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RESEARCH ARTICLE

PAH and PCB contamination in the sediments of the Venice Lagoon (Italy) before the installation of the MOSE flood defence works

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Abstract

Contamination from polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in the shallow water areas of the Venice Lagoon (415 km^2) was investigated in the surface (0–5 cm) and sub-surface (5–10 cm) sediments by collecting cores from 380 sites. The concentrations of 14 PAHs (USEPA priority pollutants) and seven PCB indicator congeners were analysed with high-performance liquid chromatography (HPLC) and capillary gas chromatography (GC), respectively. PAH and PCB concentrations ranged from 2.75 to 9980 ng g^{-1} d.w. and from 0.01 to 60.1 ng g^{-1} d.w., respectively. Their concentrations never exceeded the probable effect level (PEL) stipulated in the respective quality guidelines. In addition, the average total PAH levels expressed as B[a]P toxicity equivalents (total TEQ) were lower in the sediments of the Venice Lagoon than in other literature-reported zones in the Mediterranean. PAH profiles and ratios showed that they originated not only largely from high-temperature pyrolytic processes attributable primarily to the burning of fossil fuels but also partly from petroleum spillage. Comparison of tetra-to-hepta PCB congeners enabled the PCB profiles observed in the lagoon environment to be characterised as Aroclor 1254 and 1260 (1:1). Compared to other marine coastal areas and harbours in the Mediterranean, the Venice Lagoon sediments showed a low mean value but a wide range of concentrations. The estimation of PAH and PCB inventories indicated the low contribution of atmospheric deposition relative to local sources.

Keywords Venice Lagoon · Sediments · PAHs · PCBs · MOSE project

Introduction

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are ubiquitous, persistent organic compounds, both regarded as priority pollutants by the U.S. Environmental Protection Agency (EPA). PAHs enter the marine environment mainly from anthropogenic sources by various processes: incomplete combustion at higher temperatures of recent and fossil organic matter (pyrolytic origin), slow maturation of organic matter under certain geochemical conditions (petrogenic origin), and short-term diagenetic degradation of biogenic precursors (diagenesis) (Neff, 1979). PCBs were once widely used in a variety of industrial products, including heat exchangers and dielectric fluids, pesticides, ink, paints, paper, and plastics (UNEP 1999).

In Italy, PCBs were produced from the 1940s, reaching a peak in the 1970s (12,000 t for the decade), until 1984, with a cumulative national production of approximately 31,000 t (Maroni et al., 1991; Breivik et al. 2002). Although they have been banned in the majority of industrial countries for several decades, PCBs are still widely found in the marine environment (Covaci et al. 2002; Letcher et al. 2010).

The Venice Lagoon has been affected by various anthropogenic pollutants, including PAHs and PCBs, particularly since the development of the industrial zone of Porto Marghera in the 1930s. The industrial zone reached its maximum development in 1965 (229 industrial facilities and ca. 33,000 employees) but started to decline in the 1970s along with heavy industry in general.

Due to their hydrophobic character, PAHs and PCBs have a tendency to adsorb to organic matter particles, especially carbonaceous geosorbents (Ghosh et al. 2003; Cornelissen et al. 2005) and to accumulate in sediments. Several investigations

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have been conducted in the Venice Lagoon in order to assess the presence of PAHs and PCBs in the surface sediments. The first survey of the whole lagoon was performed in 1997, sampling from 67 sites located in the shallow water areas (MAV 1999). The sediments of specific lagoon areas were also investigated by Van Vleet et al. 1988; Fossato et al. 1998; Frignani et al. 2001; Moret et al. 2001; Frignani et al. 2003; Secco et al. 2005; Zonta et al. 2005a; Guerzoni et al. 2007; Zonta et al. 2007.

The aim of the present study was to assess the level of contamination and the distribution of PAHs and PCBs throughout the shallow water sediments of the Venice Lagoon before the construction of the MOSE system. MOSE (*MOdulo Sperimentale Elettromeccanico*, i.e. experimental electromechanical module) is designed to defend Venice and the lagoon from flooding at high tide. It consists of mobile barriers, installed in the seabed in the lagoon's three seaward inlets, which temporarily seal off the lagoon from the Adriatic Sea during high tide events (Scotti 2005). Preliminary works at the inlets began in 2003 and are now in their final stages. The works imply a modification of hydrological conditions and sediment displacement in the vicinity of the inlets and, once in operation, the system is expected to increase water residence time in the lagoon (Ferrarin et al. 2013). It is not clear how these changes will modify the transport and transfer of pollutants within the water body and affect the characteristics of the surface sediments. The information acquired with this study aims to provide a snapshot of the sediment contamination right before a seaward open lagoon is transformed and begins a "new era" of tidal regulation.

The objectives of the study were to (i) provide a detailed picture of the distribution of PAH and PCB concentrations in the surface (0–5-cm depth) and sub-surface (5–10 cm) sediments of the Venice Lagoon before the entry into service of the MOSE system; (ii) derive indications of the potential sources from the proportions of specific PAH and PCB compounds; (iii) compare the contribution of atmospheric deposition derived from previous studies to the overall accumulation of PAHs and PCBs in surface sediments; (iv) evaluate the potential toxic risk due to their presence in surface sediments together with the carcinogenic risk due to PAHs; and (v) compare sediment contamination in the Venice Lagoon with other coastal areas in Italy and the Mediterranean Sea.

Materials and methods

Study site

The Venice Lagoon (Fig. 1), which has a surface area of 550 km^2 and a mean water depth of about 1 m, is made up of islands, tidal marshes, mudflats, and a complex network of tidal channels. Shallow water areas account for ca. 75% of the whole surface area (ca. 415 km^2). The lagoon is linked to the Adriatic Sea by three inlets (Lido, Malamocco, and Chioggia), which enable the exchange of water and sediments during tidal cycles. The mean excursion is 30 and 80 cm in neap and spring tide conditions, respectively. The drainage basin, with a total area of ca. 1850 km^2 and a population of about one million inhabitants, hosts important urban areas, intensive husbandry activities, and industrial districts (Zonta et al. 2005b). Twelve main tributaries drain the catchment, providing a mean freshwater discharge of about 35.5 m^3/s to the lagoon (Zuliani et al. 2005). In addition to the pollutant load from the watershed (Collavini et al. 2005) and from the industrial zone by direct discharge or surface runoff, other pollution sources for the lagoon include waste waters from the inhabited islands (the most important being Venice, Murano, and Chioggia), water traffic, and atmospheric deposition. Located in the industrial area (Fusina) is a multi-fuel (coal and refuse-derived fuel) power plant built in the 1960s.

The various morphological units of the lagoon (Zonta et al. 1995) are affected by the impact of human activities to differing degrees, depending on local water dynamics and their position with respect to the main pollution sources (Zonta et al. 2018).

Sample collection

Sediment cores were collected at 380 sites distributed throughout the shallow areas of the lagoon (Fig. 1) in early 2008. The density of sampling sites was higher in areas where a higher pollution level was expected (i.e. around the cities of Venice, Murano, and Chioggia, in the proximity of Porto Marghera industrial district and near the mouths of the principal freshwater tributaries). The large number of sampling sites ensured coverage of at least one site every 2 km^2.

Three 50-cm-long cores were collected in each site using a piston corer and sectioned in the field. This study considered the surface (0–5 cm) and sub-surface (5–10 cm) layers, labelling them A and B, respectively. In a companion study, the samples were analysed for grain-size, total and organic carbon (TOC, OC), and heavy metals (Zonta et al. 2018).

Sample preparation

In the laboratory, triplicate samples from each depth interval were merged and sieved through a 1-mm mesh to remove any debris and thoroughly homogenised. An aliquot of sample was subsequently air dried in the dark at room temperature for 48 h on hexane-rinsed aluminium foil and then finely ground in an agate mortar. It should be noted that this procedure may lead to a concentration loss of the more volatile PAHs (Beriro et al. 2014).

The extraction was performed using a Microwave Sample Preparation System (Multiwave 3000, Anton Paar Graz,

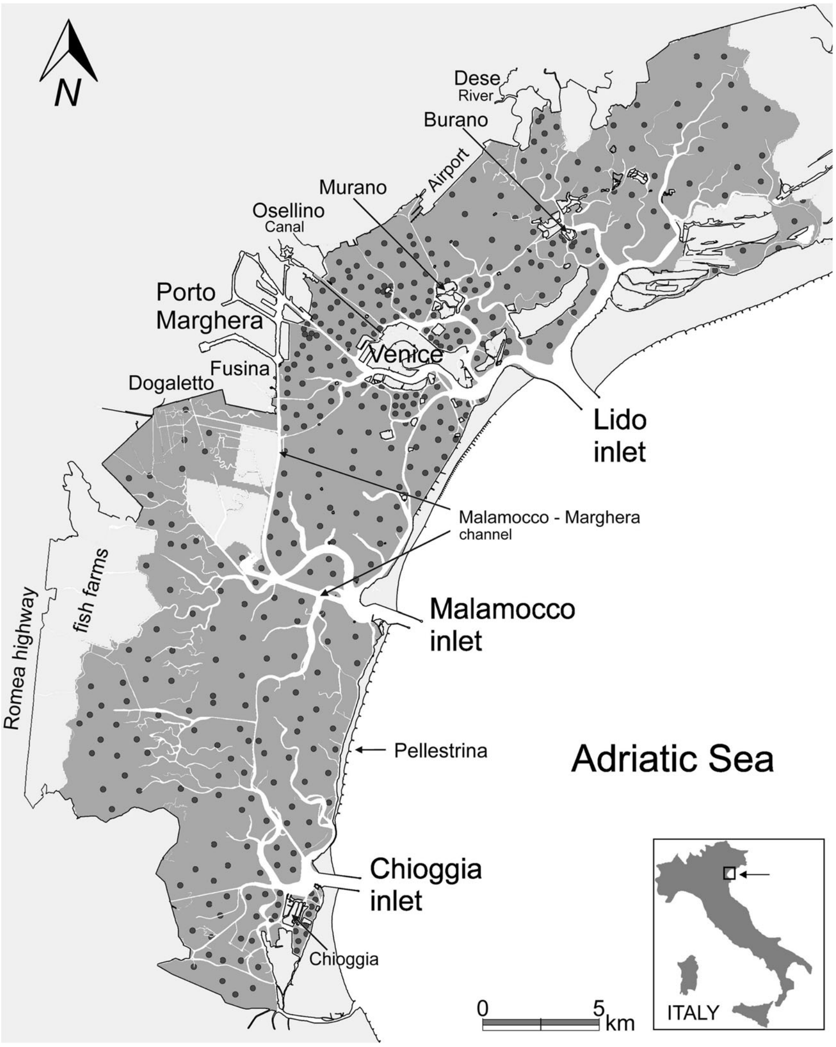


Fig. 1 Location of sampling sites and specific locations of the Venice Lagoon referred in the text

