Polychlorinated Biphenyls in Sediments of Selected Sites of the Moroccan Coastal Zone

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Introduction

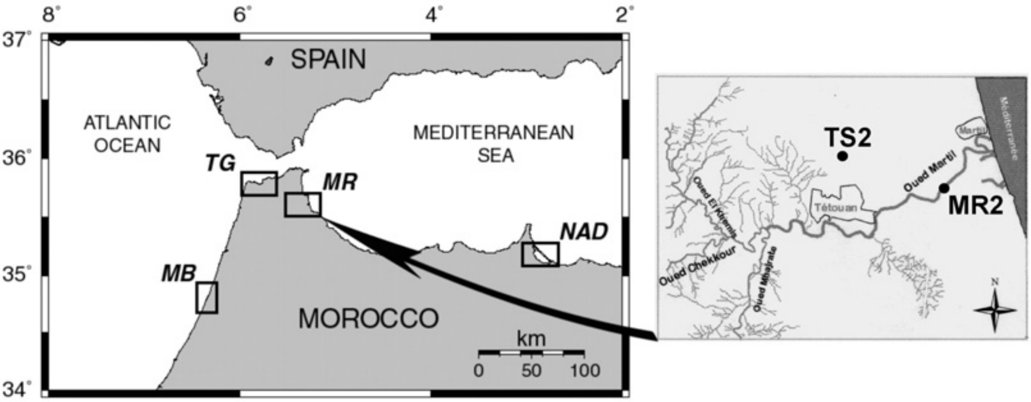
A good knowledge of sources of contaminants, distribution mechanisms, sites where chemicals tend to accumulate, potential risk and actual danger to the human and environmental health is fundamental to design a policy for the environment. In this respect, it is important to recognize that sediments can keep a record of the conditions of the environment at the time of their deposition and accumulation and hence can be used to reconstruct history and trends of contamination processes. Furthermore, actively accreting salt marshes, due to the lack of sediment reworking, may provide a relatively high resolution record of atmospheric fluxes. On the other hand, transition coastal environments are of particular importance because of their position between the inland sources and the sea, which is the final repository of all the materials mobilized from the continent.
In order to assess the level of PCB contamination in key areas of coastal Morocco we chose to analyse sediments from the Nador (NAD) and the Moulay Bousselham (MB) lagoons, the terminal tract of the Martil River (MR), the port of Tangier (TG) and a soil taken close to the industrial town of Tetouan (TS). The first two were chosen because of their high environmental value, the others as representative of zones potentially contaminated.

Materials and Methods

The four sampling areas are shown in Fig. 1. In particular, salt marsh cores were taken from the Nador and Moulay Busselham lagoons in 2000 and 2002, respectively, as representative of the delivery of airborne contaminants. Furthermore, a number of samples were collected along the banks of the Martil River in 2001, together with some soil samples around the town of Tetouan to assess the level of industrial contamination. Finally, a sediment core collected in 2003 in the Port of Tangier accounts for the influence of both harbour and civil activities. All sediment samples were obtained by manually inserting a Plexiglas tube into the sediment. The same was done in the port by a scuba diver. Sediment cores were extruded soon after collection and sectioned at intervals of 2-4 cm, with a maximum resolution close to the top.

Sediment slabs were then divided in two parts for the different analyses, put in glass vessels and stored in a refrigerator at 0°C until the arrival at the lab. Afterwards, they were conserved at -18°C until the analyses.
For PCB analyses, carried out following Moret et al.[1], sediment samples were lyophilised and 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 solutions were 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-HRMS (mass spectrometry: Thermofinnigan MAT95XP). The use of High Resolution Mass Spectrometry allowed the 3-CB congener quantification without further clean-up procedures. Five ^{13}C labeled PCBs were added to the samples before extraction, as internal standard. Crude concentration values were corrected with congener-specific instrumental response factors.
PCB concentrations were calculated as a sum of 54 congeners (45 chromatographic peaks). Accuracy was checked with respect to a certified standard (NIST®, Standard Reference Material 1941b). Precisions, calculated using the same certified standard, are in the order of 0.1% for the sum of all quantified congeners, whereas they span the interval 0.3(6-CB)-4.8(3-CB) % as far as the homologues are concerned. PCB concentrations are expressed with respect to dry weight.

