Recognizing different impacts of human and natural sources to PAHs and PCBs (including PCB-11) spatial distribution and temporal trends in sediments of the Nador Lagoon (Morocco)

Silvia Giuliani[1], Rossano Piazza[2,3], Luca Giorgio Bellucci[1], Fabio Paolo Polo[2,3], Marco Vecchiato[3,4], Stefania Romano[1], Stefano Zambon[2], Mauro Frignani[1], Bouchta El Moumni[5,6]

[1]CNR-Institute of Marine Sciences, via Gobetti 101, Bologna, Italy
[2]Dept. of Environmental Sciences, Informatics and Statistics, Univ. of Venice, Dorsoduro 2137, Venice, Italy
[3]CNR-Institute for the dynamics of Environmental processes, Dorsoduro 2137, Venice, Italy
[4] Dept. of Physical Sciences, Earth and Environment, Univ. of Siena, via Laterina 8, Siena, Italy
[5]Dept. of Earth Sciences and Oceanography, Univ. of Tangier, Tangier, Morocco
[6]Polydisciplinary Faculty of Larache, BP 745 Route de Rabat, Larache, Morocco

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ABSTRACT

The Nador Lagoon holds a major interest in present-day Moroccan socioeconomic development. However, this environment is exposed to a number of potential polluting sources, such as mine tailings, urban and industrial dumpings, and untreated wastewater inputs from surrounding cities. The aim of this study was then to assess concentrations and trends over time of persistent contaminants such as PCBs and PAHs and to identify their origin. For the first time, the non-Aroclor PCB-11 was determined. Sediment chronology and source assessment helped identifying the timing and nature of inputs and post-depositional processes controlling the two classes of contaminants. PAHs present a typical mixed petrogenic signature, with the exception of sediments deposited in the period 1930-1960 near the city of Nador, when pyrogenic inputs prevailed. PCBs show signs of microbial anaerobic degradation from 1950 to 1990, probably linked to changing hydrodynamic conditions in the southwestern part of the lagoon where agricultural inputs are dominant. The presence of PCB-11 is linked to specific productions and might be affected by some degradation processes. Presently, the different land uses (e.g., urban and agricultural areas) appear to be the key factors in controlling the level and composition of PAHs and PCBs in lagoon sediments. However, PAH and PCB levels

(values ranging from 21.6 to 108 ng g^{-1} and from 2.50 to 20.7 ng g^{-1}, for total PAHs and total PCBs, respectively) are not high enough to be a threat to aquatic organisms and human beings.

1. INTRODUCTION

Northern African countries have been experiencing a great deal of economic development, which brings about the risk of environmental contamination by both inorganic and organic chemicals. For this reason in the last decades several laws have been developed in order to achieve or maintain a Good Environmental Status of the Mediterranean marine ecosystem and to provide a legislative framework to sustainably manage human activities at all scales (e.g., the Marine Strategy Framework Directive, 2008/56/EC, and the Barcelona Convention for the Protection of the Mediterranean Sea, UNEP/MAP, 2012). In order to achieve these goals, an increasing scientific knowledge of levels, behaviour, and fate of chemicals in the marine environment and related processes is required (http://ec.europa.eu/environment/marine/good-environmental-status/index_en.htm), and the integration of environmental issues in social and economic development plans and management becomes crucial (http://www.unepmap.org/index.php?module=content2&catid=001001004).

The Nador Lagoon (NE Morocco) is a place of great social and economical interest, due to its location and environmental features that have favoured the settling of important urban sites (e.g. Ben Ansar on the North-East, Kariat Arkmane on the South East, and Nador on the South West) and production activities within and around its borders (e.g. fisheries, metallurgical industries, agriculture), at the same time increasing the touristic interest (Hamoumi and Benssaou, 2001; Chalouan et al., 2001; González et al., 2007). Potential sources of environmental pollution are strongly related to different activities that can be roughly geographically separated in: i) agriculture and its intensive cereal production in the south; ii) industry, both at Selouane (with the largest iron and steel complex in the country) and Nador (with a neighbouring metallurgic industrial area) in the west; iii) fishery in the north, with a fleet of more than 200 ships, several ports and activities related to both fish farming, and food conservation; and iv) tourism, reinforced by the lagoon's natural attraction and based on spa resorts in Kariat Arkmane in the southeast, as well as its culture, handicraft, gastronomy, etc. (Quaranta et al. 2004). Other environmental stresses in the last decades were linked to the disposal of untreated or partially treated wastewaters in the lagoon, mainly originating in the urban areas of Ben Ansar, Kariat Arkmane, and Nador and from villages located all around its shores (Bloundi et al., 2009). This latter study has indeed identified a plausible link between anthropogenic activities (mainly related to mining industry and untreated wastewater inputs) and trace metal enrichments (particularly for Zn, Pb, and As) in lagoon sediments, in accordance with previous similar researches (Bellucci et al., 2003; Águila et al., 2004; Gonzalez et al., 2007) and further confirmed by the negative impact observed on bioindicators (Ruiz et al., 2005, 2006). With respect to researches focused on trace elements' inputs, those relative to the contamination by organic pollutants in the Nador Lagoon are scarce, being focused on few locations along the Moroccan coastline and on different environmental matrices or contaminants (Azdi et al., 2006; Bloundi et al., 2008; Er-Raioui et al., 2009; Piazza et al., 2009; Scarpato et al., 2010). Despite these limits, all these studies agree in evidencing a situation of increasing contamination linked to anthropogenic activities.