Austria), in accordance with EPA recommendations (USEPA 2007a). Two grams of dried sediment was accurately weighed into lined microwave extraction vessels, and a 25-ml 1:1 acetone/hexane solvent mixture was added. Vessels were then assembled as instructed by the manufacturer, and the extraction was conducted for 15 min at 110 °C and up to 10 bars. Once cooled to room temperature, the extracts were filtered and rinsed with the same solvent mixture and then concentrated in a rotating evaporator (Rotavapor-R Buchi, Switzerland). Sulphur compounds were removed by soaking the extracts with activated copper powder.

Purification and fractionation were performed by eluting extracts through glass chromatography columns packed with silica gel/alumina/florisil (4 + 4 + 1 g). The first fraction, intended for PCB analysis, was eluted with 25 ml of *n*-hexane, while the second fraction, intended for PAH analysis, was eluted with 30 ml of 4:1 *n*-hexane/methylene chloride solvent mixture (Fossato et al. 1996, 1998). After concentration with a rotary evaporator, samples were ready for instrumental analysis.

PAH quantification

Concentrations of 14 USEPA priority PAHs (naphthalene (Naph), acenaphtene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Ft), pyrene (Py), benzo(a)anthracene (B[a]A), chrysene (Chy), benzo(b)fluoranthene (B[b]Ft), benzo(k)fluoranthene (B[k]Ft), benzo(a)pyrene (B[a]Py), dibenzo(a,h)antracene (diB[a,h]A), and benzo(g,h,i)perylene (B[g,h,i]Per)) were measured using a high-performance liquid chromatograph (PE 200, USA) coupled to a programmed fluorescence detector (HP 1046A, USA). The column used was a reverse-phase Supelcosil LC-PAH ($L = 150$ mm $\phi = 3$ cm, particles-size = 5 μm). Linear gradient elution was executed with acetonitrile-water mixture as mobile phase at a flow rate of 0.8 ml min^{-1}. The composition of the gradient started with 40% acetonitrile held constant for 4 min, rising to 100% over 11 min, and then held constant for other 10 min. The column compartment was thermo-stated at 40 °C. A wavelength programme was developed to enable optimal detection of all compounds (Table 1).

Table 1 Wavelength programme used for the detection of PAHs

Time (min)	Excitation (nm)	Emission (nm)
0.0	280	340
11.7	265	389
13.0	280	435
13.5	265	389
16.0	280	410

PCB quantification

PCB concentrations were measured by capillary gas chromatography (Carlo Erba Fractovap 4160, Italy) fitted with electron capture detectors (ECD) on a 15-m Varian VF-5-ms capillary column (0.15-mm ID, 0.15-μm film). The injector was used in splitless mode and held at 270 °C. After a conditioning period of 4 min, the column was held at 80 °C for 1 min, rising to 280 °C at a rate of 9.5 °C min^{-1}, and held at 280 °C for 4 min. The ECD temperature was maintained at 330 °C. The flow-rate of carrier (hydrogen) and make-up (nitrogen) gases was 0.6 and 30 ml min^{-1}, respectively. Total PCB concentration was determined as the sum of 7 congeners (52, 101, 110, 118, 138, 153, 180), which are appropriate indicators for a range of PCB patterns in various sample matrices and are most suitable for risk assessment of "non-dioxin-like PCBs" (EFSA 2005). In Italy, more than 90% of the production of PCBs was destined for oil for transformers, containing Aroclor mixtures 1254 and 1260 (Maroni et al. 1991; Rachdawong and Christensen 1997), in which CB-28 represents a negligible fraction (Bedard and May 1996; Newman et al. 1998). In order to ensure a more realistic estimate of total PCBs, as an alternative to CB-28, we thus determined CB-110, which accounts for 10% of total weight in Aroclor 1254 (Newman et al. 1998). The concentration was also given as total Aroclors, calculated as the sum of a 1:1 1254–1260 mixture.

Quality control

PAHs and PCBs were identified by matching retention times and quantified from the calibration curves established for each compound by analysing four external standards. For PCBs, according to EPA Method 8082A (USEPA 2007b), congener identification was confirmed for a selected number of samples, with a second analysis on a 30-m Zebron ZB capillary column (0.25-mm ID, 0.25-μm film). The average determination coefficients R^2 of the calibration curves were greater than 0.99 for both PAHs and PCBs, and the relative standard deviations of the calibration factors were always below 20% (average 10%). The linear ranges of responses were assessed from levels close to the detection limit through three orders of magnitude, for both the categories of compounds. Blanks and calibration verification with standards at one or more concentrations were run frequently for the entire procedure. Blank results indicated that the analytical procedure was free from contamination as the concentration of all compounds examined was at or near the noise level and showed no evidence of carryover. Check standards were on average within 10 and 7% of the nominal value for PAHs and PCBs, respectively.

The detection limits were 0.05–0.10 and 0.05 ng/g for PAHs and PCBs, respectively. Recovery and accuracy were validated with IAEA-417 and IAEA-159 certified sediment sample reference materials, obtaining values in the range 75–108% for all PAHs except naphthalene and 85–112% for PCBs. Naphthalene exhibited lower and more variable recovery (20–40%), due to losses in the two-rotovapor steps, and thus, results for this compound are not presented here.

Laboratory methods were also validated over time by intercalibration procedures (IAEA 2001, 2007, 2012), obtaining *Z* scores in the range 0.95–0.99 and 0.60–0.72, for PAHs and PCBs, respectively.

Data processing and statistics

For statistical processing, we choose to fill in the values below the detection limit (n.r.) with values equal to half the detection limit. This option represents a reasonable compromise between solutions that underestimate (n.r. = 0) or overestimate (n.r. = detection limit) the true value. It is also reasonable from a health/toxicity perspective, easier to perform than other more complex statistical approaches, and in agreement with the findings of various studies reported in the literature (Menichini and Viviano 2004). Correlation analysis was performed on log-transformed data sets. The frequency distributions of the elements and basic statistics were analysed with the Statistica 6.0 (Statsoft, 2001) software package for Windows.

The distribution maps of the concentrations were represented as contour plots based on Geographic Information System (GIS) technology (software QGIS). In order to reduce the bias of the mean concentrations due to the non-uniform spatial distribution of sampling sites, weighted means were calculated by an inverse distance weighted method (IDW) that takes into account the area between concentration isolines. This method was also used for calculating PAH and PCB inventories in layers A and B. The dry bulk density of sediments was calculated from porosity (Nafe and Drake 1961).

Results and discussion

Spatial distribution of PAHs and PCBs

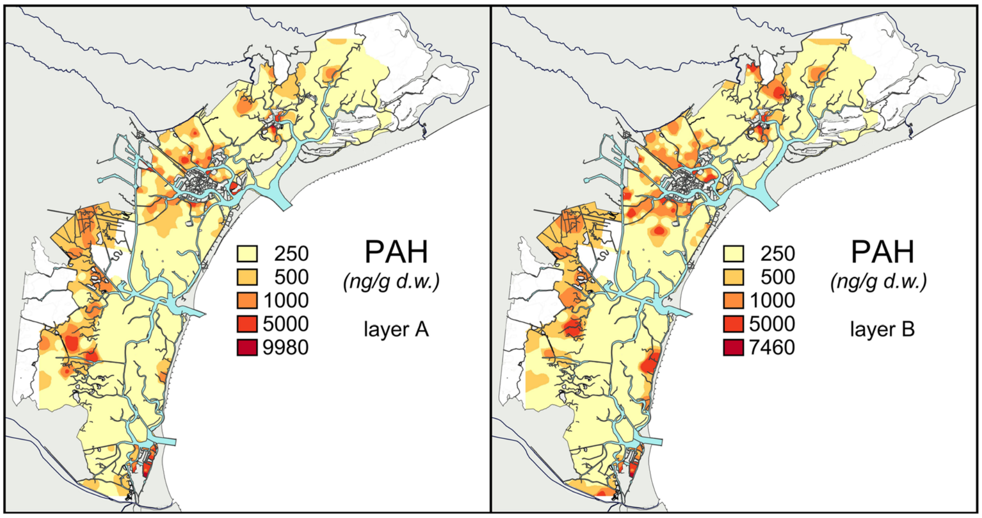
Total PAH concentrations (Table 2) ranged from 3.6 to 9980 ng/g in layer A (0–5 cm) and from 2.8 to 7458 ng/g in layer B (5–10 cm). Concentrations in both layers (Fig. 2) were highest near the city of Chioggia, in the southern lagoon, with

