Polychlorinated biphenyls in sediments of the Venice Lagoon and their toxicity with respect to other organic microcontaminants

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Introduction

Concentrations of polychlorinated biphenyls (PCBs) in sediments of the Venice Lagoon were first provided by Orio e Donazzolo (1987). They found that PCBs showed the highest concentrations in sediments from locations close to the industrial area of Porto Marghera, and that values increase constantly starting from the beginning of the 1950s, up to a maximum at the surface, approximately in 1982. Since then, other authors have discussed the presence of PCBs in sediments of the Venice Lagoon and other toxic micropollutants have been taken into consideration (Marcomini et al., 1997, and references therein). Recently, di Domenico et al. (1998) presented a summary of the results they obtained since 1992 studying heavy metal and organic micropollutant contamination (PCDDs, PCDFs, PCBs, DDE, DDT, HCB, PAHs). According to these authors, PCB concentrations show a more uniform distribution with respect to other contaminants. They found high concentrations inside both the industrial and the urban areas, with maximum values in the Ovest Industrial Channel and the Malamocco-Marghera Channel. We addressed similar problems on the basis of a more complete sampling and a greater attention to the resolution of the sediment record in terms of the thickness of the surficial layer. The aim of this paper is to discuss part of our results, with a special emphasis on PCB distribution and composition, in order to assess the principal sources. The problem of PCB toxicity, with respect to other contaminants such as dioxins and furans, is also addressed.

Materials and methods

Study area and sampling locations are shown in Fig. 1. Sediments were collected in the period 1996-1998 using either a manual piston core or a small gravity corer. All cores were extruded immediately after collection to obtain mostly 2 cm thick sections which were put in glass jars with aluminum foil caps. In a few cases sections were thicker, due to the lower sediment cohesivity. Samples were then frozen and stored at -18°C until the analysis. A separate core was taken at each location for other determinations.

PCB analyses were carried out using established HRGC-HRMS methods. Sediments were lyophilised, spiked with a series of four ^{13}C-labeled PCB isomers as internal standards (EC1400 Cambridge Isotope Laboratories, Woburn, MA) and soxhtlet extracted with toluene (EPA 3540). The sample extracts were transferred to hexane, treated with sulphuric acid (98%) and potassium hydroxide (20%) in a separatory funnel and then cleaned up using the automatic three column system, Dioxin Prep (Fluid Management System Inc.). Pre-packed disposable columns containing multilayer silica, alumina and carbon were used. PCB concentrations were calculated with respect to Aroclor (the mixture 1254+1260 1:1 represents the average composition of lagoon samples), and as a sum congeners. We considered the twelve congeners whose standards were available at

the time of the analyses (from three- to octa-CB). Four of them turned out to be dioxin-like PCBs. Here we present the results relative to the eight most relevant surficial samples: other surficial concentrations and the chronology of sediment contamination will be discussed elsewhere.

Results and discussion

Results are shown in the form of histograms in Figs. 1 and 2. The contamination of channel sediments is high, with the exceptions of the samples collected in the Sud Industrial Channel and in the Malamocco-Marghera Channel, reaching in many cases values higher than 100 μg kg^{-1}. The highest concentration was found in the Brentella Channel (2048 μg kg^{-1}) within the 1st Industrial Area. This particular location is characterised also by the maximum values of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzo furans (PCDFs) as shown by Bellucci et al. (submitted). Other locations in the 1st Industrial Area, such as the Nord Industrial Channel and the Salso Channel, do not show comparable concentrations, thus suggesting first a particular source in the Brentella Channel and, second, a limited mobility of PCBs discharged there. Surficial samples from lagoon sites are 11-205 times less contaminated with respect to the maxima found within the 1st Industrial Area. The huge difference between these concentrations confirms that the natural transfer of sediments within the industrial area and to the lagoon is not efficient.

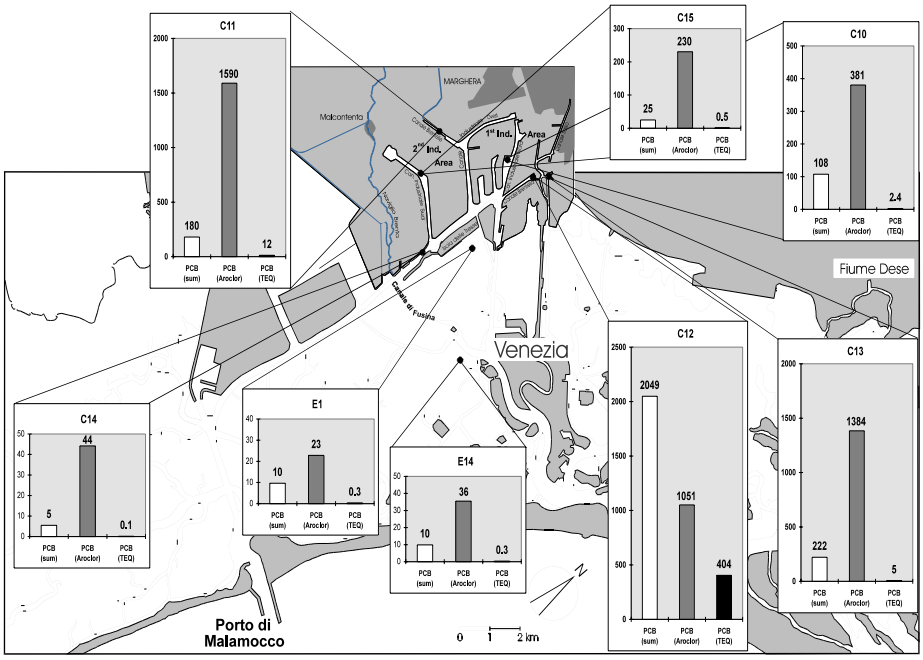

Fig. 1 - Comparison of PCB concentrations in surficial sediments, as sum of congeners, Aroclor (1254+1260 1:1) and TEQs. Concentrations are in μg kg^{-1}, TEQs in ng kg^{-1}.

