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**SEDIMENT POLLUTION AND DYNAMIC IN THE MAR PICCOLO OF TARANTO  
(SOUTHERN ITALY): INSIGHTS FROM BOTTOM SEDIMENT TRAPS AND SURFICIAL  
SEDIMENTS.**

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**Keywords:** trace elements, PCBs, PAHs, surficial sediments, bottom sediment traps, sediment dynamics, Mar Piccolo of Taranto

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## ABSTRACT

1  
2 Major and trace element, PAH, and PCB concentrations were measured in surface sediments and  
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4 sediment traps collected in the First and Second Basin of the Mar Piccolo (Gulf of Taranto) in two  
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6 periods (June-July and August-September, 2013). The aim of the study was to evaluate pollution  
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8 degree, sediment transport, and particle redistribution dynamic within the area. Results confirm the  
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10 higher contamination of sediments from the First Basin observed by previous researches, particularly  
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12 for Cu, Hg, Pb, total PAHs, and total PCBs (values up to 238, 8.98, 130, 4.69, and 1.05 mg kg<sup>-1</sup>,  
13  
14 respectively). Particle fluxes were higher in the second period of measurement (August-September:  
15  
16 average flux of particles 1.34 mg cm<sup>-2</sup> d<sup>-1</sup>) with respect to the first one (June-July: average flux of  
17  
18 particles 0.39 mg cm<sup>-2</sup> d<sup>-1</sup>). On the other hand, concentrations measured in sediment traps were  
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20 generally much higher in the first period. Advective transport of particles from the First to the Second  
21  
22 Basin has been evidenced by statistical analysis of contaminant concentrations in surficial sediments  
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24 and sediment traps. A long-range selective transport of PAHs and microbial anaerobic degradation  
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26 processes for PCBs have been also observed. These results are limited to a restricted time window but  
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28 are consistent with the presence of transport fluxes at the bottom of the water column.  
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## 1. INTRODUCTION

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38 The coastal area of Taranto (Ionian Sea, Southern Italy) is a marine ecosystem where anthropogenic  
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40 pressures are widely distributed and related to the activities of the surrounding industrial and refinery  
41  
42 plants. As a consequence, the industrial area of Taranto has been enlisted by the Italian Ministry of  
43  
44 the Environment among the 57 Sites of National Interest that require detailed characterization and  
45  
46 recovery interventions (Ministry Decree 468/01), and several scientific studies were devoted to the  
47  
48 evaluation of environmental status and quality of the marine area (Caroppo and Cardellicchio 1995;  
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50 Lerario et al. 2003; Cardellicchio et al. 2004, 2006, 2007; Buccolieri et al. 2006; Calace et al. 2008;  
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52 Annichiarico et al. 2011; Caroppo et al. 2012; Petronio et al. 2012; Buonocore et al. 2013). These  
53  
54 researches studied different contaminants (e.g. heavy metals, PAHs or PCBs) in different matrices  
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56 (atmosphere, biota, or sediments), and all agreed in identifying the Mar Piccolo in front of the city of  
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1 Taranto as a polluted area, especially in sites closer to the ILVA iron and steel factory (Annichiarico  
2 et al. 2011) and the Navy Harbour (Cardellicchio et al. 2007). Medium-high ecological risks were  
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4 calculated for marine organisms, especially benthic species and an efficient input control for quality  
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6 recovery was suggested. This request becomes even more strikingly necessary when the risks posed to  
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8 humans by local farmed mussels and sea food caught in the area are considered.  
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11 Due to their large capacity to retain pollutants from different sources, sediments act as a sink in the  
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13 aquatic environment (de Groot et al. 1976). Sediments record the composition of the overlying water  
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15 column and the accumulation with time of particle-bound pollutants (Zhang et al. 1999; Secco et al.  
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17 2005). Consequently, the analysis of sediments is a useful method to assess the human impact in the  
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19 coastal zone, and provides basic information for environmental management and risk assessment  
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21 (Forstner and Wittmann 1983; Long et al. 1995).  
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24 Knowing the magnitude of the sinking particle flux, its variability and composition is likewise  
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26 fundamental to understanding the fate and distribution of many elements in aquatic environments  
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28 (Buessler et al. 2007). Indeed, hydrophobic chemicals tend to adsorb onto particle surfaces and  
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30 follow their pathways from input sources to bottom sediments (Radakovitch et al. 2003; Buessler et  
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32 al. 2007; Giuliani et al. 2007), undergoing a series of processes that includes burial, resuspension, and  
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34 dissolution through particle remineralisation at depth (Buessler et al. 2007).  
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38 In the framework of the Italian flagship project RITMARE this paper presents the results relative to  
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40 the study of contaminants in surface sediments and adsorbed on sinking particles in the two basins of  
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42 the Mar Piccolo, Gulf of Taranto. Major and trace metals, polycyclic aromatic hydrocarbons (PAHs),  
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44 and polychlorobiphenyls (PCBs) have been measured with the aim of assess sediment quality and  
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46 evaluate transport and distribution dynamics of sediment particles.  
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## 49 50 51 52 **2. STUDY AREA**

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54 The Mar Piccolo (surface area 20.72 km<sup>2</sup>) is located north to the city of Taranto (Southern Italy, Fig.  
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56 1). It is an inner, nearly-enclosed basin with lagoon features, divided by rocky promontories into two  
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58 sections: the First Basin (western side, maximum depth 13 m) and the Second Basin (eastern side,  
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1 maximum depth 8 m). The First Basin is connected to the Mar Grande (Ionian Sea) through two  
2 channels (Canale Porta Napoli and Canale Navigabile) that represent the only pathways for water  
3 exchange. Tidal range does not exceed 30-40 cm, and water salinity is influenced by the presence of  
4 about 30 submarine freshwater springs (locally called “citri”) and outfalls of small tributary rivers  
5 (Caroppo and Cardellicchio 1995). A large cooling water intake system, installed by the ILVA steel  
6 factory during the 1970s, removes daily 120,000 m<sup>3</sup> of water from the First Basin; the outflow has a  
7 small influence on local circulation, being located in the Mar Grande (De Serio et al. 2007). The  
8 resulting hydrodynamism is quite low and determines high water stratification (Petronio et al. 2012),  
9 but density gradients are sufficient to trigger a persistent baroclinic estuarine circulation where (on a  
10 yearly averaged time scale) salty and cold water enters in the system on the bottom layer while the  
11 less salty and warmer water is outward directed on the surface (De Pascalis et al., 2015). Water  
12 renewal times of 25 and 36 days have been measured in the First and Second Basin, respectively  
13 (Umgiesser et al., 2014).

14 In addition to the contribution that comes from industrial plants, anthropogenic impacts are widely  
15 distributed along and within the study area (Calace et al. 2008; Annichiarico et al. 2011; Buonocore et  
16 al. 2013). Small rivers and “citri” drain the surrounding agricultural soils, several urban sewages from  
17 the city of Taranto and nearby towns are transported to the Mar Piccolo through a number of pipes,  
18 and the shipyard of the Italian Navy, with its dry docks, is located on the southern shores of the First  
19 Basin (Lerario et al. 2003; Cardellicchio et al. 2004, 2006; Fig. 1). In addition, the Mar Piccolo  
20 sustains the largest mussel production of Italy (ca. 30,000 tons year<sup>-1</sup>) over a total legal farm area of  
21 ca. 10 km<sup>2</sup> (Caroppo et al. 2012). Urban and industrial effluents are expected to transport organic  
22 matter, nutrients, petroleum hydrocarbons and toxic heavy metals in the Mar Piccolo. In addition,  
23 most contaminants, and especially PCBs, may be found in both the solid (waxy) and liquid (oily)  
24 forms in equipment and materials onboard old vessels (EPA, 2013) and can be transferred to the  
25 environment during routinely maintenance operations or by accidental spilling.

