Adriatic Sea in the INTERREG II Italy–Albania programme were also used in thermodynamic and network analyses to provide further insights into ecosystem health. The biopolymeric carbon load in the investigated sediments never reached very high concentrations (generally  $<3 \text{ mg}\cdot\text{g}^{-1}$ ). In these trophic conditions, ascendancy, exergy and specific exergy were strictly related to each other and an increase in all goal functions was observed at increasing resource availability. Analysis of the trophic efficiency was particularly sensitive to the environmental state in terms of sustaining complex structure and resource exploitation. In particular, specific exergy, ascendancy/capacity and Finn's cycling index were lower in areas of high anthropogenic impact.

All these findings indicate that the biochemical composition of organic matter in sediments and holistic indicators (exergy, specific exergy and ascendancy) are important when assessing the trophic state and environmental quality of coastal benthic ecosystems.

### 5.3. *Bacteria and Archaea abundance, activity and sedimentary organic matter*

The PITAGEM Project also investigated the quantitative estimate of Bacteria and Archaea and sedimentary organic matter (Supplementary Table S1a – online only) along sediment vertical profiles (1 m sediment cores) for two stations (S1 and S2, Figure 1(d)) in the inner and outer region of the Gulf of Manfredonia [11]. The aim of this study was to investigate factors that might control the prokaryotic community.

The relative importance of the Archaea and Bacteria along a 1 m vertical profile of sediment cores showed a shift in the community composition and a strong dominance of Archaea in the deeper sediment layers (from 33% in the top 0–0.5 cm to 66% in the deep layers, up to 100 cm, respectively).

The biopolymeric organic carbon content (sum of total protein, carbohydrate and lipid carbon equivalents [28]) decreased from 0 to 11 cm in the sediment core, and was unclear along the vertical profile from 11 to 100 cm, with a mean value of  $1.9 \text{ mgC}\cdot\text{g}^{-1}$  for the whole core. Proteins were the main class of biochemical organic matter, followed by carbohydrates and lipids (on average 67.7, 24.2 and 8.1%, respectively). Total prokaryotic abundance was highly correlated with biopolymeric organic carbon from 0 to 35 cm in the cores, indicating a high level of dependence between the development of a microbial community and the labile organic matter content of the sediment. Therefore, the turnover time of the organic matter in the deep-layers resulted in being very long, which meant more time was taken in the consumption of C, on average one year, with a potential effect for organic matter diagenesis and microbial loop functioning.

With regard to the findings described previously, it is possible to conclude that in marine coastal sediments the sub-superficial layers in the upper 1 m are characterised by the progressive replacement of Bacteria with Archaea and the superficial and sub-superficial assemblages are subjected to different forcing factors. This study provides new insights for better comprehension of the interactions between Bacteria, Archaea and organic matter in the benthic system.

In summary, studies involving specific point sampling for organic matter parameters have been carried out in the Gulf of Manfredonia [11] and in isolated stations in the Mid-Adriatic Depression, the southern basin and the Strait of Otranto [18,20]. More extensive, but more targeted, spatial studies (of the organic matter composition to deduce the trophic classification of the sediments and determine the degree of contamination) have been conducted along the Apulian [6,21,26,27] and Albanian shelves. Furthermore, localised studies have been carried out along the southern Italian shelf in the mouths of the main rivers and in front of the Gargano Peninsula ( $\delta^{13}\text{C}$ ) [23,24] and the city of Bari (TOC,  $\delta^{13}\text{C}$ ,  $\Delta^{14}\text{C}$  and CuO oxidation products) [25].

On the whole, research into organic matter has been carried out in separate studies of single parameters or groups of parameters and in restricted areas.

## 6. Mineralogy of superficial sediments

With regard to the mineralogy of sediments in the central and southern Adriatic Sea, previous studies can be grouped into articles and projects that used heavy and light minerals [29–33] or clay minerals [31,32,34–36] to identify areas of sediment origin and dispersion and sedimentation processes.

Pigorini [29] analysed the composition and distribution of heavy minerals, as well as the grain-size composition (Supplementary Table S1b – online only), of marine sediments for the whole Adriatic Sea to identify petrographic provinces, areas of origin for the sediments and sediment dispersion mechanisms. In the central and southern Adriatic (Figure 1(e)), he differentiated: (1) the Shelf Sand Padane Heavy Mineral Province, near the coast, to the Pescara offshore, fed mainly by Po basin sediments; (2) the Padane–South-Augite Trans-Subprovince, between the northern Adriatic shelf and the Mid-Adriatic Depression, fed by both Padane and southern sediments; (3) the South-Augite Province, in the west–central and southern Adriatic, both for muddy and sandy sediments, the principal sediment source of which is the volcanic Ofanto–Vulture Basin of the southern Apennines and the Pleistocene–Holocene volcanic ash of Vulture, Vesuvius and other volcanoes of central and southern Italy (Figure 1(e)); (4) the Coastal South-Augite Subprovince, near the coast; and (5) the Albanese Province on the eastern side of the Adriatic basin, fed by the Dinaric chain (Figure 1(e)). Pigorini [29] also individualised other secondary subprovinces (Split, Brindisi and Otranto) linked to local processes, and, using vector analysis of the heavy mineral data, a main longitudinal dispersal pattern on the shelf and a transversal one in the central and southern basins. Pigorini's study [29] was in-depth and with good coverage of many areas, however, it was limited to heavy minerals, some specific areas such as the eastern shelf or the Gulf of Manfredonia were neglected and the sampling is now dated (Supplementary Table S1b – online only).

Oeltzschner [30] studied heavy and light minerals (Supplementary Table S1b – online only) from shelf sediment of the Gulf of Manfredonia (Figure 1(e)). He found 31 different heavy minerals associated into two groups: the Ofanto mineral association, characterised by the Mount Vulture volcanic complex minerals, dominating the southern and western part of the gulf; and the Padanic–Apenninic mineral association, characterised by Padanic and Apenninic inputs supplied by the current directed south-westward along the Italian coast, in the northern and outer gulf. Based on the heavy mineral distribution, Oeltzschner [30] also supposed that the Ofanto River sediments are redistributed north and north-westward by longshore drift and near-shore currents.

