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# Determination of polychlorobiphenyl congeners (PCBs) in the surface water of the Venice lagoon

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## Abstract

The purpose of this study is to evaluate the degree of PCB contamination of Venice lagoon water. The PCB determination was made on the filtrate ("dissolved PCBs") and on the particulate collected on the filters ("particulate PCBs") by continuous liquid–liquid extraction and sonication, respectively, and by HRGC-LRMS analysis. An estimation of the procedural and "working" blanks was also made. Water samples were collected at six sites, selected to represent all the pollution situations present in the lagoon, and at a site in the Adriatic Sea. The range of the total sum ("dissolved plus particulate") of 49 congener concentrations falls between 355 and 1868 $\mathrm{pg\,l^{-1}}$; the "dissolved" fraction concentrations (250–792 $\mathrm{pg\,l^{-1}}$) are greater at six sites than that of the "particulate" fraction (105–1273 $\mathrm{pg\,l^{-1}}$). Chemometric analyses suggest that the PCB congener pattern in the Venice Lagoon is different from that in the Adriatic Sea.

*Keywords:* Venice lagoon; Water; Pollution; PCBs; GCMS; Chemometrics

## 1. Introduction

Polychlorinated biphenyls (Erickson, 1997) are a class of 209 man-made compounds with a biphenyl nucleus produced in complex mixtures (Schulz et al., 1989) with a different mean chlorination degree and used in numerous applications such as dielectric fluid in capacitors and transformers, hydraulic and heat transfer fluid and additives in pesticides, paints, copying papers, etc. World production (Breivik et al., 2002a) has been estimated at more than $1.3 \cdot 1^{-6}$ t with significant emissions (Breivik et al., 2002b) in the environment. These compounds feature a hydrophobic nature and high stability, which causes strong persistence in the environment. The degree of toxicity varies from congener to congener with values for some like those of dioxins. In the aquatic environment PCBs accumulate in sediments, particulate and biota.

The Venice Lagoon is a shallow basin, which covers an area of about 549 $\mathrm{km^2}$ along the northwest coast of the Adriatic Sea. Three entrances connect the sea to the lagoon, allowing the exchange of about 60% of the total water volume of the Lagoon each 12 h. Industrial, agricultural and urban sources cause a significant contamination level particularly in the central area. The salinity ranges from about 18 to about 36 according to distance from the lagoon inlets.

The monitoring of PCB in the Mediterranean Sea began in 1970 and has mainly focused on sediments and marine biota (Tolosa et al., 1997; Picer, 2000). However very few data have been reported on the PCB concentration in the water, particularly as regards the Adriatic Sea (Tolosa et al., 1997; Picer, 2000) and the Venice Lagoon (Moret et al., 2000).

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In this paper a methodology (Hermans et al., 1992) for the determination of PCB congener concentrations in sea water samples has been revised and used for the evaluation of the degree of contamination of Venice Lagoon water by this class of compounds. A comparison with the PCB congener concentration found in the Adriatic Sea is also made.

## 2. Materials and methods

PCBs are identified by number according to Ballschmiter and Zell (Ballschmiter and Zell, 1980).

The PCB determination was made by filtering water samples. So the PCBs were determined on the particulate collected on the filters and on the corresponding filtrate. The PCBs collected on the filters are referred to below as "particulate PCBs" and those present in the filtrate as "dissolved PCBs". The distinction is only operationally defined and the second fraction includes both the truly dissolved PCBs and those bound to material that passes through the pores of the filters.

The pentane, hexane and methylene chloride used in PCB analysis were pesticide grade (Lab-scan, Dublin, Ireland) and were used without further purification.

### *2.1. Sampling and sample treatment*

Seven water samples were collected at the end of February 2001 at six sites in the Venice lagoon and at one site in the Adriatic sea (Fig. 1). The sites were selected by subdividing the lagoon area on the basis of assumed diversities of inputs and pollution level. Site 1 is located south of the city of Venice between the island of Santo Spirito and the island of Lazaretto Vecchio and is representative of the central area of the lagoon. Site 2 is located in the urban zone (Grand Canal, opposite Ca' Rezzonico) and is affected by intensive motorboat traffic and input of untreated sewage. Site 3 is located between the Canale dei Petroli (a route for oil tankers) and the ruins of Cason Valgrande; the area is considered to be relatively unpolluted and is representative of the southern basin of the lagoon. Site 4 is located near the island of S. Giorgio in Alga and is representative of the industrial area; this area is regarded as very polluted. Site 5 is located between Marco Polo airport and the island of Carbonera; the area is polluted with agricultural inputs. Site 6 is located in the S. Felice canal near the Valle di Ca' Zane; this area is regarded as quite clean. Site 7 is located in the Adriatic Sea off the Lido island.

