

Review

DPSIR Model Applied to the Remediation of Contaminated Sites. A Case Study: Mar Piccolo of Taranto

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Abstract: The study critically analyses the complex situation of the Mar Piccolo of Taranto (South of Italy), considered one of the most polluted marine ecosystems in Europe. In order to investigate possible cause–effect relationships, useful to plan appropriate planning responses or remediation technologies to be adopted, the Driver–Pressure–State–Impact–Response (DPSIR) model was applied. Methodologically, about 100 references have been considered, whose information was organized according to the logical scheme of the DPSIR. The results showed how the Mar Piccolo is the final receptor of pollutants coming from all industrial and agricultural activities, especially due to its natural hydrogeological network conformation. The anthropic activity represents a critical impact on the ecosystem due to the subsequent marine litter. The mobility of contaminants from sediments to the water column showed the potential risk related to the bioaccumulation of organisms from different trophic levels, posing a threat of unacceptable magnitude to human safety. The paper concludes by discussing the actions currently implemented by the authorities in response to the anthropogenic impacts as well as the need for new ones concerning both plans, programs, and remediation interventions. The case study shows how the DPSIR is a useful framework to organize extensive and heterogeneous information about a complex environmental system, such as the one investigated. This preliminary organization of the available data can represent the starting point for the development of a DPSIR-based Environmental Decision Support System (EDSS) with robust cause–effect relationships.

Keywords: complex systems; holistic approach; marine sediments; pollution phenomena

1. Introduction

Economic development and industrialization have led to population growth and rapid urbanization in Europe. This economic progress allowed cities to become centers of production, commerce, and governance. On the other hand, it also generated environmental and health problems, due to the deterioration of environmental matrices caused mainly by industrial and anthropic activities. Environmental matrices, in fact, can be contaminated with metals, organic compounds (hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), aromatic solvents, polychlorinated biphenyls (PCBs)), pathogenic microorganisms (*E. coli*, coliform, and *Salmonella*), and others [1]. Several coastal-marine areas in Italy coexist with large industrial and port settlements that have led, over time, to compromise the whole marine ecosystem. Some of them have been included by the National Programme for Environmental Remediation and Recovery in the contaminated Site of National Interest (SNI) list (Ministerial Decree 468/2001) and recovery and remediation activities are planned in these areas [2].

Modern problems (e.g., pollution, urban growth, environmental risks) are complex and often transcend spatial and temporal scales. Scientific research and decisions are commonly limited to a particular scientific field or economic concern. Bovenberg and Smulders [3] developed a model on pollution-augmenting technological change. Neris et al. [4] worked on a computational code for human health risk assessment HHRISK (Human Health Risk). In addition, El Hattab et al. [5] used a Sustainable Urban Drainage Systems (SuDS) for urban drainage systems to cope with continuous population growth and urban sprawl. Ash and Fetter [6] applied the EPA's Risk-Screening Environmental Indicators Model to investigate correlations between demographic behavior trends and pollution in cities. Keller et al. [7] proposed a global assessment of chemical effluent dilution capacities from a macro-scale hydrological model. Several models have been used to describe environmental compartments, but none of them has linked together all cause–effect relations among environmental matrices. The DPSIR (Driving force–Pressure–State–Impact–Response) model [8,9] is a causal framework for describing the interactions between society and the whole environment. Establishing a DPSIR framework for an extremely compromised case is a complex task as all the various cause–effect relationships have to be carefully analyzed and environmental changes can hardly be attributed to a single cause [10]. In literature, many are the cases where the application of the DPSIR model has highlighted connections and relations essential for a complete understanding of a complex polluted site [11–17]. Lofrano et al. [11] evaluated the Sarno river development (one of the most polluted rivers in Europe) in the last 60 years (1951–2014), considering socio-economic and environmental issues, collecting information from scientific papers, public datasets, and technical monitoring reports. Caeiro et al. [12] applied the DPSIR Model to the Sado estuary in a GIS context assessing social and economic pressures. Huang et al. [13] developed a DPSIR model that incorporates GHG (Greenhouse Gases)-related indicators and evaluates their relationships using a cause–effect chain of GHG emissions in Taiwan. Lin et al. [14] used a DPSIR model and data collected from coastal wetlands in Xiamen (China), analyzing temporal changes in regional coastal wetland ecosystem structure and function from 1950 through 2005. The results showed that anthropogenic drivers of coastal wetland degradation in this region increased substantially since 1950, and this is correlated with a decline in coastal wetland function over the same period. Jago-on et al. [15] used a DPSIR framework to analyze the issues and problems of the subsurface of several Asian cities (Bangkok, Jakarta, Manila, Osaka, Seoul, Taipei, and Tokyo), and suggestions are made for additional indicators to improve our description of the stages of urban development for the future. Akbari et al. [16] used the MCDM (Multi-criteria decision making)–DPSIR approach to structure information and uncover the underlying relationships between human activities and environmental problems for desertification risk management in northeastern Iran. Some of these researches propose mathematical methodologies able to verify cause–effect correlations. Others, such as Lofrano et al. [11], suggest that before such approaches can be developed, it is essential to systematize existing data. Given the complexity of an environmental system, it is appropriate that such an arrangement should be carried out according to the individual elements of the DPSIR.

In this context, the research applies the DPSIR framework to assess the factors that contribute to the degradation of one of the most polluted marine basins in Europe. By means of a review, the main goal is to create a better understanding of the complex situation of the Mar Piccolo of Taranto (southern Italy), with a focus on cause–effect relations. The collection of information from scientific papers, public datasets, and technical reports aims at highlighting all industrial, socio-economic, and environmental issues that made Mar Piccolo a site of extreme environmental crisis.

2. DPSIR Framework of the Study

DPSIR considers a chain of causal links starting from “driving forces” (economic, environmental and human activities) through “pressures” (emissions, waste, discharges, etc.) to “states” (physical, chemical and biological situation of biota and environment) and “impacts” on targets, such as ecosystems and human health, eventually leading to political or technical “responses”.

All various cause–effect relations have to be carefully considered when developing a DPSIR framework for a complex case study, such as Mar Piccolo of Taranto.

As a first step, all data and information about the five different elements in the DPSIR chain need to be identified and collected. Responses can have a direct effect on any element of the chain: to driving forces through structural interventions, to pressures through technological and prescriptive interventions, to states through remedial actions, and to impacts through the economic compensation for the damage. Figure 1 shows a schematic representation of the DPSIR framework applied to the case study analyzed in this manuscript and described in Section 3.

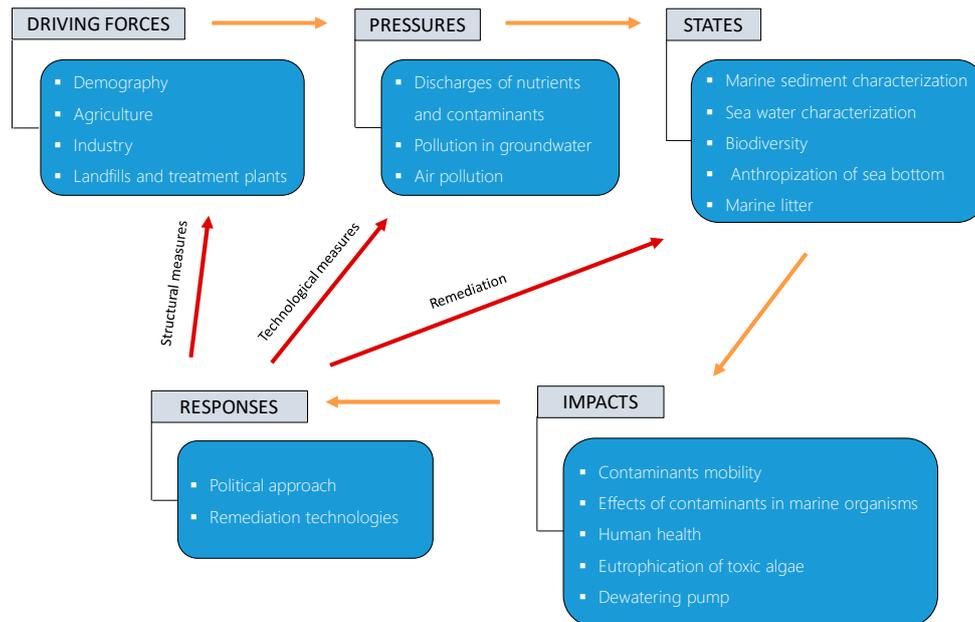


Figure 1. DPSIR framework of the study.

3. Case Study General Framing

Mar Piccolo of Taranto is an inner sea, part of the Ionian Sea, Southern Italy, and it is classified as “Contaminated Site of National Interest” established by the National Law 426 [18]. It is part of the Gulf of Taranto together with the Mar Grande, as shown in Figure 2.

With a total surface area of about 21 km², Mar Piccolo is structured in two inlets, called “First Seno” and “Second Seno”. First Seno has a maximum depth of about 15 m and Second Seno of about 10 m.

The Mar Piccolo is connected to the Mar Grande through two channels: The Navigable channel and the Porta di Napoli channel [19]. Furthermore, the Mar Piccolo is characterized by the presence of local channels, rivers, and submarine water springs called “cetri”.

This basin has been characterized by several anthropic activities in the last half-century. Severe industrial impacts made Mar Piccolo one of the most polluted environmental areas in Europe, despite an intense mussel farming culture [1].



Figure 2. (a) Map of municipalities near the Mar Piccolo of Taranto, and (b) localization of industrial activities.

4. Driving Forces

4.1. Demography

Taranto is the most populous city in the Mar Piccolo catchment area with 195,279 inhabitants in 2019. From 1861 to 1921, the population in Taranto moved from 24,528 to 97,853 units [20]. This growth was related especially to the development of the Military Arsenal and shipyards. In the same period Crispiano, Statte, and Martina Franca towns (located in the surrounding area) also recorded a doubling of the inhabitants. In 1965, the steel factory “Italsider” (today called Ex-Ilva or ArcelorMittal) was inaugurated, becoming one of the most productive steel centers in Europe. From 1961 to 1971, the city recorded a growth of 17% with a concurrent per capita income increase of 274% [20]. It is evident how economic and industrial activities led to an urban development modifying the territorial planning, with high-specialized areas around the main cities. Figure S1 (Supplementary Material) shows the population trend over the years (from 1861 to 2019) and the current population density in all cities falling into the Mar Piccolo catchment area.

4.2. Agriculture

Through the map of land use (2011), all cultivated areas have been identified and quantified through a geographic information system. ISTAT data showed information about the type of fertilizers and pesticides employed in agriculture in this area. It is well known how water bodies can collect and be impacted by the use of chemicals in agriculture. Run-off and drainage are responsible for transporting organic materials and chemicals [21] into rivers, lakes, groundwater, and sea.

Assuming run-off as the main impact to Mar Piccolo, a quantification of different types of agricultural areas falling into the catchment basin and responsible for bringing pollutants and nutrients into Mar Piccolo is shown in Figure 3.

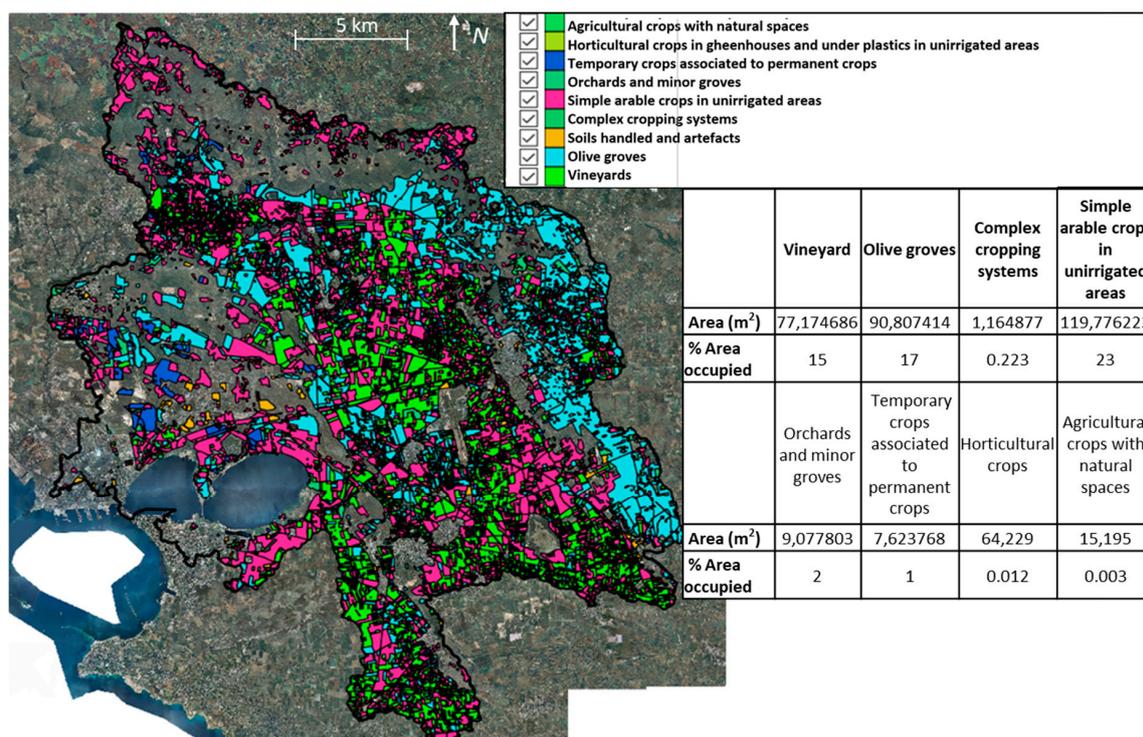


Figure 3. Types of agricultural areas falling into the Mar Piccolo catchment basin.

It is evident that vineyards, olive groves, and arable crops are the most abundant, covering 55% of the total agricultural area of the catchment basin. Furthermore, ISTAT data [22] revealed the distribution of fertilizers and phytochemicals (fungicides, insecticides, acaricides, herbicides, etc.) with an increase in soil improvers employed between 2003 and 2008 and phytosanitary products between 2013 and 2016.

4.3. Industry

Among the numerous industrial activities located in the Taranto area, the biggest one is a steel plant in terms of emissions quantity and extension of working areas [23]. It is an integrated steel process carrying out all steps of steelmaking from smelting iron ore to the rolled product. The steel factory uses water in the production cycle (about 120,000 m³/d) [24] to essentially cool the system and the materials. Both marine water from Mar Piccolo and freshwater from wells and rivers were employed in the cooling process.