### 26 **3. MATERIALS AND METHODS**

### 3.1 Sample collection and treatment

1  
2 Cylindrical polyethylene sediment traps (diameter 8,4 cm, height 25 cm, surface area  $5.5 \cdot 10^{-3} \text{ m}^2$ )  
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4 were first positioned in 5 sites (Fig. 1) on June 20<sup>th</sup>, 2013. They were retrieved 35 days after (on July  
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6 25<sup>th</sup>), and immediately substituted by others that were retrieved 49 days after (on September 12<sup>th</sup>).  
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8 After collection, samples were immediately frozen at  $-4 \text{ }^\circ\text{C}$ . Once in the laboratory, they were  
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10 defrosted and passed through a 2 mm sieve. The sediment was recovered by centrifugation, then dried  
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12 and homogenized, and divided into aliquots for different analyses.  
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16 Sediment cores were collected in 11 sites (Fig. 1) on June 20<sup>th</sup>, 2013, with a SW-104 corer  
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18 (Magagnoli and Mengoli, 1995) that preserves the sediment-water interface (Bellucci et al. 2012).  
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20 Cores were kept vertical at a temperature of  $4 \text{ }^\circ\text{C}$  until subsequent sub-sampling and analysis; the  
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22 outer sections of the slices were carefully removed in order to avoid smearing. Sediment pollution  
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24 was investigated along the entire core profile (Cassin et al. in preparation): data obtained for the  
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26 surface layer (2 cm thickness) have been utilised in this study.  
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### 3.2 Major and trace element analyses

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33 Samples were dried in an oven at  $105 \text{ }^\circ\text{C}$ , then ground to powder in an agate mortar. About 0.4 g of  
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35 each dried samples were then digested with 8 ml  $\text{HNO}_3$  in a microwave oven (Multiwave 3000, Anton  
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37 Paar, Austria). The digested samples were left cooling at room temperature, filtered through a  $0.45$   
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39  $\mu\text{m}$  nitrocellulose membrane filter, and then diluted with distilled deionised water to 40 ml in a  
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41 volumetric flask (USEPA, Method 3051A).  
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46 The concentrations of major and trace elements (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were  
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48 determined by inductively coupled plasma atomic emission spectrometry (ICP-AES; Optima 2100DV,  
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50 Perkin Elmer, USA; USEPA, Method 200.7).  
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53 Mercury analyses were carried out by atomic absorption spectrophotometry by cold vapour (Analyst  
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55 100, Perkin Elmer, USA; USEPA, Method 245.1).  
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2 The quality acceptance protocols required that one blank sample or one certified reference material  
3 (BCR-277r estuarine sediment, Community Bureau of Reference) were digested and analysed with  
4 each batch of fifteen samples. The recovery rates ranged from 88 % for Cd to 106 % for Zn.  
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6 Blanks results indicated that the analytical procedure was free from contamination as the  
7 concentrations of all metals examined were below the respective method detection limits.  
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### 10 11 12 **3.3 PAH and PCB analyses**

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14 Samples were air dried in the dark at room temperature for 48 hours on hexane-rinsed aluminium foil,  
15 then finely ground in an agate mortar.  
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19 The extraction was performed using a Microwave Sample Preparation System (Multiwave 3000,  
20 Anton Paar Graz, Austria), in accordance with the US-EPA recommendation (method 3546). Two  
21 grams of dried samples were accurately weighed into lined microwave extraction vessels. This was  
22 followed by the addition of a 25 ml 1:1 acetone/hexane solvent mixture. The extraction was  
23 performed for 15 min at temperature of 110°C and pressure of 6-10 bars, then extracts were cooled to  
24 room temperature, filtered on glass fiber filters Whatman GF/F, 47 mm in diameter (rinsed twice with  
25 hexane and acetone before heating to 450 °C for two hours in order to eliminate organic compounds)  
26 and rinsed with the same solvent mixture. They were then concentrated in a rotating evaporator  
27 (Rotavapor-R Buchi, CH), and sulphur compounds were removed by soaking the extracts with  
28 activated copper powder. All solvents were of pesticide residues grade (Romil Super Purity Solvent).  
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30 Purification and fractionation were performed by eluting extracts through chromatography glass  
31 columns packed with Silica gel/Alumina/Florisil (4+4+1 gr). The first fraction, containing PCBs, was  
32 eluted with 25 ml of n-hexane, whereas the second fraction, containing PAHs, was eluted with 30 ml  
33 of 8:2 n-hexane/methylene chloride solvent mixture. After concentration with a rotary evaporator, the  
34 samples were ready for the instrumental analysis.  
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54 PAHs were analyzed with high performance liquid chromatography (PE 200, USA), coupled to a  
55 programmed fluorescence detector (HP 1046A, USA). The column was a reverse-phase Supelcosil  
56 LC-PAH (length = 150 mm,  $\phi$  = 3 cm, particle size = 5  $\mu$ m). Linear gradient elution was executed  
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with acetonitrile-water mixture as mobile phase at a flow rate of 0.8 ml min<sup>-1</sup>. The composition of the gradient started with 40% of acetonitrile held constant for 4 minutes, it was increased to 100% in 11 minutes and then held constant for other 10 minutes. The column compartment was thermostated at 40°C. The fluorescence wavelength programme developed to enable the optimal detection of all compounds was as follows: 1) excitation = 280 nm, emission = 340 nm, time = 0 min; 2) excitation = 265 nm, emission = 389 nm, time = 11.7 min; 3) excitation = 280 nm, emission = 435 nm, time = 13 min; 4) excitation = 265 nm, emission = 389 nm, time = 13.5 min; 5) excitation = 280 nm, emission = 410 nm, time = 16 min.

PCBs were analysed by gas chromatography/mass spectrometry (GC/MS). The system consists of an Agilent 7820A GC coupled with an Agilent 5977E Series GC/MS, and software MassHunter for data analysis. The GC is equipped with a 30 m HP-5MS capillary column ( $\phi = 0.25$  mm, 0.25  $\mu$ m film) and operative conditions were the following: 1) inlet temperature = 280°C; 2) injection in splitless mode; 3) carrier gas (helium) flow = 1.8 ml min<sup>-1</sup>; 4) oven temperature programme: 70°C for 2 min, increase to 150°C at 25°C min<sup>-1</sup>, increase to 220°C at 3°C min<sup>-1</sup>, increase to 280°C at 3°C min<sup>-1</sup> (held for 10 min), total runtime = 42 min; 5) MS source temperature = 230°C; 6) acquisition mode = selected ion monitoring, beginning 10 min after initial injection.

PAH and PCB identification was based on matching retention time, and quantification was determined from calibration curves established for each compound by analyzing five external standards (Supelco Epa 610 PAH Mix and Ultra Scientific WHO/ISS PCB Mixture, respectively). Average R<sup>2</sup> of the calibration curves was greater than 0.99 for both PAH and PCB analyses, and the SD of the calibration factors was always less than 20% (average of 10%).

Sixteen US-EPA priority pollutant PAHs were determined: naphthalene (Naph), acenaphthylene (Ac), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Ft), pyrene (Py), benzo(a)anthracene (B[a]Ant), chrysene (Chy), benzo(b)fluoranthene (B[b]Ft), benzo(k)fluoranthene (B[k]Ft), benzo(a)pyrene (B[a]Py), dibenzo(a,h)anthracene (diB[a,h]Ant), benzo(g,h,i)perylene (B[g,h,i]Per), and indeno(1,2,3,c,d)pyrene (I[1,2,3,c,d]Py).

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Thirty-two PCB congeners were determined: 18, 28, 31, 52, 44, 95, 101, 99, 81, 77, 110, 151, 123, 149, 118, 114, 146, 153, 105, 138, 126, 187, 183, 128, 167, 177, 156, 157, 180, 169, 170, 189.

Detection limits, measured by calibration curve method, were 0.1 ng g<sup>-1</sup> and 0.05 ng g<sup>-1</sup> for PAHs and PCBs, respectively. Blanks were run for the entire procedure.

Recoveries and accuracies were determined through the analysis of IAEA-417 and IAEA-159 sediment sample certified reference materials. The average recovery for all PAHs (except Naph) was in the range 75-108 %, whereas the recovery for PCBs varied between 85 and 112%. Variation coefficient was about 15% for both compound classes. Recovery for Naph was lower and variable (20-40%), likely due to losses during evaporation, while Ac exhibited no appreciable fluorescence, therefore results for these compounds are not presented.

Laboratory methods were also validated by continuous intercalibration activities (IAEA, 2001, 2007).

## 4. RESULTS AND DISCUSSION

### 4.1 Pollutant concentrations in surface sediments

Concentration values obtained for surface sediments are shown in Tables 1-3, for major and trace elements, PAHs, and PCBs, respectively. In site 1A, concentrations are much lower with respect to the other sites of the First Basin, for all the analysed elements. Sedimentation processes in this site appears to be clearly influenced by the proximity of the Canale Navigabile that, since its creation in the 1880s (Fig. 1), enhanced the hydrodynamic of the area preventing the deposition of fine particles. Indeed, the surficial sediment at site 1A is mainly sandy (~ 80%) while in the other sites, the sand content does not exceed 30%; (Cassin et al., in preparation). The presence of coarser sediments at 1A might dilute the contaminant signal, as pollutants are generally adsorbed by fine particles .