About 12 l of water were collected at each site by lowering an electric rotary pump (60 $l h^{-1}$) to a depth of approximately 50–60 cm below the surface and pumping the water into a stainless steel container. The sampling was carried out with the boat in slight motion and the engine stopped.

On return to the laboratory the water samples were filtered under vacuum using GF/F ($\sim$0.7 μm) glass filters (Whatman, Maidstone, UK), replacing the filter after every filtration of 2 l of water; so the particulate from 10 l water was gathered from five filters.

### *2.2. Extraction and clean-up*

The "dissolved PCBs" were obtained by continuous liquid–liquid extraction of 10 l of the filtrate for 24 h using 200 ml of a mixture of pentane–methylene chloride, 2 + 1 v/v.

The particulate matter was extracted in a closed flask by sonication (Branson 2210, Danbury, CT, USA) for 2 h using 60 ml of a pentane–methylene chloride mixture (2:1, v/v). The supernatant mixture was removed and joined to 2 × 10 ml of pentane–methylene chloride (2:1, v/v) used for washing the filters.

The extract solutions were dried by anhydrous $Na_2SO_4$, separated from $Na_2SO_4$ by decantation, joined

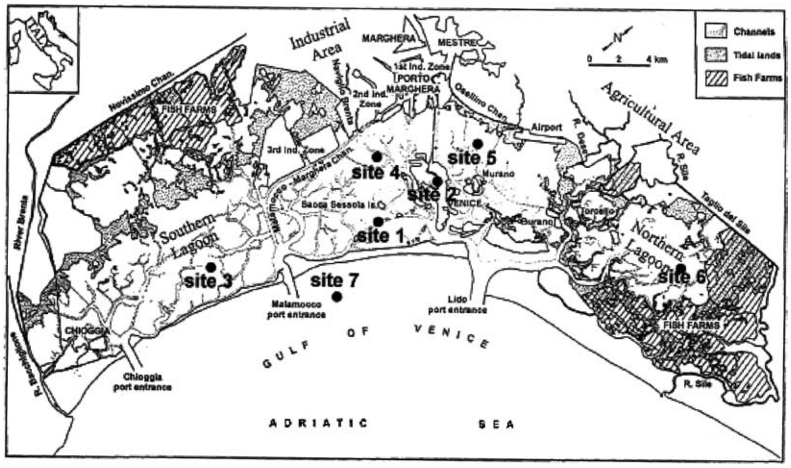

Fig. 1. Sampling sites in the Venice Lagoon, Italy.

to 2 × 10 ml of hexane used for washing the residual $Na_2SO_4$ and then reduced to 2 ml under a gentle stream of nitrogen and subjected to clean-up.

Before the extractions five carbon-13-labelled PCBs (PCB28, PCB52, PCB118, PCB153 and PCB180) were added to the water and particulate samples from a working solution (WS1) for use as internal standards in the quantification (isotope dilution GCMS), achieving a concentration of $60\,pg\,l^{-1}$ for each congener. In addition, for quality control, six PCBs (PCB30, PCB65, PCB96, PCB166, PCB189 and PCB199) were added to the samples prior to extraction from a working solution (WS2) achieving a concentration of $50\,pg\,l^{-1}$ for each compound. These PCBs have not been identified in previously analysed samples of Venice Lagoon water. The WS1 and WS2 solution was prepared by dissolving standard solutions of the PCBs (Dr Ehrenstorfer Gmbh, Augsburg, Germany) and of the carbon-13-labelled PCBs (EC-4058 mixture, Cambridge Isotope Laboratories, Andover, Massachusetts, USA) in tetrahydrofuran.

The clean-up (Erickson, 1997) of the filtrate and particulate extract solutions was performed by adsorption chromatography adding the 2 ml mixture to a glass column (*i.d.* = 6 mm) slurry packed with 2 cm (top) of pesticide grade Florisil RS 60–100 mesh (Carlo Erba, Milano, Italy) and with 1 cm (bottom) of Alumina Oxide 60 70–230 mesh (Merck, Darmstadt, Germany). Florisil and Alumina Oxide, previously washed with hexane and dichloromethane, were activated prior to use in a muffle furnace at 600 °C for 4 h. PCBs were eluted with *n*-hexane collecting 30 ml. The eluate was reduced to 100 ml under a gentle stream of nitrogen and analysed by gas chromatography–mass spectrometry (GCMS).