For light minerals, Oeltzschner [30] found that quartz, feldspar and carbonate were the main components in the Gulf of Manfredonia. In the north and the southern part of the gulf quartz prevails, between Mattinata and Manfredonia potassic feldspar prevails, whereas in the biogenic sediments high carbonates prevail. Using heavy and light mineral distributions, Oeltzschner [30] also deduced the presence of an anticyclonic current system in the gulf. Oeltzschner's study [30]

was very accurate with regards to the sampling net, but it was limited to heavy and light minerals and, after 44 years (Supplementary Table S1b – online only), the sampling can be considered out of date.

Nelson [31] analysed the mineralogy of both the clay fraction and the whole sample (Supplementary Table S1b – online only) of bottom sediments in the northern and central Adriatic Sea (Figure 1(e)). He found that fine-grained bottom sediments in the western Adriatic become enriched in montmorillonite moving away from the Po River source, along the prodelta, for continuous bottom current reworking. In the Mid-Adriatic Depression, below a depth of 150 m, Nelson [31] differentiated a bottom sediment mineral association characterised by a high Mg-calcite content which was attributed to benthic organisms living in deeper waters. In this case, the study was limited to the mineralogy of the sediments, the sampling net was very sparse and the collection is very old (Supplementary Table S1b – online only).

Viel et al. [32], in a complex study on the Apulian offshore (in the Adriatic and Ionian Seas) to identify the ecological environments [22], looked at the mineralogy and grain size (Supplementary Table S1b – online only) of Apulian offshore superficial sediments (Figure 1(e)). For the mineralogy, Viel et al. reported that biogenic debris is mainly composed of aragonite and Mg-calcite, the sandy and silty clay sediments are composed of calcite, quartz and feldspar, the most important clay mineral constituents are smectite, kaolinite and illite and the clay composition reflects the sediment and rock compositions of the watershed basins. This was a good interdisciplinary study [22] but was limited to Apulian shelf sediments.

In the INTERREG II Italy–Albania Project [33], mineralogical analyses were guided by microscopy on the sandy fraction and by X-ray diffraction on the mud (silt and clay) fraction (Supplementary Table S1a – online only) of superficial sediments from the southern Adriatic Sea (Figure 1(e)). The main components of the sandy material were lithic clasts, mineral grains, organic fragments, vegetal rests and anthropic materials. The predominant minerals of the muddy fraction were calcite, dolomite, quartz, feldspar, smectite, illite, chlorite and kaolinite.

With regard to the sandy fraction, samples from the Apulian side showed a good amount of lithic clasts (carbonates, volcanic scorias and glass), dark volcanic minerals (magnetite, pyroxene, amphibole and biotite), quartz, feldspar and organic rests. In particular, heavy minerals and volcanic scorias and glass were abundant in the northern sector, suggesting a proximal volcanic source (Vulture Mountain) and supply from the Ofanto River drainage system.

On the Albanian side, the more abundant mineral grains were quartz, feldspar, monazite, chromite, melanite, tormaline, titanite and serpentinised olivine, whereas amphibole, pyroxene and volcanic magnetite were less abundant. On the whole, the ‘Albanian’ samples reflected the supply of detrital minerals from igneous and metamorphic rocks.

The muddy fractions of both sides showed similar compositions: phyllosilicates (smectite, illite, chlorite and kaolinite) were prevalent, and tectosilicates (quartz more than feldspar) and carbonates (calcite more than dolomite) were recognised in lesser amounts.

Few differences were observed from northern to southern sectors in either the marginal area or in the deepest part of the southern Adriatic basin. More calcite was observed on the Apulian side, whereas a positive correlation between illite and chlorite was measured on the Albanian side, in keeping with the different geology of the two regions.

Veniale et al. [34] used clay mineral distribution in superficial sediments of the central and southern Adriatic Sea (Figure 1(e)) to define provenance and dispersion rather than geochemical alteration (Supplementary Table S1b – online only). They reported that clay minerals in the central and southern Adriatic basins indicate two different sources: the volcanic region of southern Italy and the Apennines. In the Mid-Adriatic Depression, clay minerals of Apenninic origin dominate, whereas in the southern Adriatic Sea clay minerals show a depth-controlled distribution, suggesting strong hydrodynamic selection. Moreover, clay minerals originating from the weathering of volcanic glass were also present. In this case, the study is limited to clay mineralogy with a

sparse sampling net excluding some areas (eastern shelf, Gallignani Sill, eastern Mid-Adriatic Depression, Otranto Strait) and the sample collection is very old (Supplementary Table S1b – online only).

Curzi and Tomadin [35] analysed central Adriatic Sea sediments (Figure 1(e)) looking at clay mineralogy and grain-size distribution (Supplementary Table S1b – online only), accompanied by seismic–stratigraphic investigations. They found that the sedimentation patterns were almost unchanged over the last 10,000 years and Apennine sediments (pelitic sediments rich in smectite) are dispersed transversally to the central basin and overlie the Padane, longitudinal, southward dispersion of fine-grained sediments (illite- and chlorite-rich sediments). Furthermore, smectite distributions suggested the presence of low-energy areas south of Ancona. This is a good example of a hydrological study based on clay mineralogy and grain size but it is limited to the central–western Adriatic Sea and the date of sampling is unknown.