As expected, the different methods used to calculate PCB concentrations provide different results: when expressed as Aroclor values are even an order of magnitude higher than the correspondent sum of congeners (as the data above). This latter, in fact, quantifies only the more toxic congeners,

and does not take into account some constituents of PCB commercial mixtures. However, the comparison between the two series of data permits some interesting observations: PCB concentrations, as sum of congeners, peak in the Brentella Channel, whereas concentrations as Aroclor follow a different pattern, in that the highest values are those relative to samples taken from channels Brentelle, Brentella and Salso, in the order. The congener profiles of Fig. 2 show that the relative importance of dioxin-like congeners in these channels is different: sample C12, taken from the Brentella Channel has a peculiar composition, with a relevant content of light PCBs. The sediment from the Salso Channel also shows a prevalence of the same fraction, whereas the other sites are characterised by a mixture of light and heavy PCBs. The sample taken at C11, in the Brentelle Channel is relatively low in light PCBs and probably rich in congeners that are not included in our set of standards. This prevalence of heavy congeners in the Brentelle Channel is probably due to some contribution from the Lusore Channel, which crosses inland urban and industrial zones. Surficial sediments at the lagoon sites E1 and E14 show the same PCB concentrations, as sum of congeners, but the value calculated as Aroclor is significantly higher at E14, thus suggesting the influence of different sources with an urban component, as hypothesised for C11.

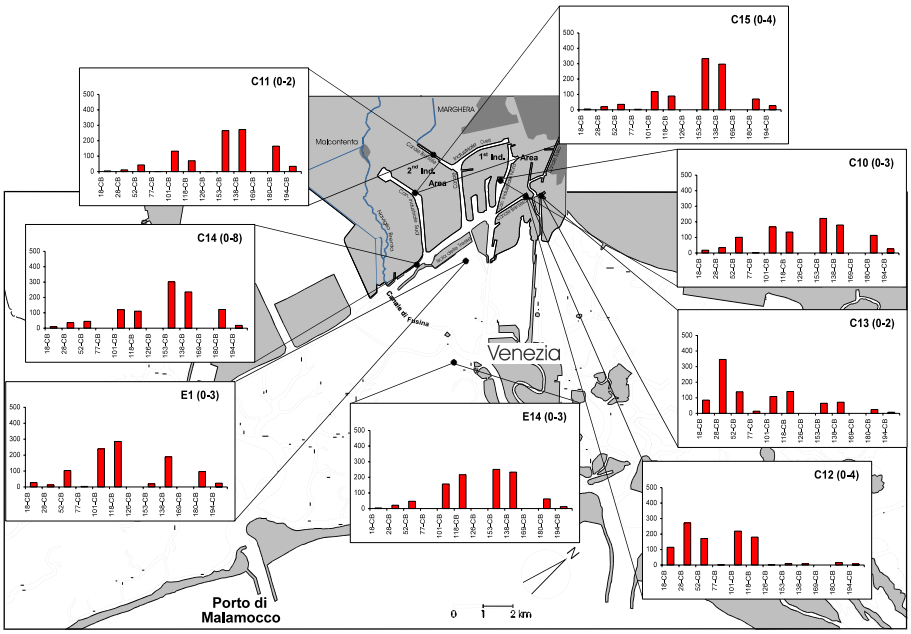

Fig. 2 - Congener profiles of PCBs in samples from the Venice Lagoon and the industrial channels.

In conclusion, the results of the two methods of calculating PCB concentrations and the congener profiles account for the influence different sources. Di Domenico et al. (1998) had suggested, on the basis of data that showed a fairly homogeneous pattern, that PCBs were related to a generic anthropogenic impact, both civil and industrial without evident distinctions. Our evidences, based

on both PCB concentration and composition, indicate that a particularly strong source was located within the 1st Industrial Area, with a probable direct discharge in the Brentella Channel.

Lately, much emphasis has been put on PCDDs and PCDFs, which have been considered the most dangerous pollutants. Since concentrations of PCBs are one to three order of magnitude higher with respect to PCDD/Fs, it is of some interest to compare the two classes of compounds on the basis of their toxicity. The international toxicity equivalency factors (TEFs) for some analysed congeners are unknown. Assuming for these TEFs a value of 10^{-5}, the TEQs of PCBs at C11, C12 and C13 are 12, 404 and 5 ng kg^{-1} dw, respectively. At the same sites PCDD/Fs give values of 24, 2857 and 566 ng kg^{-1} dw (Bellucci et al., submitted). Therefore, despite the high concentrations, TEQs of PCBs are comparable, for the less contaminated samples, or lower than those relative to PCDD/Fs. Our results, however, indicate that the sediments of the industrial area constitute a dangerous potential source of contaminants to the lagoon system.

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