### 2.3. Instrumental analysis

Analyses were performed with a fused silica capillary column (HP5 - Trace Analysis, 60 m × 0.25 mm × 0.25 μm; Hewlett Packard, Avondale, PA, USA) installed in a Hewlett Packard Model 6890 Gaschromatograph coupled to a Hewlett Packard Model 5973 Mass Selective Detector (mass analyzer: quadrupole). The injector and the transfer line temperature were maintained at 280 °C; the oven temperature program was: 70 °C (1 min), $10\,°C\,min^{-1}$ to 150 °C, 10 min at 150 °C, $3\,°C\,min^{-1}$ to 280 °C, 30 min at 280 °C. The carrier gas (helium) flow was $0.8\,ml\,min^{-1}$ (constant flow mode) and the injection mode was pulsed splitless (carrier gas flow, $2.2\,ml\,min^{-1}$ for 3 min; split valve open after 1 min). Injection volume was 3 μl. Data were acquired in the electron impact (EI) mode (70 eV) using the selected ion monitoring (SIM) technique.

The GCMS performances were tested by injecting decreasing quantities of a solution of PCB65 (solvent: hexane); injection of 0.3 pg shows a peak with signal-to-noise ratio of about 5.

### 2.4. PCB quantification

Forty-nine PCB congeners (33 as single congener and 16 as pairs of congeners) were quantified by comparison of their peak area in the chromatogram with that of the $^{13}C_{12}$ labelled PCBs with an equal number of chlorine atoms; the concentration values obtained were corrected by a factor, $F_i$, that accounts for the diversity in the GCMS response of the PCB congeners (Moret et al., 2001).

The variability of this type of matrix makes it hard to define congener quantitation limits. A practical estimation indicates values of the congener detection limits of about $1\,pg\,l^{-1}$; this concentration value is equivalent to a peak area in the chromatogram of about 400 counts. Thus PCB congeners in samples were evaluated if the peak in the sample showed at least an area of about 400 counts.

Accuracy and repeatability were estimated using the six PCBs (working solution WS2) added to samples prior to extraction.

The PCB concentrations were reported as $pg\,l^{-1}$ of dissolved PCBs and $pg\,l^{-1}$ of PCBs bound to particulate matter present in 1 l of lagoon water. Furthermore in the following tables PCBs are reported in the order of elution from the HP5-trace-analysis column.

### 2.5. Working and procedural blanks

For the evaluation of the working blanks 22 l of lagoon water were collected from the Giudecca Canal, near our laboratory, using an electric rotary pump to obtain two samples of 10 l of filtrate and two samples of five filters of the particulate suspended matter.

The two 10 l filtrate aliquots were separately extracted in succession, replacing the extracting mixture in the extraction apparatus entirely with 200 ml of fresh solution five times at 24 h intervals. So five aliquots of extracting mixture were obtained for each experiment (5 + 5 in all), which were treated and analysed as reported above.

The two samples of five filters were extracted in succession four times with 60 ml aliquots of extracting mixture. The four aliquots of extracting mixture obtained for each experiment (4 + 4 in all) were treated and analysed as reported above for the lagoon water particulate samples.

For quantification purposes the five carbon-13-labelled PCBs (working solution WS1) were added for use as internal standards before the 2 × 5 extractions of lagoon water and before the 2 × 4 extraction of the particulate samples.

The evaluation of the procedural blanks were made subjecting 200 ml (filtrate analysis) and 60 ml (particulate analysis), at first used in the extraction of 5 ready to use filters, to complete analytical procedure.

### 2.6. Data analysis

Multivariate statistical analysis was made by the well-known techniques of Principal Component Analysis PCA) and of Cluster Analysis (Massart et al., 1988; Massart and Kaufman, 1983). The data processing was performed by the Statgraphics Plus 5.1 (Manugistics, Inc., Rockville, MD, USA) software package.

## 3. Results and discussion

### 3.1. Working blanks

The trends of the average values of the sums of 49 PCB concentrations (41 peaks), obtained from the two series of extractions of filtrate samples and of the corresponding particulate, are shown in Fig. 2.

In the case of the filtrate it can be observed that the fourth and the fifth extractions show similar values of the concentration sums (average, 22.5 pg l$^{-1}$). Seven PCBs (PCB66, PCB110, PCB149, PCB153, PCB132, PCB187 and PCB180) are the congeners present in the extracts and their concentrations represent a percentage, calculated as the average of the fourth and the fifth extractions, between 6% and 19% of the concentrations found in the sample (first extraction). The seven PCBs represent the working blank and the their sum constitutes about 2% of the total measured PCB concentration in the sample (first extraction, 1000 pg l$^{-1}$). The concentrations detected in the second and third extractions, greater than that found in the following, are probably due to the recovery of residual quantities of PCBs not recovered in the extracting mixture replacement and/or not extracted by the previous extractions. The procedural blank has been estimated to be 6 pg l$^{-1}$.