As final repository of materials coming from land, atmosphere, and overlaying water masses, sediments are important in contamination studies because they give a trustworthy picture of both present-day environmental conditions and those relative to the past (e.g., Frignani et al., 2004; Giuliani et al., 2011a; Bellucci et al., 2012). In addition, they provide information on the chronology of inputs when conditions of low sediment perturbation are met. The principal aim of this paper was to partially fill the gap relative to organic contamination in sediments of the Nador Lagoon. Therefore, the research has been focused on the assessment of levels and temporal trends of two specific classes of organic contaminants: polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs).

2. STUDY AREA

The Nador Lagoon (Fig. 1) is the sole lagoon ecosystem in the Moroccan coast facing the Mediterranean Sea. It covers an area of 115 km^2 with a water depth ranging between 5 m in the north and 8 m in the south. It is separated in two basins by the Attalayoum peninsula, and is connected to the Mediterranean Sea through the artificial Bokhana inlet.

The lagoon is fed mainly by marine waters (Ruiz et al., 2006). Secondarily, it receives groundwaters from the Bou Areg Plain and by intermittent flows from inland areas through wadis; the Selouane river is the most notable and delivers large amounts of raw sewage (Gonzalez et al., 2007). Irrigation canals come from Nador, Ben Ansar and Kariat Arkmane (Fig. 1). In the lagoon, water inputs are oriented by internal currents, which follow an hourly sense from the artificial inlet toward the NW coast (Ruiz et al., 2006).

Many anthropogenic pressures are present along its shores, locations and typologies being reported in Fig. 1.

