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Highlights

- Touristic ports are driving force for the local development of coastal regions
- Touristic port activity can affect the quality of port area and the nearby coast
- Cumulative indexes and PAH content ratio were used to assess port pollution sources
- The inner basin of the ports resulted unusually more affected than the outer one;
- Hydrodynamic or other factors need to be studied for a spot-on risk assessment

Assessment and source identification of pollution risk for touristic ports: Heavy metals and polycyclic aromatic hydrocarbons in sediments of 4 marinas of the Apulia region (Italy)

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Abstract

The Apulia region in Italy has the longest Adriatic coastline; thus, maritime tourism is the driving force for its economic development. Pollution risk for four representative touristic ports of the region was assessed by determining the concentrations of 10 metals, 16 polycyclic aromatic hydrocarbons (PAHs) congeners, and the main nutrients. The cumulative mean Effects Range–Median quotient (mERMq) was used to assess the hazard degree, while the distribution patterns and content ratios of different PAH sediment concentrations were investigated to identify the pollution sources. Principal component analyses indicated an anomalous pollution trend for one of the small touristic ports assessed; this trend emerged from contamination by heavy metals and PAHs to a larger extent than expected, considering the main activity in this port, especially in its inner basin. The reason of this anomaly is thought to be the hydrodynamic and/or other stress factors.

Keywords

Hazard degree, port sediment, touristic port, heavy metals, PAHs, cumulative indices

Introduction

In a globalized economy, local development based on regional natural resources allows the regions to compete on a global scale. Maritime tourism is a driving force for the local development of regions with beaches, and touristic ports are important attraction points in such regions. Their economic benefits are based, on the one side, on environmental quality and scenic views of the nearby coastal areas and, on the other side, on the efficiency of the offered tourist services; they are therefore vulnerable to human activities that can adversely affect the ecosystem of the nearby areas. Thus, regions with beautiful sceneries, natural hydrologic structures, clean water, fresh air, and species diversity can suffer from pollution and lose their attractiveness (Mihalicˇ, 2000; Ameer A. 2008; Dias et al. 2014; Anfuso et al. 2014; Garcia et al. 2014; Dalmora et al. 2016).

The Apulia region is situated in southeast Italy and has the longest coastline. It has over 800 km of coastline, 6 certified blue-flag beaches, 30 important beach resorts, 3 regional areas of excellence, 3 marine reserves, and over 30 natural protected areas. Alongside the beach trail, many touristic ports play an important role for the local development of the region (MacCallum et al. 2011). In this context, the port expansion required to meet the increasing demands of residents and tourists would definitely facilitate touristic, commercial, and economic growth. Despite this benefit, the activities carried out in the touristic ports are also likely to cause deterioration of coastal landscape, thereby affecting the quality of marine water in the surrounding areas. (Petrosillo et al. 2010; Afuso et al. 2014; Pérez et al., 2014; Sanchís et al., 2015).

Trace metals and polycyclic aromatic hydrocarbons (PAHs) are the two major contaminant categories investigated in the marine environment, because of (1) their high toxicity and environmental persistence and (2) their consequent inclusion as priority substances in the Water Framework Directive 2000/60/EC (EC 2000). These contaminants can be introduced into the port basins through various ways, for example, ship-borne oil discharges, dry-docking operations, discharging of bilge oil, urban runoff, domestic wastewater discharges, and atmospheric deposition across the air–sea interface. After being transported into the aquatic ecosystems, these contaminants are absorbed by suspended solids and accumulate in port sediments where they become even more resistant to degradation (Zakaria et al. 2002; De Luca et al. 2005). When the concentration of these contaminants trapped in port sediments increases significantly, they are leached to the surrounding water column, thereby leading to degradation of the quality of the aquatic ecosystems (Lee et al. 2001; Tsapakis et al. 2006; Abdulla & Linden 2008; Olieviro et al. 2012; Ribeiro et al. 2013; Civeira et al. 2016; Mali et al. 2015; Mali et al. 2016).

To assess the effect of human activities on the environmental quality of marine areas in the Apulia region, four ports were selected as they represent the numerous touristic ports operating in the Apulian Adriatic coast (Figure 1a). The four selected ports – Torre a Mare (TM), Palese (PL), San Giorgio (SG), and Monopoli (MP) – are characterized by different human activities and different hydrodynamic morphologies. TM is a touristic port dealing with yachting and landing of small-sized ships. It has a particular hydrodynamic structure that facilitates an irreversible silting process of the port promoted by the materials that are periodically brought by Levante wind toward the access channel and then transported into the inner basin (Figure S1). MP is a commercial port dealing with yachting, fishery, and very important touristic/commercial activities. The latter ones are concentrated mostly in the oldest piers. PL, similar to TM, is a small-sized touristic port, currently designated for landing of small ships and yachts. SG port is a natural bay and is not equipped with yachting facilities. Nevertheless, it is used for local fishery activity or touristic needs. The distribution of 10 metals and metalloids (Al, As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, and V) and 16 priority PAHs in sediments from all the four ports was analyzed. The degree of potential health and environmental risk was assessed by calculating the cumulative mean Effects Range–Median quotient (mERMq) value, according to Long et al. (2006); this worldwide accepted method is an efficient tool that considers multiple factors affecting the hazard of sediments. In the case of the PAH contamination degree assessment, several pollution indices were used and the obtained results were compared to each other.

Finally, multivariate statistical analyses were carried out to identify specific port areas that are strongly affected by heavy metal and PAH contamination and to establish their correlation with pollution sources loading on port basins.

1. Materials and methods

2.1 Geographical, morphological, and environmental settings

The study area is a part of the Apulia region, a WNW–ESE elongated Italian region, flanked by the Adriatic Sea, and characterized by three large Meso-Cenozoic limestone landmasses from the north to south: the Gargano Promontory at the north, the Murge Plateau in the middle, and the Salento Peninsula at the south. Several minor touristic ports punctuate the entire coastline, and the four selected ports (MP, TM, SG, and PL) are located in the Murge Plateau landmass. With regard to the geomorphological features, the coastal ecosystem is constituted by micritic and calcarenitic limestones and sands, similar to most of the Adriatic coasts. Siliciclastic sediments input from the exposed region to the shelf is low since few rivers flow in Apulia, thus supplying small amounts of terrigenous material to their mouths. The only major watercourse of the area is the Ofanto river, which is 170 km long and is the longest river flowing into the South Adriatic Sea. Numerous ephemeral watercourses rhythmically affect the study area, but their contribution to the coastal sediments is scarce because of their ephemeral and torrential regime. The land use around the considered ports consists of residential neighborhoods. Numerous highly populated cities (Barletta, Trani, Bisceglie, Bari, Polignano, and Monopoli) are located alongside the coast. A prime cause of pollution is the lone incident of bombing during World War II that affected only one of the selected ports (MP port). Moreover, there are currently no heavy industrial activities in the area. The maritime transportation, fishery industry, and bathing and yachting activities are the principal environmental stressors for the quality of the harbor basins. The effect of such anthropogenic pressure can be observed often in the summer season with the increasing fishery and yachting activities. The domestic sewage water from the tourism firms operating alongside the coast is thought to affect the environment of the coastal area and related port basins.

Figure 1 near here

Caption to Figure 1 near here

2.2 Sampling

The sediment samples used in the present study were collected from May 2010 to September 2011. Sediments from the bottom of sea were sampled using a vibro-corer PF1, equipped with a liner and a support vessel and provided with the differential GPS system for positioning of sampling cores (Table S1). The sample cores were up to 1.50–2.00 m deep and could reach the rocky hard bottom of the harbor sediment. Each core was divided into several 50-cm length subcores. Aliquots of wet sediment samples were transferred from the liner into cleaned plastic bags and stored at 4°C during transportation to the laboratory.