In the case of the particulate it can be observed that the third and fourth extractions show similar values of the concentration sum (44 and 39 pg l$^{-1}$), due to thirteen PCBs (PCB20 + 33, PCB52, PCB41 + 64, PCB66, PCB95, PCB99, PCB110, PCB149, PCB118, PCB153, PCB132, PCB187, PCB180). The concentrations of these congeners vary between 6% and 21% of that present in the sample (first extraction). These values represent the working blank and their sum is about 5% of the total measured PCB concentration in the sample (first extraction). The PCB concentration value obtained in the second extraction is slightly larger than that obtained in the two following extractions, probably due to the recovery of residual quantities of PCBs. Seven of the thirteen quantified PCBs are the same found in the working blank for “dissolved PCBs”. The procedural blank has been estimated to be 8 pg l$^{-1}$.

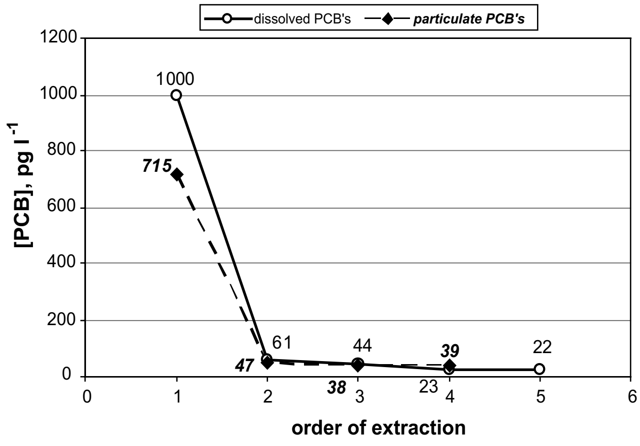

Fig. 2. Extraction curves obtained in the “working blank” evaluation of the “dissolved” PCBs and of the “particulate” PCBs.

### 3.2. Accuracy and repeatability

Accuracy and repeatability were estimated by addition of a quantity corresponding to 50 pg l$^{-1}$ of six PCBs from WS2 to the water and particulate samples, prior to extraction. The average concentrations determined in the seven filtrate and particulate samples, the relative errors and the relative standard deviations are reported in Table 1. The greatest values found for the relative error are those obtained for PCB166 in particulate samples and for PCB199 in both particulate and water samples. These PCBs are also those that show the greatest values for the relative standard deviations.

### 3.3. Lagoon surface water monitoring

The concentrations of the “dissolved” and of the “particulate” fractions together with that of the total PCB concentration, calculated as the sum of the “dissolved” and “particulate” fractions, are shown in Fig. 3. The ranges of the total and the “particulate” fraction concentrations are considerable and fall between 355 and 1868 pg l$^{-1}$ and between 99 and 1162 pg l$^{-1}$, respectively. This is due to site 3 which shows the highest concentration of the “particulate” fraction; however this sample featured a higher particulate matter content than that of the other sites, as roughly inferred from the sample filtration time. Site 5 and site 6 show the smallest “particulate” fraction concentrations; in these cases it is necessary to note that the working blank, as evaluated above, represents about 27% and 44% of the concentrations found. The “dissolved” fraction concentrations are, with the exception of site 3, larger than those of the corresponding “particulate” fractions and the range is between 250 and 792 pg l$^{-1}$. The highest value is found in the site 2 (urban zone) and this agrees with the findings of our study of the sediment contamination by PCB (Moret et al., 2001). As expected, site 6 shows the smallest value. The concentrations found in the Adriatic Sea sample are similar to that found in the la-

Table 1
Average, relative error (E.R.) and relative standard deviation (R.S.D.) of concentrations of six PCBs ($\mathrm{pg\,l^{-1}}$) added to filtrate and particulate of the seven site samples

| PCB | Filtrate | | | Particulate | | |
|---|---|---|---|---|---|---|
| | Average | R.E., % | R.S.D., % | Average | R.E., % | R.S.D., % |
| 30 | 49.6 | −0.9 | 6.9 | 49.3 | −1.5 | 5.1 |
| 65 | 52.9 | +5.8 | 7.0 | 52.2 | +4.3 | 5.4 |
| 96 | 50.3 | +0.6 | 6.2 | 51.4 | +2.8 | 7.2 |
| 166 | 47.3 | −5.4 | 10.2 | 45.1 | −9.8 | 11.0 |
| 189 | 49.3 | −1.3 | 7.8 | 49.8 | −0.4 | 8.0 |
| 199 | 44.3 | −11.4 | 8.6 | 44.4 | −11.3 | 12.1 |