Tomadin [36] used clay mineral composition (Supplementary Table S1b – online only) and distribution in the Adriatic mud sediments as tracers of sediment provenance and dispersion. With regard to the central and southern Adriatic Sea, Tomadin [36] reported that illite, smectite and their crystalline indices indicate a predominant longitudinal dispersion of fine-grained sediments, connected with the general Adriatic cyclonic circulation. He recognised two main fluxes directed south-westward along the Italian offshore: the ‘Apennine flux’, near to the coast, and the ‘Padane flux’ in the open sea; and a northernward flux, along the eastern coasts of the central and southern Adriatic basin, the ‘Albanian flux’. Furthermore, in the southern Adriatic basin, turbidity currents flow transversely to the basin and carry clay sediments from the Apulian shelf and the Albanian–Montenegrin shelf into the bathyal basin. The study is a good example of clay mineralogy applied to hydrology, even though it is limited to this parameter and the sampling time is unspecified.

Considering all past research it can be stated that many mineralogical (light minerals, heavy minerals, clay minerals) studies on superficial sediments in the central and southern Adriatic have been conducted on clay minerals in order to determine the sedimentary processes of dispersion [31,32,34–36], but the data have largely been based on and provided by low-density stations or the sampling stations are unknown. Furthermore, samples were generally collected many years ago (see Supplementary Table S1b – online only). These studies therefore need to be repeated in order to evaluate variations in the dispersion and concentration processes over time by using a closer sampling net.

Heavy minerals were studied in the central and southern Adriatic a long time ago [29], and in more detail in the Gulf of Manfredonia [30]. These studies have always aimed to determine dispersion processes and the sediment provenance.

A variety of studies have been carried out on the mineralogical composition of the bulk sample in the southern Adriatic [31–33], along the Apulian offshore [32,33] and a few studies have also been carried out in the Albanian coastal area [29,33]. These are generally associated with grain-size investigations and are mainly aimed at determining the depositional environments, the dispersion currents and the origins of the sediments. The main problem with these mineralogical studies is that they were carried out several years ago [29,30,31,34], and the composition of the areas of provenance, the processes of dispersion and the environment of deposition may have changed since. Another problem is caused by the unknown sampling time [35,36] or sampling net [36].

## 7. Pollutants in superficial sediments

With regard to pollutants, various articles have been published for superficial sediments of the central and southern Adriatic Sea [37–48], whereas recent projects treating pollutants were the INTERREG II Italy–Albania [7,49,50] and the ‘Environmental impact evaluation of the old Porto Romano (Durrës) factory site’ study [12].



Paul and Meischner [37] analysed heavy metal concentrations (Supplementary Table S1b – online only), accompanied by TOC, TP, Ca and Mg-carbonate, mineralogical composition and grain-size distribution, in superficial sediments of the whole Adriatic basin. For the central and southern Adriatic basin (Figure 1(f)), they collected superficial sediment samples along three transects between the Italian and Yugoslavian coasts (Pescara–Sibenik, Vieste–Split and Bari–Dubrovnik) and attributed heavy metal contents only to natural sedimentological processes without any pollution phenomena. The main problems of this study are that the analytical methods are out of date (Supplementary Table S1b – online only), the sampling coverage is limited to three transects (Figure 1(f)) and sampling was carried out long time ago (Supplementary Table S1b – online only), therefore, in the case of pollutants, the study does not represent the current status but could be important historically.

Helios Rybicka et al. [38] carried out trace element determinations on the clay fraction (Supplementary Table S1b – online only) of superficial sediments from the central–western Adriatic Sea and the Mid-Adriatic Depression along 50 transects from the Italian coast, between San Benedetto del Tronto and Termoli, to the mid-line (Figure 1(f)). They found a similar mineralogical composition over the area investigated and a large amount of Cr, Fe, Cu, Pb and Zn associated with the detrital fractions. Furthermore, they wrote that the resulting heavy metal concentrations did not indicate anthropogenic inputs in the investigated area. The research was very accurate as regards the geochemical investigations on the different groundmasses but it was carried out only in a restricted area.

Boniforti et al. [39], using the same samples as Helios Rybicka et al. [38], estimated the mobilisation of some elements (Supplementary Table S1b – online only) under different pH conditions in superficial sediments from the central Adriatic Sea to evaluate the bioavailability of trace elements. They concluded that marine sediment leaching may provide an estimation of ingestion effects for contaminated sediments on biota, leaching may highlight concentrations patterns that are not seen with stronger digestions, and leaching can be used for the earlier detection of anthropogenic sediment pollution. This study is mainly an evaluation of a method rather than a superficial sediment characterisation; furthermore, the investigation was carried out in only a limited area of the western–central Adriatic Sea.

Giordani et al. [40], within the framework of the ASCOP Project, analysed the sediment concentrations of some metals and nutrients (Supplementary Table S1b – online only) in two stations of the central Adriatic Sea, in the Pescara offshore, along the slope, and in the Mid-Adriatic Depression (Figure 1(f)). They found values for these variables that were generally higher than those in the northern Adriatic with an increase in concentrations from coast to offshore for Cu, Fe, organic phosphate (OP), TOC and extractable phosphate (EP). In the case of Fe and Mn, distributions do not show an anthropogenic origin but are caused by the mineralogical composition of the sediments. Furthermore, Giordani et al. [40] established background values for Cu ( $17 \text{ mg}\cdot\text{kg}^{-1}$ ), Pb ( $34 \text{ mg}\cdot\text{kg}^{-1}$ ), Zn ( $77 \text{ mg}\cdot\text{kg}^{-1}$ ) and Mn ( $452 \text{ mg}\cdot\text{kg}^{-1}$ ) in sediments from the Mid-Adriatic Depression. Unfortunately, this article is limited at only two samples and the analytical methods (Supplementary Table S1b – online only) have been updated.

Ferrara and Maserti [41] determined the mercury concentrations in water, suspended matter, plankton and sediments (Supplementary Table S1b – online only) in different stations of the Adriatic Sea. They investigated only two sites in the central and southern Adriatic (in front of Bari and in the centre of the Vieste–Split transect; Figure 1(f)) where they found Hg concentrations in sediments ( $0.08\text{--}0.05 \mu\text{g}\cdot\text{g}^{-1}$ ) comparable with those in other areas of the Mediterranean basin and lower than those of the northern Adriatic. Furthermore, the analytical methods did not recover the total content of the element.