By calculating the variation coefficient (CV%) for the concentration values in the other 10 sites (Table 4a), it can be observed that the distribution of Al, Fe, As, Cd, Cr, Mn, Ni, and Zn, has a lower spatial variability with respect to Cu, Hg, Pb, PAHs, and PCBs. For these contaminants, the ratio between the average concentrations determined in the First and Second Basin varies from 2 for Cu up to 7.1 for PAH (Table 4a). These features are in agreement with the results of previous studies on



1 surface sediment contamination in the Mar Piccolo (Cardellicchio et al. 2006; Cardellicchio et al.  
2 2007; Calace et al., 2008; Petronio et al. 2012). Comparisons between the results of the present  
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4 research and those of previous studies (specifically Calace et al. (2008) and Petronio et al. (2012) for  
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6 metals and Cardellicchio et al. (2007) for total PAHs and total PCBs) are hindered by differences in  
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8 sampling locations and subsampling thicknesses (5 cm in reference studies vs 2 cm in this research)  
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10 that integer contaminant inputs over different time intervals. Moreover, the quantification technique  
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12 used by Cardellicchio et al. (2007) to measure PCB concentrations (i.e. in reference to Aroclor 1260  
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14 mixture) affects the significance of the comparison. With these limitations in mind we proceeded with  
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16 the comparison of average values for surficial sediments in the First and Second Basins. Results of the  
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18 comparison for metals (i.e. Fe, Cu, Zn, Pb, Ni, and Hg) define a situation of stable trends and with  
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20 values generally higher in the First Basin, especially for Hg and Pb (e.g. Calace et al. (2008) report an  
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22 average concentration of 5.8 mg kg<sup>-1</sup> for Hg in surficial sediments of the First Basin, our estimate is  
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24 5.0 mg kg<sup>-1</sup>; similar results for Pb are 139 mg kg<sup>-1</sup> in Calace et al. (2008) vs 100 mg kg<sup>-1</sup> in this  
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26 research. Similar considerations can be associated to PCBs. As for PAHs, average concentrations in  
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28 surficial sediments measured in our research are lower (approximately 3 times) than those detected by  
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30 Cardellicchio et al. (2007), in both the First and the Second Basin.  
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36 Fig. 2 evidences the relevant concentration differences that occur between the First and the Second  
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38 Basin for Cu, Hg, Pb, PAHs, and PCBs (Fe is also showed as representative of the distribution of  
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40 terrigenous components). Higher concentrations in the South East part of the First Basin are  
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42 presumably linked to the presence of the Italian Navy shipyard, with its dry docks Within the Second  
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44 Basin, sediments at site 2A shows a lower quality. This site is close to the opening between the two  
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46 basins (Fig. 1) and this feature reflects the transport of polluted sediment particles from the First to  
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48 the Second Basin.  
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#### 54 **4.2. Particle fluxes and pollutant concentrations in sediment traps**

55 Particle fluxes measured from sediment traps vary between 0.28 (site 2B, first period) and 2.25 mg  
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57 cm<sup>-2</sup> d<sup>-1</sup> (site 1E, second period; Table 5) and are much higher during the second period (from 2,4 to  
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4,9 times). Conversely, concentrations are generally much higher in the first period than in the second one (Tables 1-3 and Fig. 3), for all contaminants. Indeed, Table 4b shows a decrease of concentrations in the second period from about 80% (Mn) to 50% (As, Hg, total PCBs). This scenario is consistent with varying environmental conditions between the two periods, as many different events (e.g. meteorological, naval traffic or operations) can modify water circulation and transfer of matter and pollutants to the system.

Sediment traps from the First Basin show lower concentrations than those measured in nearby sediments for Cu, Hg, total PAHs, and total PCBs, (Fig. 3) and, to a lesser extent, for As, Cd, and Pb. Conversely, sediment traps from the Second Basin during the first period show concentrations for almost all analysed chemicals that are higher than those measured in nearby sediments (Fig. 3). This might be an indication of active advective transport from the First Basin, since this is the sector that endures higher contamination. Higher concentrations in sediment traps might be also a consequence of local resuspension that favours the remobilization of finer particles where pollutants tend to concentrate. In this case, if we assume that Al concentrations are directly correlated to the content of fine particles (Covelli and Fontolan, 1997; Zhang et al., 2009), resuspended fine sediments should evidence higher values of Al than surficial sediments. This appears not to be the case in our study, since values of Al in the first period were very similar among surficial sediments and sediment traps of the Second Basin (Table 1). In addition, the presence of lateral advective transport from the First Basin is independently confirmed by the hydrodynamic scenario described by De Pascalis et al., (this issue), where bottom waters travel from the First to the Second Basin on W-E direction. The Cluster Analysis (Statistica 7, StatSoft Inc.) performed on concentrations for all analysed chemical species (Fig. 4) seems to confirm this setting: sediment traps collected at the end of the first period (TrapA) in the Second Basin are grouped together with surficial sediments from the First Basin (Cluster 1), notably those closer to the opening between the two basins (i.e. sites 1I, 1H) that, on the contrary, are not associated to the nearby sediment trap. During the second period, all sediment traps seem to be influenced by the mixed advective transport from farther locations (site 1A, 1D, 1G, and 1E; Cluster

2), as evidenced by the decrease in Al concentrations (Table 1) that can be associated to inputs of coarser materials (Covelli and Fontolan, 1997; Zhang et al., 2009).

It can be expected that lateral advective fluxes vary the composition of original PAH and PCB assemblages. In the case of PAHs, reworking following resuspension and the permanence in the water column during long-range transport can favour the accumulation of lighter congeners in the final repository (Bertolotto et al. 2003; Ruiz-Fernández et al. 2012). Similar processes, for PCBs, might enhance microbial degradation activities that increase the relative contribution of lower or higher chlorinated classes, depending if anaerobic or aerobic conditions are met (Abramowicz 1995; Giuliani et al. 2015). In the attempt to verify this hypothesis, two specific diagnostic ratios have been selected: 1) for PCBs, Cl3-4/Cl5-7 is the ratio between tri-tetra chloro-substituted biphenyls and penta-hexa-hepta chloro-substituted biphenyls, and 2) for PAHs, LMW/HMW represents the ratio between low molecular weight (2-3 rings) congeners and high molecular weight congeners. The results are shown in Fig. 5. The influence of advective fluxes on PAH differential transport and PCB microbial anaerobic degradation is confirmed for sediment trap samples collected in the Second Basin (Fig.5). Significant higher values for LMW/HMW and Cl3-4/Cl5-7 are evidenced in sediment traps at sites 2A and 2C, especially for the second period. In addition, PAH and PCB assemblages in sediment traps from the Second Basin are considerably different from those measured in nearby surficial sediments (Fig. 5), thus confirming the absence of relevant resuspension fluxes in this area, substituted by advective inputs from the First Basin.

## CONCLUSIONS

Direct measurements of contaminant concentrations (major and trace elements, PAHs, and PCBs) and data analysis on sediment traps and surficial sediments collected in the Mar Piccolo (Gulf of Taranto, Italy) in the period June-September 2013 have evidenced the connection between the two basins, despite the low hydrodynamism that characterises the area (Petronio et al., 2012).

In general, the First Basin has acted as source of more contaminated sediments, while the Second Basin was the final repository of materials transported from the First Basin. This lateral transport has

1 caused some modification of PAH and PCB original assemblages that, in the Second Basin, displayed  
2 the evidence of long-range transport and microbial degradation.

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4 Since anthropogenic sources are concentrated mainly along the shores of the First Basin, the observed  
5 distribution mechanism linking the two basins might impact also the relatively less polluted area of  
6 the Second Basin. This occurrence calls for constant monitoring, performed by current-meter and  
7 sediment transport field studies.  
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21 **Tables**  
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25 **Table 1.** Major and trace element concentrations in samples (surficial sediments and sediment traps) collected in the Mar Piccolo area. Values are in mg kg<sup>-1</sup>. Site depths (m)  
26 are also presented.  
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| Site        | 1A    | 1C    | 1D    | 1E    |       |       | 1F    |       |       | 1G    | 1H    | 1I    |       |       | 2A    |       |       | 2B    | 2C    |       |       |
|-------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Depth (m)   | 11.6  | 11.0  | 11.7  | 11.3  |       |       | 11.2  |       |       | 7.30  | 11.4  | 11.4  |       |       | 7.70  |       |       | 6.30  | 8.00  |       |       |
| Sample type | Sed   | Sed   | Sed   | TrapA | TrapB | Sed   | TrapA | TrapB | Sed   | Sed   | Sed   | TrapA | TrapB | Sed   | TrapA | TrapB | Sed   | Sed   | TrapA | TrapB | Sed   |
| <b>Al</b>   | 4906  | 27681 | 22501 | 15293 | 23344 | 19483 | 27937 | 23525 | 28521 | 19958 | 27771 | 20348 | 16261 | 27719 | 32146 | 11648 | 32359 | 26822 | 34621 | 9424  | 33544 |
| <b>As</b>   | 8.15  | 11.8  | 16.7  | 27.0  | 13.5  | 16.0  | 12.8  | 10.1  | 14.6  | 13.6  | 19.9  | 15.0  | 5.52  | 22.1  | 10.9  | 6.45  | 11.3  | 11.4  | 8.39  | 0.972 | 8.4   |
| <b>Cd</b>   | 0.247 | 0.239 | 0.346 | 0.374 | 0.267 | 0.349 | 0.253 | 0.285 | 0.351 | 0.723 | 0.473 | 0.402 | 0.251 | 0.489 | 0.421 | 0.258 | 0.558 | 0.568 | 0.427 | 0.139 | 0.358 |
| <b>Cr</b>   | 15.4  | 49.8  | 57.2  | 76.0  | 59.1  | 52.2  | 70.8  | 56.2  | 71.0  | 51.5  | 71.6  | 70.7  | 38.5  | 72.9  | 70.8  | 25.0  | 64.5  | 55.6  | 69.1  | 18.1  | 62.8  |
| <b>Cu</b>   | 17.5  | 75.8  | 86.9  | 64.6  | 59.5  | 238   | 77.6  | 56.9  | 80.7  | 119   | 105   | 79.7  | 55.1  | 119   | 73.5  | 34.2  | 66.5  | 56.6  | 46.6  | 15.6  | 52.1  |
| <b>Fe</b>   | 6768  | 33435 | 29510 | 17449 | 25331 | 27759 | 30722 | 24265 | 32867 | 25056 | 31153 | 19036 | 17215 | 34141 | 31543 | 10625 | 30597 | 28924 | 29673 | 7708  | 28115 |
| <b>Hg</b>   | 0.980 | 3.03  | 6.54  | 3.13  | 2.73  | 3.98  | 3.56  | 2.54  | 5.26  | 4.39  | 6.69  | 6.21  | 2.15  | 8.98  | 2.19  | 0.445 | 1.89  | 0.916 | 0.546 | 0.063 | 0.732 |
| <b>Ni</b>   | 8.27  | 32.8  | 42.0  | 47.1  | 37.8  | 39.4  | 48.0  | 37.4  | 46.9  | 38.0  | 49.7  | 47.4  | 26.5  | 50.4  | 49.2  | 17.7  | 48.0  | 45.3  | 47.1  | 12.1  | 45.5  |
| <b>Pb</b>   | 36.9  | 69.1  | 113   | 88.6  | 72.3  | 104   | 89.0  | 70.9  | 96.2  | 126   | 124   | 131   | 67.4  | 130   | 58.1  | 16.1  | 54.0  | 40.9  | 34.5  | 10.0  | 33.4  |
| <b>Zn</b>   | 56.8  | 372   | 261   | 143   | 197   | 313   | 384   | 205   | 259   | 312   | 291   | 250   | 194   | 354   | 261   | 111   | 254   | 229   | 243   | 68.1  | 167   |