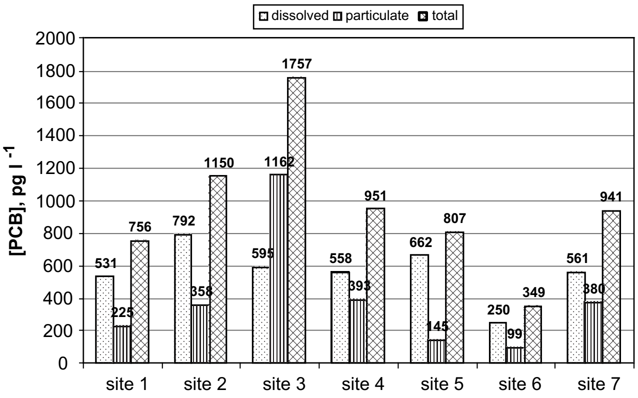

Fig. 3. "Dissolved" and "particulate" ∑PCB concentrations and total concentrations found at the seven sites in the Venice Lagoon.

goon water. These values are difficult to compare with the scarce data available on the Mediterranean sea, owing to different analytical and quantification procedures, different sampling sites and different times. The concentrations found are generally higher than ours, but also smaller, as for example in the work of Schulz-Bull et al., 1997; in this case the values are very low for the PCBs in "solution" (range: 1.7–43.9 $\mathrm{pg\,dm^3}$) and comparable to our data for the total PCBs in "suspension" (range: 190.0–615.0 $\mathrm{pg\,dm^3}$).

The congener concentrations found in the "particulate" and "dissolved" fractions of the seven samples are reported in Table 2; Figs. 4 and 5 show the homolog profiles. It can be observed that the low degree chlorination PCBs are predominant in the filtrate and the greater degree in the particulate: PCBs 17, 31 + 28, 20 + 33, 52, 44, 95, 90 + 101, 110, 149, 153, are those with a higher percentage presence in filtrate while PCBs 66, 95, 90 + 101, 110, 148, 118, 153, 138 are more present in the particulate. The homolog profiles of site 7 are an exception since they are similar and centred on the pentachloro homolog.

Table 3 reports the Euclidean distances between the sites in the multidimensional space generated by the "dissolved PCBs" matrix and by the "particulate PCBs" matrix; the data have been standardized. Considering the "dissolved PCBs" it can be observed that site 6 (the sample with the lowest value of summed PCB concentration) is, in the multidimensional space, the furthest from all the other samples; sites 1 and 4 are the closest and therefore probably the most similar. In the case of the "particulate PCBs" site 3 (the sample with the highest summed PCB concentration) is the furthest from the other samples; sites 2 and 4 are the closest and therefore probably the most similar. For all the other sites Euclidean distances highlight differences or similarities which are not characteristic.

Analysing the "dissolved PCB" data set by Principal Component Analysis (PCA) from the correlation matrix, obtained using the congener concentrations as variables and the sites as objects, it is found that the first six Principal Components (PC) explain 99.999% of the total variance, indicating that the variables (41 PCB concentrations) are quite closely correlated; the first three PCs account for 54.96%, 18.06% and 11.73% of the total variance (sum: 84.75%). The score plot obtained by the first three PCs is reported in Fig. 6. It can be noted that: on the first PC site 2 and site 6 differ from the others, which form a cluster; sites 3 and 5 differ on the second PC; site 7 differs from the others on the third PC. The fact that site 2 and site 6 are the samples that show the highest and the lowest summed concentration values suggests that the first PC considers the differences in the PCB concentrations; all the variables influence this component (loading range: 0.059–0.206) with the exception of PCB187 (loading: 0.001). PC2 and PC3 seem to consider differences in PCB concentration pattern; so sites 3 and 5 show the characteristic summed concentration values of the hexachloro homolog (Fig. 4) and site 7 a characteristic contour of the homolog concentrations. Confirmation can be found in Table 4, which reports the correlation coefficient matrix obtained from the same data matrix regarding the sites as variables and the PCBs as objects. It can be observed that sites 3 and 7 show low correlation coefficients with the other sites, especially with site 5; correlation coefficients of site 6 are greater than those of sites 3 and 7 but still lower than 0.9.