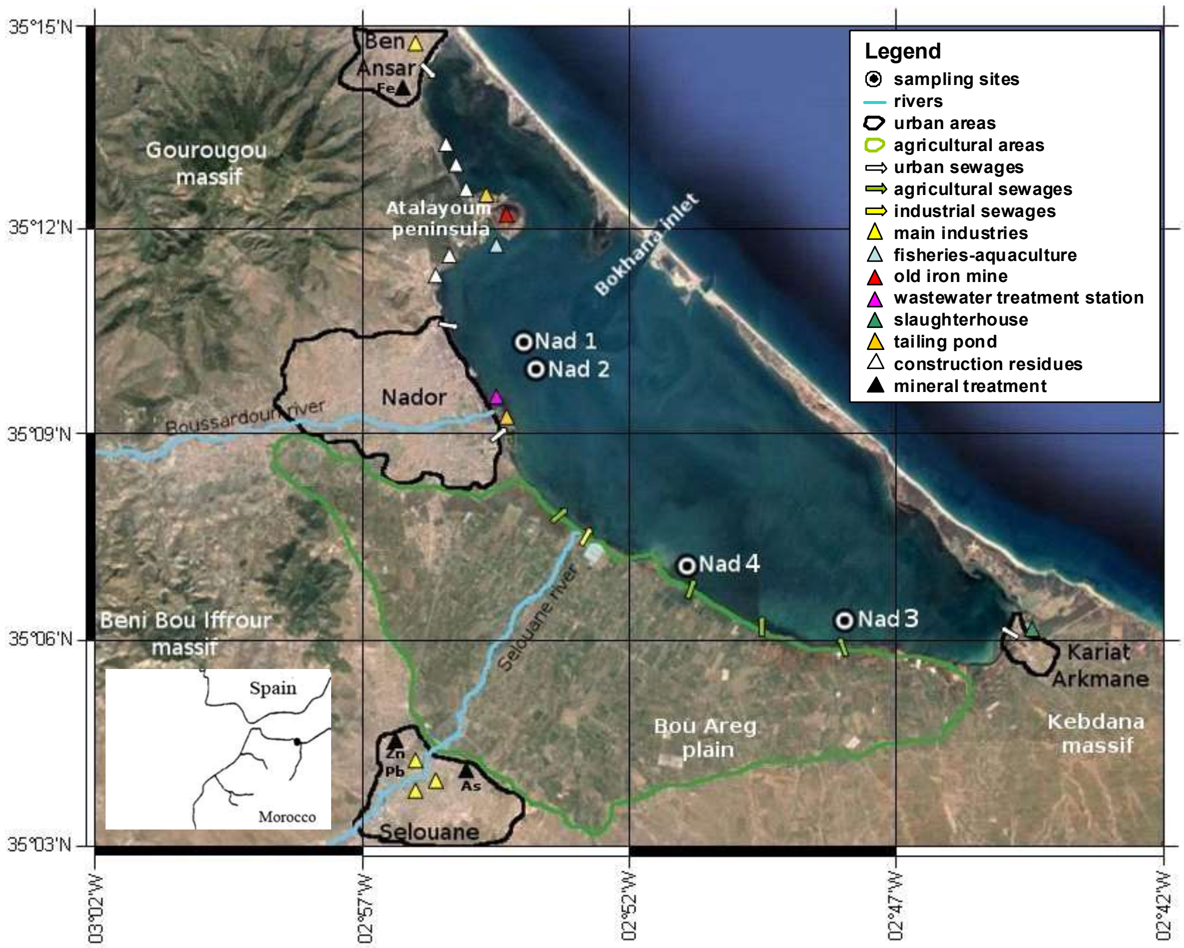


Fig. 1. Sampling sites in the Nador Lagoon. The most important human activities are indicated (Ruiz et al., 2006; González et al., 2007), as potential sources of contaminants.

3. MATERIALS AND METHODS

3.1 Sediment collection and subsampling

Sediment cores were collected by a diver in June 2009, by inserting a sharpened Plexiglas tube into the bottom at depths varying from 3.5 to 5.0 m. The four locations (Fig. 1) were selected on the basis of surficial grain size distribution reported by El-Alami et al. (1998), in order to sample fine sediment (i.e., with prevalent silt and clay fractions) that is known to interact preferentially with contaminants (e.g., Frignani et al., 2001; Ünlü and Alpar, 2006; Bellucci et al., 2012; Gibbs et al., 2014). Furthermore, fine grained materials deposit under low-energy hydrodinamic conditions that do not favour mixing and resuspension. Therefore, they are more suited for retaining chronological information (Cochran et al., 2005; Mendes et al., 2010; Bellucci et al., 2012).

The cores were extruded and carefully sectioned in 1-4 cm intervals soon after collection. Samples were stored in glass containers first at 4°C and then at -20°C before the analysis, then freeze-dried. Cores Nad 1 and Nad 3 were analysed in detail, whereas measurements on cores Nad 2 and Nad 4 were limited to the surficial (0-1 cm) layer (Tables 1-2 and Figs. 2-6).

3.2 Porosity, grain size and carbon content

Porosity was calculated from percent water content assuming a particle density of 2.5 g cm^{-3} (Berner, 1971).

Grain size analyses were carried out by wet sieving, to separate sands, after a pre-treatment with H_2O_2. Silt and clay fractions were determined as weight difference.

Total Carbon (TC) and Organic Carbon (OC) were measured by a Shimadzu TOC-5050A Analyzer, coupled with the Solid Sample Module (SSM-5000A). This instrument is based on thermical decomposition and infrared revelation. The OC percent content was determined after elimination of carbonates by treatment with HCl in a glass capsule. Samples were then heated at 120 °C for 2 hours and left overnight in an oven at 100 °C. The analyses were performed after the samples spent one day in a dryer. The Inorganic Carbon (IC) fraction was calculated as difference.

3.3 Radiotracers

The principal chronological radiotracer, ^{210}Pb, was analysed via alpha spectrometry of its granddaughter ^{210}Po, assuming secular equilibrium. The procedure was the same described in Bellucci et al. (2007). In short, 1.5-3 g of dry sediments were leached twice with hot HNO_3 8N and H_2O_2. Extracts were taken to near dryness and treated with concentrated HCl to eliminate nitric ions. Finally, the residues were diluted with HCl 1.5N, the iron reduced with ascorbic acid and Po spontaneously plated overnight on silver disks. ^{209}Po was added to the sediments at the beginning of the procedure, as internal standard and account for all efficiencies (extraction, deposition and counting). Supported ^{210}Pb (in equilibrium with ^{226}Ra naturally present in sediments) was obtained from the activities of ^{214}Pb from gamma counting. The excess ^{210}Pb ($^{210}Pb_{ex}$) was calculated by subtracting the supported fraction from the total.