2.3 Analytical methods

Sediments stored at –20°C after sampling were dried at 40°C for 48 h. Each sediment was classified according to Shepard (1954) into four classes: gravel: > 2 mm; sand: 2–0.063 mm; silt: 0.063–0.002 mm; and clay < 0.002 mm. A set of ASTM sieves was used for the granulometric separation (Romano et al., 2001).

The trace metal concentrations were measured by inductively coupled plasma mass spectrometry (ICP/MS X Series, Thermo Fisher Scientific) after sample mineralization by total acid digestion (HCl, HNO_3, and HF) (Pellegrini et al., 2001). The <63-µm fraction dried at 105 °C was used for the determination of the metal and metalloids. The results are expressed on the dry weight basis. The detection limits (LODs) were calculated from 3 replicates of procedural blanks. The LODs estimated were expressed in mg/kg and were equal to 1 ppb for all metals and metalloids analyzed. Marine Sediment Reference Material NIST 2702 (Inorganics in Marine Sediment) was used to control the analysis quality: the agreement between the analytical results for certified and measured values was satisfactory with recoveries between 80% and 100% for all metals and metalloids analyzed.

The PAHs considered for this study were as follows: naphthalene (NA), acenaphthene (Ap), acenaphthylene (Apl), phenanthrene (Phe), anthracene (An), fluoranthene (Flt), benz[a] anthracene (BaA), chrysene (Chry), benz[b]fluoranthene (BbF), benz[k]fluoranthene (BkF), benzo[a]pyrene (BaPy), benzo[e]pyrene (BePy), dibenz[a,h]anthracene (DBA), fluorene (fl), indeno[1,2,3-cd] (Ind), and pyrene (PY). These PAHs were first extracted with cyclohexane/methanol mixture and then determined by high-pressure liquid chromatography, according to Ausili's (2001) method.

Total nitrogen (N_{tot}) was determined by the Kjeldahl method (Kjeldahl, J. 1983), while total phosphorous (P_{tot}) by the elemental analysis procedure with a Perkin–Elmer 240B CHN Elemental Analyzer (Aspilla et al., 1976).

Total organic carbon (TOC) was determined by the elemental analysis procedure with a Perkin–Elmer 240B CHN Elemental Analyzer, after removing carbonates by reaction with hydrochloric acid (Nieuwenhuize et al., 1994).

All analyses were conducted in the ARPA (Apulian Regional Agency for Environmental Protection) laboratories according to standardized protocols.

2.4 Statistical analyses

Unscrambler Program (v. 9.2 Camo, Oslo, Norway) and Statistica7Software were used to perform statistical analyses. The PCA was carried out to assess geochemical associations and to ascertain the relationship among contaminants in the port sediment and their possible common sources (Lu et al., 2010; Varol et al. 2011; Silva et al. 2009; 2012; Rodriguez-Iruretagiiena et al., 2015).

2.5 Pollution risk degree for heavy metals

The pollution risk associated with heavy metal contamination was determined by calculating the mean ERM quotient (mERMq) (Long et al. 2006) on the basis of the relevant ERM values (Long et al., 1995), according to the following equations:

$$mERMq = \sum\left(\frac{ERMq}{n}\right) \qquad \text{Eq (1a)}$$

$$ERMq = \frac{Ci}{ERMi} \qquad \text{Eq (1b)}$$

where C*i* = the total content of the selected contaminant, *ERMi* = the ERM value of the selected contaminant, and n = the number of variables.

2.6 Ecological risk degree for PAHs

The diagnostic content ratio procedure (Soclo et al. 2000; Riccardi et al. 2013; Garcia et al. 2014) was used to identify the PAH origin. The diagnostic content ratios (ppb/ppb) used were Phe/An, Flt/Py, BaA/(BaA+Chry), and low-molecular-weight PAHs/high-molecular-weight PAHs (LMWPs/HMWPs).

The ecological risk associated with PAHs was calculated by the same cumulative index mERMq method (Long et al., 2006) used for heavy metals and metalloids to perform a correct comparative analysis.

2. Results and Discussion

3.1 Sediment characteristics

The sediments of the four considered ports were composed of a sandy fraction in the range of 21–97%$_w$, a coarse fraction in the range of 3–44%w, and a fine grain-sized fraction (silt and clay) in the range of 2–78%$_w$ (Table S2). The sandy fraction represents the main component for PL and SG ports, characterized by a scarce amount of fine grain-sized fraction (less than 4%$_w$). On the contrary, the fine grain-sized fraction is present in much higher amount in TM and MP samples, where differences were invariably observed between samples coming from the inner and the outer (at the entrance of the port) zones, respectively, with the amount of fine fraction higher (ranging from 17 to 78%$_w$) in the inner sites than in sediments collected at the entrance of the port (fine fraction in the range of 4–10%$_w$).

Several factors influence the distribution of fine-grained sediments in the marine ecosystem, the most important being sediment transportation and sedimentary processes (Tavakoly et al. 2011; Tavakoly et al. 2014). SG is an almost natural bay; thus, it is expected to be sandy, because it is well documented that natural bays have predominantly sandy sediments, with rare occurrences of gravel (McManus et al. 1998).

PL is sandy similar to SG, although the former is equipped with artificial port facilities (piers, breakwaters, and jetties). It seems that these facilities have a negligible effect on the hydrodynamics of the port area and thus on the fine-sized distribution of the PL sediments. The TM sediments are mainly constituted by mud sediments, especially in the inner basins and the MP port. The accumulation of mud sediments in TM and MP ports is probably facilitated by the presence of artificial port facilities such as breakwaters and headlands, which commonly protect the port structure from waves and marine currents, thereby minimizing the hydrodynamic energy inside the port area (Hancock et al. 2001). Thus, it is conceivable that the particular hydrodynamic morphology of the port affects the sediment composition.

3.2 Contaminant patterns

3.2.1 HMe distribution

Table 1 presents the statistical concentration data (minimum and maximum concentrations and standard deviations) for metals in all the 42 samples from the four considered ports. The metal distribution pattern, considering the entire database of port samples, was in the following order of concentrations: Zn>Pb>Cu>V>Cr>Ni>As>Hg>Cd, which differs substantially from both the upper crust concentrations (Wedepohl and Turekian, 1961) and the crustal average shale abundances (Wedepohl, 1995) (Table S5).

Metals & Metalloids*	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**	**V**
Wedepohl & Turekian (1961) (Upper Crust)	2.0	0.1	35.0	14.3	0.06	18.6	17.0	53.0	52.0
Wedepohl (1995) (Average crust)	1.7	0.1	126.0	25.0	0.04	56.0	14.8	98.0	65.0

Min	**3.8**	**0.05**	**0.1**	**2.7**	**0.0**	**3.9**	**5.0**	**11.0**	**10.6**
Max	**19.0**	**0.98**	**69.0**	**248.0**	**1.4**	**28.0**	**256.0**	**456.0**	**71.0**
SDev	**3.1**	**0.21**	**17.7**	**54.0**	**0.3**	**7.5**	**64.8**	**98.6**	**17.3**

Table 1. Upper crust concentrations (Wedepohl and Turekian, 1961), crustal average shale abundances (Wedepohl, 1995), and statistical concentration data (minimum and maximum concentrations and standard deviations) for metals and metalloids in all the 42 samples from the four considered ports. Concentrations are expressed in mg/kg.