The dendrogram (not reported here) obtained by analysing the data by cluster analysis (nearest neighbor

Table 2
PCB congener concentrations (pg l$^{-1}$) found in the filtrate (f) and particulate (p) of the lagoon water samples

| PCB | Site 1 | | Site 2 | | Site 3 | | Site 4 | | Site 5 | | Site 6 | | Site 7 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | f | p | f | p | f | p | f | p | f | p | f | p | f | p |
| 18 | 13 | – | 24 | – | 24 | – | 19 | – | – | – | 8 | – | 22 | – |
| 17 | 53 | – | 80 | – | 58 | – | 55 | – | 84 | 4 | 43 | – | 5 | 2 |
| 31 + 28 | 15 | 4 | 29 | 7 | 29 | – | 22 | 8 | 16 | – | 9 | – | 40 | 20 |
| 20 + 33 | 23 | 3 | 32 | 2 | 29 | – | 26 | – | 27 | – | 10 | – | 17 | 16 |
| 52 | 30 | 7 | 59 | 15 | 42 | 22 | 51 | 15 | 38 | 8 | 14 | 4 | 28 | 16 |
| 49 | 18 | 3 | 32 | 10 | 25 | 15 | 18 | 8 | 23 | 5 | 7 | 1 | 12 | 9 |
| 44 | 20 | 4 | 31 | 10 | 31 | 14 | 24 | 8 | 20 | 3 | 12 | 2 | 19 | 13 |
| 41 + 64 | 9 | 3 | 14 | 7 | 18 | 9 | 12 | 7 | 2 | 3 | 5 | – | 17 | 14 |
| 74 | 7 | 3 | 11 | 6 | 12 | 14 | 10 | 8 | 10 | 4 | 3 | 3 | 7 | 6 |
| 70 | 17 | 7 | 25 | 13 | 21 | 27 | 18 | 15 | 22 | 6 | 10 | 20 | 24 | 18 |
| 66 | 9 | 5 | 14 | 7 | 18 | 22 | 12 | 12 | 12 | – | 5 | 6 | 13 | 15 |
| 95 | 20 | 10 | 32 | 17 | 28 | 60 | 26 | 18 | 22 | 9 | 11 | – | 32 | 15 |
| 91 | 6 | 2 | 5 | 5 | 5 | 8 | 4 | 4 | – | 2 | 1 | – | 5 | 3 |
| 60 + 56 | 3 | – | 6 | 3 | 5 | 8 | 2 | 3 | 6 | 1 | – | – | 8 | 6 |
| 92 | 7 | 3 | 7 | 5 | 7 | 18 | 6 | 6 | 7 | 3 | 3 | – | 6 | 4 |
| 84 | 6 | – | 8 | – | 8 | 12 | 6 | 6 | 8 | 3 | 2 | 8 | 9 | 6 |
| 90 + 101 | 28 | 12 | 38 | 26 | 32 | 79 | 32 | 26 | 29 | 12 | 14 | 3 | 37 | 23 |
| 99 | 12 | 7 | 16 | 17 | 14 | 41 | 13 | 15 | 14 | 7 | – | – | 12 | 12 |
| 97 | 9 | 5 | 11 | 9 | 8 | 25 | 7 | 6 | 9 | 3 | 2 | 1 | 10 | 11 |
| 87 + 115 | 9 | 6 | 12 | 10 | 10 | 27 | 8 | 10 | 12 | 4 | 5 | – | 14 | 11 |
| 85 | 6 | 2 | 6 | 3 | 6 | 15 | 2 | 4 | 4 | 2 | 2 | 2 | 6 | 6 |
| 136 | 5 | 3 | 6 | 4 | 5 | 12 | 4 | 3 | 5 | 2 | 3 | 6 | 6 | 4 |
| 110 | 28 | 14 | 37 | 32 | 29 | 87 | 30 | 26 | 26 | 12 | 11 | 3 | 32 | 26 |
| 151 | 9 | 5 | 12 | 9 | 7 | 21 | 9 | 7 | 13 | 3 | 4 | 1 | 11 | 7 |
| 135 | 5 | 2 | 5 | 4 | 4 | 17 | 4 | 4 | 4 | 1 | 2 | 7 | 4 | 4 |
| 149 | 24 | 11 | 29 | 23 | 21 | 78 | 20 | 20 | 27 | 8 | 10 | 6 | 27 | 16 |
| 118 | 18 | 12 | 25 | 35 | 19 | 111 | 20 | 23 | 22 | 13 | 8 | 2 | 17 | 23 |
| 146 | 5 | 4 | 2 | 6 | 5 | 20 | 5 | 6 | 4 | – | – | 13 | 4 | 3 |
| 153 | 37 | 26 | 46 | 45 | 7 | 136 | 28 | 42 | 55 | 20 | 19 | – | 30 | 15 |
| 132 | 7 | 6 | 11 | 8 | – | 29 | 4 | 8 | 10 | 2 | 4 | – | 12 | 8 |
| 105 | 7 | 3 | 9 | 8 | 7 | 43 | 6 | 8 | 7 | 4 | 1 | 3 | 5 | 12 |
| 141 | 12 | 6 | 11 | – | 5 | 26 | 6 | 8 | 15 | 2 | – | 2 | 8 | 5 |
| 179 | 3 | 1 | 5 | 2 | – | 5 | 2 | 2 | 4 | – | – | – | 5 | 3 |
| 176 | 1 | 2 | 0 | 2 | – | 2 | 1 | 1 | 3 | – | – | 9 | 1 | – |
| 138 | 30 | 25 | 43 | 9 | 5 | 147 | 27 | 33 | 47 | – | 4 | 1 | 11 | 11 |
| 158 | 4 | 3 | 6 | – | – | 16 | 2 | 6 | 6 | 4 | 3 | – | 8 | 4 |
| 187 | 9 | 6 | 12 | 8 | 43 | 19 | 6 | 10 | 17 | 3 | 15 | – | 11 | 11 |
| 183 | 4 | 1 | 6 | 4 | – | 7 | 2 | 2 | 6 | – | – | – | 5 | 4 |
| 128 + 167 | 3 | 11 | 6 | 8 | – | 37 | 3 | 7 | – | – | – | – | – | 2 |
| 180 | – | 6 | 21 | 14 | 8 | 28 | 6 | 14 | 26 | 5 | – | – | 20 | 18 |
| 170 + 190 | – | 4 | 8 | 0 | – | 16 | – | 7 | – | – | – | – | 1 | 1 |