Figure 1: Maps of northern Morocco and the zone of Tetouan with the sampling locations.



Results and Discussion

Concentrations: Results are summarised in Table 1 as total concentration and sums of homologues. The cleanest environment is the salt marsh of the NAD Lagoon (0.96-1.19 ng g^{-1}). The MB lagoon is relatively clean (0.93-2.04 ng g^{-1}) but the trend is towards an increase of PCB contamination. The area of Tetouan is certainly more contaminated, as expected considering the presence of industrial activities. The levels (4.84-8.22 ng g^{-1}), however, remain relatively low. On the contrary, the sediment from the Port of Tangier appears very contaminated, even if the trend is towards a decrease. In particular, values of 164-452 ng g^{-1} are rather high, and can be compared with those reported for polluted sediments in Australia (0.5-790 ng g^{-1}), China (11.5-485 ng g^{-1}), India (4.8-1000 ng g^{-1}), Scotland (0.5-500 ng g^{-1}), Thailand (11-520 ng g^{-1}), Vietnam (0.2-630 ng g^{-1}), Indonesia (5.9-220 ng g^{-1}), Japan (63-240 ng g^{-1}) and Taiwan (2.3-230 ng g^{-1}) by Fillmann et al. and references therein[2].

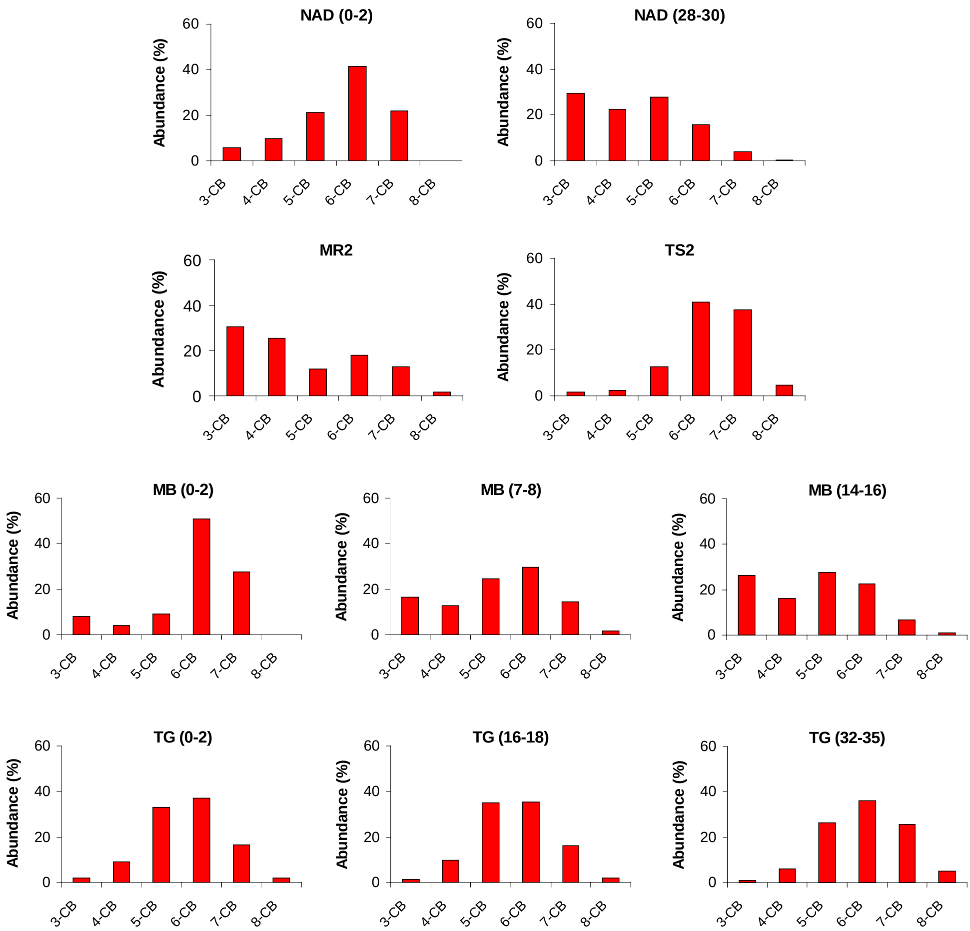
Table 1: PCB concentrations in sediment samples (values in ng g^{-1}). Depths are in cm.