Celo et al. [42] evaluated heavy metal pollution (Supplementary Table S1b – online only) in sediments along the Albanian coast (Figure 1(f)). They presented data as a log-normal distribution plot, the inflection points of which may be used as a threshold between polluted and unpolluted

sediments. They also identified the most polluted area, which was attributed to industrial activities such as mining (Mat River offshore), harbour (Harbour of Durres) and chloral-alkali plants (Vlora Bay), and they also established background levels for the Albanian coast sediments (Hg,  $0.0167 \text{ mg}\cdot\text{kg}^{-1}$ ; Cd,  $0.0471 \text{ mg}\cdot\text{kg}^{-1}$ ; Pb,  $8.76 \text{ mg}\cdot\text{kg}^{-1}$ ; Cr,  $90 \text{ mg}\cdot\text{kg}^{-1}$ ; Cu,  $10.5 \text{ mg}\cdot\text{kg}^{-1}$ ; Zn,  $40 \text{ mg}\cdot\text{kg}^{-1}$ ). In this study, the main problem is the very confined investigation area that is limited to coastal sediments of the Albania.

Di Leo [43] analysed major and trace elements (Supplementary Table S1b – online only) in superficial sediments from the Gulf of Manfredonia (Figure 1(f)) in order to investigate pollution levels. She found that only Mn and P are enriched in modern sediments and this enrichment is attributed to changes in solid discharge from rivers flowing into the gulf rather than consequence of industrial contamination. Other elements such as Ti, Fe, Ni, Cr and V are affected by anthropogenic sources but their distribution is linked to clay mineral and oxy-hydroxide distributions or to specific phases such as for the Ti. Despite the good approach used, this research is affected by a sparse sampling net and is limited to the Gulf of Manfredonia.

Martincic et al. [44] studied trace metal pollution (Supplementary Table S1b – online only) in some sites of the eastern Adriatic Sea shelf (Figure 1(f)). They found that Zn, Cd, Hg and Cu concentrations were comparable with similar unpolluted sites in the Adriatic Sea except for areas under direct anthropogenic influence. Furthermore, they found that the Pb concentrations were a factor of two higher than 1976 analyses and this was attributed to vessel traffic. Again, the main problem with this study is the very restricted area of investigation.

Fowler et al. [45], within the context of the ELNA Project, studied levels and distributions of trace metals and PCB compounds (Supplementary Table S1b – online only) in superficial sediments at four stations in the Mid-Adriatic Depression (Figure 1(f)). They found the lowest concentrations for PCB ( $1.5 \text{ ng}\cdot\text{g}^{-1}$ ), mercury ( $0.067\text{--}0.224 \text{ kg}^{-1}$ ) and other trace elements (Li, Mn, Co, Ni, Cr, Zn, As, Ba, Pb, Th, U) in sediments of the Mid-Adriatic Depression compared with northern Adriatic areas, because of the anthropogenic input of substances via the Po River. They also reported a small reduction in PCB loading in the ecosystems over the past two decades despite a significant reduction in their use over that time, indicating the persistence of these compounds in the marine environment. This article is characterised by a good analytical procedure and approach, but only a few samples in the central Adriatic Sea.

PCBs were also investigated by Pozo et al. [46] (Supplementary Table S1b – online only) in superficial sediments from two Marine Protected Areas (Figure 1(g)) of the southern Adriatic Sea. They did not find PCB enrichment, but the research was limited to only two coastal sites.

Storelli et al. [47] investigated the relationships between heavy metal concentrations in sediments (Supplementary Table S1b – online only), macroalgae and benthic species along the continental shelf of the Apulian coast (Figure 1(g)). For sediments, they found low metal levels except for Fe, which presented high values attributed to anthropogenic input. Furthermore, they found a relationship between metal concentrations in sediments and holothurians, suggesting that *Holoturia polii* could be used as bioindicator for Hg and Cu contamination. In this case, the investigation concentrated mainly on setting up a new method to evaluate marine environmental pollution rather than the characterisation of superficial sediment; in addition, the research was limited to the Apulian coastal sediments.

In the complex study on the Apulian offshore (both in Adriatic and Ionian Seas), Viel et al. [22] investigated PAH and PCB concentrations (Supplementary Table S1b – online only). De Simone and Massimino [48] found PAH concentrations close to pristine background values, higher concentrations were localised to an area in front of Brindisi and Lecce. For PCB levels, they found appreciable concentrations in coastal areas, particularly for Lindane, the distribution of which is connected with agricultural activity in the region. The work by De Simone and Massimino [48], like that of Viel et al. [22], was a good complementary and first characterisation study, however, it was limited to Apulian shelf sediments.