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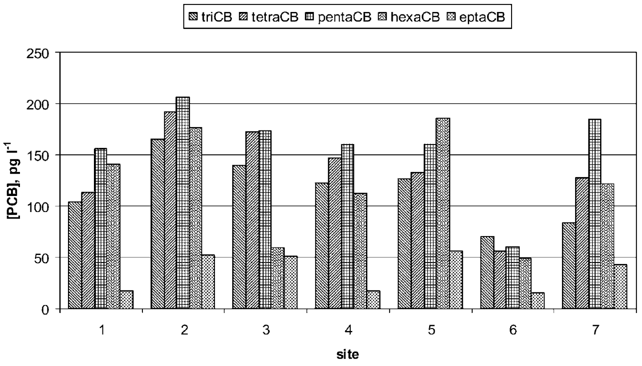

Fig. 4. Homolog profiles of the "dissolved" PCBs at the seven sites in the Venice Lagoon.

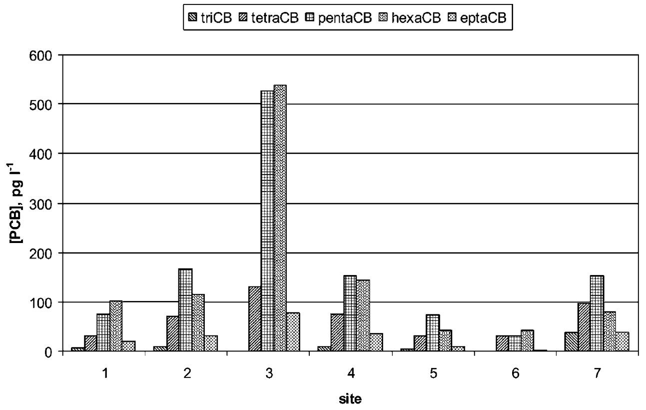

Fig. 5. Homolog profiles of the "particulate" PCBs at the seven sites in the Venice Lagoon.