Analysis of the concentration of heavy metals in each port revealed that sediments collected in TM and MP are very different from those coming from PL and SG. Figure 2 shows the mean and standard deviation values for HMe concentration calculated for each port. Higher concentrations of Pb, V, Cd, Hg, and Cu with respect to the crustal shale averages (Wedepohl, 1995) were observed in MP and TM ports, while lower HMe concentrations were determined in SG and PL samples; this finding follows the crustal average order (Wedepohl, 1995). The HMe contamination observed in MP could be explained by its commercial and touristic activities; therefore, different pollution sources could be identified (vessel batteries, discharge of wastewater, fuel and oil spills, bilge water, runoff water, etc.). On the contrary, the unusually high HMe concentrations detected in TM could be related to the particular hydrodynamic morphology of the port structure that facilitates the transport to the inner basins of fine sediments and related contaminants coming from the external coastal area.

Figure 2 near here

Caption to Figure 2 near here

In addition, differences were noted between the concentrations of heavy metals determined within the sampling sites located in the inner basin with respect to those located at the entrance of the port (Figure 3). An exception was noted for Hg, as the concentration of Hg determined within the inner sampling sites was similar to that determined at the entrance basin sampling sites. It is well known that fine particle sediments tend to trap and concentrate contaminants (Salomons and Fôrstner, 1984; Horowitz, 1991); therefore, the transport and fate of heavy metals are always associated with fine sediment dynamics. As discussed above, the morphology of the port structure facilitates the accumulation of silty sediments in the inner basin of the commercial ports, and consequently, a high level of heavy metal concentration was registered at the ports (Palanques et al. 1995; Villaescusa-Celaya et al. 2000; Fdez-Ortiz de Vallejuelo S et al. 2010; Oliveira et al. 2013).

Figure 3 near here

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3.2.2 PAH distribution

The total PAH concentration in the sediments from the four studied ports varied from 100 to 21500 ppb of dry matrix, ranging from 50 to 800 ppb for PL and SG samples and from 90 to 21500 ppb for TM and MP cores (Table S3). The lowest concentrations were observed in the sediments collected from PL and SG because they are almost uncontaminated natural bays. TM samples were moderately polluted by PAHs (90–2020 ppb) because of shipping activities, while the highest concentrations of total PAHs (up to 21460 ppb) were found in MP samples from the old basin, located near densely populated areas (Figure 4). In addition, the old basin morphology of MP produces a hydrodynamic stagnation zone in the inner harbor parts (sites MP25-MP26_MP27-MP28, Table S1), which causes the accumulation of contaminants (HMes and PAHs) in the stagnation area due to local hydraulic head gradients.

The most abundant PAHs in the sediments were those formed by 4–5 and 6 aromatic rings (mainly fluoranthrene (Fln), pyrene (Py), benzo [a] anthracene (BaA), benzo[b] pyrene (BbPy), and indene [1,2,] pyrene). The presence of HMWPs is due to their high sorption capacity and resistance to degradation (Wang et al., 2009) and has been frequently observed in marine sediments (Readman et al. 1987; Riccardi et al. 2013; Garcia et al. 2014), while the predominance of phenanthrene, fluoranthene and pyrene is symptomatic of the diesel fuel spill caused by shipping activities.

Figure 4 near here

Caption to Figure 4 near here

3.3 Assessment of ecological risk degree

3.3.1. Risk degree for HMes

The pollution risk associated with heavy metal contamination was determined by calculating the mean ERM quotient (mERMq) (Long et al. 2006) on the basis of the relevant ERM values (Long et al., 1995). The quotient provides a more realistic measurement of risk toxicity than the simple concentration data, as it weighs the magnitude by which individual metals exceed the respective ERM values, thus ranking the risk categories of the sites with multiple contaminants. The obtained results, reported in Figure 5, are presented according to the toxicity categories established by Long et al., 2006 (Table S4).

Figure 5 near here

Caption to Figure 5 near here

As expected, the calculated mERMq values showed a range from severe to moderate toxicity for the samples of MP and TM with the exception of two sampling points located at the entrance of TM port (TM_E and TM_F), while a slight toxicity was observed for the sediments from SG and PL. No sampling point with severe toxicity (mERMq value >1.5) was detected in any of the four ports.

3.2.2 Risk degree according to PAHs

PAHs can be divided into three main classes according to their features. The first one is composed of PAHs originating from incomplete combustion at high temperature of recent and fossil organic material (pyrolitic origin); the second one includes PAHs released by the slow maturation of organic matter under the geochemical gradient conditions (petrogenic origin); and the last class contains PAHs derived from short-term diagenetic degradation of biogenic precursors (diagenetic origin). However, anthropogenic activity is generally considered to be the major source of PAHs in the world (Zakaria et al. 2002). Each reported source generates characteristic PAH patterns, and it is therefore possible to identify the process that generated PAHs at a certain site.

In the present study, the diagnostic isomeric content ratios of specific PAHs were used to distinguish between the various origins and to determine pollution sources and estimate the environmental risks of the port areas. The simultaneous evaluation of four isomeric content ratios was used to distinguish pyrolitic from petrogenic processes.

Phenanthrene is the most thermodynamically stable isomer with three condensed aromatic rings, and the ratio between phenanthrene and anthracene amounts (Ph/An) is commonly used to distinguish petrogenic source from pyrolitic input (Budzinski et al. 1997). Because this ratio is temperature-dependent (Alberty and Reif, 1988), high-temperature processes such as combustion of organic matter and fossil fuels (coal and petroleum) generate PAHs characterized by a low Ph/An ratio (<10), whereas the slow maturation of organic matter during catagenesis leads to higher Ph/An ratio values (Baumard et al. 1998a; Baumard et al. 1998b; Stogiannidis and Lame, 2015). Petrogenic PAHs are introduced in the port area through accidental oil spills, discharge from routine tanker operations, municipal and urban runoff, and other sources. Thus, two different classes of sediments can be defined: the first class with a Ph/An content ratio > 10 indicating petrogenic inputs and the second one characterized by a Ph/An content ratio < 10 indicating the dominance of pyrolytic sources. Since the bordering values are not very precise and the limits between the two processes are not clear-cut (Budzinksi et al., 1997), a simultaneous comparison with other isomeric content ratios is recommended to provide a good estimation of the different PAH sources (Raoux, 1991). The isomeric content ratio between fluoranthene and pyrene concentrations (Flt/Py) is also used for PAH source identification. Values greater than 1 are characteristic of the pyrolytic origin, whereas values lower than 1 are related to petroleum hydrocarbons (Perra et al. 2009) By plotting the two ratios (Ph/An against Flt/Py), two zones with two different pollution sources, pyrolytic and petrogenic, were defined. (Figure 6). Our results show that the samples of MP and TM sediments have PAHs derived from mixed pyrolitic and petrogenic sources, while the samples collected in the two natural bays PL and SG are more of a petrogenic origin (Ph/An > 10 and/or Flt/Py > 1).

To corroborate our source identification, cross-plot for other two content ratios was carried out (Figure 7): that between chrysene and benzo[a]anthracene (Chry/BaA) and that of the LMWPs/HMWPs (Yunker et al., 2002). Chrysene and benzo(a)anthracene derived from the processes of organic matter combustion at high temperatures have a Chry/BaA content ratio of less than 1.0 (Parlanti, 1990), which is characteristic of a pyrolytic origin. On the contrary, the low maturation of organic matter during burial in the sedimentary matrix results in Chry/BaA>1.0. An LMWPs/HMWPs content ratio of less than 1.0 is characteristic of a pyrolytic source (Soclo et al., 2000), while spillage of fuel oil or light-refined petroleum products yields values of LMWPs/HMWPs >1.0 (Liu et al. 2008).