Table 2 PAHs and PCBs descriptive statistics for sediments layers "A" and "B." Concentrations in ng/g d.w.; wm—weighted mean; < d.l.—below detection limit

Layer A (0–5 cm)	Mean ± st.dev	Minimum	Lower quartile	Median	Upper quartile	Maximum
Ace	2.5 ± 4.0	< d.l.	0.5	1.2	2.9	48.1
Fl	3.6 ± 10.2	< d.l.	0.6	1.4	3.1	105.5
Phe	29.5 ± 101.5	< d.l.	4.5	9.6	23.5	1460.8
Ant	14.4 ± 46.7	< d.l.	1.8	4.1	11.0	651.7
Ft	62.2 ± 178.4	< d.l.	7.2	21.0	52.8	2032.9
Py	59.6 ± 148.4	0.3	8.3	22.5	57.6	1676.2
B[a]A	27.6 ± 68.7	< d.l.	2.8	8.0	24.0	769.4
Chy	24.6 ± 62.0	0.1	3.6	8.7	21.4	701.1
B[b]Ft	45.1 ± 98.4	< d.l.	9.4	21.7	45.1	1000.3
B[k]Ft	18.2 ± 45.1	< d.l.	2.9	7.6	17.5	489.9
B[a]Py	28.3 ± 70.8	< d.l.	4.1	10.5	27.6	824.2
diB[a,h]A	3.0 ± 7.3	< d.l.	0.4	1.3	3.2	95.1
B[ghi]Per	23.9 ± 54.3	< d.l.	5.1	9.9	21.5	598.1
PAH tot	343.9 ± 865.8	3.6	59.1	134.0	333.3	9980.3
PAH wm	260.5					
Aroclor1254	7.0 ± 8.7	< d.l.	1.0	3.5	9.8	53.3
Aroclor1260	6.2 ± 7.1	< d.l.	1.6	4.3	8.8	57.1
CB-52	0.2 ± 0.5	< d.l.	0.01	0.0	0.3	3.6
CB-101	0.8 ± 1.2	< d.l.	0.01	0.4	1.0	12.3
CB-110	0.7 ± 0.9	< d.l.	0.2	0.4	1.1	8.2
CB-118	0.6 ± 0.7	< d.l.	0.1	0.4	1.0	6.8
CB-138	1.4 ± 1.7	< d.l.	0.3	1.0	1.8	12.8
CB-153	1.3 ± 1.4	< d.l.	0.5	0.9	1.8	10.8
CB-180	0.7 ± 0.8	< d.l.	0.2	0.5	1.0	6.3
PCB tot	5.9 ± 6.2	< d.l.	1.8	3.9	8.2	47.8
PCB wm	4.6					
Layer B (5–10 cm)	Mean ± st.dev	Minimum	Lower quartile	Median	Upper quartile	Maximum
Ace	2.2 ± 3.2	< d.l.	0.4	0.9	2.9	27.2
Fl	3.6 ± 11.0	< d.l.	0.7	1.6	2.9	134.6
Phe	28.0 ± 66.9	< d.l.	5.1	11.0	23.2	681.5
Ant	18.0 ± 73.7	< d.l.	1.8	4.3	10.8	1198.8
Ft	60.3 ± 135.3	< d.l.	6.9	21.1	65.8	1572.8
Py	58.1 ± 117.9	0.2	8.2	22.6	59.1	1370.0
B[a]A	28.4 ± 58.5	< d.l.	3.1	8.6	30.1	624.6
Chy	25.0 ± 50.6	0.2	3.8	9.5	26.1	575.6
B[b]Ft	46.0 ± 78.3	< d.l.	9.8	23.0	53.4	799.5
B[k]Ft	18.5 ± 36.7	< d.l.	3.0	7.7	20.4	424.3
B[a]Py	29.7 ± 61.7	< d.l.	4.2	11.1	31.0	717.4
diB[a,h]A	2.5 ± 4.2	< d.l.	0.4	1.0	2.4	39.6
B[ghi]Per	26.2 ± 49.1	< d.l.	5.4	11.7	26.0	570.9
PAH tot	347.7 ± 675.0	2.8	61.8	143.4	382.6	7457.6
PAH wm	266.2					
Aroclor1254	6.7 ± 8.6	< d.l.	0.8	3.2	9.7	65.5
Aroclor1260	6.4 ± 8.9	< d.l.	1.5	4.4	7.8	99.3
CB-52	0.2 ± 0.5	< d.l.	0.01	0.0	0.2	3.5
CB-101	0.8 ± 1.1	< d.l.	0.01	0.4	1.1	6.6
CB-110	0.8 ± 1.2	< d.l.	0.2	0.4	1.1	14.4
CB-118	0.7 ± 0.7	< d.l.	0.1	0.4	1.0	6.7
CB-138	1.4 ± 1.7	< d.l.	0.2	0.8	1.8	11.7
CB-153	1.3 ± 1.4	< d.l.	0.4	0.7	1.8	13.2
CB-180	0.7 ± 1.0	< d.l.	0.2	0.5	0.9	10.0
PCB tot	5.8 ± 6.8	< d.l.	1.5	3.6	8.5	60.1
PCB wm	4.5					

mean values of 2300 ng/g. In this area, sediment quality is affected by urban waste discharge and road and boat traffic, being close to the harbour of the second largest fishing fleet in Italy. High values were also measured around the city of Venice and the islands of Murano and Burano, along the main shipping channels connecting the mainland and the industrial area to Venice, in the vicinity of a shipyard on the Pellestrina shore and to the south of the industrial area. Comparable values were observed in the south-western sector of the lagoon (Dogaletto) near the mainland, which is influenced by the

Fig. 2 Spatial distribution of total PAHs in sediment layers: **A** 0–5 cm and **B** 5–10 cm. For each concentration class, the upper limit is indicated



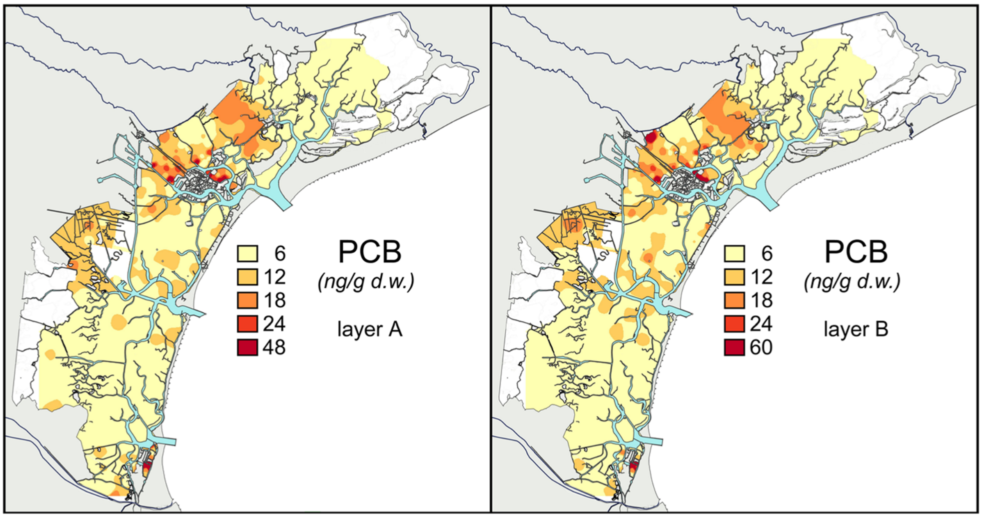
discharge of freshwater tributaries, and downwind of the Romea highway, a very busy road that connects Venice to Ravenna. A further contribution to the increase of PAH could also be the input caused by fish feeding (Hellou et al. 2005; Berntssen et al. 2015), practiced in a series of important fishing farms located near the area.

Total PCB concentrations ranged from < d.l. (detection limit) to 47.8 ng/g in layer A and from < d.l. to 60.1 ng/g in layer B (Table 2). The spatial distributions of PCB concentrations in layers A and B are shown in Fig. 3. The highest values were measured at sites near the city of Chioggia, as observed for PAH concentrations. High concentrations were also measured between the Porto Marghera industrial area and the city of Venice, to the north of Venice and Murano, and at the mouth of the Osellino Canal. Medium-to-low contamination was observed in an extensive area to the southeast of Venice airport. Enhanced PCB concentrations in the run-off water from Gdansk airport in Poland were reported by Sulej et al. (2011) and in airport soils in Croatia (Vasilić et al. 2004). We presume that this large area is moderately contaminated with PCBs delivered by run-off or atmospheric deposition from Venice airport. There were practically no differences between the distributions of concentrations in layers A and B, which confirms the absence of new sources since PCB production was banned in 1984.

On the whole-lagoon scale, no significant differences between sediment layers A and B were found for either total PAH or total PCB concentrations (Wilcoxon test $p = 0.06$ and $p = 0.39$, respectively).

However, significant differences between the two layers were seen in some areas of the lagoon. Specifically, the areas in front of the mouth of the Dese river and near the Pellestrina shipyard had lower values in layer A than layer B; while in the area in front of the fish farms, the reverse was found.