Table 3
Euclidean distances between the sites in the multidimensional space generated from the "dissolved PCB" matrix and (in italics) from "particulate PCB" matrix

| | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 | Site 6 | Site 7 |
|---|---|---|---|---|---|---|---|
| Site 1 | – | *4.20* | *14.80* | *4.17* | *3.96* | *3.96* | *6.87* |
| Site 2 | 7.430 | – | *12.40* | *3.03* | *5.84* | *6.67* | *5.07* |
| Site 3 | 7.070 | 8.602 | – | *11.78* | *16.07* | *16.93* | *12.76* |
| Site 4 | 4.351 | 7.658 | 5.804 | – | *5.49* | *6.27* | *4.72* |
| Site 5 | 6.235 | 7.611 | 9.323 | 7.024 | – | *4.41* | *7.29* |
| Site 6 | 10.383 | 15.510 | 12.179 | 9.919 | 12.756 | – | *8.31* |
| Site 7 | 6.591 | 7.506 | 8.034 | 7.314 | 7.686 | 12.798 | – |

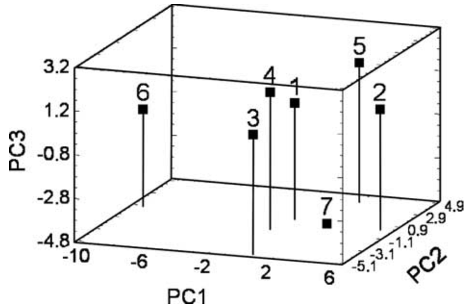

Fig. 6. Three-dimensional principal component score plot obtained from the data correlation matrix of the seven samples of filtrate.

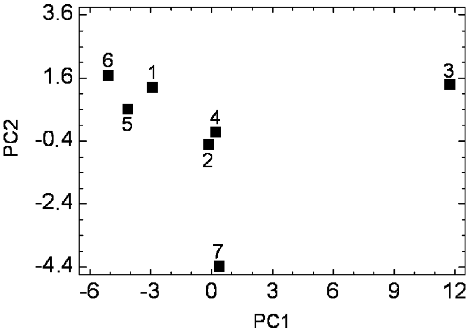

Fig. 7. Two-dimensional principal component score plot obtained from the data correlation matrix of the seven samples of particulate.

method) leads to similar conclusions, showing again that the most different sites are site 6, site 2 and site 7.

Analysing the "particulate PCB" data set by PCA from the correlation matrix, obtained using the congener concentrations as variables and the sites as objects, it is found that the first six PCs account for 100.00% of the total variance, indicating that also in this case the variables are quite closely correlated; the first two PCs account for 77.04% and 10.93% (sum: 87.97%) of the total variance. The score plot obtained by the first two PCs is reported in Fig. 7. As previously, it can be noted that the first PC considers the differences in the PCB concentrations at the sites with the highest value at site 3 and the lowest at site 5 and site 6; all the variables influence this component (loading range: 0.053–0.177) with the exception of PCB31 + 28 and PCB20 + 33. These PCBs influence the second PC with loading values of −0.459 and 0.436, respectively; this justifies the difference of site 7 on the second component. In this case the correlation matrix (Table 4) obtained from the same data matrix regarding the sites as variables and the PCBs as objects shows correlation levels lower than those found in the "dissolved PCB" case; in particular site 6 and site 7 show low correlation with the other sites.

The dendrogram (not reported here) obtained analysing the data by cluster analysis (nearest neighbor method) again shows a separation of site 3 and site 7 and two clusters consisting of sites 1, 5 and 6 and sites 2, 4.

## 4. Conclusions

The analysis of water samples collected in the Venice Lagoon shows a PCB pollution level similar to that found in the North Adriatic Sea sample with the exception of the sample collected in the Northern Lagoon.

Table 4
Correlation matrix obtained from "dissolved PCBs" and (in italics) "particulate PCBs" data set using sites as variables

| | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 | Site 6 | Site 7 |
|---|---|---|---|---|---|---|---|
| Site 1 | – | *0.754* | *0.938* | *0.935* | *0.616* | *0.623* | *0.487* |
| Site 2 | 0.950 | – | *0.791* | *0.861* | *0.913* | *0.557* | *0.723* |
| Site 3 | 0.720 | 0.772 | – | *0.932* | *0.676* | *0.617* | *0.510* |
| Site 4 | 0.937 | 0.970 | 0.815 | – | *0.777* | *0.690* | *0.646* |
| Site 5 | 0.917 | 0.920 | 0.625 | 0.842 | – | *0.452* | *0.620* |
| Site 6 | 0.869 | 0.857 | 0.826 | 0.829 | 0.841 | – | *0.450* |
| Site 7 | 0.534 | 0.572 | 0.544 | 0.616 | 0.397 | 0.407 | – |

Some differences have been highlighted both in the "dissolved PCB" fraction and in the "particulate PCB" fraction. In particular it can be stated that site 7 (North Adriatic sea) appears to be different from all the other sites, fact which is ascribable to a different pattern of homolog concentrations. This finding indicates a different source of the PCB pollution for the Venice lagoon.

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