For ^{137}Cs determinations, 5-10 g of dry sediments were put in standard geometries and gamma counted. The accuracy was tested with respect to the IAEA river sediment certified standard (Bellucci et al., 2007).

3.4 PAHs and PCBs

PAHs and PCBs were analysed on all surficial samples and on selected levels from cores Nad 1 and Nad 3 that appeared most interesting, based on the ^{210}Pb profiles.

Aliquots of about 3 ± 0.01 g of dry sediment were spiked with known amounts of labelled compounds mixtures (3 ^{13}C-labelled PAHs at 500 pg μL^{-1} and 21 ^{13}C-labelled PCBs at 40 pg μL^{-1}) as internal standards. PCB isotope-labelled solutions (EC-1434, EC-1426, EC-4187, EC-4188, EC-4189, CLM-2477, CLM-2722, CLM-3757, CLM-2451) were purchased from CIL (Cambridge Isotope Laboratories, Inc., Andover, Massachusetts, USA). PAH and PCB native standard solutions (M-1668-A, PAH Mix 9) were acquired from Accustandard Inc. (New Haven, USA) and Dr. Ehrenstorfer GmbH (Augsburg, Germany). The samples were then extracted by means of Pressurized Liquid Extractor (PLE, FMS, Fluid Management System Inc., Watertown, MA) equipped with stainless steel cells, using dichloromethane/acetone (1:1 v/v) in presence of anhydrous sodium sulphate, diatomaceous earth and activated metallic copper. Extractions were performed at 100°C, 1500 psi with 2 static cycles of 7 min. Clean-up was carried out by injecting samples onto a disposable neutral silica column in an automated system (PowerPrep™, FMS) and by eluting with 30 ml of *n*-hexane and 30 ml of 1:1 *n*-hexane:dichloromethane. Purified samples were reduced to 100 μL under a gentle nitrogen flow at 23 °C (Turbovap II®, Caliper Life Science, Hopkinton, MA, USA) and spiked with a known amount of the recovery standard solution containing ^{13}C-Chrysene at 1000 pg μL^{-1} and ^{13}C-PCB 47 and ^{13}C-PCB 141 at 40 pg μL^{-1}. Determinations were made by HRGC-LRMS (7890A-5975C, Agilent Technologies). The gas chromatographic separation was carried out on a 60-m HP-5MS column (0.25 mm I.D., 0.25 μm; Agilent Technologies, Avondale, USA). Quantification was achieved using internal standards and isotopic dilution. Results were corrected by applying the instrumental response factors obtained from standard solutions. Full analytical details on extraction, clean-up stage and instrumental analysis can be found in Piazza et al. (2013). All concentrations and activities were calculated on a dry weight basis.

The following fifteen PAH congeners were quantified: acenaphthylene (Ac), acenaphthene (Ace), fluorene (F), phenanththrene (Phe), anthracene (An), fluoranthene (Flu), pyrene (Py), benzo(a)anthracene (BaAn), chrysene (Ch), benzo(b)fluoranthene (BbFlu), benzo(k)fluoranthene (BkFlu), benzo(a)pyrene (BaPy), benzo(g,h,i)perylene (BghiPe), indeno(1,2,3,c,d)pyrene (IPy), and dibenzo(a,h)anthracene (DahAn). Naphthalene was not quantified because its ubiquitary presence (Klotz et al., 2011) leads to very high analytical errors. The 3 ^{13}C-labelled PAHs used as internal standards were Acenaphthene, Phenanthrene, Benzo(a)pyrene.