Figure 6 near here

Caption to Figure 6 near here

Figure 7 near here

Caption to Figure 7 near here

The ecological risk associated with PAHs (organic pollutants) was calculated by the mERMq method (Long et al., 2006). The obtained results are comparable with the mERMq values calculated for metals and metalloids. The mERMq values for organic pollutants fitted well with those determined for metals and metalloids, and the strong relationship (R^2=0.89) between them suggests a common contamination source for both these classes of contaminants (Figure 9). Nevertheless, the high PAH mERMq values found in MP and TM harbors indicate a severe PAH pollution risk for the two commercial ports.

Figure 8 near here

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Figure 9 near here

Caption to Figure 9 near here

3.3.3 Total organic carbon and total nitrogen.

The C/N ratio of organic matter in surficial marine sediments has been frequently used as an indicator of terrigenous addition to marine sediments (Trask, 1955; Pocklington, Leonard, 1979; Faganelli et al. 1988; Mayers, 1994; Sánchez et al. 2013). The C/N content ratio for each sample site was calculated as an organic carbon source indicator, and the obtained results are plotted in Figure 10. The C/N ratios ranged from 14 to 49 and increased with the increasing fine fraction within the sediment samples. These C/N ratios are much higher than the typical C/N values reported for most coastal sediments (C/N=6–10) (Faganelli et al. 1988; Oliveira et al. 2011; Oliveira et al. 2012) indicating that the organic matter inputs to harbor sediments are highly affected by terrestrial and anthropogenic sources, especially in the case of TM and MP.

Figure 10 near here

Caption to Figure 10 near here

3.4 Principal Component Analyses

To identify the common pollution sources and to relate them with the determined contamination degree, a PCA was performed on the entire dataset, as a non-supervised technique for comparing the compositional patterns between sediment samples and for identifying factors influencing them. The analysis was carried out for each contaminant class. For this purpose, two datasets were considered: the first one was constituted by a matrix with 10 variables in columns (Zn, Pb, Cu, V, Cr, Ni, As, Hg, Cd, and Al) and the sediment samples in rows (42), and the second one was a matrix with 16 PAHs in columns and the 42 samples in rows.

Before the analysis, the data were pretreated by scaling and mean-centering.

For metals and metalloids, a model with two PCs (76% and 9% of explained variance, respectively) was selected, explaining 85% of the total variance, since the results did not significantly change when the third principal component (PC3 = 5% of explained variance) was considered using the Full Cross Validation method (Figure 11).

Figure 11 near here

Caption to Figure 11 near here

The score plot in the space formed by the two PCs (Figure 11(a)) reveals the existence of two different groups of sediments with two different pollution profiles. The first group was formed by sediment samples from MP and TM ports. The loading plots show the influence of almost all heavy metal concentrations on this group. The second group includes all sediments collected from the natural bays (SG and PL) and the sampling sites located at the entrance of the two ports of TM and MP (TM_E/TM_F and MP_23) indicated by the black arrows in Figure 11(a). This group was not affected by any metal concentrations. Two subclusters are noted in the loading plots: the samples of the inner basin of MP and TM ports are affected by As and Hg amounts [distinguished by strong positive loadings on PC2 (Hg: 0.46; As: 0.453)]; both of them are considered as metals with a high level of toxicity in environmental studies. The second subcluster in the loading plots is influenced by Cd, Cu, Pb, V, and Zn concentrations, characterized by lower positive loadings on PC2 and higher positive loadings on PC1. The PC space configuration suggests that these metals may have a common source, probably fossil fuel combustion, losses of fuel during maneuvering of vessel within the port (Cd and Pb), and use of metal antifungal products (Cu, V, and Zn).

A PCA of PAH congeners was also carried out to analyze their sources, and the obtained results confirmed the HMe trend. Further, in this case, a model with two PCs was considered since they explain 95% of the total variance (93% and 3% of the explained variance by each respective PC) (Figure 12 (a) and (b)). The score and loading space configurations of PC1 and PC2 show that the natural bays (PL and SG) results are not affected by any PAH congener, while the two ports (TM and MP) are influenced by the PAH content. In particular, 2- to 3-ring PAHs with low molecular weight affected TM samples, while the MP port was influenced predominantly by 4- to 6-ring PAHs with high molecular weight.

Figure 12 near here

Caption to Figure 12 near here

3.5 Pollution source identification

By performing the ratio analyses, cumulative indices, and multivariate statistical analyses used to identify possible sources of heavy metals and PAHs, the following considerations can be proposed:

i) The strong pollution determined for Pb, Cd, Cu, Zn, and Hg within the ports (MP and TM) suggests that fuel additives and combustion and corrosion of alloys used in vessel components are the main pollution source for these metals. Cu and Cd can also be related to the use of antifungal organometallic compound and to the maritime batteries, often spilled on the bottom sea area.

ii) The C/N ratio was high for MP and TM and was moderately high for SG, with only PL showing a normal C/N ratio with respect to the unpolluted marine ecosystem (i.e., C/N in the range from 6 to 10). The high C/N ratio could be due to domestic and municipal wastewater discharge in the coastal area, especially for TM and MP ports.

iii) On the basis of PAH ratio analyses, the main sources of PAHs in the sediments of MP and TM ports are anthropogenic with a dominant effect of pyrolytic genesis. The PAH contamination trend is similar to that found for metal pollution. In addition, only for the TM port, besides fossil fuels burned by yachts and vessels, PAHs may have other petrogenic sources such as petrol, coal, grass, and wood.

iv) The higher mERMq values for PAHs with respect to those determined for metals and metalloids suggest that the major risk for the four considered port basins is constituted by organic pollutants. Because of their high carcinogenic effect, the meticulous identification and prevention of fuel losses within the port area should be strictly and continuously monitored.

4. Conclusion

The different distribution patterns determined within the four studied tourist ports showed that multiple sources contributed to the increase in the content of pollutants (metals and PAHs), and human activity is one of the main sources of contamination of the coastal area. Generally, low hazard degrees were determined for the natural bay (SG) and one of the touristic ports (PL) that are not subjected to heavy anthropogenic activities. With regard to TM and MP, heavy metal pollution was moderate, but large risk indices were estimated for PAHs, which should be considered of high concern. In fact, the mERMq values calculated for PAHs suggest a relatively elevated level of toxicity of TM and MP sediments. A special consideration should be made for the TM port. In fact, although TM is a small touristic port, its hazard degree resembles that of MP, which, on the contrary, is a bigger port characterized by a higher extent of commercial and touristic activities. The serious threats determined for TM sediments are probably related to the hydrodynamic port structure that facilitates the entrance of contaminated fine sediments from the outer area and hampers their exit from the inner basin. This anomalous behavior observed for TM suggests that other factors such as hydrodynamic parameters may play a role in determining pollution risk. Further investigations are warranted to verify this hypothesis.