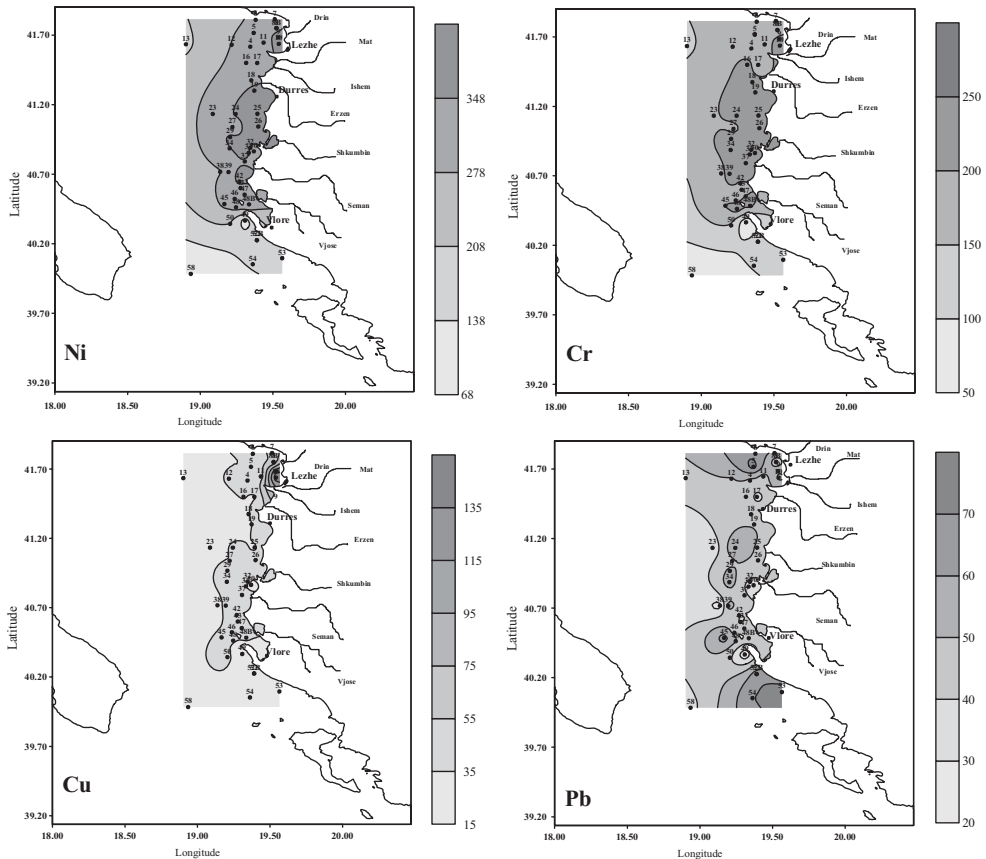


Figure 4. Spatial distribution of Ni, Cr, Cu, Pb in total superficial sediments in the INTERREG II Italy–Albania. Metal concentrations are expressed in  $\text{mg kg}^{-1}$ .

Trace metal concentrations and speciation and PAH distribution (Supplementary Table S1a – online only) have also been determined for coastal sediment samples collected in Albania and the Italian offshore (Figure 1(g)) within the framework of the INTERREG Italy–Albania Project [7,49,50].

The mean concentrations of Cd, Cu, Zn and Pb are similar to the data reported for Dinaric chain-derived sediments by Bogner et al. [51], whereas those for Ni, Cr and Mn are higher. Moreover, in some selected areas such as the Drin and the Shkumbin Bay, concentrations of Cr, Fe, Ni and Cu (Figure 4) are significantly higher than background levels, probably because of discharging mines and smelter activities [52].

The relationship between heavy metal content and grain size has also been considered. All metals, except Cu and Cd, accumulated in the finest fraction, which constituted up to 95% of most of the considered sediments.

A good correlation has been found for Ni, Cr, Fe, Zn and Cu in the entire area and also the principal component analysis suggested a common origin for these metals in the analysed sediments.

Moreover, Albanian coastal sediments have been shown to be highly influenced by river inputs, as confirmed by the decreasing of concentrations moving from coast to offshore. In particular, Fe and Ni became more homogeneous, whereas Cr, Cu, Cd, Zn and Mn showed relative maxima corresponding to Drin and Shkumbin (Cr) or to the mouth of the Drin (Cu, Zn, Mn and Cd). Pb

represents an exception to the general trend among the heavy metals, meteoric and atmospheric inputs being important for this metal (Figure 4).

With regards to speciation, a selective extraction procedure (Supplementary Table S1a – online only) carried on sediments collected along the Albanian coast gave information on heavy metal bioavailability and mobility.

All metals were mostly associated with the most refractory phases, i.e. the residual, which has a negligible environmental impact and constitutes up to 80% of the total concentration. This confirms the hypotheses on the main origin of the high heavy metal content found in the sampled area, i.e. the mineralogical composition of the coastal shelf and direct discharge into the sea of the solid particles from rivers flowing through a hydrographic basin with a prevalence of serpentine soils.

Nevertheless, Cr, Cu, Ni and Mn are present in significant amounts in the labile fraction, particularly in the Drin Bay area. This reveals a recent river input for these metals, related to mining and industrial wastewater discharge. In particular, the concentration of bioavailable Ni exceeds Effect Range Low (ERL) values ( $21 \text{ mg} \cdot \text{kg}^{-1}$ ), suggesting a possible toxic effect on the benthic community, and Cr levels were 10 times Italian coastal values, where reduced bacterial activities were observed related to the labile Cr concentration [27]. In the case of Mn, the highest values found in the labile phase (which comprises carbonates) can be also justified by the sediment richness in organogenic carbonate debris [33]. The case of labile Cu is very interesting, it clearly overlaps Cr distribution, with the highest values ( $\sim 17 \text{ mg} \cdot \text{kg}^{-1}$ ) near the Drin mouth and the lowest ( $< 1.7 \text{ mg} \cdot \text{kg}^{-1}$ ) south of Durres. This can be ascribed to mining activity, because in the north of Albania serpentine soils, volcanogenic massive sulphides and copper deposits can be found [29]. Moreover, Drin Bay sediments, together with those from Vlora Bay and Karavasta Lagoon, show higher protein/carbohydrate ratios than other Albanian sites, indicating sediments rich in organic matter of recent origin (excretion, dead organisms, etc.) [27]. The richness of recent organic matter in Drin Bay sediments supports the presence of a Cu labile percentage higher than in other investigated areas, suggesting an important role for such organic matter in binding Cu carried by local rivers.

In conclusion, the trace metal study in the INTERREG Italy–Albania Project allows us to state that sediments in the sampled area are not heavily polluted, with the exception of those collected in Drin Bay.