PCB total concentrations were calculated as a sum of 127 congeners (107 chromatographic peaks), including the non-Aroclor CB-11: 3 monochlorobiphenyls (CB-1, -2, -3), 10 dichlorobiphenyls, (CB-10+4, -7+9, -6, -5+8, -11, -12, -15), 17 trichlorobiphenyls (CB-19, -18, -17, -24+27, -16+32, -34, -29, -26, -25, -31, -28, -20+33, -22, -37), 23 tetrachlorobiphenyls (CB-45, -46, -69, -52, -49, -47+48, -44, -42+59, -41+64+71, -40, -67, -63, -74, -70, -66, -56+60, -81, -77), 24 pentachlorobiphenyls (CB-104, -103, -93+95, -91, -92, -84+90+101, -99, -119, -83, -97, -87+115, -85, -110, -82, -107, -123, -118, -114, -105, -126), 22 hexachlorobiphenyls (CB-136, -151, -135+144, -147, -149, -134, -131, -146, -153, -

132, -141, -137, -138+164, -158, -129, -128+167, -156, -157, -169), 17 heptachlorobifenyls (CB-179, -176, -178, -187, -183, -185, -174, -177, -171, -173, -172, -180, -193, -191, -170+190, -189), 7 octachlorobiphenyls (CB-197, -199, -196+203, -195, -194, -205), 3 nonachlorobiphenyls (CB-208, -207, -206) and CB-209. Calculated concentrations for all congeners are reported in the Supporting Material.

Precision, measured as standard deviation of replicated analyses of the same sample, was always below 10% for total PAHs and total PCBs. It ranged from 7% to 21% for the groups of PCB homologues and from 0.4% (CB-183) to 25% (CB-84+101+90) when every single PCB congener was considered. Accuracy was estimated through repeated analyses of NIST 1941b Reference Standard Material. Results were always within the certified analytical uncertainty. For PAHs, 54% of the values were accurate within 1σ, 87% within 2σ.

4. RESULTS

4.1 Sediment features

Sediment porosities vary from a minimum of 0.56 to a maximum of 0.81 (Figs. 2 and 3). Core trends for Nad 1 and Nad 3 show higher values at surface, resulting from the relative higher water content in the most recent unconsolidated layers. Values in Nad 1 remain quite constant (~0.77) from 1 to 22 cm depth, then decrease to ca. 0.72 down to the core bottom, with an isolated relative peak of 0.76 at 39 cm depth (Fig. 3). Downcore porosity trend in Nad 3 presents a quite constant decrease from surface to 6 cm depth, increasing to 0.76 at 7 cm depth then setting to almost constant values of approximately 0.60 from that point downward (Fig. 3).

The analyzed sediments are predominantly fine grained (sand content varies from 0 to 38%, Figs. 2 and 3), in agreement with the indications of El-Alami et al (1998). Nad 1 presents constant downcore sand contents around 2% (Fig. 3), whereas Nad 3 is clearly separated in two parts: the most surficial one (from 0 to 7 cm depth) is almost totally composed by fine sediments (≥ 96%, Fig. 3), whereas the deeper layers are characterized by sand contents averaging 31% (Fig. 3).