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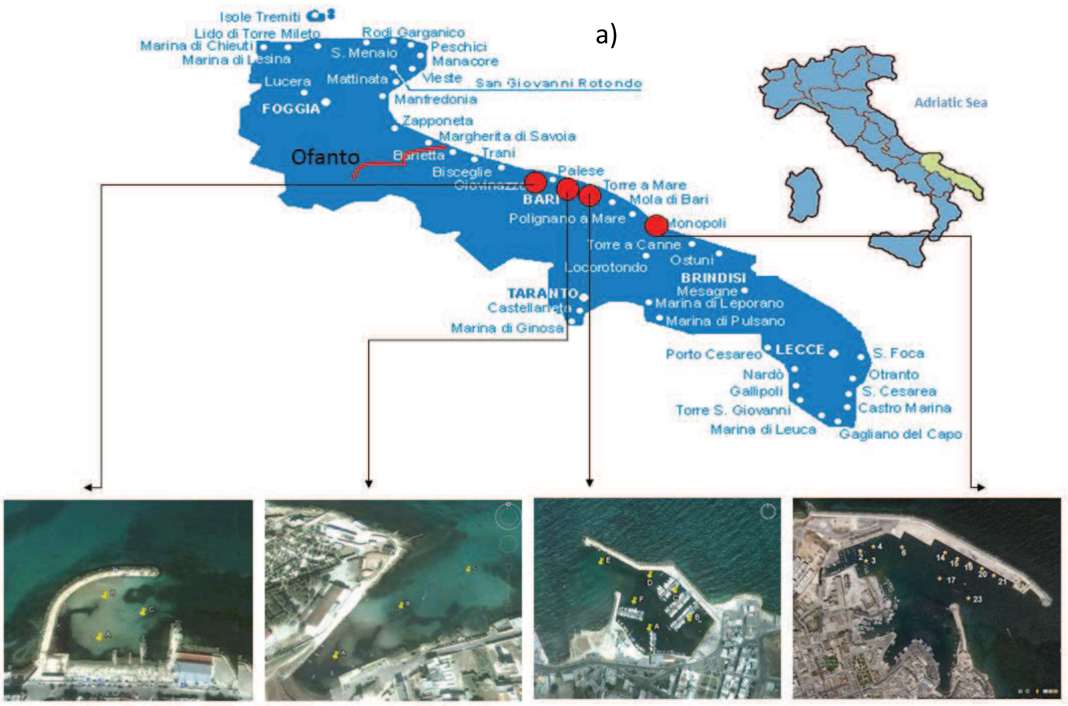
Metals & Metalloids*	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**	**V**
Wedepohl & Turekian (1961) (Upper Crust)	2.0	0.1	35.0	14.3	0.06	18.6	17.0	53.0	52.0
Wedepohl (1995) (Average crust)	1.7	0.1	126.0	25.0	0.04	56.0	14.8	98.0	65.0
Min	**3.8**	**0.05**	**0.1**	**2.7**	**0.0**	**3.9**	**5.0**	**11.0**	**10.6**
Max	**19.0**	**0.98**	**69.0**	**248.0**	**1.4**	**28.0**	**256.0**	**456.0**	**71.0**
SDev	**3.1**	**0.21**	**17.7**	**54.0**	**0.3**	**7.5**	**64.8**	**98.6**	**17.3**

Table 1. Upper crust concentrations (Wedepohl and Turekian, 1961), crustal average shale abundances (Wedepohl, 1995) and statistical concentration data (minimum and maximum concentrations and standard deviations) for metals and metalloids in all of the 42 samples of the four considered port. Concentrations are expressed in mg/kg.

Figure(s)



b) c) d) e)

Figure 1

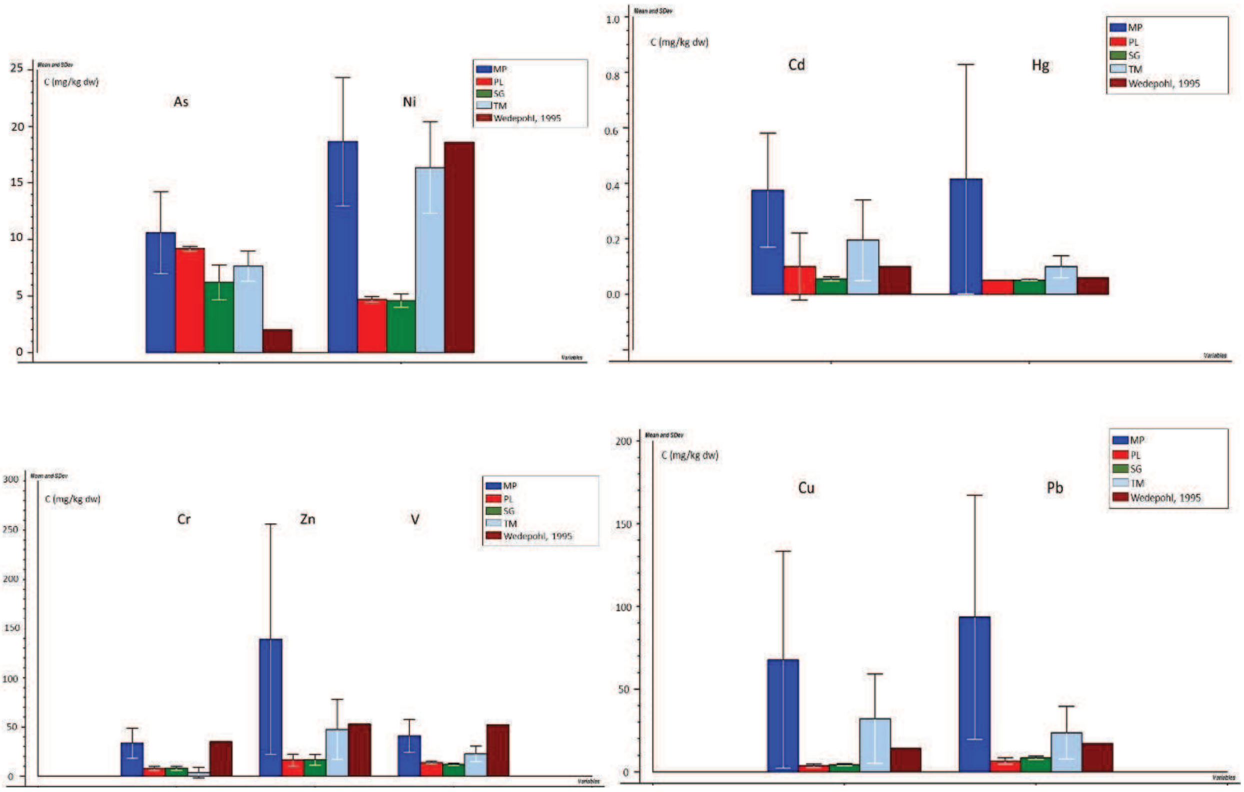
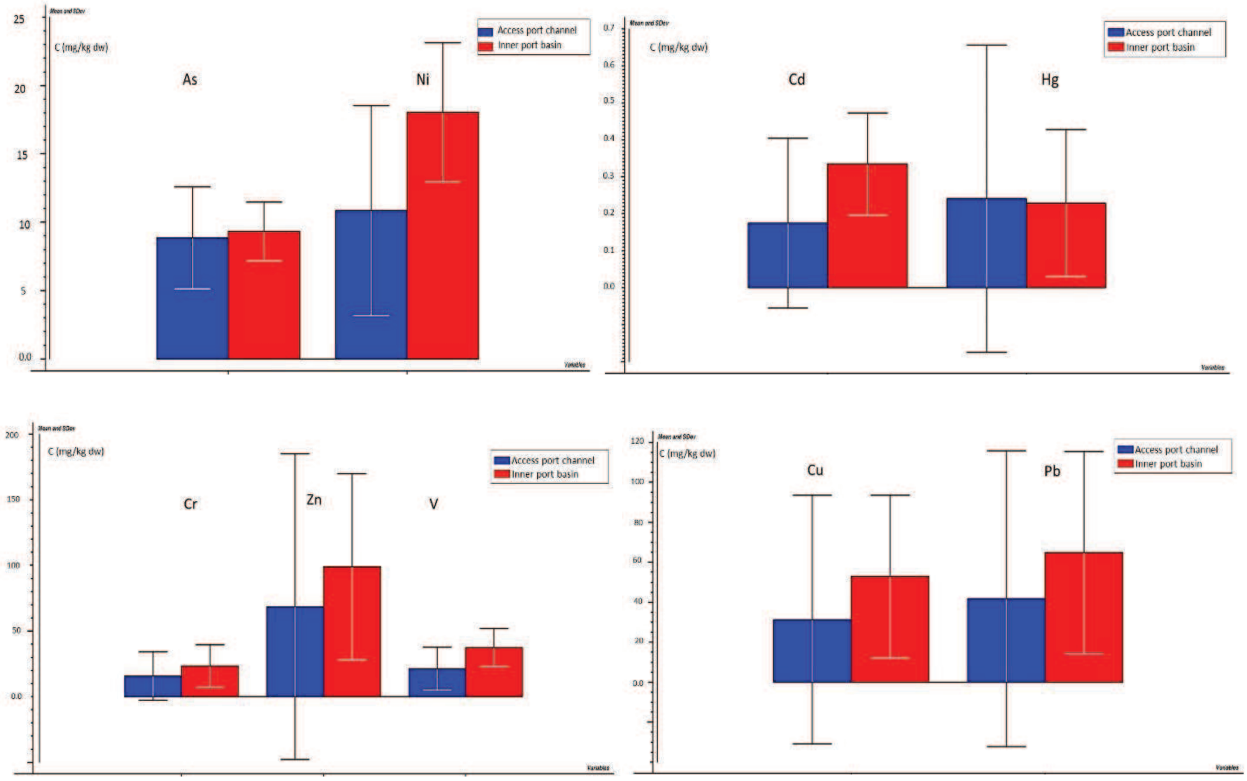