The industrial and anthropogenic impacts can also be attributed to the presence of the Italian Navy shipyard with its dry docks on the south side of the first bay, and to a petroleum refinery station and a concrete factory on the west side, as shown in Figure 2 [25].

The oil refinery started its operation in 1967, occupying an area of about 200 ha. The refinery plants have been gradually modernized, following the change in demand. In its present configuration, it is made up of the original hydro-skimming refinery, the thermal conversion of residues, and the residual hydration plant. CO₂ emissions reached 1800 kt/y in 1996 [26].

The cement plant, in operation since 1947, has a capacity of 900 kt/y and uses 15% of the untreated blast furnace slags that come from the steel production [27].

Additional relevant activities can also be identified, such as intensive mussel farm production (with 30,000 tons/y), fishing-boat activity in both bays and some sewage discharge pipes and small rivers with surrounding agricultural activities draining nutrients into the basin [28].

Other smaller emission sources can be found in this territory, related to both the main industrial activities and the local economy. The above industrial activities use the harbor of Taranto to download primary goods and to deliver final products. These tasks are often related to emissions of particulate matter. Combustion processes during wharf operations also produce pollutants emissions. The typical urban emissions are superimposed with the industrial ones located in the proximity of the city boundaries.

4.4. Landfills and Waste Treatment Plants

Legal dump sites falling into the Mar Piccolo catchment area were identified and localized. They represent a possible source of contamination due to leachate moving into the subsoil and reaching groundwater, but also to biogas production.

Municipal solid waste reaches the landfills localized in Massafra, Manduria e Castellaneta (out of the Mar Piccolo catchment area). Special wastes, instead, are sent to Grottaglie, Statte, Massafra, and Taranto landfills and to several dumping and treatment plants, as visible in Figure S2 in Supplementary Material [29]. Notarnicola et al. [27] showed a provincial yearly production of 3.17 Mt of special waste and a total recovery or disposal of 3.99 Mt per year. This indicates that over 800 kt of waste that originates from outside the province is managed within it. There are also several illegal landfills, generally of small size, located on the territory. The latter are frequently secured by local authorities, derogating from national laws.

A waste-to-energy plant is in the municipality of Massafra (about 12 km from the Mar Piccolo). The plant was designed for an electric power of 10.0 MWe. The electricity is the result of the combustion process of about 100,000 tons/year (permitted value) of solid recovered fuel coming from regional mechanical-biological plants [30].

5. Pressures

5.1. Discharges of Nutrients and Contaminants

Nutrients and contaminants produced by the abovementioned driving forces could reach the Mar Piccolo basin through surficial/deep groundwater, run-off, rivers, and citri, following the hydrographic network, as shown in Figure S2 in Supplementary Material. Citri are submarine freshwater springs, which may bring contamination in particular cases [1].

Furthermore, an Italian national research group [31] localized the thermal anomalies to identify the possible submarine sources and pathways of pollution, as shown in Figure 4. After a field survey, they identified and registered all discharges into the Mar Piccolo, both natural and anthropic, shown by the red dots in Figure 4b. However, many sewage discharges were reduced, shown by the grey triangles in Figure 4b. The natural water springs were sampled, shown by the blue triangles in Figure 4b to analyze the water quality entering the basin [31]. Information about contamination by metals and PCBs and annual average outflow is available in Table 1.

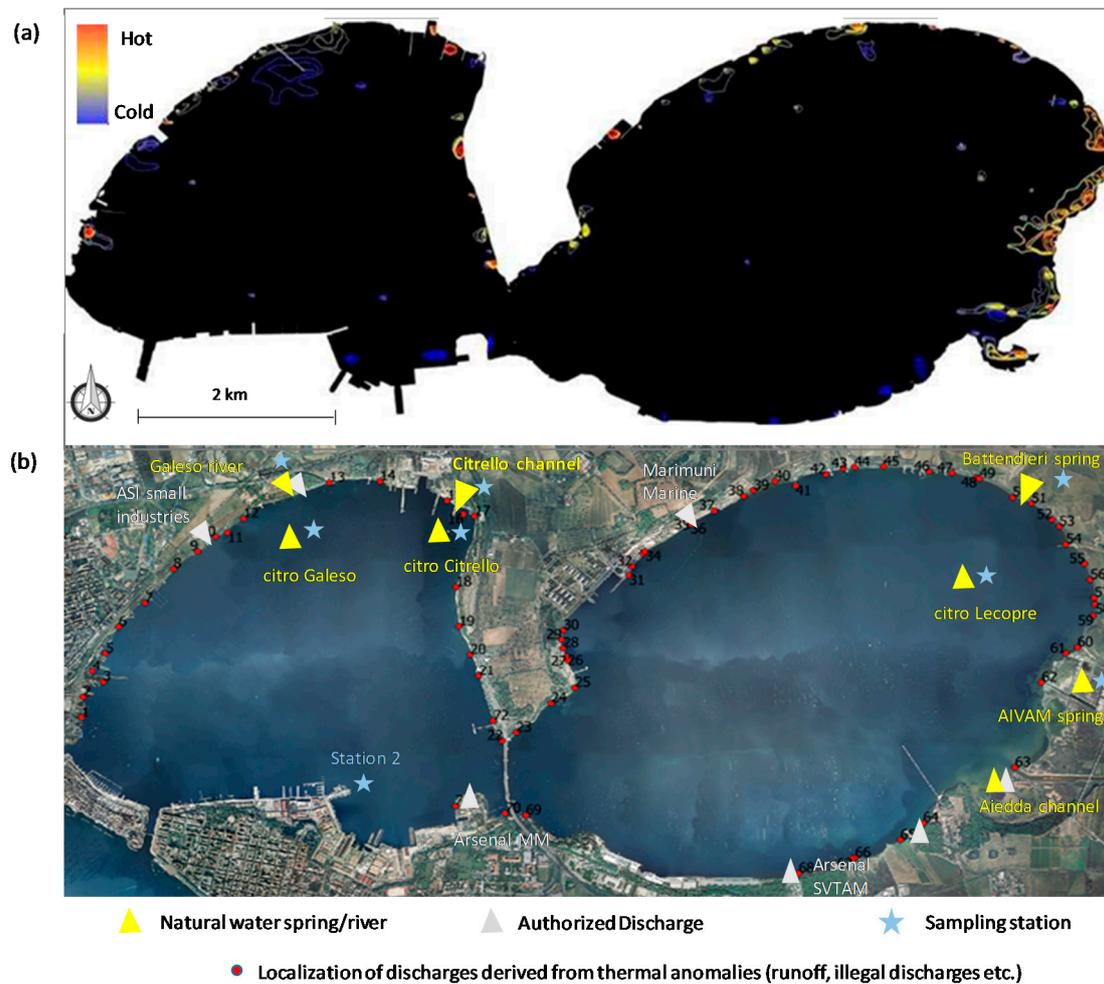


Figure 4. (a) Map of thermal anomalies and (b) localization of discharges (adapted from [31]).

Mar Piccolo is subjected to both private (Military Arsenal) and public sewage discharges. The Aiedda channel discharges the wastewaters of eight municipalities into the second bay of Mar Piccolo [19], as shown in Figure 4b. A total amount of 100,000 equivalent inhabitants is estimated to discharge into Mar Piccolo. About 18,272 m³/d are released, of which about 85% into the second bay, with an amount of organic matter equal to 6.7 t/d of BOD₅ (Biochemical Oxygen Demand in five days) [32]. The daily release of nitrogen and phosphorus into the basin has been quantified as 17.2 t/d and 0.3 t/d, respectively [33].

5.2. Pollution in Groundwater

ARPA Puglia, the Regional Agency for Environmental Protection in the Apulia region, carried out a monitoring campaign in 2008 to evaluate water quality especially in the industrial area [34]. The main aim was to track the role of groundwater as transport carrier of contaminants arriving into Mar Piccolo. However, some uncertainty exists about the relationship of the multi-layered aquifer of industrial area and groundwater flow in the Mar Piccolo [35].

The superficial groundwater, particularly, may be affected by the infiltration of contaminants due to not-controlled sewage discharges, industrial waste abandoned, excessive well pumping varying the water table, excessive use of chemical products in agriculture, but also the karstic nature of soil and subsoil. As shown in Figure 4, Mar Piccolo represents the final collector of both underground streams and surface watercourses, deeply connected to superficial phenomena, often reflecting hazardous chemical situations.

In a groundwater sampling campaign carried out by ARPA Puglia [31], concentrations in main submarine springs in both First and Second Seno showed acceptable values for both metals and PCBs.

5.3. Air Pollution

The results of the Regional Air Quality Plan of the Apulia Region, drawn up by ARPA [36] and the monitoring of sedimentable dust carried out by the provincial department ARPA of Taranto have shown that in the Province of Taranto the atmosphere is subject to considerable pressures, such as production activities, demographic concentration, and transports. The point emissions can also produce, through diffusion phenomena, an impact on a large scale on the quality of water and soil (through fallout), on the health of the population, on the development of fauna and vegetation, and the state of cultural heritage.

An air pollution assessment study was conducted by Gariazzo et al. [23] for the most relevant emission sources located in the area of Taranto, as shown in Figure 5a.

SO₂, NO_x, CO, and primary PM₁₀ concentration fields were calculated by means of the 3D Lagrangian particle dispersion model (SPRAY) model for the studied area covering both winter and summer seasons. Results are shown in Figure 5b, highlighting the extension of the impact of emitted pollutants to a large area of the local territory, including the First Inlet of Mar Piccolo. This study indicated a prevailing contribution of industrial activities on the estimated ground concentrations of SO₂ and PM₁₀. NO_x contribution pointed out a more diffuse responsibility, with industry and traffic sources mainly involved, followed by domestic heating and port activities. Because of the diffusion phenomena, Taranto is considered an area at high risk of environmental crisis, where the high concentration of industries has produced substantial emissions into the atmosphere, with a significant excess of mortality for lung and pleuric tumors [37].

Furthermore, during the last few years, several exceedances of PM₁₀ and benzo(a)pyrene limit values were recorded in Taranto city. A study of these critical pollution events showed a close correlation with the wind coming from the industrial site to the adjacent urban area [38]. In fact, the wind action can presumably contribute to bring air pollutants towards the Mar Piccolo area. Trizio et al. [38] showed that at least 65% of PM₁₀ exceedances at monitoring sites, close to the industrial area, were related to wind day conditions (with at least 3 consecutive hours of wind coming from 270–360 ± 2 deg. with an associated speed higher than 7 m/s). Consequently, in 2012 an integrated environmental permit and a regional air quality plan were enacted to reduce pollutant emissions from the industrial plants [39].

More recent investigations have demonstrated the efficacy of the regional measures with a decrease in air pollution concentration in the Taranto area [40,41].

However, studies about the direct correlation between air pollutants and fall out into Mar Piccolo water are still missing.

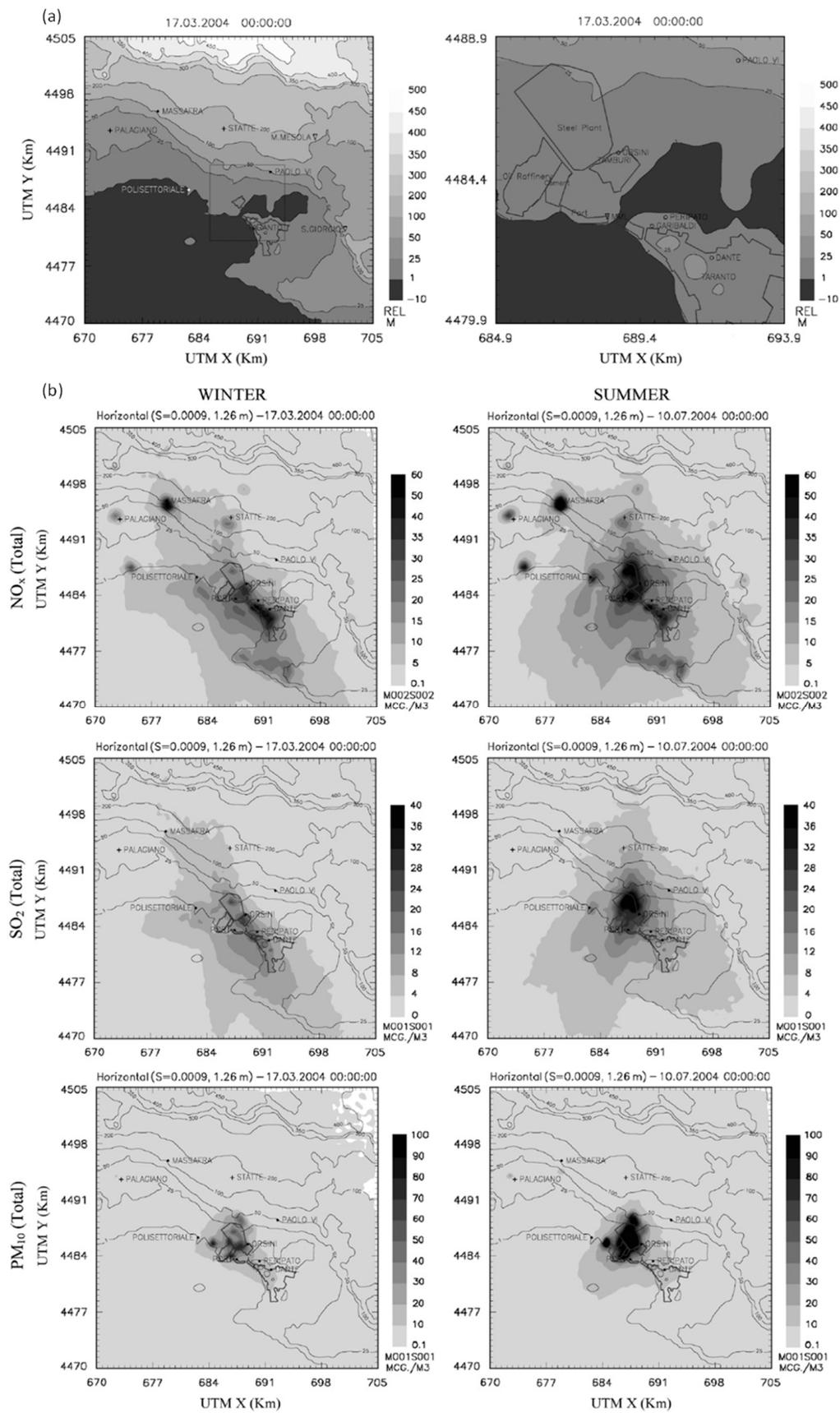


Figure 5. (a) Map of the studied area with a large and zoomed view showing location (UTM 33 [Km]) of the monitoring stations and the main industrial harbor and urban areas. (b) Average concentration maps of NO_x, SO₂, and primary PM10, predicted by the SPRAY model in winter and summer seasons [23].