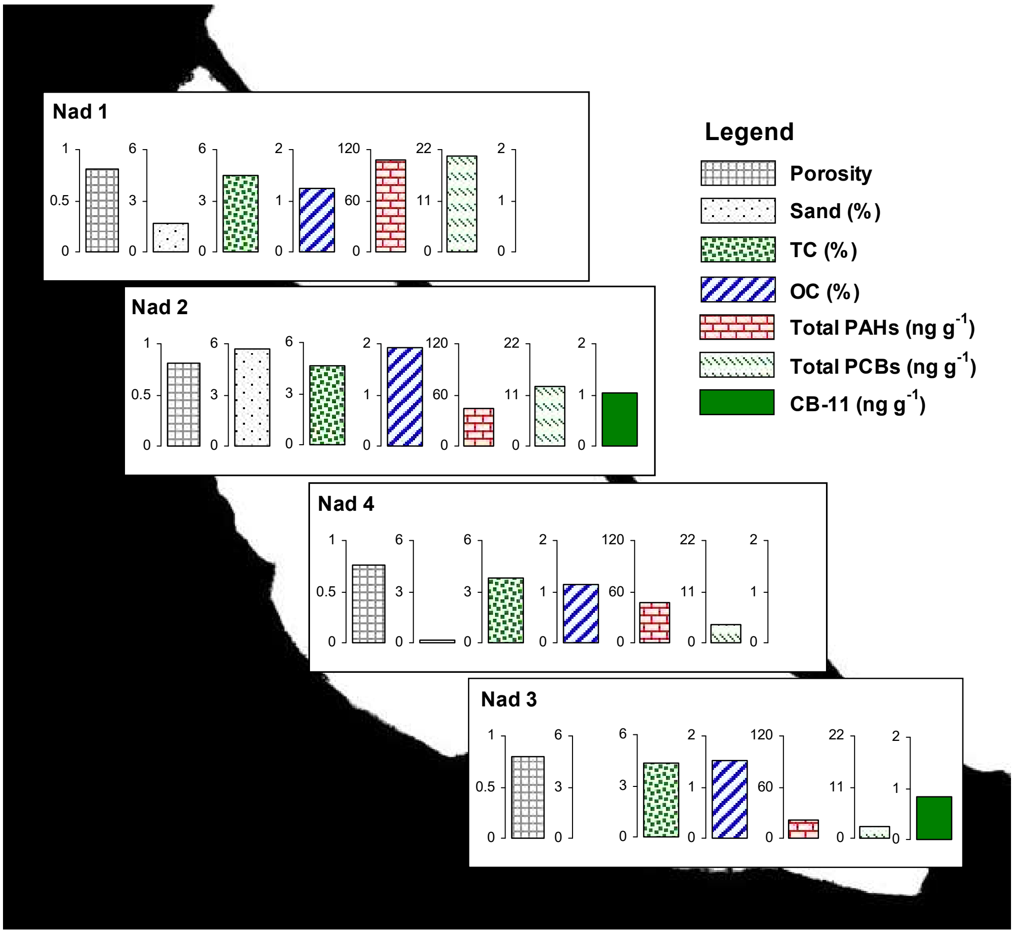


Fig. 2. Surficial distribution of porosity, sand content, TC, OC, total PAHs, total PCBs, and CB-11 in cores Nad 1, Nad 2, Nad 4 and Nad 3.

TC varies from 3.53 to 5.28 % and downcore trends in Nad 1 and Nad 3 are relatively constant (Figs. 2 and 3). OC percent content ranges from a minimum of 0.71 to a maximum of 2.87 (Figs. 2 and 3). Downcore values are more scattered than TCs and present relative mimina at both the surface and 22-33 cm depth in core Nad 1, whereas the surficial 2 cm of core Nad 3 shows the higher values of the entire sedimentary sequence (Figs. 2 and 3).

Depth profiles of ^{210}Pb and ^{137}Cs for cores Nad 1 and Nad 3 are shown in Fig. 4, with the relative analytical errors. In core Nad 3 the maximum ^{210}Pb value is at surface (53.5 Bq kg^{-1}, Fig. 4), whereas Nad 1 displays its maximum at 5 cm depth (110 Bq kg^{-1}). This is probably the result of some post-depositional processes (such as bioturbation or physical mixing) that have reworked the topmost layer of the core. Supported ^{210}Pb is 20 and 11 Bq kg^{-1} in cores Nad 1 and Nad 3, respectively. ^{137}Cs maxima are located at 22 and 14 cm depth in Nad 1 and Nad 3, respectively.