With regard to the PAHs investigated in the INTERREG Italy–Albania Project [7], of the 16 PAHs indicated as priority pollutants by the US Environmental Protection Agency (EPA), only pyrene, fluoranthene, benzofluoranthene, chrysene and benzoanthracene were found in some of the sediments considered for metal analysis. The concentration was very low ( $2\text{--}8 \text{ ng} \cdot \text{g}^{-1}$ ) and, moreover, there was no evidence of river input influencing PAH distribution, as found for heavy metals.

In this case, as in the article by De Simone and Massimino [48], the investigation was a good complementary and first characterisation study, the only problem was that it was limited to Albania offshore sediments.

Pesticides were investigated in the research ‘Environmental impact evaluation of the old Porto Romano (Durres) factory site’ [12].

In the north of Durres (Albania), 1 km from the sea, a chemical and pesticide factory was active in the past. Its mainly produced Lindane (HCH- $\gamma$ ), and as a consequence of these past activities, the area is highly polluted with HCH.

In order to assess the presence of Lindane in sea sediments in this area (Supplementary Table S1a – online only), to protect human health, 16 superficial sediment samples were collected along the Albanian and Montenegro coast, north-east of Durres, in November 2007 (Figure 1(g)).

Sediment samples showed a concentration range from 1 to  $22 \text{ ng} \cdot \text{g}^{-1}$  HCH. The higher Lindane concentrations were encountered in the north of the investigated area (Figure 5). This pattern is attributed to the eastern Adriatic superficial current flowing northward and forming eddies along

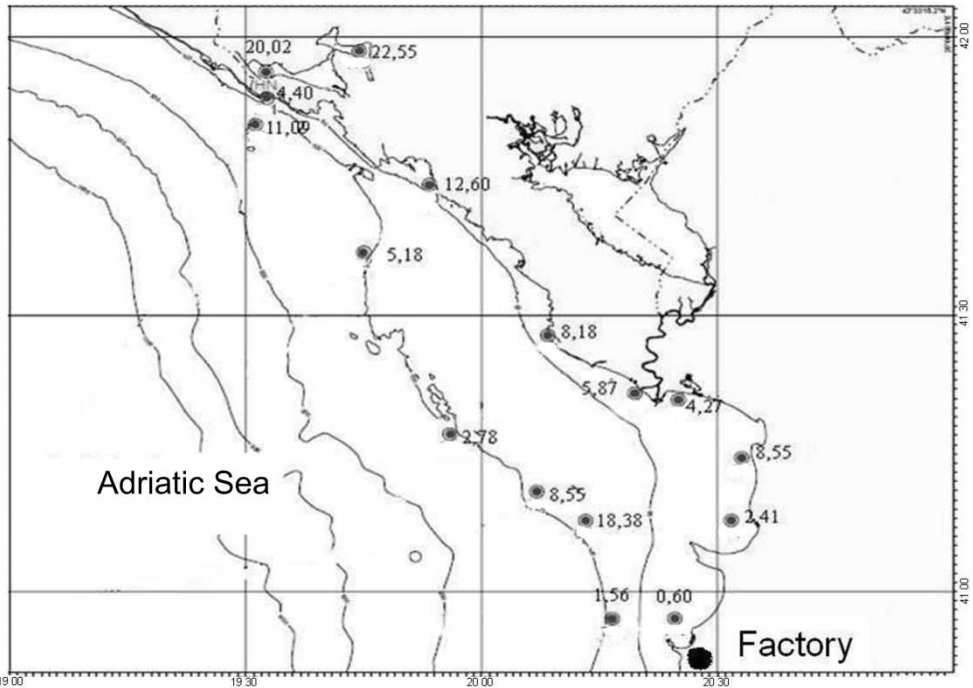


Figure 5. Position and concentration ( $\text{ng}\cdot\text{g}^{-1}$ ) of Lindane in the 16 sediment samples (circled points) and the position of the pesticide factory.

the coast; this current transports and deposits the Lindane-containing suspended particles flowing out from the factory channel.

By analysing all pollution research, we can see that data for heavy metals in central and southern Adriatic Sea sediments show a low density covering in coastal Italian and Albanian areas and the Mid-Adriatic Depression [37–47]. Furthermore, the data were generally obtained a long time ago, using methods that have changed a great deal over the years and cannot therefore be compared (Supplementary Tables S1a,b – online only). Moreover, data are almost absent in the southern area of the Adriatic basin. Other chemical species of anthropogenic logical origin were studied: PCBs in the Mid-Adriatic Depression [45] and other localised areas [46], pesticides along the Albanian coast [12], and PAHs in a few stations along the southern Apulian [7,48] and Albanian coasts [7], although there are no data concerning the concentration of tin organic compounds in the central and southern Adriatic. On the whole, both the areal and temporal coverage for all these pollutants are very sparse.

## 8. Grain-size distributions in superficial sediments

The most complete, but also the oldest, maps of grain-size distribution of superficial sediments from the central and southern Adriatic Sea are those by Pigorini [29], Gallignani and Selli [53] and Colantoni [54,55]; other superficial areal sediment grain-size distribution in specific and localised areas of the central and southern Adriatic Sea have been shown by Curzi and Tomadin [35] for the central–western Adriatic Sea, by Sigl [56], Colantoni and Gallignani [57] and Spagnoli et al. [9] for the Gulf of Manfredonia, by Gallignani [58] and Viel et al. [32] for the Apulian offshore, and by Loiacono [33] for the southern basin.

Pigorini [29] presented two grain-size distribution maps (sand fraction and generalised gross lithology) in which he characterised the shelf sands in the central and southern western Adriatic Sea, the predominant mud deposition area in the central and southern basins and a bathyal elongated sand area of reworked sediments. Pigorini's [29] sampling net was accurate enough, even though some specific areas, such as the eastern shelf and the Gulf of Manfredonia, were neglected (Figure 1(h)), furthermore the sampling was carried out long time ago (Supplementary Table S1b – online only) and some coastal environments may be changed.

