POLYCHLORINATED BIPHENYLS IN SEDIMENT CORES FROM THE NORTHERN VENICE LAGOON

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Introduction

The knowledge of Venice Lagoon sediments contaminated by polychlorinated biphenyls (PCBs) has greatly improved in the last years. Following the pioneer work of Orio and Donazzolo[1], information was provided by several authors [2-6]. In particular, the results show that the canals of the industrial area are highly contaminated (up to 41,639 μg kg^{-1}) but the highest concentrations in lagoon sediments are much lower, ranging between 0.3 and 77 μg kg^{-1}. Furthermore, sediment chronologies[3,6] show that the inputs peaked in the 1970s and early 1980s, with just one recent contaminating event[6], and present trends suggest a decrease of the inputs due to environmental regulations and closure of many industrial plants. However, despite this fairly recent information, several aspects of PCB contamination remain to be explored. In particular, most of the available data were calculated with respect to both Aroclor (the mixture 1254+1260 1:1 represent the average composition of PCBs in sediments of the Venetian area) and as a sum of a limited number of congeners. Frignani et al.[5,6] discussed the results obtained from a wide series of both surficial and core samples and reported the congener profile is not the same everywhere: a mixture with a significant component of less chlorinated PCBs contaminates two of the industrial canals. This paper discusses the PCB contamination in a zone of the northern Venice Lagoon not subject to direct PCB sources, in comparison with a polluted industrial canal. In this case PCB total concentrations were obtained by the quantification of all PCB congeners. The temporal evolution of the PCB delivery to the environment is obtained from concentration depth profiles in sediment cores.

Study area, sampling and analytical methods

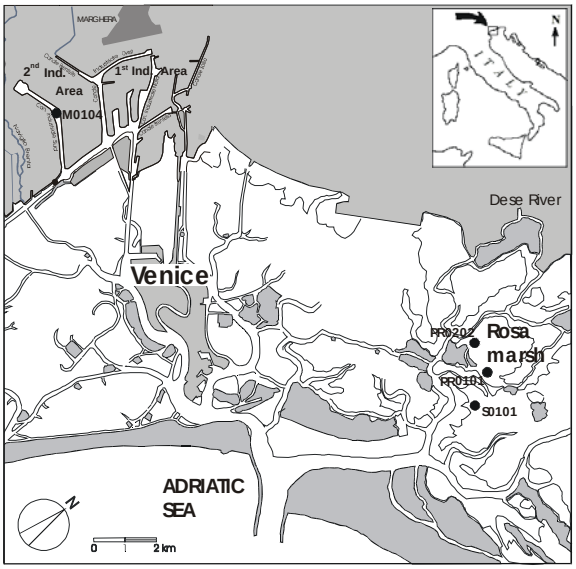
Samples were obtained in June 2000 and January 2001 from the locations shown in Fig. 1. We collected a core in the Sud Industrial Canal (M0104A) because it is heavily polluted by PCBs[6]. Two cores were also taken from the Palude della Rosa (PR0101B and PR0202A), which is a brackish water mud flat were several experiments were performed to study suitable methods of environmental recovery[7]. Another core was taken from the nearby Scanello Channel (S0101B) because it represents a rather different setting within the area.

Sampling was carried out in May 1996 (E1) and March 1997 (C11) by means of a manual piston corer. Cores were immediately frozen and stored at -18°C. Before the analysis cores were extruded and cut to obtain 2-10 cm thick sections. These were dried at room temperature, then homogenized and extracted in a sonication bath with 50 ml of a mixture of pesticide grade n-hexane-dichloromethane (4:1, v/v). The solution, was dried by anhydrous Na_2SO_4 and reduced to 25 ml under a gentle stream of nitrogen. After sulfur removal by several treatment with 2 ml of

mercury, the extracts were purified by solid-liquid chromatography (stationary phase Alumina Oxyde/Florisil, eluent n-exane) and then reduced to 0.5 ml. PCB analyses were carried out by HRGC-LRMS following Moret et al.[8]. PCB concentrations were calculated as a sum of 54 congeners (45 chromatographic peaks). Precision is typically 5 %, whereas the deviation with respect to the certified standards (NIST®, standard Reference Material 1941a) is always lower than 10 %.

Inferences on sediment chronologies were obtained from activity-depth profiles of ^{210}Pb and ^{137}Cs, which were determined by alpha counting of ^{210}Po and non destructive gamma spectrometry[6], respectively. Organic carbon (OC) contents were determined using a CHN analyzer, after elimination of the carbonate fraction with HCl directly in a silver capsule. Grain size analyses were carried out by wet sieving, after a pre-treatment with H_2O_2. All concentrations were calculated with respect to dry weight.

