DISTRIBUTION OF POLYCHLORINATED BIPHENYLS IN DATED SEDIMENTS CORES FROM THE VENICE LAGOON AND THE INDUSTRIAL AREA OF PORTO MARGHERA

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Introduction

Data on the contamination of sediments of the Venice Lagoon by polychlorinated biphenyls (PCBs) have been provided by several authors[1-5]. In particular, the results provided by di Domenico et al.[3] show a high contamination within the canals of the industrial area (up to 5500 µg kg^{-1}) and moderate values in lagoon sediments (from 0.3 to 77 µg kg^{-1}). Furthermore, the PCBs present in the canals of Venice (290-610 µg kg^{-1}) can have concentrations that are at least one order of magnitude higher than in a sample taken in front of the industrial area of Porto Marghera (13 µg kg^{-1}). More recently, Frignani et al.[4] discussed the results obtained from a wide series of surficial samples. They found that the congener profile is not the same everywhere: a mixture with a significant component of less chlorinated PCBs contaminates the canals Brentella and Salso, within the 1st industrial area. Marcomini et al.[5] discussed PCB distributions in three cores representing industrial, urban (Venice) and lagoon environments. They found maximum values in the period between the end of the 1960s and the beginning or middle of the 1980s. In two cases the top sediment had been lost due to erosion or dredging. However, not many attempts have been made so far to achieve a detailed chronology of the inputs. Therefore, this paper discusses the vertical distribution of PCBs in two sediment cores from the central Venice Lagoon and the nearby industrial area to reconstruct past and present trends.

Study area, sampling and analytical methods

Study area and sampling locations are shown in Fig. 1. The industrial district has been reported as the major responsible of the lagoon pollution[1-7]. Nevertheless, the scientific literature about the pollution of this area and its relationship with the lagoon environment is rather scarce. The lagoon site E1 was chosen because it can be directly influenced by industrial pollution[4,6,7], and C11 represents the Brentelle Canal, where plants of a major petrochemical industry discharged without treatments until 1980[6-7].

Sampling was carried out in May 1996 (E1) and March 1997 (C11) by means of a manual piston corer. Cores were immediately extruded to obtain 2-4 cm thick sections which were put in glass jars with aluminum foil caps. Samples were then frozen and stored at -18°C until the analysis.

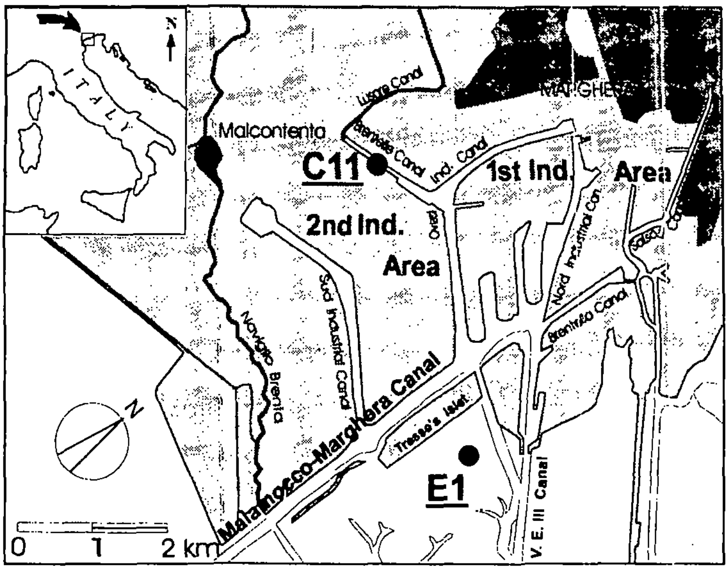

Fig. 1 - Study area and sampling locations.

PCB analyses were carried out using established HRGC-HRMS methods, described in detail by Frignani et al.[4]. PCB concentrations were calculated with respect to Aroclor (the mixture 1254+1260 1:1 generally represents the average composition of lagoon samples), and as a sum of 12 congeners whose standards were available at the time of the analytical work (from three- to octa-CB: 18, 28, 52, 77, 101, 118, 126, 153, 138, 169, 180, 194).