Gallignani and Selli [53] (Supplementary Table S1b – online only) and Colantoni [54,55] showed grain-size distribution maps similar to that given by Pigorini [29] with the addition of biogenic sandy calcarenites and biogenic concretions in the Gulf of Manfredonia and along the Apulian coast. Unfortunately, these articles do not report the sampling net used and the collection time.

Curzi and Tomadin [35], in conjunction with mineralogy (see Section 6), carried out a study on grain size (Supplementary Table S1b – online only) in the central–western shelf and the Mid-Adriatic Depression of the Adriatic Sea (Figure 1(h)). In these areas, they characterised belts sub-parallel to the coast with different grain-size composition (present sands, silt–clay, clay–silt, relictic sands) and the area of Mid-Adriatic Depression with prevalent clay. As stated for the mineralogical observations, this is a good example of a hydrological study based on clay mineralogy and grain size but is limited to the central–western Adriatic Sea and the date of sampling and analytical methods used are unknown.

Sigl [56] analysed the sediment grain-size composition of the Gulf of Manfredonia (Figure 1(h)) in combination with mineralogical (carbonate content) and current-meter studies to determine the distribution patterns and the direction of sediment transport (Supplementary Table S1b – online only). He identified a 'littoral sand zone', close to the coast, a 'pro-littoral transition zone' (polymodal and poorly sorted sandy to silty sediments), an outer 'mud zone' (polymodal and very poorly sorted silty to clayey sediments), and the 'scogliera zone' with differentiated bottom relief constituted by mud banks, reef-like organic structures and highly eroded limestone outcrop and composed of recent silty mud, authigenic organic debris, terrigenous relict sands and recent carbonates rich in aragonite and Mg-calcite. Sigl [56] also recognised six sediment types (sand, silty sand, sandy silt, silt, mud and clay) in the Gulf of Manfredonia, with decreasing grain size with increasing water depth or distance from shore, and attributed this to wave action. Furthermore, he characterised a southward directed tongue of silt caused by the southward flowing western Adriatic current and hypothesised a clockwise current system distributing river sediment load predominantly north-westward. The sampling coverage and approach of this study were exhaustive, but, as for other works the sampling time was fairly long ago (Supplementary Table S1b – online only).

Colantoni and Gallignani [57] studied the grain-size composition (Supplementary Table S1b – online only) of surface sediments in the Gulf of Manfredonia (Figure 1(h)) in conjunction with geophysical investigations. They characterised three elongated belts: the coastal sands and the silty-clays, characterised by present-day sedimentation, and the offshore sands. Furthermore, they characterised also the 'scogliera' zones with rough morphology. Colantoni and Gallignani [57] used also scuba diving for *in situ* studies of microtopography and to collect samples and photographs. In this way, they characterised three different seafloor types: sands with rhizomes of *Posidonia*, sands and pebbles, and reef-like organogenous concretions. Finally, they also found a supply of fine materials that deposit on the biogenic structures and killed the *Posidonia* prairies. In this case, the study presents a rather sparse sampling that is 40 years old.

Spagnoli et al. [9], in the context of the PITAGEM Project, also analysed the grain size (Supplementary Table S1a – online only) of superficial sediments from the Gulf of Manfredonia (Figure 1(h)). They characterised areas with different grain size and biogeochemical composition (see Section 3 for more details): the north-eastern area, fed by the southward directed western Adriatic current, the central and eastern part of the gulf, with a mixed feeding, the south-western

area, fed by the Ofanto River sediments and the biogenic deposits. As for the geochemical comments, it should be noted that the study presents a good sampling net and is interdisciplinary, but is limited to the Gulf of Manfredonia.

Galignani [58] discussed the grain size of surface sediments (Supplementary Table S1b – online only) of the south-western Adriatic shelf between Bari and Torre Canne (Figure 1(h)). In this study, he reported, moving seaward from the coast: coastal sands, a coralligenous bank, clay, clayey sands and sands. Only the coastal sands and clay are related to present-day sedimentation. Even though it presents a good sampling coverage, this study is limited to grain-size analyses and because it was carried out 38 years ago can now be considered out of date (Supplementary Table S1b – online only).

Viel et al. [32], in addition to the study on mineralogy (see Section 6), investigated the grain size (Supplementary Table S1b – online only) of the superficial sediments from the Apulian offshore (Figure 1(h)). With regard to the grain-size composition, they found two main types of superficial sediment: those which are predominantly bioterritic, i.e. composed of biogenic debris, and those with a higher lithogenic grain content, which are composed of either sandy or silty-clay sediments. As for the mineralogical comments, this is a good interdisciplinary study but is limited to Apulian shelf sediments.

In the INTERREG II Italy–Albania Project 100 superficial samples were collected for grain-size analyses (Figure 1(h)) [32]. The gravel (>2 mm), sand (0.005–2 mm) and mud (<0.005 mm) fractions were separated (Supplementary Table S1a – online only). Most samples are from coastal or inner shelf bottoms, secondarily from the outer shelf or deep sea area (Figure 1(h)). The analysed sediments, lacking gravel, were classified according to Nota binary classification (1958) [59]; mud (<5% sand), sandy mud (5–30% sand), very-sandy mud (30–50% sand) and muddy sand (>50% sand). This classification allows recognition of the main depositional mechanisms: traction (sands) or suspension (muds). The result is a sedimentological and environmental hydrodynamic map (Figure 6). The coarsest sediments can be interpreted as relict sediments, the mud is related to suspended load from settling of terrigenous grains, the mixed sand–mud sediment may be related to dilute turbulent flows or hemipelagites.

In general, on the Albanian side, mud was dominant: it was very abundant in the coastal area of the northern sector as far as the middle shelf (depth 100 m), whereas in the outer shelf (as far as 200 m) sediments were sandy muds and muddy sands.