43 **Sed** = surficial sediment; **TrapA** = sediment trap first period; **TrapB** = sediment trap second period.  
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**Table 2.** PAH congener concentrations (ng g<sup>-1</sup>) in surficial sediments and sediment traps collected in the Mar Piccolo area.

| Site                  | 1A          |             | 1C          | 1D          | 1E         |             |            | 1F         |             |             | 1G          | 1H          | 1I         |             |            | 2A         |            |            | 2B         | 2C        |            |  |
|-----------------------|-------------|-------------|-------------|-------------|------------|-------------|------------|------------|-------------|-------------|-------------|-------------|------------|-------------|------------|------------|------------|------------|------------|-----------|------------|--|
| Sample type           | Sed         | Sed         | Sed         | TrapA       | TrapB      | Sed         | TrapA      | TrapB      | Sed         | Sed         | Sed         | TrapA       | TrapB      | Sed         | TrapA      | TrapB      | Sed        | Sed        | TrapA      | TrapB     | Sed        |  |
| <b>Ace</b>            | 1.34        | 4.45        | 21.0        | 13.2        | 7.98       | 8.5         | 12.5       | 9.80       | 5.78        | 2.85        | 7.19        | 1.59        | 4.75       | 5.38        | 7.39       | 1.87       | 3.64       | 3.2        | 16.1       | 0.579     | 0.217      |  |
| <b>Fl</b>             | 13.9        | 16.8        | 18.0        | 8.91        | 9.00       | 8.74        | 9.06       | 8.44       | 16.0        | 7.54        | 15.0        | 15.2        | 5.57       | 13.6        | 6.71       | 1.59       | 3.03       | 3.36       | 7.15       | 0.845     | 1.06       |  |
| <b>Phe</b>            | 110         | 168         | 134         | 92.7        | 42.7       | 73.8        | 49.7       | 32.9       | 130         | 63.7        | 197         | 60.6        | 20.2       | 98.7        | 46.2       | 5.35       | 16.0       | 28.1       | 26.0       | 4.27      | 8.33       |  |
| <b>Ant</b>            | 52.9        | 69.9        | 59.0        | 8.61        | 14.4       | 31.3        | 7.58       | 9.51       | 52.4        | 22.2        | 89.4        | 13.4        | 5.60       | 38.9        | 5.67       | 1.46       | 6.95       | 10.9       | 3.78       | 3.08      | 2.88       |  |
| <b>Ft</b>             | 251         | 497         | 333         | 181         | 129        | 235         | 127        | 87.0       | 327         | 226         | 841         | 122         | 48.6       | 205         | 66.2       | 17.1       | 48.0       | 85.7       | 22.4       | 3.91      | 24.5       |  |
| <b>Py</b>             | 268         | 555         | 372         | 187         | 136        | 262         | 136        | 68.8       | 357         | 254         | 940         | 126         | 53.2       | 232         | 133        | 15.3       | 55.2       | 95.7       | 16.7       | 3.17      | 24.2       |  |
| <b>B[a]Ant</b>        | 131         | 233         | 145         | 72.4        | 56.7       | 123         | 54.7       | 42.4       | 159         | 107         | 344         | 48.8        | 22.6       | 87.6        | 28.6       | 9.02       | 22.3       | 41.6       | 6.61       | 1.41      | 10.0       |  |
| <b>Chy</b>            | 151         | 271         | 174         | 116         | 82.9       | 143         | 85.9       | 57.0       | 185         | 144         | 393         | 63.7        | 32.3       | 92.4        | 42.5       | 13.9       | 22.4       | 47.2       | 11.8       | 3.28      | 10.6       |  |
| <b>B[b]Ft</b>         | 133         | 305         | 242         | 153         | 128        | 220         | 117        | 99.1       | 261         | 214         | 506         | 164         | 54.0       | 218         | 58.9       | 19.2       | 48.5       | 55.8       | 23.1       | 5.59      | 18.8       |  |
| <b>B[k]Ft</b>         | 67.2        | 146         | 101         | 65.8        | 51.8       | 98.7        | 47.3       | 38.1       | 126         | 102         | 175         | 57.8        | 19.1       | 97.4        | 22.8       | 7.54       | 18.6       | 23.9       | 18.2       | 1.60      | 8.75       |  |
| <b>B[a]py</b>         | 141         | 172         | 91.3        | 46.7        | 91.4       | 111         | 14.2       | 47.1       | 105         | 159         | 258         | 101         | 87.6       | 91.7        | 20.0       | 13.4       | 32.7       | 42.8       | 5.59       | 2.97      | 11.2       |  |
| <b>diB[a,h]Ant</b>    | 4.24        | 1.24        | 8.6         | 18.8        | 2.79       | 17.3        | 4.74       | 6.40       | 17.9        | 0.944       | 3.33        | 11.1        | 5.93       | 8.65        | 0.520      | l.d.l.     | 4.74       | 0.736      | 1.57       | l.d.l.    | l.d.l.     |  |
| <b>B[g,h,i]Per</b>    | 163         | 321         | 193         | 157         | 114        | 218         | 113        | 75.7       | 293         | 207         | 379         | 141         | 34.7       | 274         | 61.2       | 10.4       | 41.9       | 38.6       | 38.9       | 1.64      | 14.2       |  |
| <b>I[1,2,3,c,d]Py</b> | 158         | 282         | 248         | 97.3        | 91.4       | 205         | 92.1       | 67.4       | 247         | 251         | 543         | 128         | 29.6       | 161         | 55.9       | l.d.l.     | 32.8       | 50.1       | l.d.l.     | l.d.l.    | 21.8       |  |
| <b>Total PAHs</b>     | <b>1646</b> | <b>3042</b> | <b>2140</b> | <b>1218</b> | <b>957</b> | <b>1755</b> | <b>871</b> | <b>650</b> | <b>2282</b> | <b>1761</b> | <b>4691</b> | <b>1054</b> | <b>424</b> | <b>1624</b> | <b>556</b> | <b>116</b> | <b>357</b> | <b>528</b> | <b>198</b> | <b>32</b> | <b>157</b> |  |

**Sed** = surficial sediment; **TrapA** = sediment trap first period; **TrapB** = sediment trap second period; l.d.l. = lower than detection limit.