6. States

6.1. Marine Sediment Characterization

There were several characterizations of marine sediments in the last few decades.

From 2005 to 2009, the Italian institute for environmental protection and research (ISPRA), carried out a sampling campaign in both bays of the Mar Piccolo for a total number of 1517 samples, as shown in Figure 6.

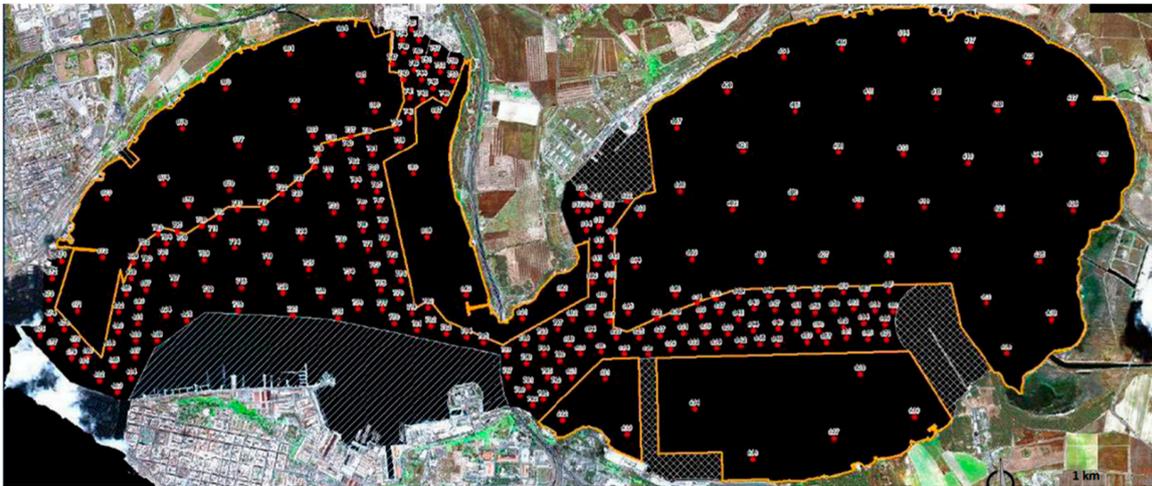


Figure 6. Maps of the sampling points from 2005 to 2010 [42].

The following analyses were performed on the sediment samples:

- Granulometry, water content, specific weight, pH, redox potential, metals and trace elements (Al, As, Cd, total Cr, Fe, Hg, Ni, Pb, Cu, Zm, V), polychlorinated biphenyls, organochlorine pesticides, PAHs, light hydrocarbons $C \leq 12$, heavy hydrocarbons $C > 12$, total nitrogen, total phosphorus, cyanides, and total organic carbon (TOC) on 1023 samples;
- Organotin compounds on 106 samples;
- Aromatic solvents (BTEX), phenols on 112 samples;
- Sb, Cr VI, Se and St on 138 samples;
- Microbiological parameters (fecal streptococci, salmonella, sopite-reducing spores:) on 128 samples;
- Dioxins and furans and asbestos on 23 samples;
- Ecotoxicological tests (*Vibrio fischeri* e *Brachionus plicatilis*) on 20 samples.

Figures 7 and 8 show chemical concentrations with reference to the Italian Legislative Decree [43] and the ICRAM intervention values for the Taranto area [44]. Observing the analytical results, the sediment environmental quality state were complex and characterized mainly by inorganic pollutants in high concentrations in all the First Bay and some parts of the Second one. All surficial layers (0–50 cm) appeared to have a spread contamination by heavy metals and hot spots in some areas (Military Arsenal and Citro Citrello etc.), as shown in Figure 7. Organic compounds are present but in a smaller percentage both in terms of area and amount, as shown in Figure 8. For what concerns metals and trace elements, mercury (Hg) is the element which showed the highest concentrations in most samples. Even zinc (Zn) exceeded many of the concentrations in the limit intervention values [44] in both bays. Copper (Cu) and lead (Pb) showed similar concentration trends both in surficial and deep levels. Arsenic appeared in the first centimeters of sediments. For what concerns organic compounds, their concentrations were lower than metals, and PCBs were the most abundant, especially in the first

bottom layer (0–50 cm) in the First Bay, as shown in Figure 8. A similar distribution is given by PAHs, mostly present on the north-west side of the First Bay.

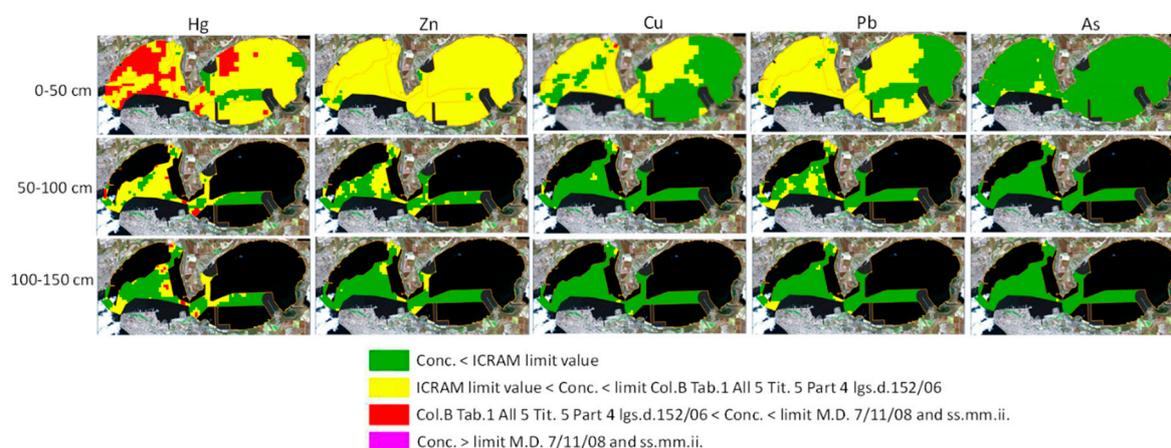


Figure 7. Inorganic compound concentrations map (adapted from [42]).

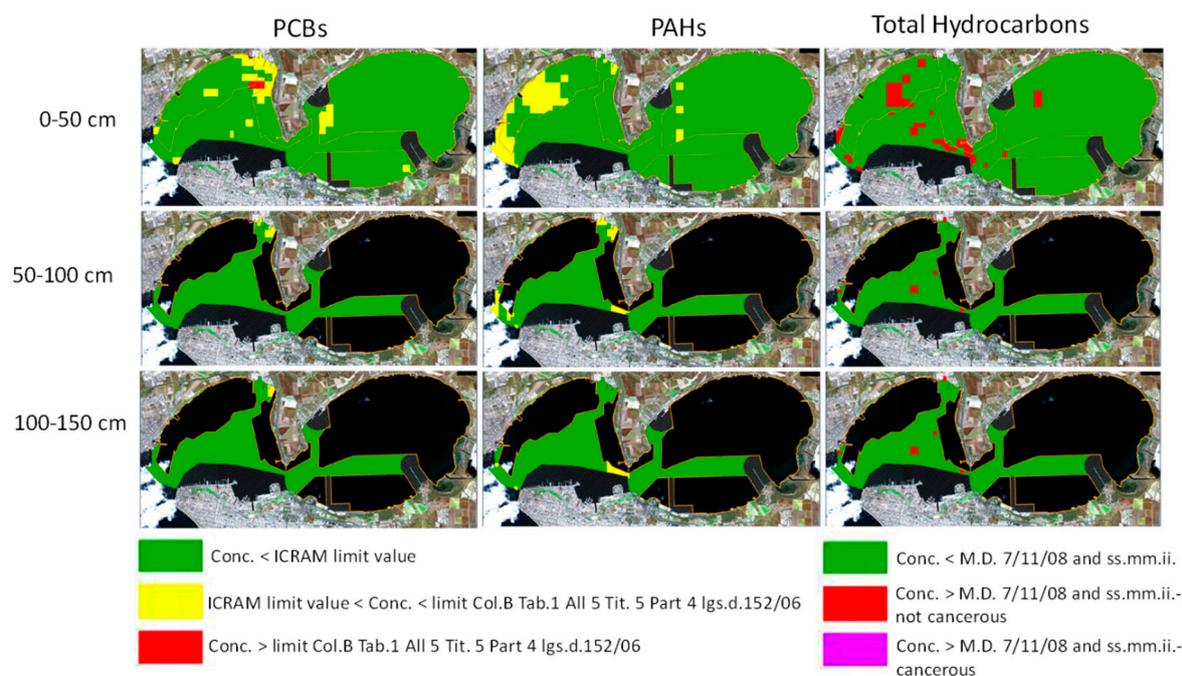


Figure 8. Organic compound concentrations map (adapted from [42]).

Total hydrocarbons were present especially in the first layer of the First Bay in the area for mussel farming, near both the bridges on the west side but also in the entrance/exit channel between the two Bays.

In 2016, the Special Commissioner for urgent measures of remediation, environmental improvements, and redevelopment of Taranto, appointed by the Italian government, promoted an investigation campaign aimed at the multidisciplinary characterization of the First Bay. In the field of the actions promoted by the Italian Government to select the most sustainable remediation strategies, a multidisciplinary investigation of the site was carried out, involving the reconstruction of the geological set-up of the basin, the analysis of the chemical contamination, and the geo-mechanical properties of the sediments collected up to 30 m below the seafloor [45]. In particular, chemical analyses to determine the concentrations of metals, PAHs, and PCBs in the 3m-deep samples were carried out [46].

It was observed that metal concentrations decreased with sampling depth, as shown in Figure S3 in Supplementary Material. Except for Ni and V, all the other metal concentration levels (in at least one site) were higher than the limits of site-specific law [46]. PAH levels were higher than the instrument detection limit in sites 1, 7, 8, 10, 13, 14, 15, 16, 17, 18, and 19, and sites 4 and 6 for PCBs. Additionally, for organic compounds, concentrations followed a decreasing trend with sampling depth, excluding the borehole no. 7. PAHs exceed limits in several areas (i.e., S01, S02, S04, S05, S06, S07, S015, S016, and S18), reaching the maximum values of 18,000 $\mu\text{g}/\text{kg}$ d.w. (dry weight) and 36,000 $\mu\text{g}/\text{kg}$ d.w., respectively in sample S06 and S05 [45].

Furthermore, the data obtained from chemical characterization and bioassays were integrated within a Weight of Evidence (WOE) [47,48] model in an overall quantitative risk assessment. Figure 9 shows the distributions of the Integrated Hazard Index (IHI) [49] at various depths below the seafloor. In the top layer, the integration of data identified the highest risk in areas near the naval arsenal (i.e., sites 4, 6, 7) and the central area (i.e., sites 5, 11, 16, 19). Additionally, the sites 10, 12, 14, and 19 are close to the areas of mussel-culture and fishery activities, raising concerns about environmental and health issues. However, the class of hazard tends to decrease with depth, except for stations S03 and S09. This could be due to the hydrodynamic conditions of the Navigable Channel and Citro Citrello water spring.

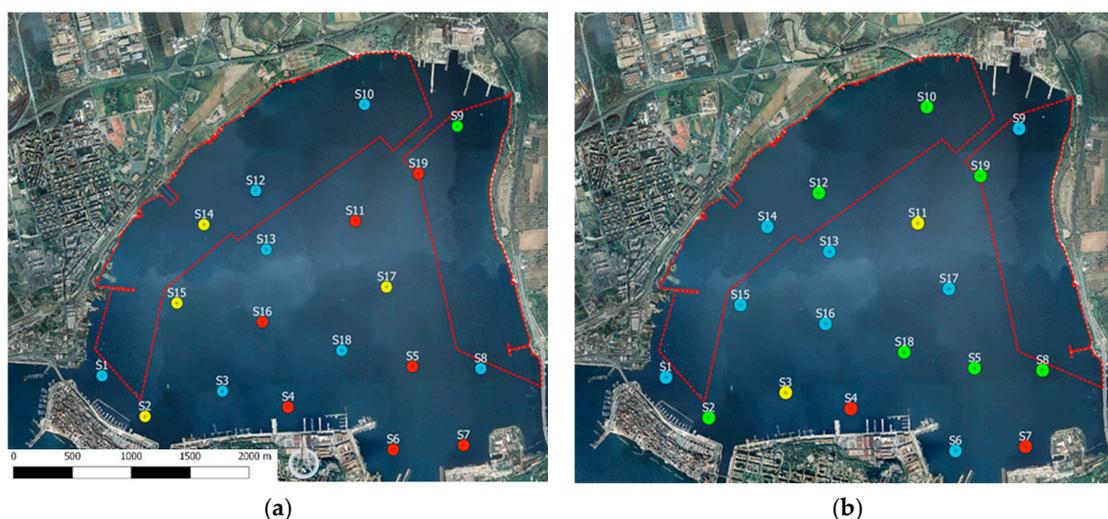


Figure 9. Area of investigation for the First Bay in the Mar Piccolo of Taranto in the sampling campaign in 2016 and spatial distributions of the Integrated Hazard Index (IHI): (a) 0.0–1.5 m below seafloor; (b) 1.5–3.0 m below seafloor. (Class of hazard: ● Absent (IHI < 20); ● Slight (20 < IHI < 40); ● Moderate (40 < IHI < 60); ● Major (60 < IHI < 80); ● Severe (IHI > 80). In red, the mussel-culture areas [46]).

Concerning eco-toxicological analyses, Costa et al. [50] applied a multi-organism and multi-endpoint approach, exposing organisms from different trophic levels to elutriate and whole contaminated sediment. The battery of bioassays considered consisted of a microalgal growth inhibition test (*Dunaliella tertiolecta*), acute and sublethal assays on crustaceans' larvae and juveniles, and rotifers (*Amphibalanus amphitrite*, *Artemia salina*, *Corophium insidiosum* and *Brachionus plicatilis*), and embryotoxicity test on echinoderms (*Paracentrotus lividus*). Despite the high levels of sediment contamination, an unexpectedly very low toxic effect was observed in the biological compartment, even considering the sublethal end-point (larval swimming speed alteration).

In line with the findings of Costa et al., Todaro et al. [46] performed toxicity bioassays on *Vibrio fischeri*, algae *Phaedactylum tricornutum*, and shellfish *Mytilus galloprovincialis*. Even in this case, the obtained biological response unexpectedly highlighted that the level of contamination seems not to affect the biological compartment in a considerable manner.