Fig. 3 Spatial distribution of total PCBs in sediment layers: **A** 0–5 cm and **B** 5–10 cm. For each concentration class, the upper limit is indicated



In addition, concentrations of PAHs with five or more aromatic rings (B[b]Ft, B[k]Ft, B[a]Py and B[ghi]P) were significantly higher in layer B than layer A (Wilcoxon test $p = 0.03$, 0.02, 0.04, 0.01, respectively). This might be due to their higher resistance to biodegradation compared to low molecular weight compounds (Cerniglia 1992). No significant differences with depth were observed for individual PCB congeners.

Analysis of correlation among TOC, grain-size, and both organic pollutant concentrations, performed on log-transformed values did not show significant relationships ($p > 0.05$).

The mean concentration of PAHs in the sediments of the Venice Lagoon (Fig. 4, left) was lower than that of the highly contaminated area of Taranto (Mar Piccolo, Gulf of Taranto; Cardellicchio et al. 2006, 2007) and those of other harbour areas, such as Napoli, Italy (Sprovieri et al. 2007), Rovinj, Croatia (Bihari et al. 2006), and harbours in southern France (Baumard et al. 1998). It was comparable to values reported for coastal areas, such as the Gulf of Trieste, Italy (Notar et al. 2001) and the Istanbul Strait, Turkey (Karacik et al. 2009), but was higher compared to the values found in other lagoon systems (Trabelsi and Driss 2005; Perra et al. 2009; Acquavita et al. 2014). The range of concentrations measured in the sediments of the Lagoon of Venice was wide (4 orders of magnitude), with the highest values comparable to those of the above-mentioned harbours.

Mean PCB concentration (Fig. 4, right) was lower than the values reported for the inner channels of the industrial zone of the Venice Lagoon (Frignani et al. 2001), Mar Piccolo near Taranto, Italy (Cardellicchio et al. 2007), Keratsini harbour, Greece (Galanopoulou et al. 2005), and Alexandria harbour, Egypt (Barakat et al. 2002), but higher than values reported for coastal areas, such as the Caspian Sea (De Mora et al. 2004) and Adriatic Coast, Albania (Koci 1998). PCB concentration was lower than values reported for other Mediterranean lagoons (Mandalakis et al. 2014; Jayed et al. 2015).

Estimation of toxicological and carcinogenic risk

Sediment quality guidelines (SQGs) provide a scientifically valid basis for evaluating the potential effects of sediment-associated contaminants on aquatic organisms. The threshold effects level (TEL) and probable effects level (PEL) (MacDonald et al. 1996) have been used to estimate the potential effect of PAHs and PCBs in the surface sediments (0–5 cm) on the biota of the Venice Lagoon, as have the limits for Venice sediment established by the Ministry of the Environment (Ministero dell'Ambiente 1993). The latter system identifies four classes corresponding to increasingly strict constraints for sediment disposal: non-polluted (A), moderately polluted (B), polluted (C), and highly polluted (> C). Table 3 shows the percentage distribution of samples with respect to SQGs and national limits.

The PEL was never exceeded by PAHs or PCBs, and the TEL was exceeded only in a small number of sites for PAHs (8, i.e. 2.1%) and PCBs (10, i.e. 2.6%), highlighting the absence in the lagoon of zones where effective incidence on biota would be expected. Although the concentrations never

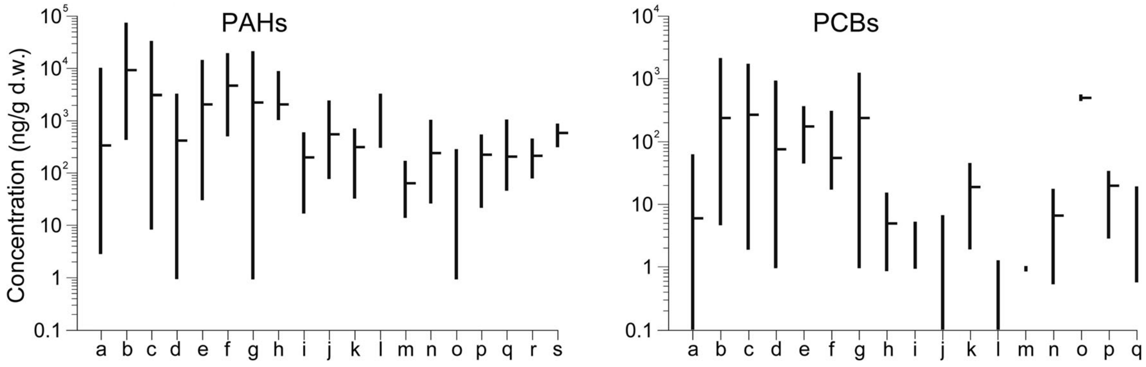


Fig. 4 Mean concentrations and their ranges (ng/g d.w.) of PAHs (left) and PCBs (right) in sediments from harbours and coastal areas of the Mediterranean. PAH: **a** this study, **b** Gulf of Taranto, Italy (Cardellicchio et al. 2006), **c** Naples Harbour, Italy (Sprovieri et al. 2007), **d** Istanbul Strait, Turkey (Karacik et al. 2009), **e** Rovinj, Croatia (Bihari et al. 2006), **f** East Mediterranean Sea (Yilmaz et al. 1998), **g** West Mediterranean Sea (Baumard et al.1998), **h** Alexandria, Egypt (Mohamed et al. 2016), **i** North Adriatic Sea (Caricchia et al. 1993), **j** Thyrrenian Sea (Pinto et al. 1995), **k** Gulf of Trieste, Italy (Notar et al. 2001), **l** Gulf of Lion, France (Lipiatou and Saliot 1991), **m** Cretan Sea (Gogou et al. 2000), **n** Spanish Coast (León et al. 2014), **o** Orbetello Lagoon, Italy (Perra et al. 2009), **p** Venice Lagoon, Italy (Secco et al. 2005), **q** Marano-Grado Lagoon, Italy (Acquavita et al. 2014), **r** Bizerte Lagoon, Tunisia (Trabelsi and Driss 2005), **s** Berre Lagoon, France (Kanzari et al. 2012). PCB: **a** this study, **b** industrial canals of Venice Lagoon, Italy (Frignani et al. 2001), **c** Mar Piccolo of Taranto, Italy (Cardellicchio et al. 2007), **d** Naples Harbour, Italy (Sprovieri et al. 2007), **e** Keratsini Harbour, Greek (Galanopoulou et al. 2005), **f** Tripoli, Lebanon (Merhaby et al. 2015), **g** Alexandria Harbour, Egypt (Barakat et al. 2002), **h** Adriatic Sea (De Lazzari et al. 2004), **i** Adriatic Coast (Koci 1998), **j** Caspian Sea (De Mora et al. 2004), **k** Barcelona Coast, Spain (Castells et al. 2008), **l** Crete, Estearn Mediterranean Sea (Mandalakis et al. 2014), **m** Varano Lagoon, Italy (Fabbrocini et al. 2017), **n** Venice Lagoon, Italy (Secco et al. 2005), **o** Berre Lagoon, France (Kanzari et al. 2012), **p** Etang de Thau, France (Castro-Jiménez et al. 2008), **q** Oualidia Lagoon, Morocco (Jayed et al. 2015)

Table 3 SQGs (NOAA marine, MacDonald et al., 1996), limits of classes A and B according to Protocol for the Venice Lagoon (Ministero dell'Ambiente, 1993) for PAHs and PCBs, and classification of sediments (0–5-cm depth, in % of sites) according to these guidelines

Layer A	TEL/PEL ng/g d.w.	< TEL	TEL-PEL	> PEL	A	B
PAH tot	1684÷16,770	97.9	2.1	0.0	94.2	5.8
PCB tot	22÷189	97.4	2.6	0.0	80.8	19.2

exceeded the "B" limit, it is worth noting that 5.8 and 19% of sites would respectively be considered as moderately polluted due to PAH and PCB concentrations if the sediment was to be subjected to disposal after dredging.

The carcinogenicity of certain PAHs, due to the production of active metabolites that can covalently bind to DNA (USEPA 1993), has been documented (Harvey 1991, 1997). The toxicity of PAHs is expressed in terms of toxic equivalency factors (TEFs) with respect to benzo[a]pyrene, the latter being the only known potentially carcinogenic PAH for which toxicological data are sufficient for derivation of a carcinogenic potency factor (Peters et al. 1999).

TEF values for benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenzo [a,h]anthracene, and chrysene are 0.1, 1, 0.1, 0.01, 1, and 0.001, respectively (USEPA 1993). The total toxic benzo[a]pyrene equivalent (total TEQ) of the mixture was then calculated from the sum of the concentrations of individual compounds (conc_i) multiplied by their relative toxicity (TEF_i):

$$\text{Total TEQ} = \Sigma \text{BaP}_{eq}\text{dose}_i,$$

where

$$\text{BaP}_{eq}\text{dose}_i = \text{TEF}_i \text{x conc}_i,$$

In this study, total TEQ calculated for sediment layer A varied from 0.3 to 1070, with a mean of 39. The PAH congeners contributing most to total TEQ were (in order): BaPy (69.0%) > BbFt (13.3%) > diBahA (10.8%) > BaA (6.3%) > BkFt (0.5%) > Chy (0.1%).

The mean total TEQ was lower than the majority of values reported in other studies (Table 4). Nevertheless, the maximum total TEQ value suggested that the most PAH-polluted areas of the Venice Lagoon represented a possible hazard.

PAH and PCB composition and sources

Each type of source gives rise to characteristic PAH patterns, making it possible to infer the processes that generate the compounds (Soclo et al. 2000). PAH profiles and ratios have been widely used to detect PAH sources (Gogou et al. 1996; Mantis et al. 2005; Rossini et al. 2007; Sprovieri et al. 2007). In this study, to minimise possible confusion due to differences in volatility, water solubility, adsorption, and degradation by photo-oxidation, profiles and ratio calculations were restricted to PAHs within a given molecular mass (Yunker et al. 2002).