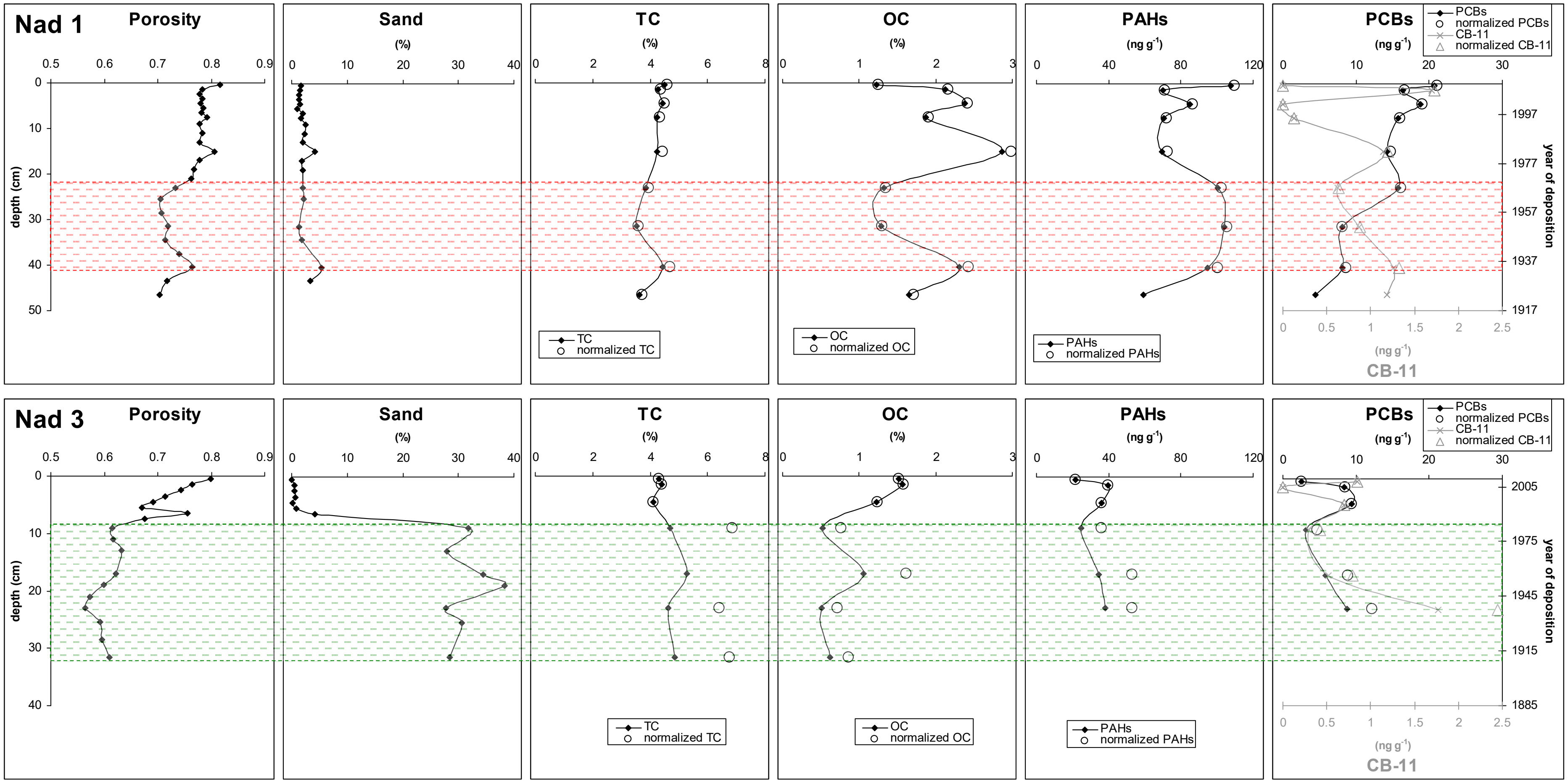


Fig. 3. Depth distribution of porosity, grain size (as sand % content), TC, OC, total PAHs, total PCBs, and CB-11 in cores Nad 1 and Nad 3. Open circles identify values of TOC, total PAHs, total PCBs, and CB-11 normalized for a 100% fine sediment. The red area in core Nad 1 comprises a sediment layer characterized by lower porosity and higher PAH concentrations. The green area in core Nad 3 defines the boundaries of a coarser sediment layer. Profiles are reported also versus the established year of deposition (see Figure 4).