6.2. Sea Water Characterization

A study about water and sediments around citri, conducted by an Italian research center [31], revealed contamination by metals and PCBs, especially in citro Citrello and the station near the Military Arsenal, as shown in Table 1. In Figure 4b, the sampling stations are depicted with blue stars.

The concentration values comply with the Italian discharge limits in superficial waters [44].

Table 1. Metals and PCBs concentrations in the Mar Piccolo water sampling stations [31].

Source	(µg/L)								(ng/L)	Outflow (Annual Average) [51] (m ³ /s)
	Cd	Cu	Ni	Pb	Hg	Mn	Fe	Zn	PCB _{tot}	
Citro Galeso	0.007	0.753	0.293	0.041	0.011	0.031	9.515	3.74	0.2	0.75
Citro Citrello	0.011	1.042	0.242	0.156	0.009	0.027	10.616	0.772	1.84	0.35
Citro Lecopre	0.008	0.701	0.036	0.131	0.005	0.016	8.39	0.483	0.21	0.65
Station 2	0.043	1.958	0.831	0.248	-	1.97	39.39	6.73	1.08	-
Galeso river	0.003	0.218	0.043	0.055	0.002	-	-	-	0.06	-
Citrello channel	0.002	0.395	0.039	0.043	0.002	-	-	-	0.36	-
Battendieri spring	0.003	0.217	0.073	0.067	0.004	-	-	-	-	-
“AIVAM” spring	0.004	0.07	0.039	0.045	0.003	-	-	-	0.06	-

Narracci et al. [52] evaluated the toxicity level in three selected sampling stations of the Mar Piccolo by Microtox[®] system, vibrios, total, and fecal coliform densities. The results showed sediments characterized by an elevated level of toxicity, while the interstitial water of the same sites showed bio-stimulatory phenomenon.

Vibrios and coliforms were more abundant in water than in sediment samples. The most often isolated strains were: *Vibrio alginolyticus*, *Vibrio mediterranei*, *Vibrio metschnikovii*, and *Vibrio splendidus* II, as shown in Figure S4 in Supplementary Material.

Concerning the convention of 28 May 2013 between the Special Commissioner of the Italian government for urgent measures of reclamation, environmental improvements, and the redevelopment of the Taranto area and the Apulia Regional Environmental Agency, the results of the investigation of contaminants in the Mar Piccolo water column are shown in Figure 10. Samples were taken in 26 stations in the First Bay. The analytical concentrations were compared to the quality standards of the Ministerial Decree n. 260/2010 [31].

For cadmium (limit 0.20 µg/L), in two stations the concentration was 0.40 ± 0.01 µg/L and in another two sites, 0.30 ± 0.01 µg/L. The total chromium (limit 4.00 µg/L) and lead (limit 7.20 µg/L) did not show exceedances. For what concerns PCBs (limit 600 pg/L), the two stations near the dewatering pump recorded the maximum levels (about 4652 ± 140 pg/L) and also those near citro Citrello (about 2251 ± 65 pg/L).

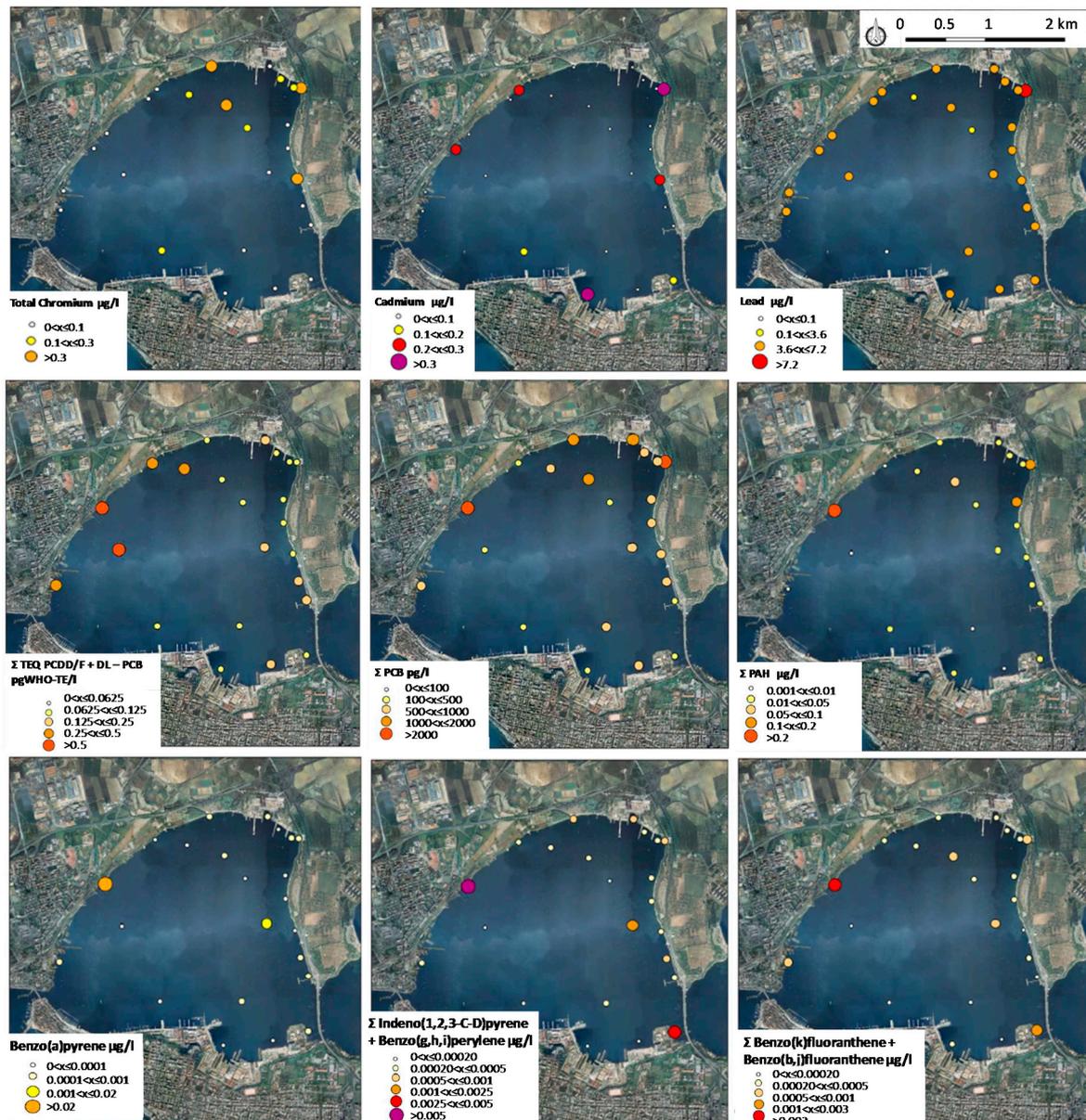


Figure 10. Analytical values of contamination in water column for heavy metals, PAHs, and PCBs (adapted from [31]).

6.3. Biodiversity

In 1969 Parenzan [53] identified submerged meadows of oceanic *Posidonia* but later this seagrass species started to be compromised [31] by industrial and anthropic impacts.

In the SPICAMAR project by the Italian CONISMA [31], a 2-year monitoring plan of the seabed allowed for the production of a biocenotic map, as shown in Figure 11.

Many species were identified, but it is noteworthy to highlight the presence of several protected species according to the SPA/BIO protocol (Barcelona convection), such as *Tethya citrina*, *Geodia cydonium*, *Pinna nobilis*, *Maja squinado*, *Paracentrotus lividus*, *Epinephelus marginatus*, *Aphanius fasciatus*, *Signatus sp.*, *Hippocampus hippocampus* H. *guttulatus* and the marine turtle, *Caretta Caretta*.

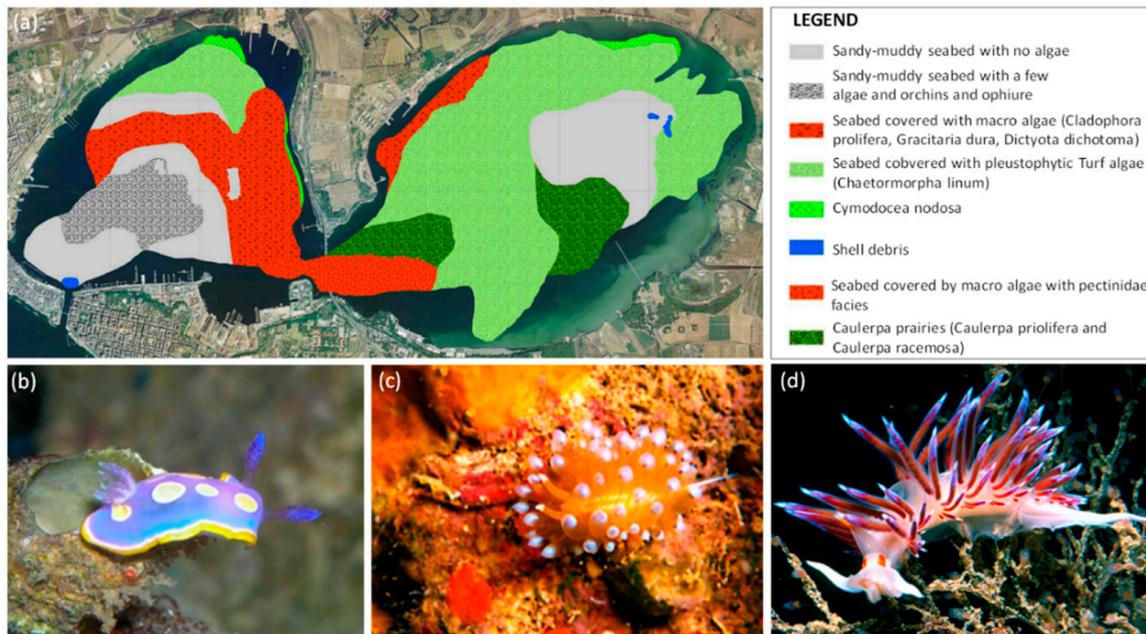


Figure 11. (a) Biocenotic map, (b) *Chromodoris luteorosea*, (c) *Janolus cristatus*, (d) *Cratena Peregrina* [31].

6.4. Anthropization of Sea Bottom

In July 2013, a Digital Terrain Model (DTM) of the Mar Piccolo seabed was obtained thanks to morphological and bathymetric surveys (single beam, multibeam, side-scan sonar) [31].

In the First Inlet, three anomalies were identified, as shown in Figure 12a. Two mainly related to anthropic excavations and one probably linked to the Leonardo da Vinci shipwreck. In 1921, in fact, the Italian Navy Ministry documents report that an accident in the Italian dreadnought occurred and a channel, 2.500 m long and 45 m wide, was dug for the vessel retrieval, handling 300.000 m³ of mud, as shown in Figure 12b [54].

The seafloor of the Mar Piccolo Basin was investigated by Bracchi et al. [54], using remote-sensing techniques, diving observations, and underwater trawled video camera inspections. The main result was a map of the distribution of anthropogenic impacts, as shown in Figure 13, produced by a variety of human activities, both in the water column and on the seafloor, and their spatial relationship with present benthic communities. For instance, they classified the Mar Piccolo seafloor using eight categories of anthropic impacts, associated with mussel farming activity, hydraulic engineering (dredging and buoys), navigation (wrecks and anchoring scars) and undefined traces. Among them, the main ones were:

- Long-line mussel farm (44.10 ha area) with the use of buoys and ropes, as shown in Figure 12c;
- Pole mussel farm with (42.45 ha area) with the use of three wooden or metallic poles driven into the seabed;
- Mussel frame structures-based farm (10.69 ha area), with a metallic net made up of poles and ropes to contain boxes of fishermen;
- Traces of anchorage (24.87 ha area) mainly related to mussel farming and military activities.

They also found that, in terms of absolute coverage, the benthic association most affected is the pleustophytic algae, although in terms of percentage the most affected is shell debris (76%).

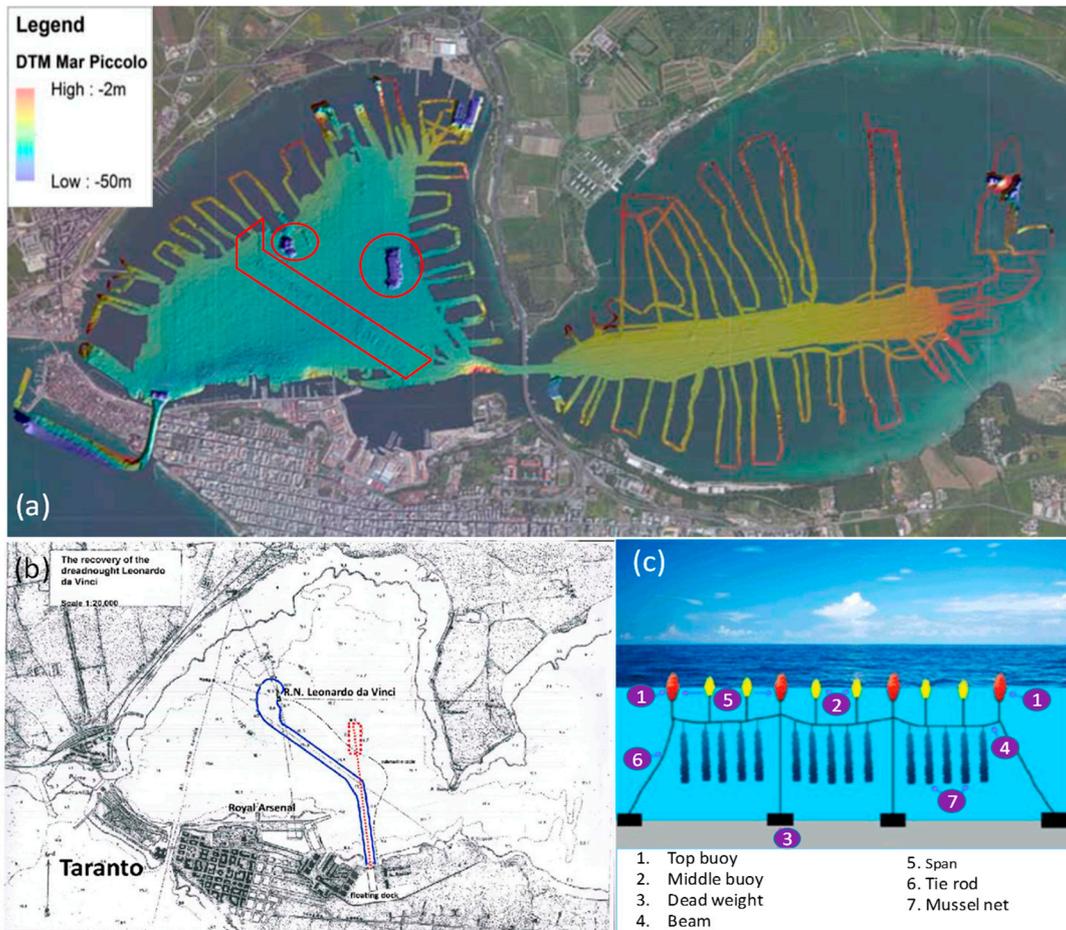


Figure 12. (a) DTM of the Mar Piccolo seabed [31], (b) Leonardo da Vinci vessel retrieval channel [54], and (c) longline mussel farming system.