To determine their relative composition, PAHs were subdivided into five isomer groups: the mean concentrations of isomers with molecular masses of 178, 202, 228, 252, and 276 were calculated. The concentration of isomers decreased in the order 202 > 252 > 228 > 178 > 276; this profile is commonly observed in sediments adjacent to urbanised and industrialised areas. PAHs with a mass of 178 and 202 predominate in kerosene and diesel exhaust fumes. In gasoline and diesel soot, mass 202 or 252 is generally the dominant constituent (Rogge et al. 1993; Wang et al. 1999; Oros and Simoneit 2000). Hence, a PAH profile dominated by masses 202 and 252 (usually with mass 202 predominant) is indicative of pyrolytic PAHs of anthropogenic origin (Gogou et al. 1996).

The ratios of PAH isomers with molecular masses of 178 and 202 are also commonly used to distinguish between combustion and petroleum sources (Budzinski et al. 1997; Soclo et al. 2000), while isomers with a molecular mass of 228 are

Table 4 A comparison of mean total TEQs in sediments from selected coastal areas

	Mean TEQcarc (ng g^{-1})	Range	References
This study	39	0.3–1070	
Barents Sea (Russia)	92	18–300	Savinov et al. (2003)
Meiliang Bay (China)	407	94–856	Qiao et al. (2006)
Napoli Harbour (Italy)	932	2–4723	Sprovieri et al. (2007)
Coastal lagoons (Vietnam)	22	2–98	Giuliani et al. (2008)
Istanbul Strait (Turkey)	48	0.1–382	Karacik et al. (2009)
Mangrove Wetland (India)	59	7–119	Dominguez et al. (2010)
Kaohsiung Harbour (Taiwan)	151	3.9–1970	Chen et al. (2012)
Coastal Lagoon (Italy)	1144	4.3–7880	Guerra (2012)
Bizerte Lagoon (Tunisia)	11	3.1–53.7	Barhoumi et al. (2014)
Red Sea (Egypt)	8	nd-72	Aly Salem et al. (2014)

often used to corroborate the assignment of combustion sources (Yunker and Macdonald 2003).

When the primary PAH source is combustion, the less stable or kinetic PAH isomers tend to be enhanced with respect to the more stable or thermodynamic PAH isomers of the same molecular mass (Yunker and Macdonald 1995).

For isomers with a molecular mass of 178, anthracene/anthracene + phenanthrene ratios below 0.1 are usually taken as an indication of unburned petroleum, while a ratio higher than 0.1 indicates a dominance of combustion effects (Yunker and Macdonald 2003). For isomers with a molecular mass of 202, low fluoranthene/fluoranthene + pyrene ratios (< 0.4) indicate petroleum, intermediate ratios (0.4–0.5) indicate combustion of liquid fossil fuel (petrol and crude oil), whereas ratios > 0.5 are characteristic of grass, wood, or coal combustion (Yunker and Macdonald 2003). Ratios > 0.5 are also often observed in atmospheric deposition samples (Rossini et al. 2007, Gambaro et al. 2009).

For isomers with a molecular mass of 228, benz(a)anthracene/benz(a)anthracene + chrysene ratios < 0.20 imply petroleum, from 0.20 to 0.35 either petroleum or combustion and > 0.35 combustion (Yunker and Macdonald 2003).

The present study showed the clear dominance of combustion sources in the Venice Lagoon, with more than 73% of samples simultaneously fulfilling the three criteria for the ratios mentioned above. This feature is also supported by the presence of acenaphthene in 95% of samples, which is specific to combustion sources (Yunker and Macdonald 1995).

Among the zones of the lagoon with a higher presence of PAHs in the surface sediment, five areas with three different source patterns were identified (Fig. 5).

Sediments in zones LF1 and LF2 showed a distribution of isomers dominated by classes 202 and 252 (with $202 > 252$ and 178 isomers making up around 10%). They were also characterised by a 202 ratio < 0.5. Given the intense boat traffic in these zones, sediment showed the characteristic PAH fingerprint for liquid fossil fuel combustion.

The two zones CD1 and CD2 showed a distribution of isomers similar to the previous two, but the 202 ratio was always > 0.5, indicating a prevalence of coal combustion sources and/or the occurrence of significant atmospheric deposition (Rossini et al. 2007). Both areas are located downwind of the industrial zone and the Fusina power plant.

In contrast, the 178 and 252 isomers are dominant in the sediments of zone CO, which is under the direct influence of the industrial zone. The 202 ratio was mostly > 0.5 and the 178 isomers accounted for almost 30%, suggesting the combined effects of combustion and unburned oil.

As observed in other studies (e.g. Viñas et al. 2010, León et al. 2014), the distribution of PAHs in sediment seems to be dependent on proximity of emission sources rather than on sediment characteristics.

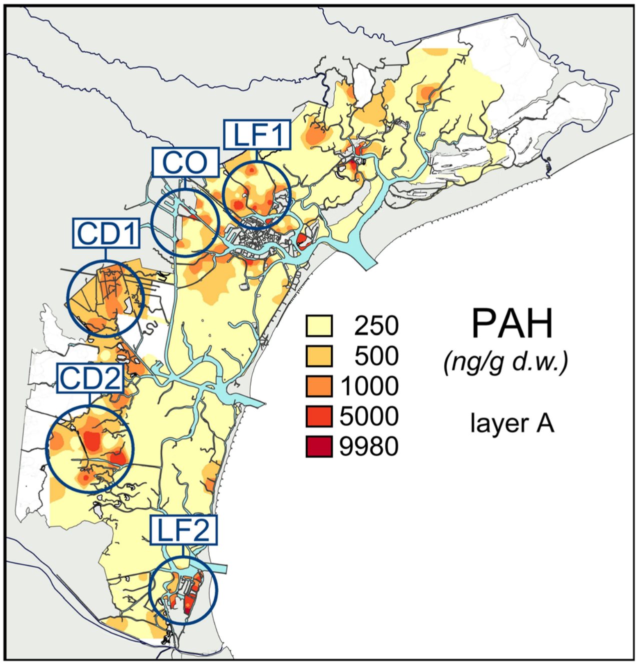


Fig. 5 Typology of PAH congener ratios, characteristic for likely sources, in selected areas of the Venice Lagoon (LF = liquid fuel, CD = combustion/deposition, CO = combustion/oil)

Regarding PCB congeners, the most abundant (24 and 23%) were two hexachlorobiphenyls (CB-138 and CB-153), followed by two pentachlorobiphenyls (CB-101 and CB-110) and a heptachlorobiphenyl (CB-180), accounting for 13, 13, and 12%, respectively. The resulting PCB pattern (hexa-PCBs > penta-PCBs > hepta-PCBs > tetra-PCBs) is in agreement with what has been reported by other authors for the Venice Lagoon (Secco et al. 2005) and for other Mediterranean zones (Galanopoulou et al. 2005, Castro-Jiménez et al. 2008). A different composition was found in other areas (Jayed et al. 2015) in which lower chlorinated PCBs (3–4 Cl atoms) were predominant. This could be due either to the different grain-size and organic matter content of the sediment (Pierard et al. 1996) or to the different composition of the main sources.

To evaluate the similarity of the PCB pattern with that of the principal commercial mixtures, the composition (weight %) of chlorobiphenyl PCB homologues in the sediment samples was compared with that of Aroclors 1254 and 1260 (Fig. 6). The comparison confirmed that a 1:1 mixture of 1254 + 1260 best represents the PCB composition of the lagoon sediments, as suggested previously (Frignani et al. 2001).

PAH and PCB inventories

Given the high number of sampling sites, our results were suitable for reliable quantification of PAHs and PCBs in the shallow water sediments of the Venice Lagoon. The inventories

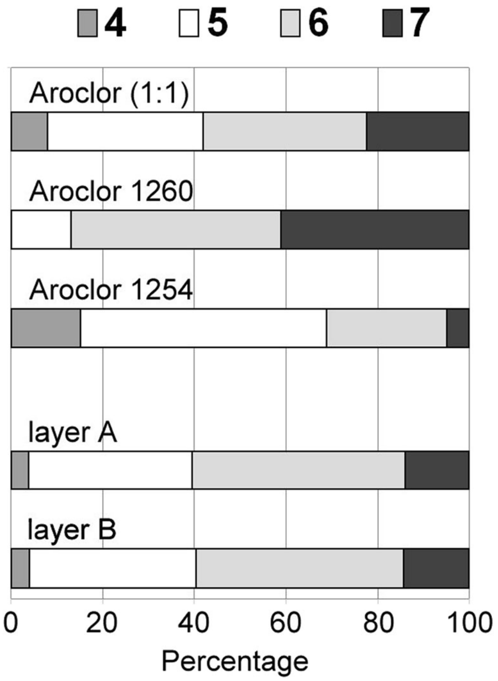


Fig. 6 Mean composition (by wt%) of chlorobiphenyl homologues of PCBs in the Venice Lagoon sediments compared with those of Aroclors 1254 and 1260. Data for Aroclors from Erickson (1997)

were calculated for both surface (0–5 cm) and sub-surface (5–10 cm) sediment layers (Table 5).

A comparison of the amounts of PAHs and PCBs in the surface sediment and rates of atmospheric deposition was tentatively carried out for the northern basin of the Venice Lagoon. The northern basin (shown in Fig. 1) is the only part of the lagoon that is mainly in deposition conditions (Sarretta et al. 2010), and we assumed that the total PAH and PCB atmospheric fallout accumulated in sediments.