Figure 1: **Study area and sampling locations.**



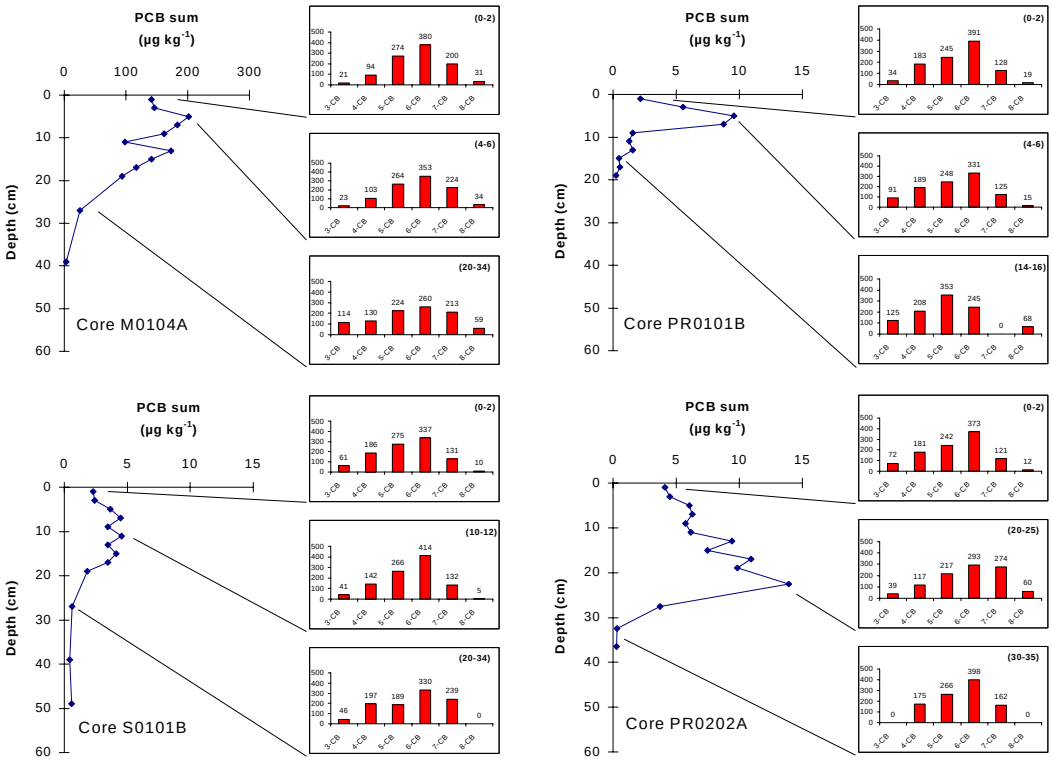
Results and Discussion

Sediment features. Sampled sediments are mainly fine (silt or clayey silt) with layers of sandy silt. The coarser sediment is located at depth in core M0104A with a content of 35 % of sand that accounts for the influence of a relatively intense water dynamics. OC concentrations range from 0.73 to 2.93 % in cores PR0101B and PR0202A, with the highest values in the latter. However, none of these parameters suggest major discontinuities.

PCB distributions. PCB downcore distributions are displayed in Fig. 2. PCB concentrations in the industrial canal range between 3.4 and 202 μg kg^{-1}. The values in sediments of in the northern lagoon are much lower: from close to detection limits to 4.6, 8.8 and 13.9 μg kg^{-1} in cores S0101B, PR0101B and PR0202A, respectively. The concentration-depth profiles of the four cores are rather different and two of them present a clear peak value. As already reported for other

sediments[5,6], neither grain size nor organic carbon drive the downcore distribution of PCBs. Therefore, trends in pollutant delivery are more effective than changes in sediment characteristics. The depth profile in core M0104A shows two peak values but the environment is likely disturbed and the pattern may not be a function of the chronology of the inputs. The distribution at S0101B is characterized by several maximums distributed between 4 and 18 cm depth. This pattern can be due to the effects of bioturbation or physical mixing, as revealed by radiotracer profiles.

Fig. 2: PCB downcore distributions and homologue profiles at the four study sites.



Core PR0101B contains a low ^{137}Cs inventory: 0.05 vs. 0.10-0.12 Bq cm^{-2} reported by Frignani et al.[9] for salt marsh sediments of the northern lagoon. This evidence, and the lack of a Chernobyl peak, suggest that this sediment has lost its upper part. Both the ^{210}Pb depth profile and what seems the bomb testing peak (1963) suggest an accumulation rate of 0.46 cm y^{-1} and the peak contamination can thus be dated back to 1953-1959. On the other hand the peak values in core PR0202A were found at ca. 25 cm depth that corresponds, assuming the above accumulation rate, to the end of the 1950s. The concentrations remain relatively high until the middle 1970s. Regarding this, it must be noted that the accumulation rate could be overestimated because no attempt was made to account for the effect of mixing and bioturbation. Furthermore, we know that

low concentrations can be found before the 1930s, when these compounds were first commercialized. In fact, these chemicals were the undesirable by-products of highly polluting industries, present within the 1st Industrial Area since the early 1920s.
Homologue profiles. The congener concentrations were grouped to obtain profiles such as those of Fig. 2 that show the permil contribution of homologues to the PCB assemblage. In core M0104A the patterns of homologues suggest a decrease, over time, of the relative contribution of 5-, 6- and 7-CBs. Meanwhile the 6-CBs dominate (>30 %) down to 20 cm depth where they decrease and contemporarily 3-, 4- and 8-CBs increase. These changes may not be due only to processes of anaerobic degradation, which are supposed to produce only less chlorinated congeners. In core PR0101B the homologue profiles show again the decrease of the less chlorinated congeners and increase of the heavier fractions. Homologue profiles of cores S0101B and PR0202A also show minor but significant changes through time. These variations are more evident in core PR0202A where at 35 cm depth the 3- and 8-CBs disappear.
In conclusion, the results confirm that a profound difference exists between the contamination of sediments from the industrial district and the lagoon. This contamination reached maximum values in the 1960s and 1979s and is decreasing since then. The patterns of congeners show that the effects of anaerobic degradation are not very important and probably the differences could be in part attributable to the composition of the inputs and hence of the sources. The lack of a consistent portion of upper sediment at station PR0101B is probably the effect of the recovery experiment carried out in the Palude della Rosa in the 1990s.

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