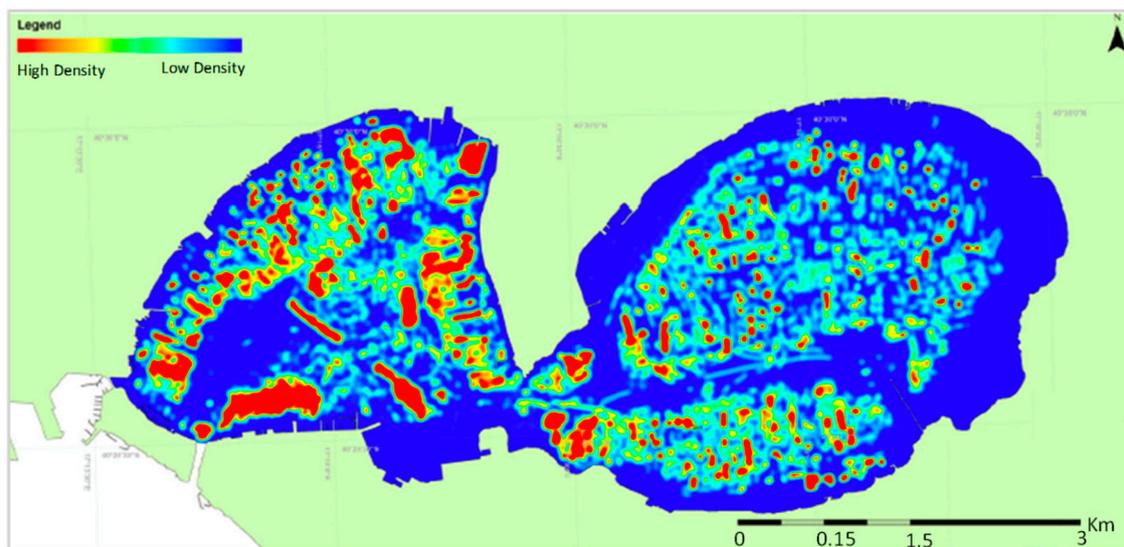


Figure 13. Map of the distribution of anthropogenic impacts in the seafloor [55].

6.5. Marine Litter

The term “marine litter” identifies all human-created waste that has been discharged into the coastal or marine environment, representing a serious risk to the ecosystems.

In 2015, with the technical support of the Coast Guard, all quantities and typologies of waste in the First Bay were analyzed. Later, in 2016, waste collecting and removal activities started and were operated by Sogesid [56], as part of the convention with the Special Commissioner of the Italian government for urgent measures of reclamation, environmental improvements, and redevelopment of the Taranto area. The area considered was represented by three main hotspots close around the so-called “old town” [57], as easy access for cars to the coast. Results showed that the most common litters were abandoned cars, tires, waste related to mussel farming and fishing activities, and urban waste, as shown in Table 2.

Table 2. Typology and quantity of mega-litter observed at three critical areas in the Mar Piccolo [57].

Litter Typology	Total
Car and truck	90
Parts of car	34
Motorcycle	13
Battery	20
Tire	234
Bicycle	5
Wreck with hull	91
Wreck with motor	13
Industrial propeller/fan	3
Drum and large barrel	14
Medium and small barrel/tin	25
Fishing net and rope	n.d.

Not all of the litter is visible and float on the water; heavy products fall onto the seafloor and, in that case, fouling phenomena can occur. Marine mega-litter removal was also planned to avoid further impacts, such as runoff of percolation waters, polluting spills, or silting in areas not confined. However, the high number of fishing nets, ropes, and plastic nets for mussel farming, and their entanglement, did not allow for quantifying exactly their amount.

7. Impacts

7.1. Contaminants Mobility

It is extremely important to understand the mobility and availability of pollutants in environmental matrices. Di Leo et al. [58] investigated the effects of sediment resuspension on the fate of PCBs. Sediments and water were collected nearby the most contaminated site in the Mar Piccolo basin.

PCBs in sediments after resuspension increased by 15%. Instead, after resuspension, PCBs in the dissolved phase increased from 0.82 to 4.82 ng/L and from 0.22 to 202.21 ng/L in the particulate one. In addition, the dissolved phase in water was found enriched in light-to-mid-weight compounds, and, conversely, the particulate phase was enriched in heavier congeners after the resuspension. A correlation was found with the dissolved organic carbon (DOC) that increased from 1.31 to 8.55 mg/L, likely influencing the fate of metals and PCBs in the dissolved and particulate phases.

The Italian research center of Taranto investigated the role of granulometry, bioavailability, and mobility of pollutants [31]. They considered two stations in the Arsenal area for sediment sampling:

The granulometry of Station 1 was represented by: 6.2% gravel, mostly made of biological material, 20% sand, 74% mudstone (silt and clay);

The granulometry of Station 2 was represented by: 7% gravel, 15% sand, 78% mudstone.

It is evident that the high percentage of fine and extremely fine fractions in sediments of the Mar Piccolo leads to a higher possibility to connect with pollutants [59].

Concerning PCBs, Station 2 was found to be more contaminated than Station 1. In fact, the sum of PCB Σ 28 in Station 1 was equal to 1986 ng/g d.w. and 3278 ng/g d.w. in Station 2. In both cases, however, values exceeded the ICRAM threshold limit, equal to 190 $\mu\text{g}/\text{Kg}$ d.w. (sum of PCB 28, 52, 77, 81, 95, 99, 101, 105, 110, 118, 126, 128, 138, 146, 149, 151, 153, 156, 169, 170, 177, 180, 183, 187).

Even in this case, it is interesting to quantify PCBs contained in the mudstone fraction. In particular, 43% and 52% of PCBs were detected in the fraction $<63 \mu\text{m}$, respectively, in Station 1 and 2.

Values of As, Cu, Pb, Zn, and Hg in both stations exceeded ISPRA threshold limits (as 20 mg/Kg d.w.; Hg 0.8 mg/Kg d.w.; Pb 50 mg/Kg d.w.; Cu 45 mg/Kg d.w.; Zn 110 mg/Kg d.w.).

Table 3 shows the amount of metals detected in all sediment and the mudstone fraction ($<63 \mu\text{m}$).

Table 3. Metal concentration in sediments and percentage of metals in the mudstone fraction [31].

Metals	Sediment Station 1	Metal Fraction $<63 \mu\text{m}$	Sediment Station 2	Metal Fraction $<63 \mu\text{m}$
	(mg/kg d.w.)	(%)	(mg/kg d.w.)	(%)
As	34.36	35	115.30	39
Cd	4.29	30	1.69	28
Cr	133.41	34	77.84	38
Cu	177.00	38	536.00	43
Fe	49,653.00	38	28,513.00	42
Ni	75.76	39	54.73	45
Zn	430.00	50	815.00	57
Pb	121.00	64	392.00	70
Al	38,672.00	33	22,803.00	38
Mn	439.00	51	386.00	57
Sn	15.31	13	6.86	16
V	134.37	31	72.84	34
Se	5.92	52	2.01	47
Hg	5.37	64	40.61	75

They also carried out a speciation analysis by using the method of Tessier et al. [60], according to which the suspended sediment samples are subjected to a sequential extraction procedure designed to partition the particulate trace metals into five fractions: (F1) exchangeable; (F2) bound to carbonates; (F3) bound to Fe/Mn oxides; (F4) bound to organic matter; F5) residual.

No evident differences were noted in the distribution percentage of geochemical fractions between the two stations.

Figure 14 shows that more than 80% of Cu is linked to the organic matter (F4), and only a small amount is associated with residual. Cr, V, and Ni are found mainly in the residual fraction (about 70%), and a small amount is connected to iron oxides and Mn and a smaller quantity to organic matter.

Lead is found essentially bound to iron and manganese oxides (about 60%) and organic matter (about 25%). The small quantity of lead in the residual fraction confirmed the anthropic origin.

Zinc shows a similar behavior of Pb and, according to Ankley and Schubauer-Berigan [61], it decreases with sulfides increasing in sediments. Arsenic was found mainly bound to organic matter and residual fractions (50% and 40%, respectively). Lastly, about 70% Mn was present as an oxide.

Calace et al. [62] showed a correlation between Pb bound to Fe/Mn oxides and Mn in its reducible form. This highlights that any red-ox variation in the environment could lead to the reduction in manganese oxides, promoting remobilization mechanisms for metals, such as Cu, Pb, and Zn.

Mercury was detected by using the Bloom method [63]. Results showed that up to 90% of the total Hg derived from complexes species (Hg elementary and/or bound to amorphous organic compounds with sulfur, amalgam Hg-Ag, or crystalline phases of Fe/Mn oxides), leachable with HNO_3 12N.

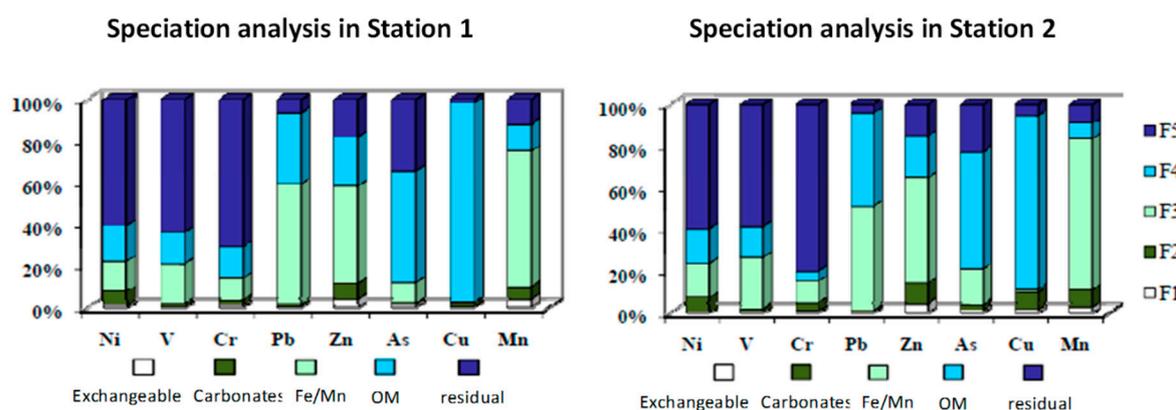


Figure 14. Results of the speciation analyses in Stations 1 and 2 (by using the Tessier approach).

7.2. Effects of Contaminants in Marine Organisms

Cavallo and Stabili [64] evaluated the degree of pathogenic microbial pollution, vibrios, fecal coliforms, and *Escherichia coli* densities in mussels (*Mytilus galloprovincialis*) collected in 30 sampling sites in the Mar Piccolo. *Vibrio alginolyticus* appeared as the predominant component of the total culturable vibrios. Some *Vibrio* species, such as *V. mediterranei*, *V. parahaemolyticus*, *V. diazotrophicus*, *V. nereis*, and *V. splendidus*, were present both in water and in mussel samples; however, other vibrios were found in mussels (*V. vulnificus*, *V. cincinnatiensis*, *V. orientalis*, *V. anguillarum*, *V. marinus*, *V. hollisae*). As this research suggested, it is fundamental to isolate potential pathogenic vibrio species to avoid the transmission of infection to man and other marine organisms.

Bioaccumulation data showed severe results. Di Leo et al. [65] and Giandomenico et al. [66] presented spatial and seasonal variations data on the PCDD/Fs and DL-PCBs in mussels of Mar Piccolo. The main results indicated that PCDD/Fs and DL-PCBs contamination in mussels was higher in the First Bay, with DL-PCBs as the dominant chemicals in all samples, followed by PCDFs and PCDDs. Another finding showed a relevant increase in dioxin and dioxin-like PCB TEQs during the summer. Two peaks were reached in June (8 ± 2 pgTEQ/g ww) and in July (11 ± 3 pgTEQ/g ww), above the legislation limit of 6.5 pg WHO₂₀₀₅-TEQ g⁻¹ ww. Nevertheless, the exceeding limits in the first inlet, set by the EC Regulation, have involved the prohibition of mussel sale and commercialization from this basin. Concerning the bio-accumulation of metals, Cardellicchio et al. [67] analyzed samples of *Mytilus galloprovincialis* collected monthly, determining, by atomic absorption spectrophotometry (AAS), the metals (Cd, Cu, Pb, Zn, Fe and As) in the whole soft tissue of mussels. Even in this case, seasonal changes in metal concentrations were observed, exhibiting maximum values in later winter to early spring, followed by a progressive decrease during the summer. Their research indicated that the metal content was within the permissible range established for safe consumption by humans.

All the above observations raise several questions about the potential mobility of pollutants and their risks for the surrounding environment.

The Italian national research group of Taranto carried out bioaccumulation tests to investigate the potential gathering of pollutants by mussels. Experiments were developed both ex situ (in a laboratory) and in situ (in a station in the Arsenal area in the First Bay). For bioaccumulation tests, clean *Mytilus galloprovincialis* were used.

Ex situ tests were conducted in laboratory in a fish tank filled with 280 L of marine water and 30 kg of marine sediments collected from the same station used in the in situ tests. Figure S5 in the Supplementary Material shows how mussels were suspended on a grid during the testing period.

Every 7 days, a resuspension event was induced and at days 1, 15, 30, and 45, a defined quantity of mussels was collected. A similar approach was taken for the in situ experiments. At the test station, mussels were collected at the same periods and resuspension events were induced every 7 days through the help of divers.

Tables 4 and 5 shows the percentage increase in metals in mussels at T15, T30, and T45 days in reference to T0 in both ex situ and in situ experiments.

Table 4. Percentage increase (%) of metals at T15, T30, and T45 in reference to T0 for the in situ and ex situ bioaccumulation tests [31].