**Table 3.** PCB congener concentrations (ng g<sup>-1</sup>) in surficial sediments and sediment traps collected in the Mar Piccolo area. Chlorination classes are in parentheses

| Site              | 1A         |            | 1C         |            | 1D         |            | 1E         |            |            | 1F         |            |            | 1G         |             | 1H         |             | 1I         |             |            | 2A          |             |       | 2B    |     | 2C     |       |        |
|-------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|-------------|------------|-------------|------------|-------------|------------|-------------|-------------|-------|-------|-----|--------|-------|--------|
| Sample type       | Sed        | Sed        | Sed        | TrapA      | TrapB      | Sed        | TrapA      | TrapB      | Sed        | Sed        | Sed        | TrapA      | TrapB      | Sed         | TrapA      | TrapB       | Sed        | TrapA       | TrapB      | Sed         | Sed         | TrapA | TrapB | Sed | TrapA  | TrapB | Sed    |
| <b>18 (3-CB)</b>  | l.d.l.     | 2.69       | 0.379      | l.d.l.     | 1.25       | 0.829      | l.d.l.     | 1.82       | l.d.l.     | 2.96       | l.d.l.     | l.d.l.     | 1.69       | 0.772       | 4.39       | 1.55        | 1.07       | l.d.l.      | l.d.l.     | 1.48        | l.d.l.      |       |       |     | l.d.l. | 1.48  | l.d.l. |
| <b>28 (3-CB)</b>  | l.d.l.     | 2.20       | 3.23       | 8.54       | 1.45       | 4.84       | 7.48       | 3.08       | 3.84       | 1.75       | 2.69       | 10.8       | 1.50       | 4.09        | 6.54       | 1.18        | 0.559      | 0.334       | 7.15       | 1.17        | 0.532       |       |       |     |        |       |        |
| <b>31(3-CB)</b>   | l.d.l.     | l.d.l.     | l.d.l.     | 9.08       | 1.74       | l.d.l.     | 6.63       | 4.51       | l.d.l.     | l.d.l.     | l.d.l.     | 10.3       | 1.76       | l.d.l.      | 5.84       | 0.949       | l.d.l.     | l.d.l.      | 5.73       | 0.784       | l.d.l.      |       |       |     |        |       |        |
| <b>44 (4-CB)</b>  | 4.84       | 2.68       | 17.3       | 5.50       | 1.92       | 8.87       | 5.57       | 2.27       | 7.82       | 7.27       | 9.35       | 8.9        | 1.83       | 21.6        | 4.63       | 1.04        | 0.220      | 0.479       | 5.95       | 0.989       | 0.479       |       |       |     |        |       |        |
| <b>52 (4-CB)</b>  | 4.95       | 12.6       | 14.2       | 7.94       | 2.63       | 9.81       | 7.07       | 3.80       | 9.06       | 21.2       | 12.3       | 12.8       | 5.21       | 17.0        | 6.07       | 1.59        | 2.94       | 1.19        | 5.98       | 1.16        | 1.12        |       |       |     |        |       |        |
| <b>77 (4-CB)</b>  | l.d.l.     | l.d.l.     | l.d.l.     | 5.75       | 2.31       | l.d.l.     | 6.36       | 2.15       | l.d.l.     | l.d.l.     | l.d.l.     | 10.6       | 2.61       | l.d.l.      | 5.16       | 1.22        | l.d.l.     | l.d.l.      | l.d.l.     | 1.07        | l.d.l.      |       |       |     |        |       |        |
| <b>81 (4-CB)</b>  | l.d.l.     | l.d.l.     | l.d.l.     | 5.35       | 2.10       | l.d.l.     | 6.01       | 2.01       | l.d.l.     | l.d.l.     | l.d.l.     | 9.17       | 1.65       | l.d.l.      | 4.66       | 1.07        | l.d.l.     | l.d.l.      | l.d.l.     | l.d.l.      | l.d.l.      |       |       |     |        |       |        |
| <b>95 (5-CB)</b>  | 14.2       | 28.8       | 21.3       | 7.99       | 4.77       | 22.2       | 8.24       | 4.63       | 28.8       | 52.1       | 51.0       | 13.9       | 9.03       | 54.3        | 6.18       | 1.99        | 2.60       | 4.75        | 6.02       | 1.41        | 3.37        |       |       |     |        |       |        |
| <b>99 (5-CB)</b>  | 10.9       | 30.5       | 20.5       | 14.2       | 10.5       | 22.7       | 14.6       | 9.65       | 31.2       | 41.0       | 29.6       | 30.2       | 18.3       | 47.6        | 12.0       | 3.90        | 7.80       | 6.28        | 7.26       | 2.13        | 5.58        |       |       |     |        |       |        |
| <b>101 (5-CB)</b> | 21.1       | 38.4       | 26.2       | 12.4       | 8.63       | 32.3       | 13.7       | 7.98       | 50.6       | 73.6       | 42.0       | 24.6       | 17.6       | 77.9        | 9.76       | 3.58        | 8.73       | 7.84        | 6.96       | 1.97        | 5.46        |       |       |     |        |       |        |
| <b>105 (5-CB)</b> | 1.77       | 9.71       | 6.69       | 6.62       | 2.62       | 7.46       | 7.54       | 2.66       | 10.3       | 17.5       | 11.7       | 11.6       | 3.83       | 15.8        | 6.50       | 1.49        | 2.24       | 0.527       | 7.80       | 1.37        | 1.41        |       |       |     |        |       |        |
| <b>110 (5-CB)</b> | 8.76       | 17.0       | 12.9       | 9.12       | 5.30       | 12.3       | 10.0       | 5.45       | 25.6       | 38.1       | 19.6       | 14.8       | 10.3       | 38.2        | 7.14       | 2.27        | 3.06       | 2.76        | 7.47       | 1.71        | 2.56        |       |       |     |        |       |        |
| <b>114 (5-CB)</b> | 3.91       | 5.31       | 7.11       | l.d.l.     | l.d.l.     | 4.39       | 5.98       | 1.88       | 6.57       | 14.1       | 8.48       | l.d.l.     | 0.909      | 17.0        | 7.11       | l.d.l.      | 0.172      | 0.987       | l.d.l.     | 1.21        | 0.650       |       |       |     |        |       |        |
| <b>118 (5-CB)</b> | 10.4       | 24.3       | 19.3       | 17.1       | 11.0       | 18.6       | 19.8       | 11.1       | 30.8       | 30.9       | 25.3       | 36.2       | 20.0       | 45.1        | 15.1       | 4.10        | 8.99       | 3.72        | 9.57       | 2.43        | 3.52        |       |       |     |        |       |        |
| <b>123 (5-CB)</b> | 18.8       | 41.5       | 33.5       | l.d.l.     | l.d.l.     | 41.2       | l.d.l.     | 0.31       | 47.1       | 55.8       | 46.0       | l.d.l.     | l.d.l.     | 78.4        | l.d.l.     | l.d.l.      | 11.3       | 7.86        | l.d.l.     | l.d.l.      | 7.60        |       |       |     |        |       |        |
| <b>126 (5-CB)</b> | 2.89       | l.d.l.     | 6.42       | 6.19       | 1.73       | 3.81       | 7.02       | 1.77       | 7.29       | 4.62       | l.d.l.     | 11.5       | 2.28       | 14.1        | 5.89       | 1.34        | 5.07       | l.d.l.      | l.d.l.     | l.d.l.      | l.d.l.      |       |       |     |        |       |        |
| <b>128 (6-CB)</b> | 3.21       | 7.04       | 5.92       | 7.23       | 2.86       | 3.16       | 8.59       | 3.11       | 10.1       | 11.6       | 10.1       | 12.3       | 3.93       | 17.5        | 7.81       | 1.57        | 0.62       | 0.441       | 8.42       | 1.64        | 0.375       |       |       |     |        |       |        |
| <b>138 (6-CB)</b> | 28.6       | 55.7       | 47.0       | 33.7       | 26.1       | 51.7       | 35.2       | 24.8       | 66.0       | 78.3       | 58.7       | 67.8       | 42.7       | 103         | 25.1       | 6.40        | 13.0       | 10.8        | 8.79       | 3.29        | 8.53        |       |       |     |        |       |        |
| <b>146 (6-CB)</b> | 5.66       | 14.5       | 13.7       | 6.50       | 5.55       | 12.9       | 7.17       | 6.00       | 18.7       | 18.9       | 20.2       | 14.9       | 9.22       | 30.9        | 5.00       | 1.67        | 5.03       | 3.93        | 1.44       | 0.718       | 3.03        |       |       |     |        |       |        |
| <b>149 (6-CB)</b> | l.d.l.     | l.d.l.     | l.d.l.     | 19.8       | 14.7       | l.d.l.     | 20.7       | 13.5       | l.d.l.     | l.d.l.     | l.d.l.     | 37.6       | 24.8       | l.d.l.      | 12.1       | 4.11        | l.d.l.     | l.d.l.      | 8.11       | 2.38        | l.d.l.      |       |       |     |        |       |        |
| <b>151 (6-CB)</b> | 5.61       | 13.9       | 12.0       | 9.53       | 6.12       | 13.1       | 9.95       | 5.57       | 15.8       | 14.6       | 15.6       | 20.0       | 9.82       | 26.9        | 6.91       | 1.95        | 3.04       | 2.03        | 5.99       | 1.35        | 1.85        |       |       |     |        |       |        |
| <b>153 (6-CB)</b> | 35.7       | 65.2       | 55.5       | 51.6       | 44.0       | 67.4       | 52.9       | 39.5       | 80.3       | 81.8       | 73.0       | 107        | 65.8       | 127         | 35.1       | 11.43       | 23.8       | 18.4        | 10.6       | 4.98        | 13.82       |       |       |     |        |       |        |
| <b>156 (6-CB)</b> | 6.78       | 8.13       | 16.0       | 6.18       | 2.42       | 7.80       | 5.94       | 2.12       | 14.9       | 14.3       | 16.4       | 9.79       | 3.11       | 30.4        | 4.44       | 1.11        | 1.57       | 1.92        | l.d.l.     | 0.984       | 1.13        |       |       |     |        |       |        |
| <b>157 (6-CB)</b> | 4.86       | 5.94       | 9.23       | 5.32       | 1.69       | 7.56       | 5.76       | 1.73       | 11.1       | 6.98       | 1.06       | 9.32       | 2.16       | 17.0        | 4.79       | 1.11        | 1.24       | 0.793       | l.d.l.     | 1.05        | 0.239       |       |       |     |        |       |        |
| <b>167 (6-CB)</b> | 4.90       | 5.72       | 10.2       | 7.21       | 2.34       | 6.80       | 7.83       | 2.31       | 10.1       | 5.98       | 10.1       | 12.2       | 2.94       | 17.6        | 6.02       | 1.36        | 0.77       | 0.298       | 6.98       | 1.29        | 0.452       |       |       |     |        |       |        |
| <b>169 (6-CB)</b> | l.d.l.     | l.d.l.     | l.d.l.     | 13.0       | 9.43       | l.d.l.     | 27.2       | 10.7       | l.d.l.     | 2.64       | 1.35       | 32.0       | 1.15       | 0.00        | 9.79       | 4.11        | l.d.l.     | l.d.l.      | l.d.l.     | 1.97        | l.d.l.      |       |       |     |        |       |        |
| <b>170 (7-CB)</b> | 10.8       | 16.2       | 16.6       | 16.4       | 11.5       | 16.9       | 15.2       | 9.97       | 20.4       | 16.1       | 21.3       | 25.9       | 13.3       | 27.3        | 7.68       | 1.84        | 2.89       | 2.08        | 4.90       | 1.14        | 2.03        |       |       |     |        |       |        |
| <b>177 (7-CB)</b> | 9.58       | 11.2       | 19.9       | 10.1       | 6.26       | 10.4       | 10.5       | 5.87       | 13.2       | 14.2       | 16.5       | 18.1       | 8.07       | 20.5        | 6.13       | 1.47        | 3.91       | 1.01        | 5.40       | 1.12        | 1.25        |       |       |     |        |       |        |
| <b>180 (7-CB)</b> | 32.0       | 49.4       | 53.5       | 38.5       | 30.0       | 57.0       | 35.0       | 25.3       | 42.1       | 39.8       | 58.8       | 66.3       | 35.7       | 92.6        | 15.4       | 4.22        | 11.7       | 7.52        | 7.47       | 2.34        | 7.54        |       |       |     |        |       |        |
| <b>183 (7-CB)</b> | 8.50       | 13.4       | 14.6       | 9.34       | 5.37       | 15.9       | 9.20       | 4.63       | 16.7       | 11.8       | 17.3       | 17.2       | 6.40       | 27.7        | 6.08       | 1.62        | 2.57       | 2.22        | 5.94       | 1.15        | 1.65        |       |       |     |        |       |        |
| <b>187 (7-CB)</b> | 17.0       | 42.1       | 39.4       | 31.6       | 25.1       | 41.7       | 32.5       | 23.4       | 42.8       | 31.6       | 45.1       | 61.2       | 33.6       | 71.8        | 17.9       | 5.33        | 12.8       | 9.87        | 7.49       | 2.72        | 8.77        |       |       |     |        |       |        |
| <b>189 (7-CB)</b> | 1.56       | 3.60       | 1.04       | 4.58       | 1.36       | 1.39       | 4.89       | 1.30       | 1.09       | 0.37       | 2.46       | 7.76       | 1.35       | 3.27        | l.d.l.     | l.d.l.      | l.d.l.     | l.d.l.      | l.d.l.     | l.d.l.      | l.d.l.      |       |       |     |        |       |        |
| <b>Total PCBs</b> | <b>277</b> | <b>528</b> | <b>504</b> | <b>386</b> | <b>253</b> | <b>503</b> | <b>415</b> | <b>245</b> | <b>623</b> | <b>710</b> | <b>626</b> | <b>725</b> | <b>363</b> | <b>1045</b> | <b>277</b> | <b>76.6</b> | <b>138</b> | <b>98.0</b> | <b>151</b> | <b>47.0</b> | <b>82.9</b> |       |       |     |        |       |        |