Organic carbon (OC) content and grain size composition of samples have been reported by Frignani et al., who discussed also sediment chronologies[6].

Results and Discussion

Sediment features. The X-radiographs, together with grain size composition and OC concentrations, show that both cores present a major discontinuity[7]. In fact, core C11 (Fig. 2) at ca. 26 cm depth shows the passage from coarse sediment below to fine sediment above. This seems to mark the closure of a major outfall, which caused a drop in the hydrodynamics of the system. In the lagoon core E1 a high content of organic carbon (>15%) in the form of vegetal remains is found below 23 cm depth. It accounts for the effect of the discharge of allochthonous continental material at the time of the construction of the 1st Industrial area, followed by regular sedimentation.

Core Chronologies. Core chronologies have been established using ^{210}Pb and ^{137}Cs activity-depth profiles[6]. For core C11 the mean recent accumulation rate (1.55 cm y^{-1}) was calculated only from the depth of the ^{137}Cs peak due to the Chernobyl accident (1986), because the accretion of canal sediments is so fast that ^{210}Pb is useless. In the case of E1, ^{137}Cs and ^{210}Pb derived sediment accumulation rates were similar (ca. 0.34 cm y^{-1}) but could be overestimated because no attempt was made to account for the effect of mixing and bioturbation[6]. Independent information confirms that the chronology of core C11 is very reliable and also that of E1 has a good approximation. In particular, the lithologic change at the base of E1 matches quite well with the dates reported in Fig. 3.

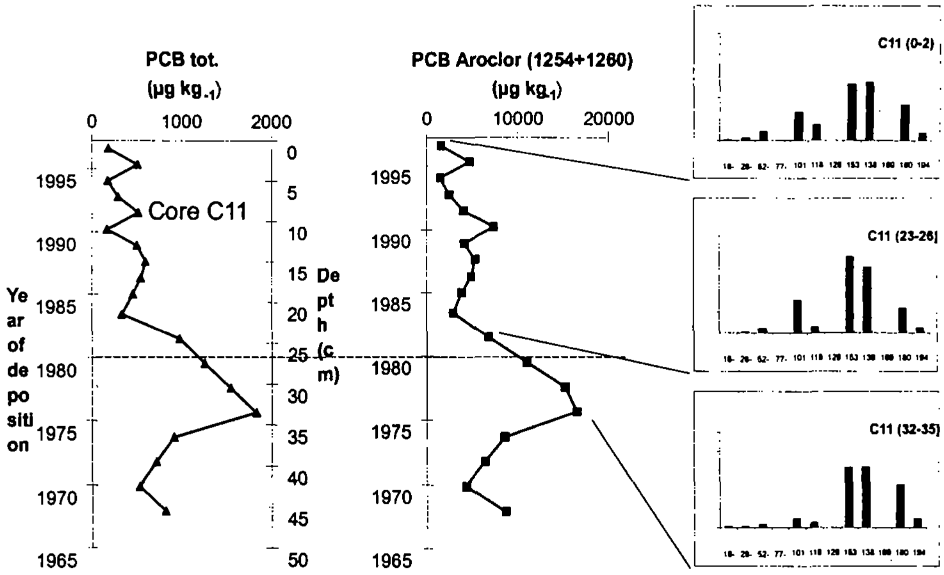

Fig. 2 - PCB downcore distributions and congener profiles at site C11 (Lusore-Brentelle Canal). The dashed line represents a physical discontinuity.

PCB distributions. PCB downcore distributions are displayed in Figs. 2 and 3. As discussed by Frignani et al.4, the different methods used to calculate PCB concentrations provide different results: when expressed as Aroclor values are much higher (2,3-10 times) than the correspondent sum of congeners. In spite of this difference, the two series of data are generally strictly related and we will discuss especially the data as Aroclor, which are closer to the actual total concentrations.