Metal	Experiment Typology	T15	T30	T45	Metal	Experiment Typology	T15	T30	T45
As	In situ	21	27	47	Pb	In situ	160	204	268
	Ex situ	2	19	38		Ex situ	198	260	323
Cd	In situ	-16	26	19	Al	In situ	-4	5	-1
	Ex situ	10	26	7		Ex situ	-4	6	10
Cr	In situ	29	146	240	Mn	In situ	23	113	204
	Ex situ	1	42	201		Ex situ	5	13	52
Cu	In situ	-19	102	69	Sn	In situ	125	175	175
	Ex situ	-31	25	36		Ex situ	425	400	525
Fe	In situ	40	59	62	V	In situ	126	149	187
	Ex situ	18	49	51		Ex situ	9	117	187
Ni	In situ	12	33	40	Se	In situ	8	29	19
	Ex situ	81	172	189		Ex situ	10	-8	-3
Zn	In situ	23	151	208	Hg	In situ	100	550	600
	Ex situ	52	148	268		Ex situ	700	1250	1350

Table 5. Percentage increase (%) of PCBs (sum of congeners) at T15, T30, and T45 in reference to T0 for the in situ and ex situ bioaccumulation tests [31].

Pollutants	Experiment Typology	T15	T30	T45
Σ PCB (ng/g wet weight)	In situ	31	37	56
	Ex situ	7	14	41
Σ PCB _{TARGET} (28, 52, 101, 153, 138, 180) (ng/g wet weight)	In situ	26	29	46
	Ex situ	6	10	30

The highest percentage increase is given by mercury, especially ex situ with 1350%. A study by Gagnon and Fisher [68] identified the principal mercury source for bivalves in contaminated sediments.

However, all metals showed an increase in both ex situ and in situ samples during the investigation period.

Concerning PCBs, an increase of 56% was the highest value recorded, exceeding the threshold limit (Regulation CE no. 1259/2011: the sum of PCB congeners 28, 52, 101, 153, 138, 180 = 75 ng/g w.w.).

Even though the speciation analysis (in Section 7.1) showed that most metals present in sediments are not naturally available, but any red-ox modification, caused by resuspension phenomena, could involve metal release into the water column with highly toxic effects for the pelagic trophic web [31].

7.3. Human Health

Great attention has been focused in Europe on the importance of food safety and the relation between diet and human health. Nowadays, it is fundamental to monitor contaminants in the food chain and their impact on human beings, because of the increased use of man-made chemicals due to our modern lifestyles.

Giandomenico et al. [69] investigated contamination levels and public health risks, associated with consuming seafood harvested from the Mar Piccolo areas, as shown in Figure 15.

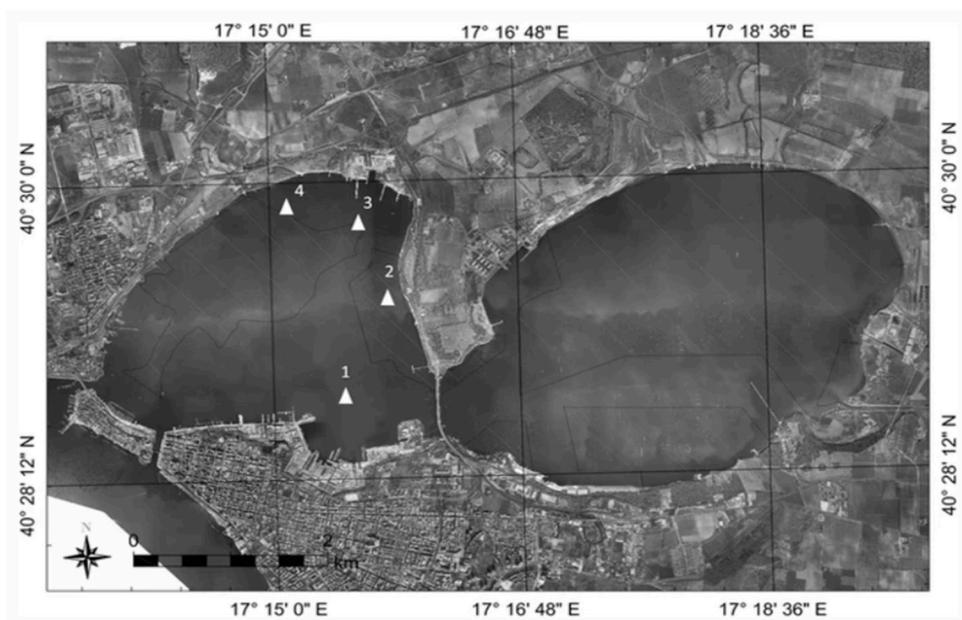


Figure 15. Location of the sampling stations [69].

They analyzed concentrations of some metals (Cd, Cu, As, Hg, Pb) and PCBs in edible marine organisms from different trophic levels and feeding behavior for bivalve mollusks (*Mytilus galloprovincialis* and *Chlamys glabra*), gastropod mollusks (*Hexaplex trunculus*), and some commercial species of fish (*Trachurus trachurus*, *Boops boops*, *Sarpa salpa* and *Gobius niger*).

In reference to the permissible limits set by EC Regulations, Cd and Pb levels were over the limit in the *H. trunculus* (in all sampling stations) and in the fish *T. trachurus*, respectively, as shown in Table 6.

Table 6. Mean values of As, Cd, Cu, Hg and Pb (mg/kg wet weight) and wet/dry ratio in soft tissues of marine organisms ($n = 3$; S.D. range = 7–12%).

Site	Organism	W/D	Cd	Cu	As	Hg	Pb
St. 1	<i>Mytilus galloprovincialis</i>	5.1	0.09	1.79	3.19	0.06	0.24
	<i>Chlamys glabra</i>	7.5	0.36	2.97	2.76	0.1	1.22
	<i>Hexaplex trunculus</i>	3.4	1.67	50.95	40	0.34	0.21
St. 2	<i>Mytilus galloprovincialis</i>	5.6	0.07	1.85	2.82	0.02	0.22
	<i>Chlamys glabra</i>	7.8	0.25	5.23	2.41	0.02	0.36
	<i>Hexaplex trunculus</i>	3.8	1.49	45.59	35.8	0.3	0.19
St. 3	<i>Mytilus galloprovincialis</i>	5.7	0.06	1.7	2.74	0.02	0.26
	<i>Chlamys glabra</i>	6.1	0.28	2.11	2.61	0.02	0.43
	<i>Hexaplex trunculus</i>	3.5	1.17	17.9	17.8	0.22	0.2
St. 4	<i>Mytilus galloprovincialis</i>	5.7	0.09	1.96	2.8	0.02	0.27
	<i>Chlamys glabra</i>	7	0.3	2.56	2.59	0.02	0.59
	<i>Hexaplex trunculus</i>	3.7	1.53	35.15	34.5	0.25	0.17
	<i>Boops boops</i>	4.17	N.D.	0.29	0.99	0.08	0.03
	<i>Gobius niger</i>	4.34	N.D.	0.38	1.82	0.14	0.18
	<i>Sarpa salpa</i>	4.76	N.D.	0.17	15.9	0.09	0.21
	<i>Trachurus trachurus</i>	3.45	0.05	260.9	4.15	0.44	1.03
	Range		N.D.–1.67	0.17–260.92	0.99–40.03	0.02–0.44	0.03–1.22

S.D. standard deviation, W/D wet/dry ratio, N.D. not detectable.

Additionally, PCBs were over the legal limit in all sampled species except for *M. galloprovincialis* in one station, *C. glabra*, and the herbivorous fish *S. salpa*, as shown in Table 7.

Table 7. Mean values of PCB congeners ($\mu\text{g}/\text{kg}$ wet weight), wet/dry ratio, and fat content (%) in soft tissues of marine organisms ($n = 3$; S.D. range = 8–15%).

Site	Organism	W/D	% Fat	28	52	101	118	153	138	180	$\Sigma 7\text{PCBs}$	$\Sigma 6\text{PCBs}$
St. 1	<i>Mytilus galloprovincialis</i>	5.1	1.2	0.25	0.43	10.69	10.31	30.71	17	2.45	71.84	61.53
	<i>Chlamys glabra</i>	7.5	0.4	0.17	2.65	2.81	7.11	31.55	13.8	11.19	69.28	62.17
	<i>Hexaplex trunculus</i>	3.4	0.7	0.26	0.56	59.53	9.29	85.94	33.26	26.56	215.41	206.12
St. 2	<i>Mytilus galloprovincialis</i>	5.6	1	1.41	4.36	15.98	17.46	34.68	20.77	2.02	96.68	79.21
	<i>Chlamys glabra</i>	7.8	0.3	0.08	0.05	1.47	3.22	15.33	3.83	3.56	27.55	24.33
	<i>Hexaplex trunculus</i>	3.8	1.2	0.13	0.18	26.76	19.97	108.05	29.55	16.74	201.39	181.42
St. 3	<i>Mytilus galloprovincialis</i>	5.7	0.7	1.04	7.46	24.4	27.02	62.89	37.04	5.91	165.75	138.74
	<i>Chlamys glabra</i>	6.1	0.3	0.2	0.3	1.69	6.82	17.31	7.64	3.66	37.61	30.79
	<i>Hexaplex trunculus</i>	3.5	1.7	0.31	0.29	52.6	32.46	186.66	34.8	24.2	331.31	298.86
St. 4	<i>Mytilus galloprovincialis</i>	5.7	0.8	0.67	2.6	13.7	15.44	36.95	21.51	2.16	93.02	77.58
	<i>Chlamys glabra</i>	7	0.6	0.3	0.17	2.69	2.24	13.37	3.4	0.43	22.6	20.36
	<i>Hexaplex trunculus</i>	3.7	1.5	0.35	5.81	35.22	32.59	172.05	45.92	45.27	337.22	304.62
	<i>Boops boops</i>	4.2	0.6	N.D.	0.12	3	1.78	105.6	30.13	29.4	170.03	168.25
	<i>Gobius niger</i>	4.3	0.4	0.31	0.58	3.1	4.91	37.39	22.29	15.23	83.81	78.9
	<i>Sarpa salpa</i>	4.8	1.1	N.D.	0.08	2.34	2.31	23.22	10.97	7.4	46.32	44.01
	<i>Trachurus trachurus</i>	3.5	4.3	0.1	3.67	29.62	14.7	174.54	92.77	41.89	357.26	342.55
	Range			N.D.–1.41	0.05–7.46	1.47–59.53	1.78–32.59	13.37–186.66	3.40–92.77	0.43–76.75	22.60–357.26	20.36–342.55

S.D. standard deviation, W/D wet/dry ratio, N.D. not detectable.

In the fish *T. trachurus*, for example, the concentrations of six target PCBs were five times higher than the EC limit. They also estimated the intakes of the trace elements included in this study through seafood consumption by the population. The results showed that they exceeded the provisional tolerable weekly intake recommended by the Joint FAO/WHO Expert Committee on Food Additives for both Cd and Hg in the *H. trunculus* and *T. trachurus*, especially in children. Moreover, the hazard quotient (HQ) for Hg and Cd was >1 in children for *T. trachurus* and *H. trunculus* consumption. For non-dioxin-like PCB (NDL-PCB), the estimated intakes were always above the “provisional guidance value” (70 ng/kg body weight) [70] for all sampled organisms.

The exceeding limits in the First Bay, set by the EC Regulation, involved the prohibition of mussels sale and commercialization from this basin since 2011 [65,71].

7.4. Eutrophication of Toxic Algae

One of the main issues worldwide caused by anthropogenic inputs is eutrophication, especially in areas with limited water exchange [72], salt marshes, and lagoons [73].

The comparison with a 20-year dataset revealed a drastic decrease in nutrient concentrations after the year 2000, validating the functionality of the treatment plants discharging into Mar Piccolo basin. The reduction in nutrient inputs (up to −90% in the first inlet) changed the biogeochemical characteristics of Mar Piccolo from being relatively eutrophic to moderately oligotrophic [74].

Phytoplankton dynamics were investigated by Caroppo et al. [75] concerning environmental parameters, with particular reference to harmful algal blooms (HABs). They found that the relocation of the main urban sewage outfalls had positive effects on the environment, reducing sewage detritus and nutrient loadings by 25% and increasing the Mar Piccolo water transparency.

A recovery of shallow water *phytobenthos* occurred [76]. Seagrasses, for instance, are indicators of good environmental status. It was observed that the phytoplankton composition changed, with nano-sized species, indicators of oligotrophic conditions, becoming dominant over micro-sized species. However, even though phytoplankton dynamics were affected by the closure of the sewage outfalls, it did not preserve the Mar Piccolo from HABs and anoxia crises. They also detected about 25 harmful species throughout the years, such as the potentially domoic acid producers, *Pseudo-nitzschia* cf. *galaxiae*, and *Pseudo-nitzschia* cf. *multistriata* [77].

7.5. Dewatering Pump

Another anthropic impact is present in the First Inlet: the dewatering pump belonging to the steel factory. Used for cooling down blast furnace circuits, it withdrew about 35 m³/s of the Mar Piccolo water in the last thirty years [18,77]. Such water usage has modified circulation in the First Bay, causing a higher salinity level, due to the input of water from Mar Grande, but also a different environment for the biological species [1], as shown in Figure 2. Scroccaro et al. [19] applied a finite element model to the Taranto sea, finding a modification on the local circulation due to the water pump in that area. Amenio et al. [78] adopted the Trapping Index (TI), defined as the normalized product between the water renewal and transit times. In this way, they identified areas where both these time scales were high, and the dewatering pump, as well as other hot spots, was found vulnerable for the system.

8. Responses

8.1. Political Approach

The sections D–P–S–I were essential to fully understand the critical framework of the Mar Piccolo area in all respects, laying the groundwork for proper measures to be taken.

Many responses were given about the Mar Piccolo over the years but many more are still under study and testing. The main first interventions to give to a site with an environmental and sanitary crisis consist in responses with a structural-normative nature. Afterwards, on-site actions are essential after preliminary studies and plans.

In 1986, with the national Law no. 349 of 8 July 1986, all Taranto territorial and marine zones were declared “area of high risk of environmental crisis”.

After an application made by the Apulia Region in 1988, with the Deliberation of the Italian Council of Ministers of 30 November 1990, a part of the province of the Taranto area (made of Taranto, Crispiano, Massafra, Montemesola municipalities) was declared “area of high risk of environmental crisis”, reiterated with the Deliberation of 11/06/1997.

Then, the Council of Ministers required the Italian Ministry of the Environment, in agreement with the Apulia Region and other local bodies, to draw an action plan up to remediate the Taranto province area. The plan, approved in 1997, defined typologies and costs of remedial interventions after preliminary characterization studies of all environmental matrices and sources of pollution.