**Sed** = surficial sediment; **TrapA** = sediment trap first period; **TrapB** = sediment trap second period; l.d.l. = lower than detection limit.

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**Table 4.** Descriptive statistic of the distribution of contaminant concentrations in: (a) surficial sediments and (b) sediment traps of the Mar Piccolo. CV% = Percentage Coefficient of Variation; F/S = ratio of mean concentration values between First and Second Basin; MeanA/Mean B = ratio of mean concentration values between the two periods.

| <b>(a)</b> | <b>Al</b> | <b>As</b> | <b>Cd</b> | <b>Cr</b> | <b>Cu</b>  | <b>Fe</b> | <b>Hg</b>  | <b>Mn</b> | <b>Ni</b> | <b>Pb</b>  | <b>Zn</b> | <b>IPA</b> | <b>PCB</b> |
|------------|-----------|-----------|-----------|-----------|------------|-----------|------------|-----------|-----------|------------|-----------|------------|------------|
| Mean       | 26636     | 14.6      | 0.45      | 60.9      | 100        | 30156     | 4.2        | 366       | 43.8      | 89.1       | 281       | 1834       | 486        |
| St. Dev.   | 4720      | 4.2       | 0.14      | 8.9       | 54         | 2848      | 2.7        | 63        | 5.6       | 36.8       | 61        | 1361       | 305        |
| CV%        | 18        | 29        | 32        | 15        | 54         | 9         | 63         | 17        | 13        | 41         | 22        | 74         | 63         |
| Min        | 19483     | 8.4       | 0.24      | 49.8      | 52         | 25056     | 0.7        | 263       | 32.8      | 33.4       | 167       | 157        | 83         |
| Max        | 33544     | 22.1      | 0.72      | 72.9      | 238        | 34141     | 9.0        | 460       | 50.4      | 129.8      | 372       | 4690       | 1045       |
| Ratio F/S  | 0.8       | 1.6       | 0.9       | 1.0       | <b>2.0</b> | 1.0       | <b>4.7</b> | 1.4       | 0.9       | <b>2.5</b> | 1.4       | <b>7.1</b> | <b>6.1</b> |

| <b>(b)</b>               | <b>Al</b> | <b>As</b> | <b>Cd</b> | <b>Cr</b> | <b>Cu</b> | <b>Fe</b> | <b>Hg</b> | <b>Mn</b> | <b>Ni</b> | <b>Pb</b> | <b>Zn</b> | <b>IPA</b> | <b>PCB</b> |
|--------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|------------|------------|
| <b>First period (A)</b>  |           |           |           |           |           |           |           |           |           |           |           |            |            |
| Mean                     | 26069     | 14.8      | 0.38      | 71.5      | 68.4      | 25685     | 3.13      | 366       | 47.8      | 80        | 256       | 779        | 391        |
| St. Dev.                 | 8099      | 7.2       | 0.07      | 2.6       | 13.5      | 6849      | 2.08      | 106       | 0.9       | 36        | 85        | 408        | 213        |
| CV%                      | 31        | 49        | 19        | 4         | 20        | 27        | 66        | 29        | 2         | 45        | 33        | 52         | 55         |
| <b>Second period (B)</b> |           |           |           |           |           |           |           |           |           |           |           |            |            |
| Mean                     | 16840     | 7.3       | 0.24      | 39.4      | 44.2      | 17029     | 1.59      | 293       | 26.3      | 47        | 155       | 437        | 197        |
| St. Dev.                 | 6505      | 4.7       | 0.06      | 18.3      | 18.9      | 7893      | 1.24      | 201       | 11.5      | 31        | 62        | 382        | 132        |
| CV%                      | 39        | 65        | 24        | 46        | 43        | 46        | 78        | 69        | 44        | 66        | 40        | 87         | 67         |
| Mean A/Mean B            | 0.6       | 0.5       | 0.6       | 0.6       | 0.6       | 0.7       | 0.5       | 0.8       | 0.6       | 0.6       | 0.6       | 0.6        | 0.5        |

**Table 5.** Dates of samplings, weight of collected particles and derived fluxes from sediment trap measurements in the Mar Piccolo.