Figure 2



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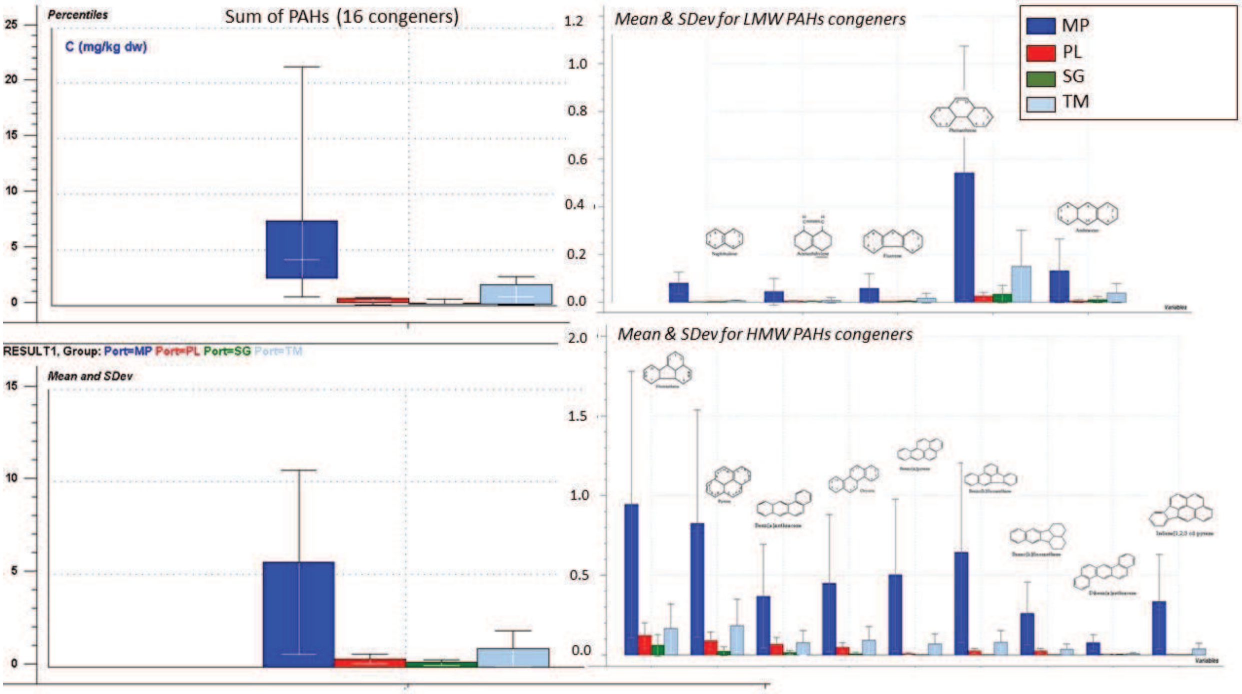


Figure 4

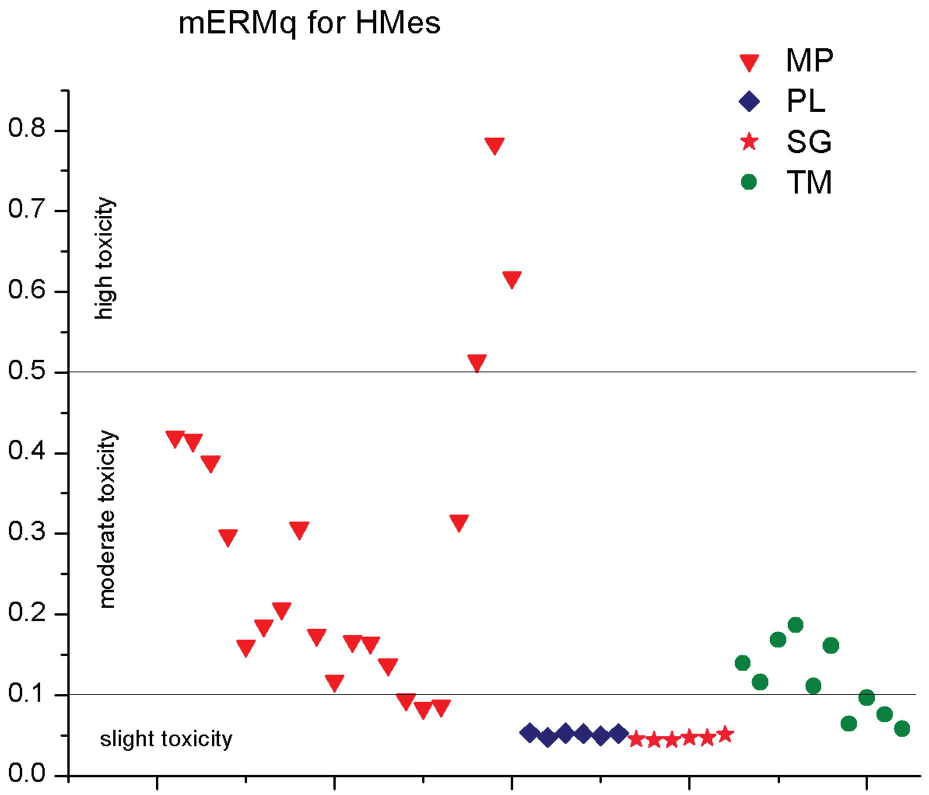
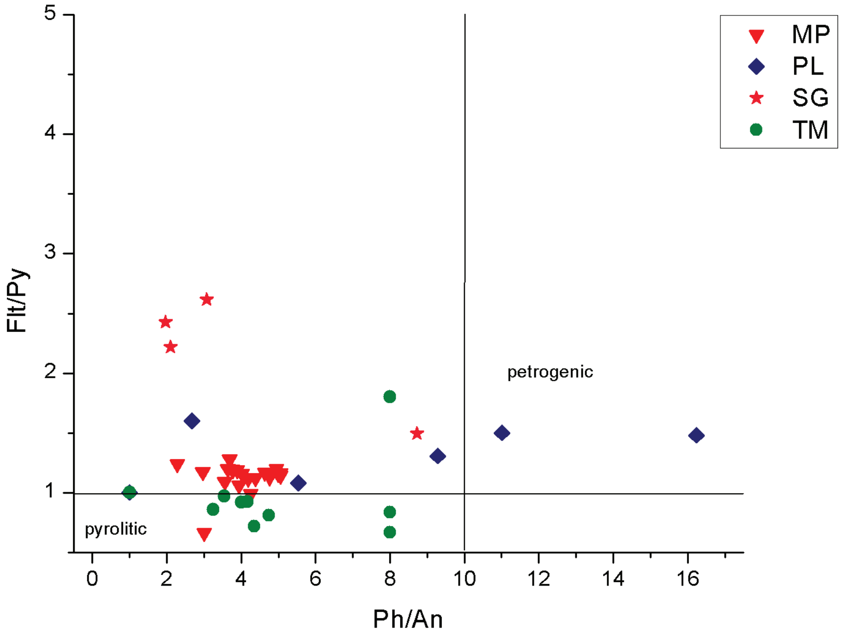