With the Decree of 10 January 2000, the Italian Ministry of the Environment defined the perimeter of the Contaminated Site of National Interest (SIN) of Taranto where the Mar Piccolo is also included, as shown in Figure 16.

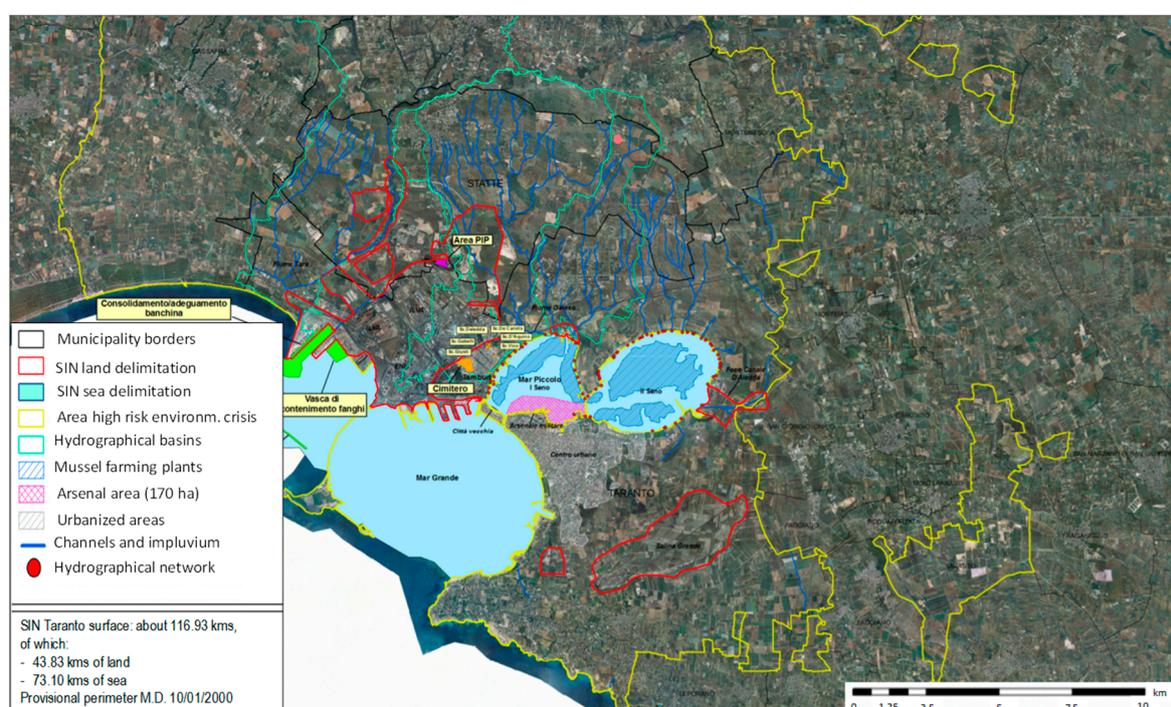


Figure 16. Localization of SIN Taranto (Ministerial Decree 10 January 2000).

With subsequent Decree no. 468 of 18 September 2001, the Italian Ministry of the Environment approved the “National Program of remediation and environmental restoration of contaminated sites of national interest” defining priority interventions in terms of the identification of economic resources and definitions of a public tender for the implementation of the measures.

After the results of a monitoring plan started in 2011 by the Italian Local Health Authority for the evaluation of contamination by PCDD/F and DL/PCB in M. Galloprovincialis of Mar Piccolo and Mar Grande, the ordinance no. 1989 of 22 July 2011 declared the prohibition of harvesting and handling mussels in the First Inlet.

On 26 July 2012, the Italian Ministry of the Environment and the Protection of Territory and Sea, the Italian Ministry of Infrastructures and Transports, the Italian Ministry of Economic Development, the Italian Ministry for the Territorial cohesion, the Apulia Region, the Taranto province, Taranto Municipality, and the Special Commissioner of the Port of Taranto, signed a protocol of understanding aimed at:

- Planning all the complex remediation strategies of all the sites with clear reachable objectives and times of approval, and the realization of interventions;
- Developing infrastructural interventions complementary to remediation actions;
- Identifying measures designed to increase the level of employment;
- Identifying incentives for local companies interested in adopting innovative environmental technologies;
- Identifying incentives for new investments, even for industrial requalification of the area;
- Carrying out and completing studies about environment and health connected to the presence of industrial plants in order to identify and realize measures of mitigation, reduction, and prevention.

In 2014, with a Decree of the President of the Council of Ministers, the Special Commissioner of the Italian government for urgent measures of reclamation, environmental improvements, and the redevelopment of the Taranto area was nominated and, starting from 2015, was scientifically supported by the Polytechnic University of Bari, the National Research Council and the University of Bari.

Concerning the interventions to the Mar Piccolo area already carried out or that are in progress, these are:

- Remediation of the Mar Piccolo shores;
- Sustainable removal and disposal of anthropic materials on the sea bottom;
- Cleanup of unexploded ordinance and other explosive remnants;
- Mitigation actions to impacts derived from wastewater discharges;
- Intervention on abatement of contamination sources;
- Remediation plan and/or permanent safety measures for contaminated sediments;
- Protection, monitoring, and translocation of species of conservation interest;
- Removal of the floating fish farm.

In 2016, the Ordinance no. 188 of the President of the Apulian Regional Council established the possibility to collect mussels present in the First Bay for human consumption, by the 31st of March of each year, only after sanitary results conformed to chemical thresholds for dioxins and PCBs.

It is fundamental to underline the importance of structural and political-strategic responses, preparatory for technological and remedial interventions.

8.2. Remediation Technologies

The technological response in terms of remediation interventions is closely related to a new development strategy for the study area. As described above, Taranto has always had an industrial vocation against agricultural and tourist activities. Lately, with the crisis in heavy industry and steel, a new development strategy has been discussed. There are several hypotheses, among which are those of converting part of the heavy industry towards greener forms and, at the same time, promoting forms of circular economy [27] or abandoning heavy industry to promote tourism, not extensive agricultural activities with less environmental impact and the fish industry.

Any new development strategy must include a technological response in terms of remediation. In order for these remediation interventions to be long-lasting, the current pressures on the study area should be identified and controlled/regulated, starting with the control of discharges.

The remediation interventions described below are part of this context.

Extensive research has been conducted on remediation treatment technologies. In our study, we consulted both project reports and scientific articles [79–85].

In situ remediation with a capping system involves the placement of a clean substrate to isolate contaminants (physical capping) or reactive amendments to chemically react and reduce contaminant availability and mobility (reactive capping) [86]. Reactive amendments tend to increase contaminant binding by modifying sediment geochemistry and can provide degradation and/or adsorption of contaminants while allowing upward groundwater flow.

The results of the experimental investigation have shown that reactive capping could represent an interesting option for in situ remediation technology for contaminated sediments in the Mar Piccolo [87]. Reactive Permeable Mats (RPM) with organoclay (OC) or active carbon (AC) were used. RPM represents an innovative capping technology and consists of using the amendments encapsulated in a non-woven core matrix, bound between two geotextiles [88]. After 20 days from the placement of the capping system, the results show that PAH concentrations in water decreased from an initial 0.1 µg/L to near 0.04–0.06 µg/L for the column apparatus with a cap. Moreover, a reduction of 60% (RPM with AC) and 40% (RPM with OC) in the original PAH contamination was recorded.

The effectiveness of different capping materials for PAH contaminated marine sediments was evaluated by Bortone et al. [25] through numerical modelling in a long observation period (≥ 10 months). The results demonstrated that, without the capping system, PAH concentrations in water increased over the time, reaching high levels of contamination far above the Italian regulatory limits in water. Conversely, in the condition with capping, the long-term effectiveness over time was guaranteed, not reaching the threshold limit set at 0.05 µg L⁻¹.

Concerning ex situ technologies, dredging and subsequent chemical treatments are the most common techniques adopted in a remediation plan. However, sustainability and protection of the marine ecosystem should be the first objective for any decision-maker. Dredging, in fact, entails sediment, resuspension phenomena, and off-site sediment transport for treatment or disposal [89]. For heavily polluted sediments, or if dredging is compulsory to reach a desired bathymetric level, ex situ technologies for sediment remediation become the most appropriate choices. However, after dredging any remaining contaminants in seabed, sediments can be sequestered or isolated with either a low-permeability cap or a permeable in situ layer. In these cases, the “beneficial reuse” of dredged materials is highly encouraged [90]. The stabilization/solidification (S/S) of contaminated sediments is an appealing technology for both chemical and mechanical improvement (i.e., contaminant immobilization, compressibility reduction, and strength improvement). Todaro et al. [87] explored the possibility of re-using dredged contaminated sediments from the Mar Piccolo as a resource via S/S treatment. After 28 days from preparation, the sediment mixtures with Portland cement (10%) and active carbon or organophilic clay (5%) complied with the acceptance criteria for reuse in terms of leachability. Barjoveanu et al. [91] suggested that the ex situ S/S treatment could contribute to improving the current situation of the Mar Piccolo and that the marine sediment S/S operation generates a complex environmental profile which is dominated by the treatment phase, which, in turn, shows that the optimization of this stage could lower these impacts. Furthermore, Todaro et al. [92] investigated the effects of a treatment with cement and lime enhanced by the addition of green additives, such as active carbon and biochar, for chemical remediation. The last one is a promising and cheap adsorbent material, which is the by-product of—mainly—agricultural waste pyrolysis. The first results suggested that appropriate mix designs and curing times could allow for the reuse of sediments by both improving their geotechnical characteristics and making them environmentally acceptable in accordance with end-of-waste criteria. However, the addition of binders increased the pH of the mixtures with a consequent high leachability of different metals. The mobility of the metals appeared to be also governed by the curing time. The performance of the mixtures in terms of immobilized metals was influenced by the presence of organic contaminants (e.g., organic matter, PAHs, and PCBs). As a lesson, high organic matter and fine-grained particles can negatively affect the effectiveness of S/S treatment in terms of metal immobilization. Regarding the sediments of the first basin of the Mar Piccolo, after the addition of the binders (Portland cement/Calcium oxide), a significant increase in release was observed [93] due to the consequent rise of pH values (>10).

Recently, nanotechnology has emerged as an efficient, cost-effective, environment-friendly, and promising technology for soil remediation [89]. De Gisi et al. [94] studied the effectiveness of nZVI treatment for the decontamination of marine sediments polluted by heavy metals, using the commercial product Nanofer 25s. Experimental activities were conducted on sieved sediment with a size < 5 mm and the treatments with nZVI included 2, 3, and 4 g of product per kg of dry matter

(DM) in the case of low dosage and 5, 10 and 20 g for kg DM in the case of high dosage. The optimal amount of nZVI to be potentially used for sediment reclamation was selected (4% and 5% in the case of low and high dosages, respectively). According to the results, nZVI was more suitable to be used for specific elements removal rather than to be applied for a generalized contamination, meaning that a mix of techniques can be suggested for whole sediment remediation.

The institute for Coastal Marine Environment of the National Research Council CNR IAMC—UOS of Taranto proposed (with the Life4MarPiccolo project [95]) an alternative methodological approach to traditional intervention and remediation techniques, based on the design and implementation of a pilot wastewater treatment plant using the technology of microfiltration. The study is centered on the reclamation process of the Mar Piccolo of Taranto on a marine area of 3000 sqm, using a pilot system based on the use of membrane technology, defined internationally as Best Available Technologies (BAT).

Lastly, much interest has lately been given to monitored or assisted natural attenuation as a bioremediation treatment. It arose after extensive studies in numerous real scale sites about the reductive dechlorination of PCBs, such as the Hudson River (NY, USA), Silver Lake (MA, USA), Waukegan Harbor (IL, USA), and Acushnet Estuary (MA, USA) [96,97]. PCB biodegradation was followed for one year in microcosms containing marine sediments collected from the Mar Piccolo chronically contaminated by this class of hazardous compounds [98]. Results suggested that the autochthonous microbial community living in the Mar Piccolo sediment is able to efficiently sustain the biodegradation of PCBs in anaerobic conditions (the concentrations of the most representative congeners detected in the original sediment decreased by approximately 33% after only 70 days of anaerobic incubation without any bioaugmentation treatment).

However, this approach is very sensitive to the correct realization of a detailed conceptual model of the site and requires analytical or numerical simulations of the natural recovery [99].

9. Discussion

The Mar Piccolo ecosystem is undoubtedly unique on the world scene, as derived from the extensive literature previously described. It is a paradigmatic example of how economic activities affect the environment over time. The available information described above represents the starting point for planning suitable remediation actions.

The first level of discussion concerns the comparison of the results of our study with those of similar cases reported in the literature. By reviewing other case studies affected by severe contamination, as shown in Table 8, the critical situation of the Mar Piccolo of Taranto is evident. Pb, As and Hg, together with the organic pollutants, appear with a severe concentration, especially in sediments.

The comparison of our DPSIR approach with those present in the literature, as shown in Table 9, shows a level of response based on a qualitative pre-treatment survey. Only the Sarno River case is similar.

Table 8. Comparative sediment and water concentrations of PAHs, PCBs and Metals in marine basins worldwide.

Site and Reference	Environmental Matrices	Total PAHs	Total PCBs	Metals
Mecoacán Lake Estuarine, Mexico [100]	water	0.3–2.8 µg/L	-	-
Venice lagoon, Italy [101]	sediments	0.1–36 mg/kg	0.1–59 µg/kg	Cu (0.1 mg/kg), Zn (12 mg/kg)
Naples harbor, Italy [102]	water	19.6–178.9 ng/L	1.2–10.5 ng/L	-
Guánica Bay, Puerto Rico [103]	sediments	9–31,774 ng/g	1–899 ng/g	As (1–1121 mg/kg), Cd (0.01–3 mg/kg), Co (1–30 mg/kg), Cr (7–1798 mg/kg), Cu (12–5743 mg/kg), Pb (19–3083 mg/kg), Ni (4–362 mg/kg), Hg (0.01–139 mg/kg), V (37–2114 mg/kg) and Zn (17–7234 mg/kg).
Lake Chaohu, China [104]	sediments	9.637–4663.143 ng/g	0.11–3059.9 ng/g	As (1.28–12.80 mg/kg), Cd (0–0.11 mg/kg), Cr (3.48–1930 mg/kg), Cu (0.89–102 mg/kg), Hg (0–0.19 mg/kg), Ni (4.88–709 mg/kg), Pb (0.20–31.90 mg/kg) and Zn (2.21–153 mg/kg).
Our study [31]	water	-	672 ± 1293 pg/g	Cd (0.966 ± 0.481 mg/kg), Cu (30.9 mg/kg), Hg (0.570 ± 0.510 mg/kg), and Zn (122.5 ± 53.2 mg/kg).
Mar Piccolo of Taranto, Italy [46]	sediments	>0.2 pg/L	4652 pg/L	Cd (>0.3 µg/L), Cr (>0.3 µg/L) and Pb (>7.2 µg/L).
		56–36,370 µg/kg	20–9391 µg/kg	As (3.77–48 mg/kg), Cd, (0–1.5 mg/kg), Cu (9.1–172.7 mg/kg), Hg (0–16.7 mg/kg), Ni (23.33–60.66 mg/kg), Pb (24.42–272.54 mg/kg), V (25.67–95.61 mg/kg), Zn (38.51–602.89 mg/kg).