Core C11 provides a chronological information spanning the period 1965-1997. At depth in the core the maximum value of PCBs (16556) dates ca. 1976, and the peak ends in 1982. Starting from 1983, the concentration spans between 7500 and 1000 μg kg-1, with one of the minimum values at the surface. In lagoon sediments concentrations are much lower. After a maximum at the end of the 1930s (26 μg kg-1) the values increase again starting from 1967, and reach a new maximum in the early 1970s. In the topmost sediment a slight decrease is shown by the sum of congeners, whereas the Aroclor values are almost constant. Low concentrations can be found before the 1930s, when these compounds were first commercialised. We know that these chemicals were the undesirable by-products of highly polluting metallurgical industries, present within the 1st Industrial Area since the early 1920s.

To understand the effects of changes in sediment composition on downcore pollutant distributions we normalised some data against the content of fine particles (clay plus silt) and OC. Results show that trends in pollutant delivery are more effective than changes in sediment characteristics. For example, when a nearby outfall was closed in the Lusore-Brentelle Canal, a shift of sediment grain size composition occurred at C11, but the newly accumulating finer sediment was less contaminated than the older one. The high OC content at the base of core E1 does not significantly affect PCB concentrations that reach minimum values just at and below the discontinuity (Fig. 3).

Sources. The data provided by Frignani et al.[4] clearly indicate that major sources were located in the canals Brentella, Lusore-Brentelle and Salso. The former canal was affected by a very significant input, which is very peculiar in that it is rich in less chlorinated congeners (18, 28, 52, 101, 118). On the other hand, it is possible that a certain contribution of PCBs to the

Lusore-Brentella Canal is provided by the runoff of 170 ha of industrial land, with a selection of the heavy congeners that are richer in the sediment at C11. At site E1, which is influenced by the contaminants stored in sediments of the 1st Industrial Area, the profiles of PCB congeners (Fig. 3) suggest the predominance of the heavy components (from 126 to 194) in the past, and then an increase of the light cogeners.

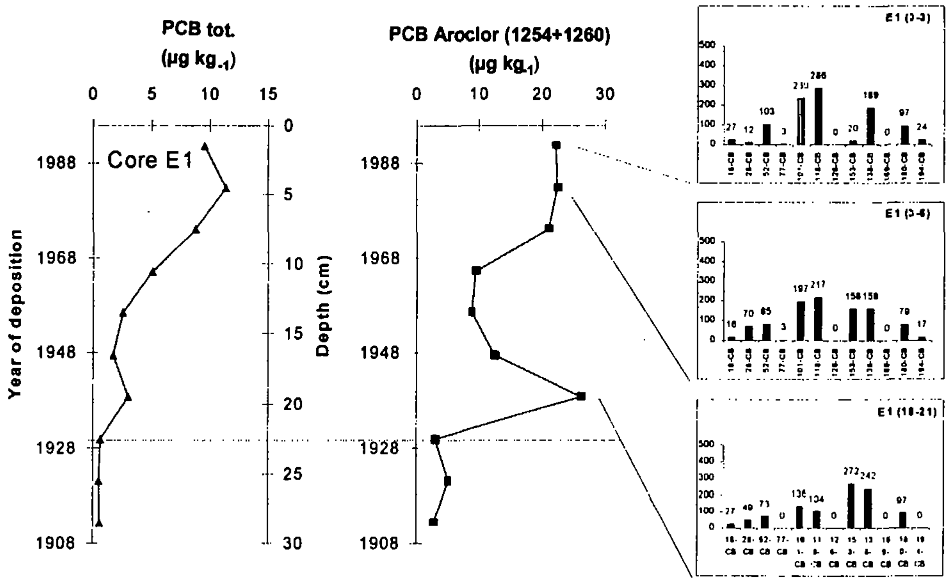

Fig. 3 - PCB downcore distributions and congener profiles at lagoon site E1. The dashed line represents a lithological discontinuity.

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