Figure 5



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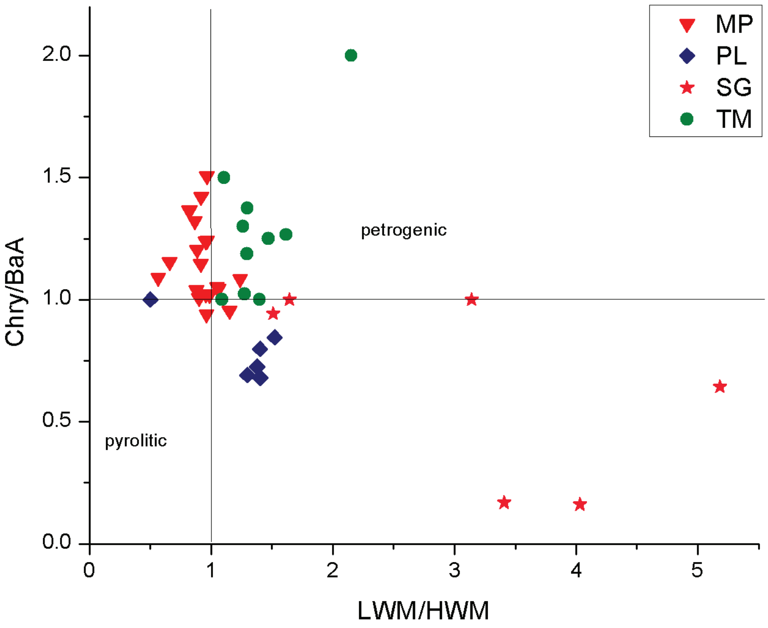

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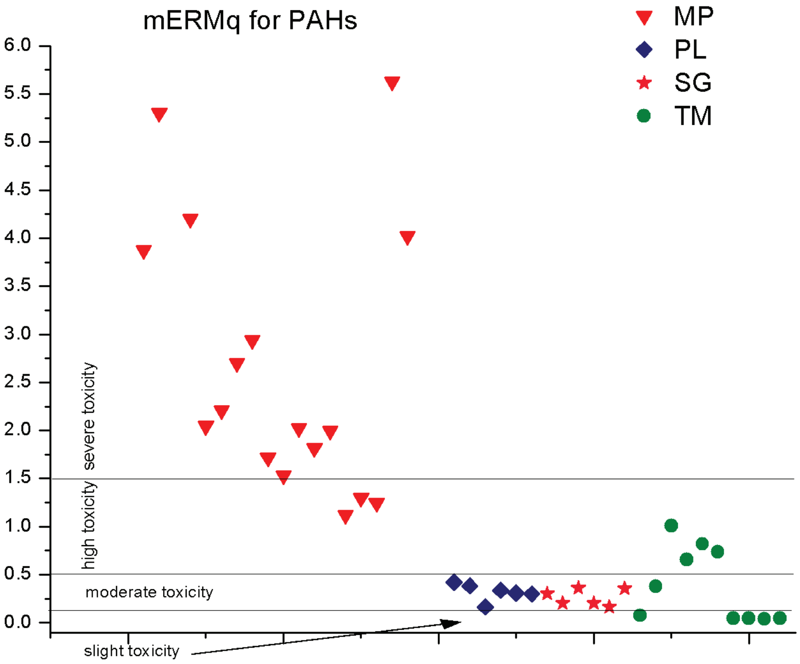

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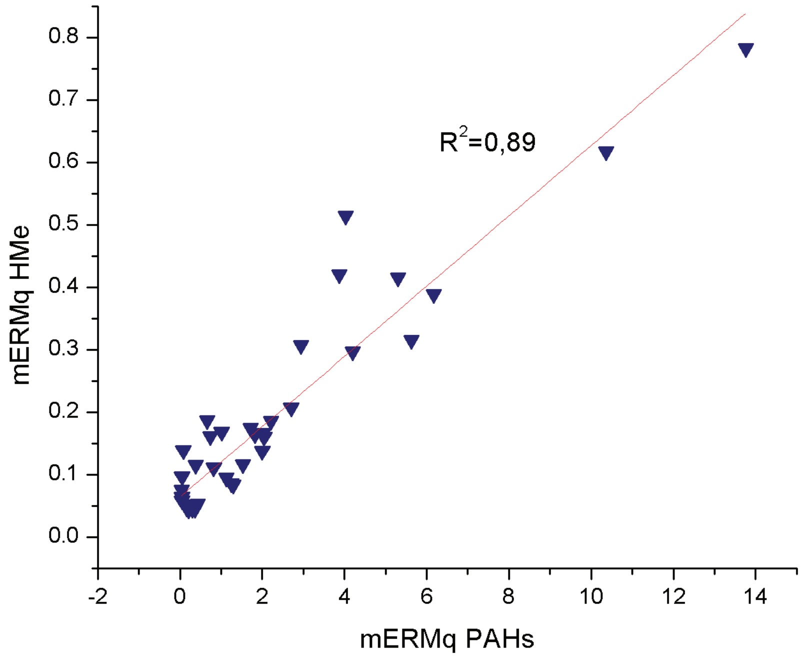