| Site              | placement date | recovery date | mass of particulate fraction (g d.w.) | fluxes of particles (mg cm <sup>-2</sup> d <sup>-1</sup> ) |
|-------------------|----------------|---------------|---------------------------------------|--|
| <b>1E - TrapA</b> | 20/06/2013     | 25/07/2013    | 0.890                                 | 0.459  |
| <b>1E – TrapB</b> | 25/07/2013     | 12/09/2013    | 6.11                                  | 2.25   |
| <b>1F - TrapA</b> | 20/06/2013     | 25/07/2013    | 0.880                                 | 0.454  |
| <b>1F – TrapB</b> | 25/07/2013     | 12/09/2013    | 2.91                                  | 1.07   |
| <b>1I - TrapA</b> | 20/06/2013     | 25/07/2013    | 0.650                                 | 0.335  |
| <b>1I – TrapB</b> | 25/07/2013     | 12/09/2013    | 3.20                                  | 1.18   |
| <b>2A - TrapA</b> | 20/06/2013     | 25/07/2013    | 0.840                                 | 0.433  |
| <b>2A – TrapB</b> | 25/07/2013     | 12/09/2013    | 3.20                                  | 1.18   |
| <b>2B - TrapA</b> | 20/06/2013     | 25/07/2013    | 0.540                                 | 0.278  |
| <b>2B – TrapB</b> | 25/07/2013     | 12/09/2013    | 2.77                                  | 1.02   |

## Figure captions

**Fig. 1.** Study area with sampling sites for surficial sediments and sediment traps. Locations of freshwater submarine springs (citri) and main discharges are derived by Caroppo et al. (2012) and De Pascalis et al. (2015).

**Fig. 2.** Distribution maps of the concentration of Cu, Hg, Pb, total PAHs, total PCBs ( $\text{mg kg}^{-1}$ ), and Fe ( $\text{g kg}^{-1}$ ) in surface sediments of the Mar Piccolo.

**Fig. 3.** Concentrations of total PAHs, total PCBs, and major and trace elements, in sediment traps and nearby surficial sediments.

**Fig. 4.** Results of the Cluster Analysis performed on concentrations for total PAHs, total PCBs, major and trace elements in surficial sediments and sediment traps.

**Fig. 5.** Plot of C13-4/C15-7 vs LMW/HMW. C13-4 = sum of tri and tetra chloro-substituted biphenyls (Table 3); C15-7 = sum of penta, hexa, and hepta chloro-substituted biphenyls (Table 3); LMW = sum of low molecular weight PAHs (Ac, Ace, F, Phe, An); HMW = sum of high molecular weight PAHs (Flu, Py, BAn, Ch, BbFlu, BkFlu BaPy, BPe, IPy, DahAn).