Sample (depth)	Total	3-CB	4-CB	5-CB	6-CB	7&8-CB
Nador (0-2)	0.96	0.06	0.09	0.20	0.40	0.21
Nador (28-30)	1.19	0.35	0.27	0.33	0.19	0.05
Moulay B. (0-2)	2.04	0.16	0.09	0.19	1.04	0.56
Moulay B. (7-8)	0.93	0.15	0.12	0.23	0.28	0.15
Moulay B. (14-16)	0.80	0.21	0.13	0.22	0.18	0.06
Martil River (0-2)	4.84	1.49	1.25	0.58	0.88	0.64
Tetouan Soil 2 (0-3)	8.22	0.13	0.19	1.04	3.37	3.49
Port of Tangier (0-2)	164	3.32	14.9	54.2	60.7	30.5
Port of Tangier (16-18)	210	3.15	20.3	73.6	74.5	38.8
Port of Tangier (32-35)	452	3.90	26.9	119	163	139

As far as the Alboran Sea (western Mediterranean) is concerned, literature data were summarised by Picer[3] who reported a concentrations interval of 0.3-323 ng g^{-1}. On the other hand, concentrations spanning the intervals 1.07-3.00, 2.11-9.90, and 5.48-11,405 ng g^{-1} were found in surficial salt marshes, subtidal sediments and industrial canal sediments of the Venice Lagoon[1,4,5]. However, it should be emphasized that the comparison of PCB concentrations cannot be straightforward, because the authors used different analytical procedures, and determined different series of congeners or expressed the concentration with respect to Aroclor standard mixtures.

Sources and trends: Concentrations show a clear gradient as a function of type and distance of the source. In fact, the contamination of the port is the effect of direct releases of PCBs from the town, the ships and the infrastructures. Differently, the zone of Tetouan, with the Martil River, is only slightly contaminated and the levels are situated in the lower part of the literature intervals mentioned above. In turn, the lagoon salt marshes, far from direct sources, are rather unpolluted. Here contaminants are probably delivered through atmospheric wet and dry deposition.
The homologue profiles of PCBs in our samples are shown in Fig. 2. The analysis of these profiles, and the use of a Principal Component Analysis on the homologue distributions, suggest the following inferences: 1) the MB surficial sample has a composition that is similar to that of Aroclor 1260. The other samples, downcore, are not similar to any of the commercial mixtures; 2) in the NAD the two samples from the same core are different, with the presence of less and more chlorinated PCBs in the surficial and deep sample, respectively; 3) the Martil River sample and the Tetouan soil, taken close to each other, are very different because in the first the lower chlorinated biphenyls prevail, whereas the composition of the other is dominated by the high molecular weight PCBs being not very dissimilar to Aroclor 1260; 4) the three levels in the Port core are relatively similar to each other, even if the deep sample contains less 5-CB and more 7- and 8-CB than the others. These profiles, are different from those of all commercial Aroclor mixtures.

Figure 2: Homologue profiles of PCB in all sediment samples. In brackets the depth in core (cm).



In conclusion, the levels of PCBs in sediments of selected sites of the coastal zone of Morocco were found to vary widely, depending of the type and closeness of the sources. The Port of Tangier appears heavily contaminated but with a decreasing trend. In all cases but two, PCBs appear to be a mixture of congeners not easily referable to specific commercial products. This may be due to a multiplicity of sources, as in the case of the Port of Tangier, or to fractionation processes caused by differential transport and interaction rates within the environment. A further discussion of the PCB data will benefit by the assessment of both sediment characteristics and core chronologies.

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