The estimated amounts of PAHs and PCBs in the surface sediments (layer A) of the northern basin were 2770 and 34 kg, respectively. On the basis of literature data (Cochran et al. 1998; Ciavola et al. 2002; Bellucci et al. 2007; Zonta et al. 2018), the mean sedimentation rate in this basin was assumed to be 0.2 cm year^{-1}, and thus, the 5-cm surface sediments would be accumulated in about 25 years.

From data collected between November 1998 and July 1999, Rossini et al. (2005b) estimated the annual rates of atmospheric PAH and PCB deposition for the whole lagoon surface area (550 km^2) at 104.5 and 0.52 kg, respectively, corresponding to 17.9 and 0.09 kg for the 94 km^2 of the northern basin. These values can be considered as the upper limit, as the mean deposition includes values from the Porto Marghera industrial area. Based on these numbers, atmospheric deposition accounts for 16.1 and 6.6% of the total inventory of PAHs and PCBs in the sediments, respectively (Table 5). Atmospheric fallout can also be inferred from measurements at two sites located on opposite sides of the northern basin (data collected in 1998/99 (Rossini et al. 2005a), and in 2003/04 (Rossini et al. 2005b)). Using these data, the mean fallout in the northern basin was 13.8 (PAHs) and 0.06 kg/year (PCBs), respectively, accounting for 12.5 and 4.4% of the total flux into sediments. Atmospheric deposition in this semi-enclosed basin seems to be relatively less important than for the lagoon as a whole (Rossini et al. 2005a; Bettiol et al. 2005), probably because of the predominance of input from the catchment area.

Table 5 PAH and PCB inventories in sediments of the Venice Lagoon and estimation of the atmospheric contribution for the northern basin inventories

	Surface area	PAH tot Layer A	PAH tot Layer B	PCB tot Layer A	PCB tot Layer B	References
Sediment inventory	km^2	kg	kg	kg	kg	
Lagoon (sampled area)	415	8500	8630	193	189	This work
Northern basin	94	2770		34		This work
Atmospheric fallout		kg/year		kg/year		
Lagoon	550	104.5		0.52		Rossini et al. 2005b
Northern basin	94	17.86		0.09		
		kg in 25 years		kg in 25 years		
Northern basin % of atm. contribution to sediment inventory	94	446.5		2.23		
		16.1%		6.6%		
Atmospheric fallout northern basin		kg/year		kg/year		
	94	13.83		0.06		Rossini et al. 2005a, b
		kg in 25 years		kg in 25 years		
		345.6		1.50		
% of atm. contribution to sediment inventory		12.5%		4.4%		

Conclusions

The study provides an assessment of PAH and PCB contamination in the upper sediment layer of the Venice Lagoon, which is the most comprehensive to date. Neither PAH nor PCB concentrations represent a risk to the biota (TEL exceeded in only 2.1% of sites), although for the purposes of disposal after dredging, sediments should be considered moderately polluted in 5.8 and 19% of sites for PAH and PCB concentrations, respectively. These more polluted areas are linked to specific sources, being located around inhabited islands or in the proximity of the industrial zone, harbours, and the mouths of the lagoon's freshwater tributaries. Slightly higher PCB concentrations in the northern part of the lagoon can possibly be attributed to runoff from Venice airport. In general, the distribution of persistent organic pollutants is thus more dependent on proximity to sources than on sediment characteristics.

A clear dominance of combustion sources is observed in the distribution of PAH concentrations on the basis of isomer ratios. Nevertheless, a signal reflecting both unburned oil sources and atmospheric fallout with the fingerprint of coal combustion is evident in specific zones of the lagoon and can be interpreted as the effect of the presence of the industrial zone.

Compared to other Mediterranean areas, PAH concentrations had lower maximum values than those measured in harbours and higher than those measured in majority of coastal systems. PCB concentrations were comparable to Mediterranean coastal sediments, but generally lower in comparison with other Mediterranean lagoons.

Based on high-density sampling, the PAH and PCB inventories in the surface layer of the whole of the shallow area of the lagoon were calculated. The estimate for the northern basin of the lagoon suggests a modest contribution of atmospheric deposition to the sediment inventory (12–16% for PAHs and 4–7% for PCBs).

The resulting picture of PAH and PCB distributions in the sediments provides a reference for future monitoring of changes that may arise as a result of the entry into service of the MOSE system, as well as the general evolution of pollution in the Venice Lagoon sediments.

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References

Acquavita A, Falomo J, Predonzani S, Tamberlich F, Bettoso N, Mattassi G (2014) The PAH level, distribution and composition in surface sediments from a Mediterranean lagoon: the Marano and Grado lagoon (northern Adriatic Sea, Italy). Mar Pollut Bull 81:234–241

Aly Salem DMS, Morsy FA-EM, El Nemr A, El-Sikaily A, Khaled A (2014) The monitoring and risk assessment of aliphatic and aromatic hydrocarbons in sediments of the Red Sea, Egypt. Egyptian Journal of Aquatic Research 40(4):333–348

Barakat AO, Kim M, Qian Y, Wade TL (2002) Organochlorine pesticides and PCBs residues in sediments of Alexandria Harbour, Egypt. Mar Pollut Bull 44:1421–1434

Barhoumi B, LeMenach K, Devier MH, Ameur WB, Etcheber H, Budzinski H et al (2014) Polycyclic aromatic hydrocarbons (PAHs) in surface sediments from the Bizerte Lagoon, Tunisia: levels, sources, and toxicological significance. Environ Monit Assess 186(5):2653–2669

Baumard P, Budzinski H, Garrigues P (1998) Polycyclic aromatic hydrocarbons (PAHs) in sediments and mussels of the western Mediterranean Sea. Environ Toxicol Chem 17:765–776

Bedard DL, May RJ (1996) Characterization of the polychlorinated biphenyls in the sediments of Woods Pond: evidence for microbial reductive dechlorination of Aroclor 1260 in situ. Environmental Science & Technology 30:237–245

Bellucci LG, Frignani M, Cochran JK, Albertazzi S, Collavini F, Cecconi R, Hopkins H (2007) ^{210}Pb and ^{137}Cs as chronometers for salt marsh accretion in the Venice Lagoon-links to flooding frequency and climate change. J Environ Radioact 97(2–3):85–102

Beriro DJ, Vane CH, Cave MR, Nathanail CP (2014) Effects of drying and comminution type on the quantification of polycyclic aromatic hydrocarbons (PAH) in a homogenised gasworks soil and the implication for human health risk assessment. Chemosphere 111:396–404

Berntssen MHG, Ørnsrud R, Hamre K, LiePolyaromatic KK (2015) Polyaromatic hydrocarbons in aquafeeds, source, effects and potential implications for vitamin status of farmed fish species: a review. Aquac Nutr 21(3):257–273

Bettiol C, Collavini F, Guerzoni S, Molinaroli E, Rossini P, Zaggia L, Zonta R (2005) Atmospheric and riverine inputs of metals, nutrients and persistent organic pollutants into the lagoon of Venice. Hydrobiologia 550(1):151–165

Bihari N, Fafandel M, Hamer B, Kralj-Bilen B (2006) PAHs content, toxicity and genotoxicity of coastal marine sediments from the Rovinj area, northern Adriatic, Crotia. Sci Total Environ 366:602–611

Breivik K, Sweetman A, Pacyna JM, Jones KC (2002) Towards a global historical emission inventory for selected PCB congeners—a mass balance approach. 1. Global production and consumption. Sci Total Environ 290:181–198

Budzinski H, Jones I, Bellocq J, Piérard C, Garrigues P (1997) Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. Mar Chem 58:85–97

Cardellicchio N, Buccolieri A, Giandomenico S, Lerario VL, Lopez L, Pizzulli F (2006) Distribution and occurence of polycyclic aromatic hydrocarbons (PAHs) in sediments from the Mar Grande and Gulf of Taranto (Ionian Sea, southern Italy). Ann Chim 96:51–64

Cardellicchio N, Buccolieri A, Giandomenico S, Lopez L, Pizzulli F, Spada L (2007) Organic pollutants (PAHs, PCBs) in sediments from the Mar Piccolo in Taranto (Ionian Sea, Southern Italy). Mar Pollut Bull 55(10–12):451–458

Caricchia AM, Chiavarini S, Cremisini C, Martini F, Morabito R (1993) PAHs, PCBs, and DDE in the northern Adriatic Sea. Mar Pollut Bull 26(10):581–583

Castells P, Parera J, Santos JF, Galceran MT (2008) Occurrence of polychlorinated naphthalenes, polychlorinated biphenyls and short-chain chlorinated paraffins in marine sediments from Barcelona (Spain). Chemosphere 70:1557–1565

Castro-Jiménez J, Deviller G, Ghiani M, Loos R, Mariani G, Skejo H, Umlauf G, Wollgast J, Laugier T, Héas-Moisan K, Léauté F, Munschy C, Tixier C, Tronczyński J (2008) PCDD/F and PCB multi-media ambient concentrations, congener patterns and occurrence in a Mediterranean coastal lagoon (Etang de Thau, France). Environ Pollut 156:123–135

Cerniglia CE (1992) Biodegradation of polycyclic aromatic hydrocarbons. Biodegradation 3(2–3):351–368

Chen CF, Chen CW, Dong CD, Kao CM (2012) Assessment of toxicity of polycyclic aromatic hydrocarbons in sediments of Kaohsiung Harbor, Taiwan. Sci Total Environ 463-464:1174–1181