On the Apulian side in the northern sector (Manfredonia–Monopoli), it was possible to note the same grain-size distribution as in the Albanian northern sector: mud in the marginal areas (coast and inner shelf), and sandy mud or muddy sand in outer shelf. In the southern sector (south of Monopoli), the whole shelf was dominated by sandy mud, whereas the slope and deepest basin (730–1200 m) sediments were muds or sandy muds.

In conclusion, the sediments of the southern Adriatic Sea bottom were mainly muds; in very few samples the sand exceeded 50%. Some differences were evident in the cross-profiles between the northern and southern sectors. In the latter, the coastal sediments appeared sandy, whereas in the deepest area the muds were common. By contrast, in the northern sector mud is dominant in the coastal areas; coarser sediments are frequent in the shelf. It is likely that during the Holocene both the northern Albanian and Apulian coasts received more and finer-grained sediments from rivers, whereas the coarser sediments of the outer shelf may be interpreted as relict sediments, not in equilibrium with the present-day sedimentary conditions.

For the grain-size data, it can be stated that although there is ample spatial and temporal data for the Gulf of Manfredonia [9,33,56,57] and along the Apulian offshore [32,33,58], less is available for the Albanian shelf [33] or other localised areas [35]. Grain-size data for the rest of the basin are sparse and were obtained a long time ago [29,53–55], so it would be useful to repeat the studies carried out several years ago and use a greater spatial frequency because the inputs, processes of dispersion, and environments of depositions may indeed have changed in the meantime.

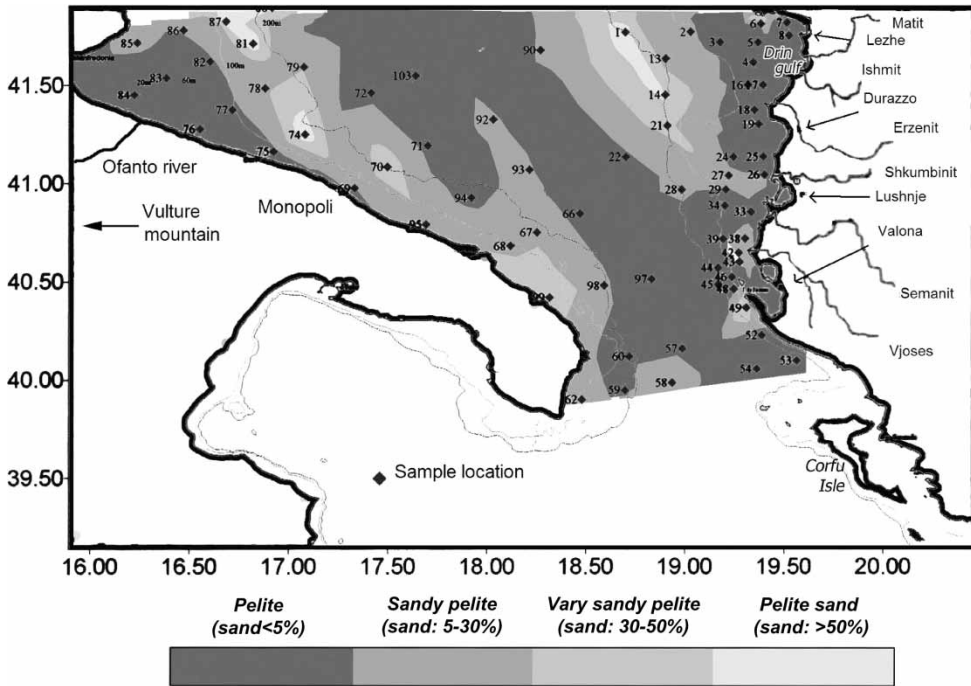


Figure 6. Grain-size classification of superficial sediments from the southern Adriatic Sea elaborated in the INTERREG II Italy–Albania Project. Pelite (<5% sand), sandy pelite (5–30% sand), very sandy pelite (30–50% sand) and pelitic sand (>50% sand). Black dots indicate sampling stations. Grain-size classification according to Nota (1958) [59].

## 9. Conclusions

This study aimed to present the current status of geochemical (major and trace elements), biochemical (total organic matter, TOC, TN, OP, isotopic carbon composition, Bacteria, Archaea, and various organic compounds) and mineralogical (minerals on bulk sample, heavy minerals and clay minerals) parameters, grain-size composition, principal pollutants (heavy metals, PAHs, PCBs and pesticides), early diagenesis studies and sediment–water interaction processes (benthic fluxes) in superficial bottom sediments from the central and southern Adriatic Sea by combining information provided by authors who have taken part in recent research projects and information from the literature. Using these two sources of information, it was possible to identify where there is full knowledge of the parameters considered and in which areas these parameters have been studied, where relevant knowledge is lacking, and especially where interdisciplinary studies would be useful.

On the whole, the biogeochemical, mineralogical, pollution and grain-size studies in the central and southern Adriatic Sea superficial sediments are limited to specific areas, are partial, generally only consider individual parameters without being interdisciplinary in nature and, with the exception of some more recent projects (ASCOP, PRISMA 1, PITAGEM and INTERREG II Italy–Albania), were generally carried out long time ago. Consequently, there are no holistic studies of the parameters and their temporal development for the whole of the central and southern Adriatic Sea.

Last, but not least, with the exception of studies on the nature of the organic substances ( $\delta^{13}\text{C}$ ) in sediments from central and southern Adriatic, there are no studies of the isotopic geochemistry aimed at determining the provenance of the sediments (such as  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ ) or



other processes regarding the diagenetic selection (such as  $^{56}\text{Fe}/^{54}\text{Fe}$ ). Furthermore, there is a complete lack of studies on particular pollutants such as organotins.

Based on previous findings and as a main and final conclusion of this review, it can be stated that it would be very useful to carry out an interdisciplinary and holistic study regarding all the parameters investigated (geochemistry, organic matter, early diagenesis, mineralogy, pollutants, grain size), adding the unknown parameters (some isotopes and pollutants) for superficial sediments of the central and southern Adriatic Sea.

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