Figure 1

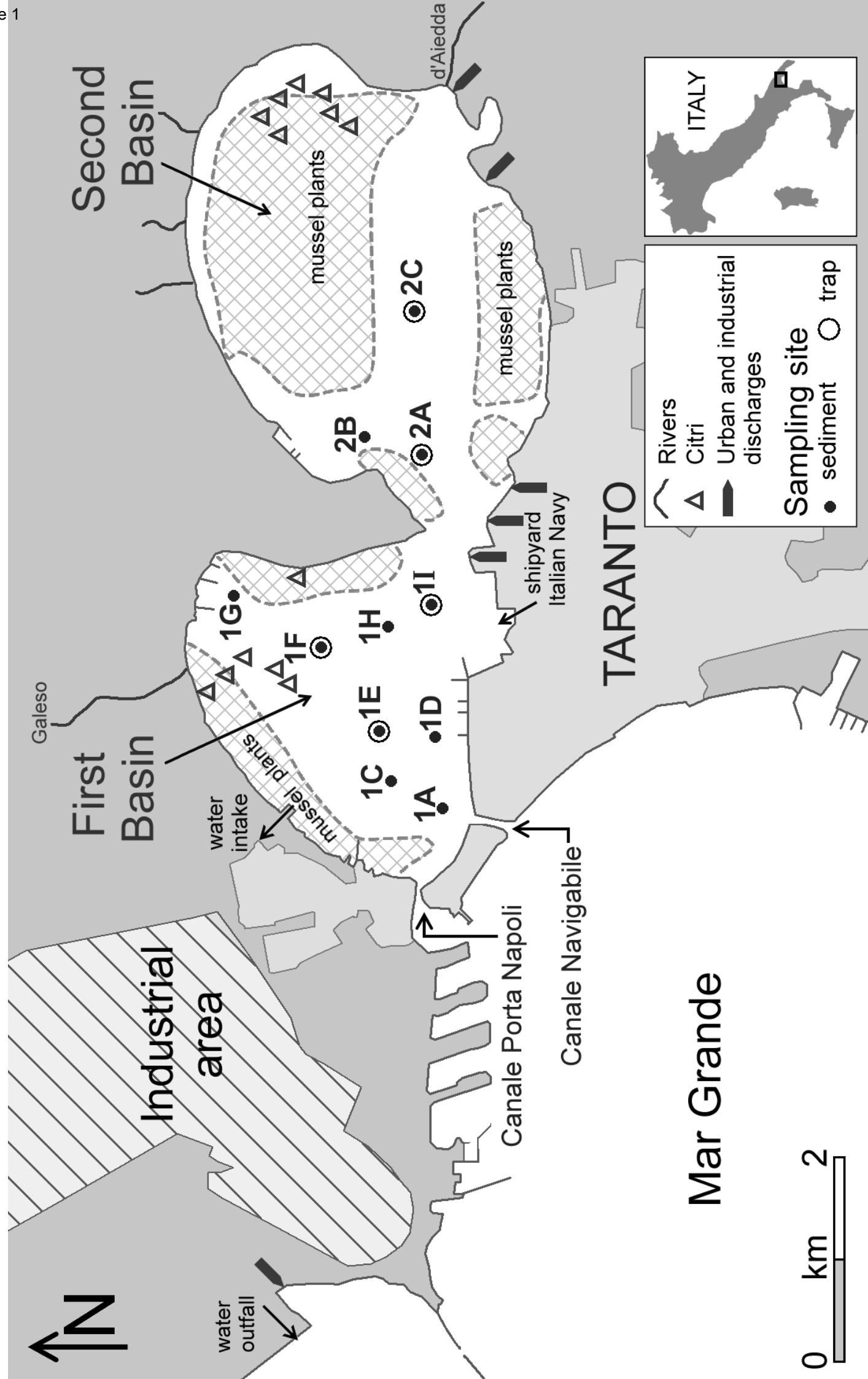


Figure 2

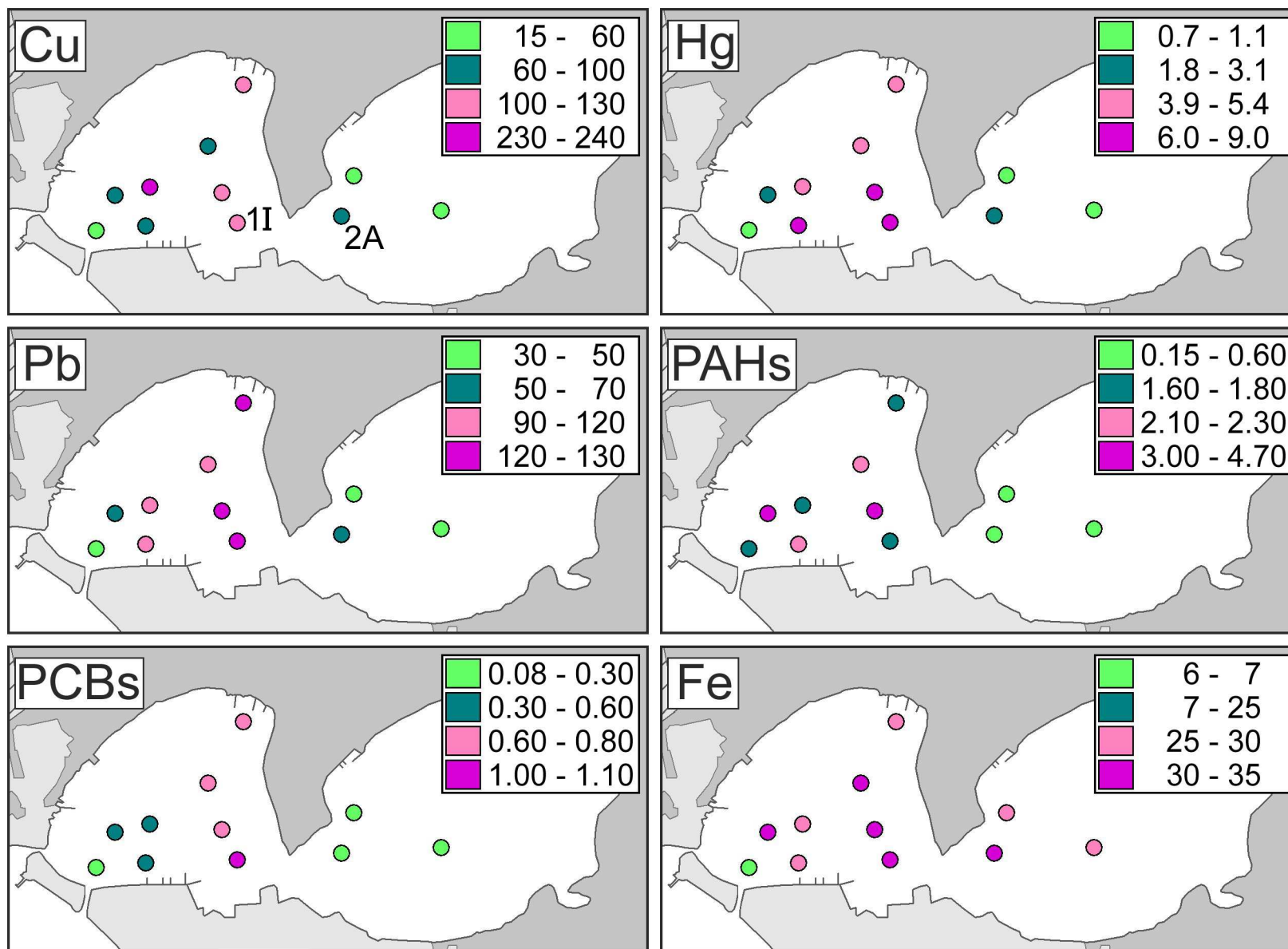


Figure 3

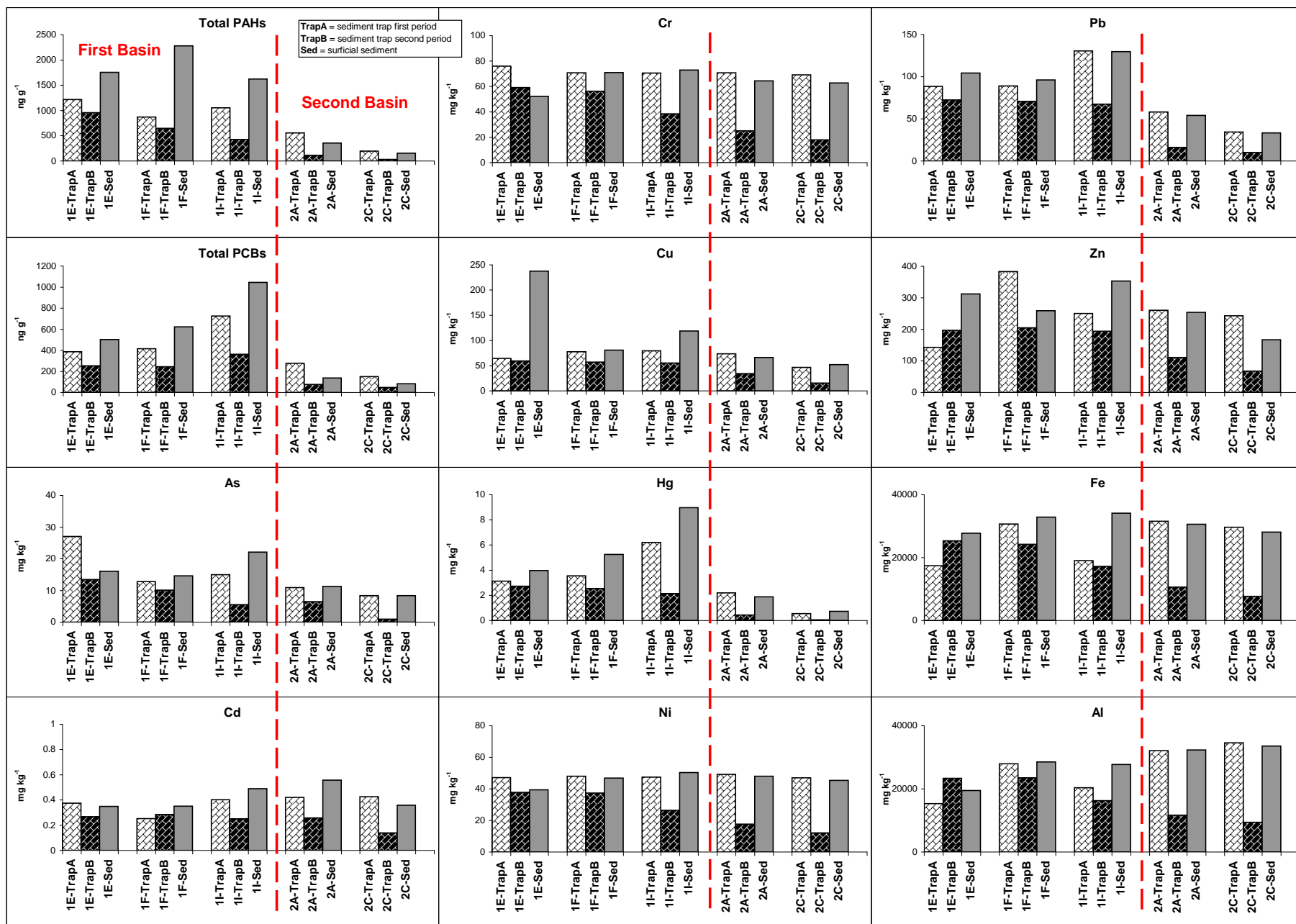


Figure 4

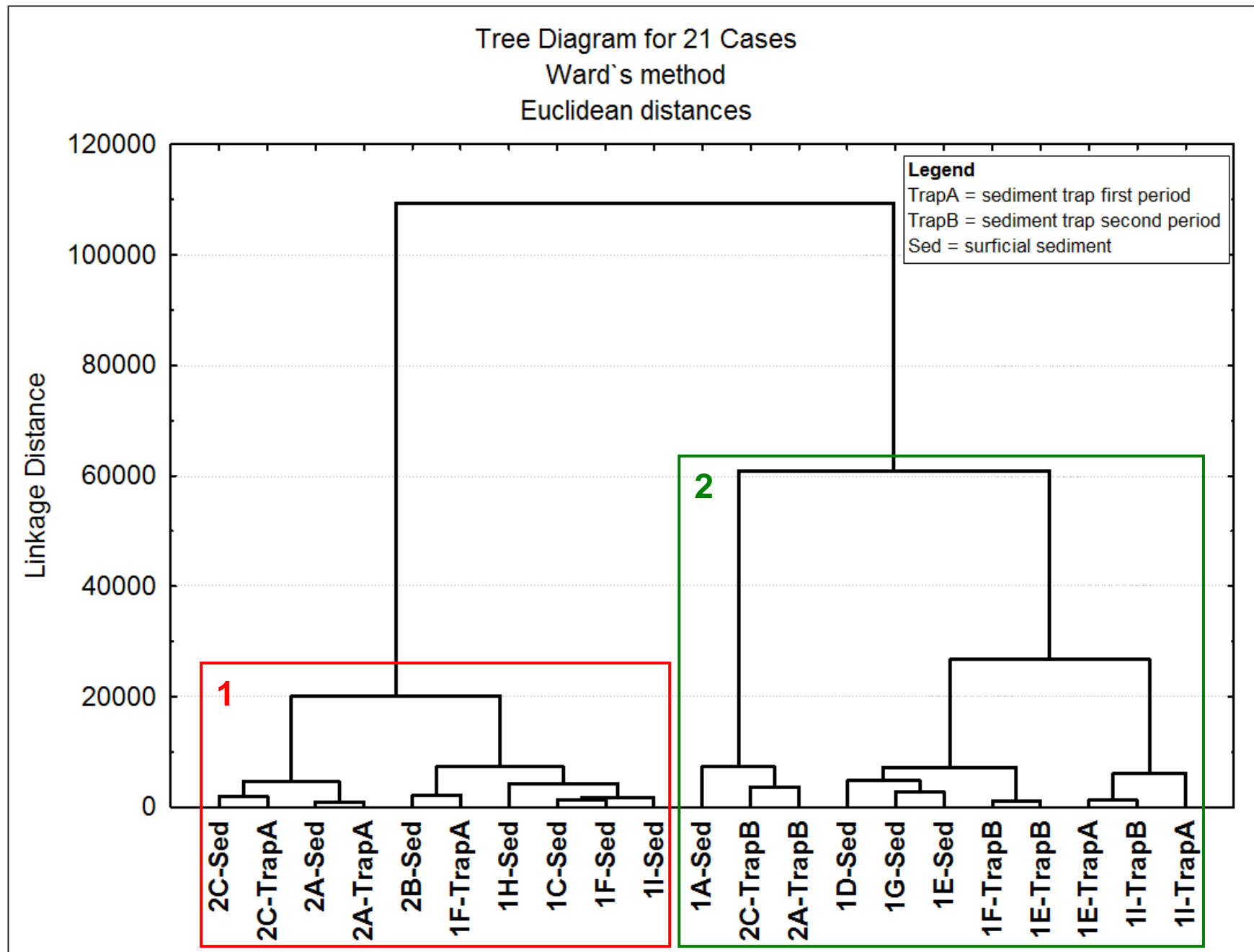




Figure 5