Ciavola P, Organo C, Lèon VL, Mitchell PI (2002) Sedimentation processes on intertidal areas of the Lagoon of Venice: identification of exceptional floods events (acqua alta) using radionuclides. J Coast Res 36:139–147 ISSN 0749-0208

Cochran JK, Frignani M, Salamanca M, Bellucci LG, Guerzoni S (1998) Lead-210 as a tracer of atmospheric input of heavy metals in the northern Venice Lagoon. Mar Chem 62:15–29

Collavini F, Bettiol C, Zaggia L, Zonta R (2005) Pollutant loads from the drainage basin to the Venice Lagoon (Italy). Environ Int 31:939–947

Cornelissen G, Gustafsson Ö, Bucheli TD, Jonker MT, Koelmans AA, van Noort PC (2005) Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. Environ Sci Technol 39(18):6881–6895

Covaci A, Van de Vijver I, De Coen W, Das K, Bouquegneau JM, Blust R, Schepens P (2002) Determination of organohalogenated contaminants in liver of harbour porpoises (Phocoena phocoena) stranded on the Belgian North Sea coast. Mar Pollut Bull 44:1152–1169

De Lazzari A, Rampazzo G, Pavoni B (2004) Geochemistry of sediments in the northern and central Adriatic Sea. Estuar Coast Shelf Sci 59: 429–440

De Mora S, Villeneuve J-P, Sheikholeslami MR, Cattini C, Tolosa I (2004) Organochlorinated compounds in Caspian Sea sediment. Mar Pollut Bull 48:30–43

Domínguez C, Karkar SK, Bhattacharya A, Chatterjee M, Bhattacharya BD, Jover E, Albaigés J, Bayona JM, Alam MA, Satpathy KK (2010) Quantification of source identification of polycyclic aromatic hydrocarbons in core sediments from Sundarban Mangrove Wetland, India. Arch Environ Contam Toxicol 59:49–61

EFSA (2005) Opinion of the Scientific Panel on Contaminants in the food chain on a request from the Commission related to the presence of non-dioxin-like polychlorinated biphenyls (PCB) in feed and food. Adopted on 8 November 2005. EFSA J 284:1–137. https://doi.org/10.2903/j.efsa.2005.284

Erickson MD (1997) Analytical chemistry of PCBs. Lewis Publishers, New York 688 pp

Fabbrocini A, Cassin D, Santucci A, Scirocco T, Specchiulli A, D'Adamo R (2017) Early chemical and ecotoxicological responses of the Varano Lagoon (SE Italy) to a flood event. Ecotoxicol Environ Saf 144:178–186

Ferrarin C, Ghezzo M, Umgiesser G, Tagliapietra D, Camatti E, Zaggia L, Sarretta A (2013) Assessing hydrological effects of human interventions on coastal systems: numerical applications to the Venice Lagoon. Hydrol Earth Syst Sci 17:1733–1748

Fossato VU, Campesan G, Craboledda L, Dolci F, Stocco G (1996) Organic micropollutants and trace metals in water and suspended particulate matter. In: Lasserre P, Marzollo A (eds) Venice Lagoon ecosystem, vol 1. Unesco, Murst 8 p

Fossato VU, Campesan G, Dolci F, Stocco G (1998) Trends in chlorinated hydrocarbons and heavy metals in sediments of Venetian canals. Rapp Comm int Mer Médit 35:258–259

Frignani M, Bellucci LG, Carraro C, Raccanelli S (2001) Polychlorinated biphenyls in sediments of the Venice Lagoon. Chemosphere 43: 567–575

Frignani M, Bellucci LG, Favotto M, Albertazzi S (2003) Polycyclic aromatic hydrocarbons in sediments of the Venice Lagoon. Hydrobiologia 494:283–290

Galanopoulou S, Vgenopoulos A, Conispoliatis N (2005) DDTs and other chlorinated organic pesticides and polychlorinated biphenyls pollution in the surface sediments of Keratsini harbour, Saronikos Gulf, Greece. Mar Pollut Bull 50:520–525

Gambaro A, Radaelli M, Piazza R, Maria Stortini A, Contini D, Belosi F, Zangrando R, Cescon P (2009) Organic micropollutants in wet and dry depositions in the Venice Lagoon. Chemosphere 76:1017–1022

Ghosh U, Zimmerman JR, Luthy RG (2003) PCB and PAH speciation among particle types in contaminated harbor sediments and effects on PAH bioavailability. Environ Sci Technol 37(10):2209–2217

Giuliani S, Sprovieri M, Frignani M, Cu NH, Mugnai C, Bellucci LG (2008) Presence and origin of polycyclic aromatic hydrocarbon in sediments of nine coastal lagoons in central Vietnam. Mar Pollut Bull 56:1504–1512

Gogou A, Stratigakis N, Kanakidou M, Stephanou EG (1996) Organic aerosols in eastern Mediterranean: components source reconciliation by using molecular markers and atmospheric back trajectories. Org Geochem 25:79–96

Gogou A, Bouloubassi I, Stefanou EG (2000) Marine organic geochemistry of the eastern Mediterranean: 1. Aliphatic and polyaromatic hydrocarbons in Cretan Sea surficial sediments. Mar Chem 68: 265–282

Guerra R (2012) Polycyclic aromatic hydrocarbons, polychlorinated biphenyls and trace metals in sediments from a coastal lagoon (northern Adriatic, Italy). Water Air Soil Pollut 223:85–98

Guerzoni S, Rossini P, Sarretta A, Raccanelli S, Ferrari G, Molinaroli E (2007) POPs in the Lagoon of Venice: budgets and pathways. Chemosphere 67:1776–1785

Harvey RG (1991) Polycyclic aromatic hydrocarbons: chemistry and carcinogenesis. Cambridge University Press, Cambridge 396 pp

Harvey RG (1997) Polycyclic aromatic hydrocarbons. Wiley-VCH, New York 667 pp

Hellou J, Hayab K, Steller S, Burridge L (2005) Presence and distribution of PAHs, PCBs and DDE in feed and sediments under salmon aquaculture cages in the Bay of Fundy, New Brunswick, Canada. Aquat Conserv Mar Freshw Ecosyst 15:349–365

IAEA (2001) World-wide and regional intercomparison for the determination of organochlorine compounds, petroleum hydrocarbons and sterols in sediment sample. International Atomic Energy Agency I.A.E.A - 417

IAEA (2007) World-wide and regional intercomparison for the determination of organochlorine compounds, petroleum hydrocarbons and sterols in sediment sample. International Atomic Energy Agency I.A.E.A - 159

IAEA (2012) World-wide and regional intercomparison on the determination of organochlorine compounds, polybrominated diphenyl ethers and petroleum hydrocarbons in sediment sample. International Atomic Energy Agency I.A.E.A - 459

Jayed M, Benbrahim S, Bakkas S, Ramdani M, Flower R (2015) Accumulation of organochlorines in the European clam (*Ruditapes decussatus*) and sediment of the Oualidia Lagoon (Morocco). Bull Environ Contam Toxicol 94:614–621

Kanzari F, Syakti AG, Asia L, Malleret L, Mille G, Jamoussi B, Abderrabba M, Doumenq P (2012) Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorine, and organophosphorous pesticides in surface sediments from the Arc River and the Berre Lagoon, France. Environ Sci Pollut Res 19:559–576

Karacik B, Okay OS, Henkelmann B, Bernhöft S, Schramm KW (2009) Polycyclic aromatic hydrocarbons and effects on marine organisms in the Istanbul Strait. Environ Int 35(3):599–606

Koci K (1998) The trend of POP pollution in the Albanian Adriatic Coast. Case Study PCBs (1992–1996). UNEP/IFCS, pp 101–106

León VM, García I, Martínez-Gómez JA, Campillo JA, Benedicto J (2014) Heterogeneous distribution of polycyclic aromatic hydrocarbons in surface sediments and red mullet along the Spanish Mediterranean coast. Mar Pollut Bull 87:352–363

Letcher RRJ, Bustnes JO, Dietz R, Jenssen BM, Jørgensen EH, Sonne C, Verreault J, Vijayan MM, Gabrielsen GW (2010) Exposure and effects assessment of persistent organohalogen contaminants in arctic wildlife and fish. Sci Total Environ 408(15):2995–3043

Lipiatou E, Saliot A (1991) Fluxes and transport of anthropogenic and natural polycyclic aromatic hydrocarbons in the western Mediterranean Sea. Mar Chem 32:51–71

MacDonald DD, Carr RS, Calder FD, Long ER, Ingersoll CG (1996) Development and evaluation of sediment quality guidelines for Florida coastal waters. Ecotoxicology 5:253–278

Mandalakis M, Polymenakou PN, Tselepides A, Lampadariou N (2014) Distribution of aliphatic hydrocarbons, polycyclic aromatic hydrocarbons and organochlorinated pollutants in deep-sea sediments of the southern Cretan margin, eastern Mediterranean Sea: a baseline assessment. Chemosphere 106:28–35

Mantis J, Chaloulakou A, Samara C (2005) PM10-bound polycyclic aromatic hydrocarbons (PAHs) in the Greater Area of Athens, Greece. Chemosphere 59:593–604

Maroni M, Colombi A, Carrer P, Barbieri F, Foà V, Del Frate G, Bossi G (1991) Stima delle giacenze di PCB in Italia e loro soluzioni di smaltimento. Acqua-Aria 8:761–767 In Italian

MAV (1999) Mappatura dell'inquinamento dei fondali lagunari. Studi ed indagini. Relazione finale, luglio 1999. Consorzio Venezia Nuova. In Italian

Menichini E, Viviano G (2004) Trattamento dei dati inferiori al limite di rivelabilità nel calcolo dei risultati analitici. Rapporti ISTISAN 04(15) In Italian