Table 9. Comparative DPSIR frameworks in literature.

Site and Reference	Driving Forces	Pressures	States	Impacts	Responses
Sarno river, Italy [11]	- Demography - Agricultural land use - Industrial development	- Water consumption and wastewater - Waste production - Air pollution	- Genotoxic effects - Contamination of matrices - High concentration nutrients - Presence of illicit drugs	- Risk to trophic chain, horticultural products, and animal fed	- Water and wastewater management - Waste management - Air pollution prevention
Asian cities (Bangkok, Jakarta, Manila, Osaka, Seoul, Taipei, and Tokyo) [15]	- Population growth - Industrialization	- Wastewater discharge - Oil leakage - leachate from landfills - Water demand - Groundwater use - Land use change	- Chemical contamination - Microbial contamination - Salinity - Decrease GW levels - Decrease GW recharge	- Human health risks - Impacts on organisms - Land subsidence - Flooding - Damage to infrastructure	- Change in consumption and production - Improve sanitation and waste disposal - Alternative source of water - Improve water quality - Control pumping areas - Flood control

Table 9. Cont.

Site and Reference	Driving Forces	Pressures	States	Impacts	Responses
Choghakhor wetland, Iran [105]	<ul style="list-style-type: none"> - Agricultural activities - Water requirement of lowland - Tourism - Settlements and urban areas - Mining activities in upland - Population Growth - Drought 	<ul style="list-style-type: none"> - Construction of deep and semi-deep wells - Drainage of the agricultural wastewater containing pesticides and fertilizers - Uncontrolled development of fields, gardens and water harvesting - Water transfer with channel by the edge of wetland - Excavation and construction of the channel in margin of wetland - Increased tourists despite lack of facilities - Sprawl growth and dacha building without infrastructure and sanitary sewage disposal - Land use change and eliminating the vegetation - Sewage and waste production - Mining and creating dust and aerosols - Excessive harvesting of wetland biological resources - Illegal fishing and hunting 	<ul style="list-style-type: none"> - Drying the springs - Declining groundwater table - Increasing in organic and inorganic contaminants (Eutrophication) - Decreasing the quality water and dissolved oxygen - Increased sediment load - Loss of the surrounding wetland habitats - Increasing waste and reducing habitat quality - Leakage and infiltration of wastewater into groundwater and contamination despite high density springs - Groundwater and surface water contamination - Habitat loss and increase flooding potential - Reducing the quality and quantity of habitat - Accumulation of pollution disturbs the stability of the hydrological regimes 	<ul style="list-style-type: none"> - Disturbance in hydrological Regimes - Decreasing the biochemical products - Reducing the water regulation - Biodiversity loss and reduction in habitats - Reducing primary and biomass production - Reducing the educational opportunities 	<ul style="list-style-type: none"> - A comprehensive environmental assessment of water transition system - Developing master plans for tourists with environmental and potential of landscape consideration - Reduction in usage of pesticides and fertilizers and conscious of their correct application, decrease the unhealthy consequences - Development of continuity plans and wildlife nurture and give authorization in hunting to restrict illegal hunting - Mitigate drought impacts and apply solutions, such as optimized selection of land use, selection of improved variety of crops, change in the tillage technology, land restoration, and proper irrigation - Focus on impacts of water development plans and programs

Table 9. Cont.

Site and Reference	Driving Forces	Pressures	States	Impacts	Responses
Jiangsu province, China [106]	<ul style="list-style-type: none"> - Total food crops output - Population density - Urban built-up area - Industrial sector 	<ul style="list-style-type: none"> - Disproportion of arable land area in total land area - Total power of agricultural machinery per unit sown area - Chemical fertilizer use - Pesticide use - Irrigation - Acid rain 	<ul style="list-style-type: none"> - Scarcity of wild higher plants - Scarcity of wild higher animals - Disproportion of woodland, garden and grassland area in total 	<ul style="list-style-type: none"> - Farming output value per chemical fertilizer use - Food crops output per unit sown area - Tourism income - Housing area per capita in rural area - Proportion of rural population with new cooperative medical insurance 	<ul style="list-style-type: none"> - Government agricultural expenditure per unit sown area of crops - Agricultural loans per unit sown area of crops - Number of agricultural science and technology personnel - Years of rural education
Mar Piccolo of Taranto, Italy [Our study]	<ul style="list-style-type: none"> - Demography - Agriculture - Industry - Landfills and treatment plants 	<ul style="list-style-type: none"> - Discharges of nutrients and contaminants - Pollution in groundwater - Air pollution 	<ul style="list-style-type: none"> - Marine sediment characterization - Sea water characterization - Biodiversity - Anthropization of sea bottom - Marine litter 	<ul style="list-style-type: none"> - Contaminant mobility - Effects of contaminants in marine organisms - Human health - Eutrophication of toxic algae - Dewatering pump 	<ul style="list-style-type: none"> - Political approach - Remediation technologies

A second element of discussion concerns the affordability of the adopted data. Generally, the monitoring of an environmental system, such as a river or the suitability of a treatment technology in terms of the removal of a target contaminant, involves setting the time frame for the analysis. The adoption of sampling and analysis methods, well recognized or established by law, provides reliable data, and especially comparable with that derived from similar monitoring or technological experimentation in other parts of the world. Clearly, this rarely happens in the case of DPSIR, due to the complexity of the case study addressed. The heterogeneity of the data and its acquisition in different temporal instants are an intrinsic weakness of the DPSIR approach, as highlighted by Lewison et al. [17].

Based on the comparisons in Table 9, a third element of discussion concerned the importance of developing reliable cause–effect relationships between the different elements of DPSIR. In this direction, the literature hardly ever shows universal solutions that can be adopted for any complex environmental system. Therefore, in order to highlight the potential of the DPSIR approach, one of the possible relationships has been investigated; in particular, we focused the attention on the relations between contamination sources and the environmental quality of marine sediments. Previous statistical studies [1,107], in fact, applied Principal Components Analysis and Cluster Analysis in order to find information about the existing site-clusters with similar pollution characteristics and to identify the most important discriminant contaminants (variables) within the same cluster, as shown in Figure S6a in Supplementary Material.

All the surficial layer, the so-called young sediments, appear with a spread contamination, as shown in Figure 17a, suggesting that the primary sources of contamination could be still active. The presence of contamination even in the deeper layers (hot spots) could act as “secondary sources of contamination” if appropriate containment measures are not taken, as shown in Figure 17b. Correlations between nutrients and metals, as shown in Figure S6b in Supplementary Material, showed that the excessive presence of nutrients and organic matter, in the Mar Piccolo water, could act as a carrier for many contaminants concentrated in the fine fraction of sediments with a high percentage of organic matter. Furthermore, Mali et al. [107] used ANOVA analyses in order to assess the impact of the main factors. They pointed out that the nature and origin of organic matter within different layers, the rates of dilution by terrigenous sediments, the grain size fractions and aggregation phenomena, and the original composition of the sediment parent rocks can represent the main factors controlling the contaminant pattern. Therefore, either the seasonal intrusion of freshwater-carrying terrestrial detritus from citri or, most likely, the high land runoff, often detected at the end of the rainy winter period [108,109], could influence the behavior of pollutants.

It is possible to do research within the same part of DPSIR, as in the case, for example, of the responses part, as shown in Figure 1, where the problem of choice of the most suitable technologies for the remediation of the Mar Piccolo, is addressed. Necessarily, the best technologies will have to take into account not only technical aspects linked to their actual applicability (are they able to decontaminate sediments?), but also economic and social aspects. Consequently, the use of a multi-criteria approach, able to take into account both the different criteria (performance of the technologies in terms of contaminant removal, timing of the remediation work, costs, social impacts of the intervention, acceptability of the intervention, etc.) and the different stakeholders involved in such a decision making problem (administrations, environmental protection bodies, clusters of citizens, industrialists and traders, environmentalists, etc.) represent a mandatory solution, as highlighted in OECD-JRC [110].

The key to the development of robust new relationships is in the accurate initial data setup. The use of statistical techniques, as in the case of “contamination sources and marine sediments environmental quality”, relationship is fundamental, as highlighted in Sabia et al. [111].

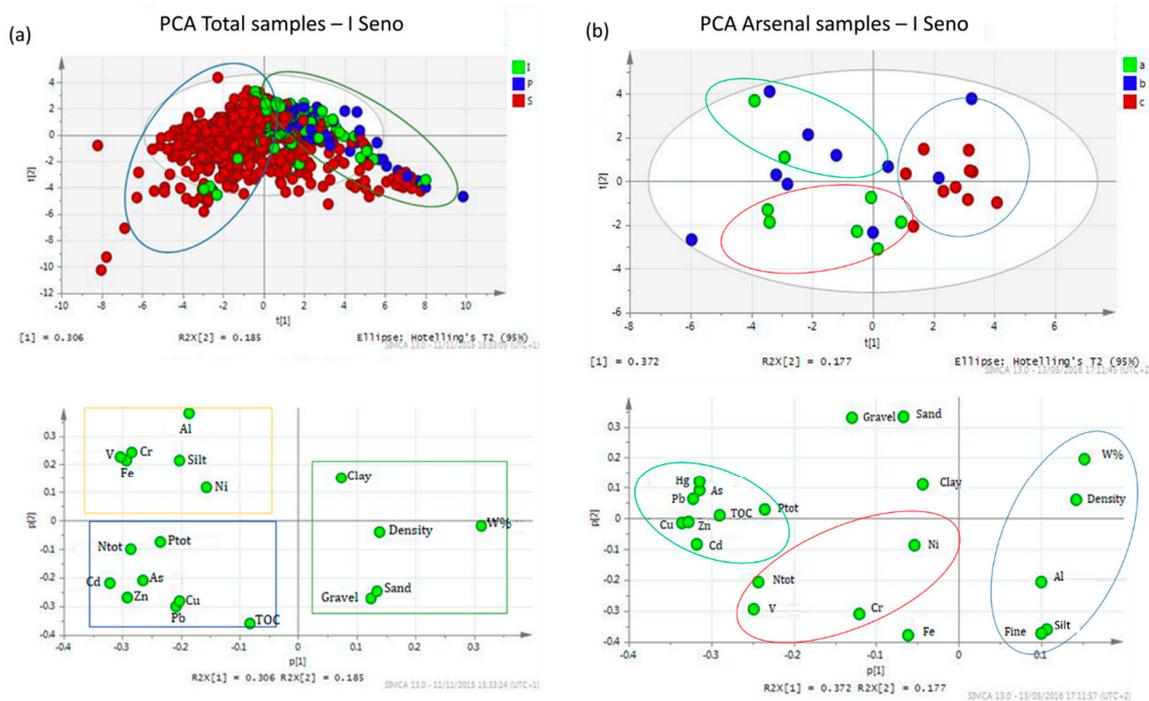


Figure 17. (a) Total dataset projection of Score plot (samples) and Loading plot (variables) on space PC1/PC2; (b) Arsenal dataset projection of Score plot (samples) and Loading plot (variables) on space PC1/PC2 (S = Surficial = layers 0–10 cm (a), 10–30 cm (b), 30–50 cm (c); I = Intermediate = layers 100–120 cm; P = Deep = layers 180–200 cm, 280–300 cm) [1].

10. Conclusions

Considering the case study of the Mar Piccolo in Taranto, the existing information and knowledge were synthesized in order to understand the major issues affecting this marine basin in the last half-century and how to respond to them. Following the DPSIR approach, used as global framework of the analysis, it was possible to gauge the potential responses to be implemented, although they are strongly constrained by the new development strategy for the investigated areas. The revised data revealed how the Mar Piccolo is a strongly anthropized environment, as a final receptor of a series of pollutants coming from all urban, industrial and agricultural activities, municipal wastewater treatment plants, and other anthropic activities, especially due to its natural hydrogeological network conformation. Mussel farming represents a historical economic activity for Taranto but also, unfortunately, a critical impact on the ecosystem due to subsequent marine litter. The mobility of contaminants from sediments to the water column showed the potential risk related to the bioaccumulation of organisms from different trophic levels, posing a threat of unacceptable magnitude to human safety. Some responses, already taken by the Apulia Region and the Special Commissioner of the Italian Government, were reported, while others have been hypothesized and, above all, related to the reclamation interventions. Together with the adoption of appropriate remediation solutions, which, however, require site-specific in-depth studies based on lab scale and pilot scale investigations, it is necessary to redesign a new development strategy of the area under investigation. The control and regulation of the driving forces, such as wastewater discharges, assumes a fundamental role to ensure that the results of the remediation can last over time.

While generalizing in order to provide reliable environmental decision support tools, consistent cause–effect relationships should be developed. Future lines of research should include the development of tools operating in the individual parts (e.g., state, impacts, responses), and the development of relations between the different parts of DPSIR.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2076-3417/10/15/5080/s1>, Figure S1: Population trend in cities falling into Mar Piccolo catchment area from 1861 to 2019 and (b) population density index (ratio between the number of inhabitants and area of town); Figure S2: Localization of treatment and disposal sites for special waste, hydrogeological network, and lithotypes; Figure S3: Metal concentrations (mg/kg) for As, Cd, Cu, Hg, Ni, Pb, V, Zn, and organic contaminants concentrations ($\mu\text{g}/\text{kg}$) for PAHs and PCBs in sediments (blue bars are used for samples taken at 0–1.5 m below the seafloor and red bars for samples taken at 1.5–3.0 m below seafloor). The red dashed lines indicate the site-specific law (ICRAM, 2004) [45]; Figure S4: (a) Localization of investigation stations and (b) percentages of *Vibrio* species isolated in water samples [47]; Figure S5: (a) Ex situ bioaccumulation tests and (b) in situ bioaccumulation tests (Adapted from [30]); Figure S6: (a) Dendrogram for 20 variables with identification of two main clusters and (b) first cluster correlations (TOC, As, Cd, Hg, Pb, Cu, Zn) [1].

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