Figure 9

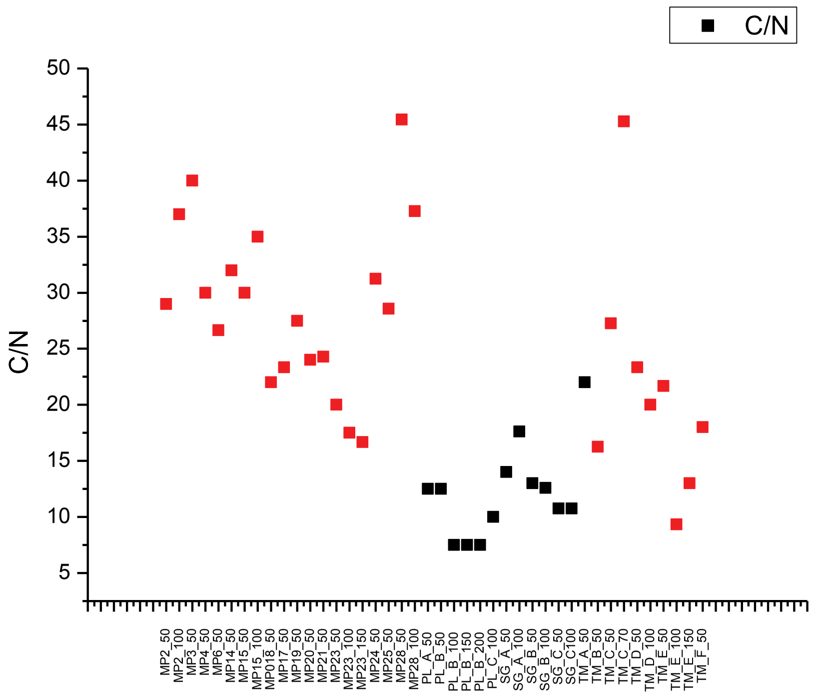

Figure 10

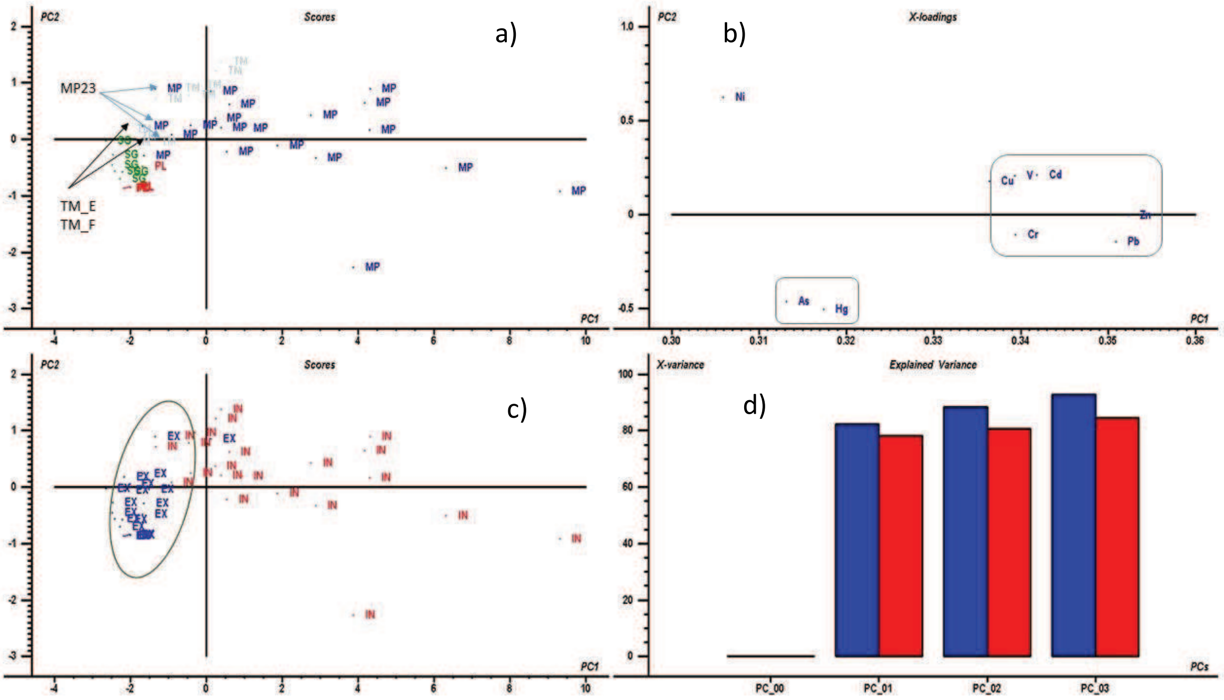

Figure 11

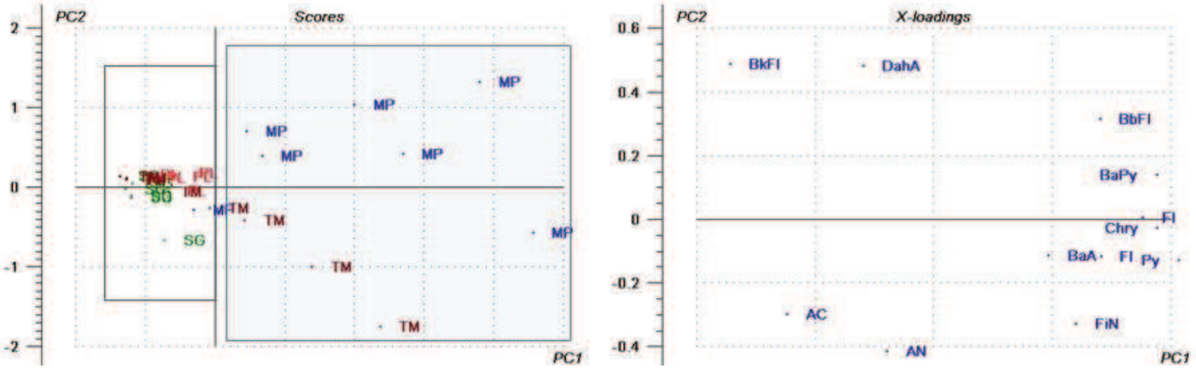

Figure 12

Figure's captions

Figure 1: Map of study area and sampling sites within port; a) Apulian Coast; b) sampling sites of PL port, c) sampling sites of SG bay, d) sampling sites of TM port, e) sampling sites of MP port.

Figure 2. Means and Standard Deviations of concentration of heavy metals calculated from data obtained in all sampling stations for each port (mg·kg^{-1}). Color code: blue = MP; red = PL; green = SG; light blue = TM; brown = Wedepohl values).

Figure 3. Means and Standard Deviations (SDev) of concentration of heavy metals metals calculated from data obtained, the red ones from sampling sites located in the inner basins of the four ports, and the blue ones from sites located in the entrance areas (all the concentration are expressed in mg·kg^{-1}).

Figure 4. Means and Standard Deviations (SDev) of concentration of PAHs calculated from data obtained in all sampling stations for each port (mg·kg^{-1}). Color code: blue = MP; red = PL; green = SG; light blue = TM).

Figure 5. Distribution of mERMq for HMes the four considered ports.

Figure 6. Cross plot of Ph/An content ratio values against Flt/Py content ratio values for sediments from different ports (MP, TM, SG and PL)

Figure 7. Cross plot of LMWPs/HMWPs content ratio against Chry/BaA content ratio or sediments from different ports (MP, TM, SG and PL).

Figure 8. The distribution of mERMq values obtained for PAHs within sediments samples

Figure 9. Cross plot of mERMq values for PAHs and Metals.

Figure 10. C/N content ratio values for each sampling site of the four ports.

Figure 11. Score (a and c) and Loading (b) plot of PC1/PC2 projection. Explained variance (d) of selected PCs. In figure (a) red, green, blue and light blue points indicate samples coming from PL, SG, MP and TM bays, respectively. In figure (c) points of TM and MP located at the port entrance and all sample points coming from SG and PL are represented in blue, while inner points of MP and TM are represented in red.

Figure 12. Score plot and Loading plot of the projection of PC1/PC2 for PAHs. Red and green points indicate samples coming from PL and SB bay respectively, while blue and brown indicates samples coming from MP and TM respectively. See section 2.3 for the meaning of the PAH abbreviations in the loadings plot. (c) (d)