Merhaby D, Net S, Halwani J, Ouddane B (2015) Organic pollution in surficial sediments of Tripoli Harbour, Lebanon. Mar Pollut Bull 93(1):284–293

Ministero dell'Ambiente (1993) Criteri di sicurezza ambientale per gli interventi di escavazione, trasporto e impiego dei fanghi estratti dai canali di Venezia. In Italian

Mohamed LA, El Zokm GM, El Deeb KZ et al (2016) A new record for aliphatic and polycyclic aromatic hydrocarbon accumulation in the surficial sediments of El Mex Bay, Alexandria, Egypt after 19 years from the first one. Egypt J Aquat Res 42:375–383

Moret I, Piazza R, Benedetti M, Gambaro A, Barbante C, Cescon P (2001) Determination of polychlorobiphenyls in Venice Lagoon sediments. Chemosphere 43(4):559–565

Nafe JE, Drake CL (1961) Physical properties of marine sediments. Columbia University. Lamont Geological Observatory. Technical Report n.2, CU3-16 I NObsr 85077 Geology

Neff JM (1979) Polycyclic aromatic hydrocarbons in the aquatic environment: sources, fates, and biological effects. Applied Science Publishers, London, p 262

Newman JW, Becker JS, Blondina G, Tjeerdema RS (1998) Quantitation of aroclors using congener-specific results. Environ Toxicol Chem 17:2159–2167

Notar M, Leskovsˇek H, Faganeli J (2001) Composition, distribution and sources of polycyclic aromatic hydrocarbons in sediments of the Gulf of Trieste, northern Adriatic Sea. Mar Pollut Bull 42:36–44

Oros DR, Simoneit BRT (2000) Identification and emission rates of molecular tracers in coal smoke particulate matter. Fuel 79:515–536

Perra G, Renzi M, Guerranti C, Focardi S (2009) Polycyclic aromatic hydrocarbons pollution in sediments: distribution and sources in a lagoon system (Orbetello, Central Italy). Transitional Waters Bulletin 3:45–58

Peters CA, Knightes CD, Brown DG (1999) Long-term composition dynamics of PAH containing NAPLs and implications for risk assessment. Environ Sci Technol 33:4499–4507

Pierard C, Budzinski H, Guarrigues P (1996) Grain size distribution of polychlorobiphenyl in coastal sediment. Environ Sci Technol 30: 2776–2778

Pinto B, Pellegrini D, Gabellino M, Ausili A (1995) Harbour and coastal sediment chemistry and toxicity: a preliminary assessment of dredging activities. J Aquat Ecosyst Health 4:249–255

Qiao M, Wang CX, Huang SB, Wang DH, Wang ZJ (2006) Composition, sources and potential toxicological significance of PAHs in the surface sediments of the Meiliang Bay, Taihu Lake, China. Environ Int 32:28–33

Rachdawong P, Christensen ER (1997) Determination of PCB sources by a principal component method with nonnegative constraints. Environ Sci Technol 31:2686–2691

Rogge WF, Hildemann L, Mazurek MA, Cass GR, Simoneit BRT (1993) Sources of fine organic aerosol: 2. Noncatalyst and catalyst-equipped automobiles and heavy duty diesel trucks. Environ Sci Technol 27:636–651

Rossini P, Guerzoni S, Matteucci G, Gattolin M, Ferrari G, Raccanelli S (2005a) Atmospheric fall-out of POPs (PCDD-Fs, PCBs, HCB, PAHs) around the industrial district of Porto Marghera, Italy. Sci Total Environ 349:190–200

Rossini P, Guerzoni S, Molinaroli E, Rampazzo G, De Lazzari A, Zancanaro A (2005b) Atmospheric bulk deposition to the lagoon of Venice. Part I. Fluxes of metals, nutrients and organic contaminants. Environ Int 31:959–974

Rossini P, Matteucci G, Raccanelli S, Favotto M, Guerzoni S, Gattolin M (2007) Polycyclic aromatic hydrocarbons in atmospheric depositions around the Venice Lagoon. Polycycl Aromat Compd 27(3): 197–210

Sarretta A, Pillon S, Molinaroli E, Guerzoni S, Fontolan G (2010) Sediment budget in the Lagoon of Venice, Italy. Cont Shelf Res 30:934–949

Savinov VM, Savinova TN, Matishov GG, Dahle S, Næs K (2003) Polycyclic aromatic hydrocarbons (PAHs) and organochlorines (OCs) in bottom sediments of the Guba Pechenga, Barents Sea, Russia. Sci Total Environ 306:39–56

Scotti A (2005) Engineering interventions in Venice and in the Venice Lagoon. In: Fletcher CA, Spencer T (eds) Flooding and environmental challenges for Venice and its lagoon: state of knowledge. Cambridge University Press, UK, pp 245–255

Secco T, Pellizzato F, Sfriso A, Pavoni B (2005) The changing state of contamination in the Lagoon of Venice. Part 1: organic pollutants. Chemosphere 58:279–290

Soclo HH, Garrigues P, Ewald M (2000) Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. Mar Pollut Bull 40: 387–396

Sprovieri M, Feo ML, Prevedello L, Manta DS, Sammartino S, Tamburrino S, Marsella E (2007) Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy). Chemosphere 67:998–1009

Sulej AM, Polkowska Ż, Namieśnik J (2011) Contamination of runoff water at Gdańsk airport (Poland) by polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Sensors 11(12):11901–11920

Trabelsi S, Driss MR (2005) Polycyclic aromatic hydrocarbons in superficial coastal sediments from Bizerte Lagoon, Tunisia. Mar Pollut Bull 50(3):344–348

UNEP Chemicals (1999) Guidelines for the identification of PCBs and materials containing PCBs (PDF). United Nations Environment Programme. p. 40. Retrieved 2007-11-07

USEPA (United States Environmental Protection Agency) (1993) Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons, EPA/600/R-93/089

USEPA (United States Environmental Protection Agency) (2007a) Method 3546, Microwave Extraction, Revision 0

USEPA (United States Environmental Protection Agency) (2007b) Method 8082A, polychlorinated biphenyls (PCBs) by gas chromatography, Revision 1

Van Vleet ES, Fossato VU, Sherwin MR, Lovett HB, Dolci F (1988) Distribution of coprostanol, petroleum hydrocarbons, and chlorinated hydrocarbons in sediments from canals and coastal waters of Venice, Italy. Org Geochem 13(4):757–763

Vasilić Ž, Periš N, Wilken M, Drevenkar V (2004) Polychlorinated biphenyls, dibenzo-p-dioxins and dibenzofurans in soil samples from airport areas of Croatia. Int J Environ Anal Chem 84(14–15):1093–1103

Viñas L, Franco MA, Soriano JA, Gonzales JJ, Pon J, Albaiges J (2010) Sources and distribution of polycyclic aromatic hydrocarbons in sediments from the Spanish northern continental shelf. Assessment of spatial and temporal trends. Environ Pollut 158:1551–1560

Wang Z, Fingas M, Shu YY, Sigouin L, Landriault M, Lambert P, Turpin R, Campagna P, Mullin J (1999) Quantitative characterization of PAHs in burn residue and soot samples and differentiation of pyrogenic PAHs from petrogenic PAHs—the 1994 Mobile Burn Study. Environ Sci Technol 33:3100–3109

Yilmaz K, Yilmaz A, Yemenicioglu S, Sur M, Salihoglu I, Karabulut Z, Karakoc FT, Hatipoglu E, Gaines AF, Phillips D, Hewer A (1998) Polynuclear aromatic hydrocarbons (PAHs) in the eastern Mediterranean Sea. Mar Pollut Bull 36(11):922–925

Yunker MB, Macdonald RW (1995) Composition and origins of polycyclic aromatic hydrocarbons in the Mackenzie River and on the Beaufort Sea shelf. Arctic 48:118–129

Yunker MB, Macdonald RW (2003) Alkane and PAH depositional history, sources and fluxes in sediments from the Fraser River Basin and Strait of Georgia, Canada. Org Geochem 34:1429–1454

Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org Geochem 33(4):489–515

Zonta R, Argese E, Costa F, Zaggia L (1995) Useful tracer parameters to investigate the environmental conditions in areas of the Venice Lagoon. Wetl Ecol Manag 3:139–147. https://doi.org/10.1007/bf00180021

Zonta R, Zaggia L, Collavini F, Costa F, Scattolin M (2005a, UK) Sediment contamination assessment of the Venice canal network (Italy). In: Fletcher CA, Spencer T (eds) Flooding and environmental challenges for Venice and its lagoon: state of knowledge. Cambridge University Press, pp 603–615

Zonta R, Costa F, Collavini F, Zaggia L (2005b) Objectives and structure of the DRAIN project: an extensive study of the delivery from the drainage basin of the Venice Lagoon (Italy). Environ Int 31:923–928

Zonta R, Botter M, Cassin D, Pini R, Scattolin M, Zaggia L et al (2007) Sediment chemical contamination of a shallow water area close to the industrial zone of Porto Marghera (Venice Lagoon, Italy). Mar Pollut Bull 55:529–542

Zonta R, Botter M, Cassin D, Bellucci LG, Pini R, Dominik J (2018) Sediment texture and metal contamination in the Venice Lagoon (Italy): a snapshot before the installation of the MOSE system. Estuar Coast Shelf Sci. https://doi.org/10.1016/j.ecss.2018.03.007

Zuliani A, Zaggia L, Collavini F, Zonta R (2005) Freshwater discharge from the drainage basin to the Venice Lagoon (Italy). Environ Int 31:929–938