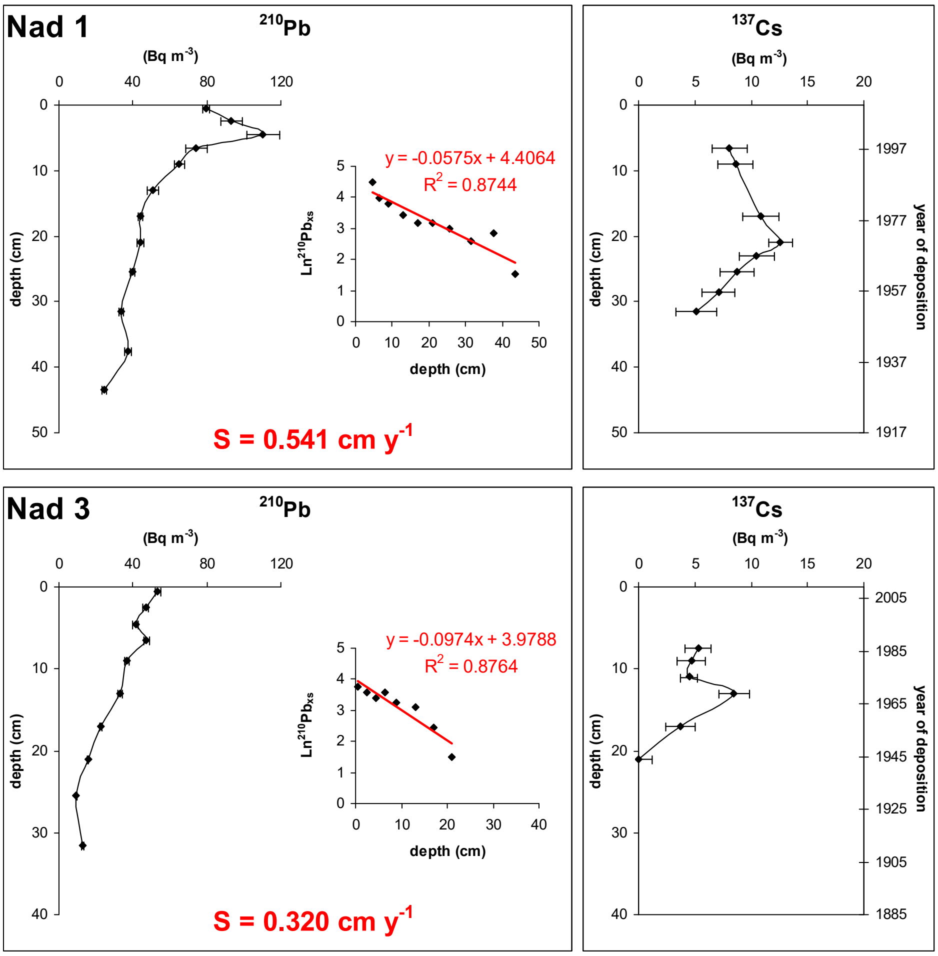


Fig. 4. Activity-depth profiles of ^{210}Pb and semilogaritmic plots of excess ^{210}Pb vs depth in cores Nad 1 and Nad 3. Calculated sediment accumulation rates (S, in cm y^{-1}) are reported, as well as ^{137}Cs profiles vs. depth and time. The first 2 cm of core Nad 1 have been excluded from calculation due to probable sediment mixing and reworking.

4.2 PAHs

Total PAH concentrations (ng g^{-1}) are shown in Fig. 2 for surficial samples and in Fig. 3 for cores Nad 1 and Nad 3. Values measured in surficial samples show a clear gradient from the northernmost site Nad 1 (108 ng g^{-1}) to 2-4 (43-47 ng g^{-1}) and 3 (22 ng g^{-1}, Fig. 2). Total PAHs in core Nad 1 are at their maximum at surface, but relatively higher values are found also between 22 and 42 cm depth (95-104 ng g^{-1}, Fig. 3). On the contrary, total PAHs in core Nad 3 are highest at 2 cm depth (39.5 ng g^{-1}, Fig. 3). Table 1 reports the concentration of PAH congeners (ng g^{-1}) in sediment cores and surficial samples. Phenanthrene is by far the most important PAH in all analysed samples (8.32-59.2 ng g^{-1}), followed by fluoranthene and pyrene in core Nad 1 (<d.l.–14.6 and 1.19–15.2 ng g^{-1}, respectively) and by acenaphthene in core Nad 3 and sites Nad 2 and Nad 4 (< d.l.–9.11 ng g^{-1}).

Table 1. Concentrations of PAH congeners (ng g^{-1}) and TEQs (ng g^{-1}) in both surficial and downcore sediment samples from the Nador Lagoon.

core	level (cm)	Ac	Ace	F	Phe	An	Flu	Py	BaAn	Ch	BbFlu	BkFlu	BaPy	BghiPe	IPy	DahAn	TEQ[a]
Nad 1	0-1	0.297	<d.l.	4.86	59.2	<d.l.	9.08	15.2	1.52	5.29	2.13	0.837	1.63	2.84	3.66	1.14	3.39
	1-2	0.412	<d.l.	1.88	38.2	1.40	4.67	4.93	1.07	3.22	2.83	1.27	1.59	3.15	3.89	1.38	3.62
	4-5	0.356	<d.l.	2.48	46.9	0.72	6.14	7.28	1.30	3.50	3.04	1.23	1.79	3.91	4.77	1.63	4.18
	7-8	0.270	<d.l.	3.59	40.5	<d.l.	<d.l.	5.60	1.22	3.21	2.88	1.14	1.94	4.00	4.66	1.78	4.45
	14-16	0.284	3.00	2.25	31.8	<d.l.	6.03	5.94	1.58	4.22	3.23	1.37	1.99	2.58	4.57	0.897	3.68
	22-24	0.553	0.716	2.46	26.2	1.11	14.6	12.6	3.68	8.21	6.51	2.80	3.70	6.95	7.33	2.82	7.97
	30-33	0.255	0.890	2.87	32.7	1.15	13.0	10.1	3.93	8.04	6.97	3.42	4.48	6.77	7.23	2.39	8.41
	39-42	<d.l.	5.90	3.03	28.8	1.18	10.4	7.70	2.52	5.53	6.82	2.62	3.39	7.35	7.09	2.53	7.21
	45-48	<d.l.	0.839	2.16	25.7	1.08	7.14	5.11	1.42	3.48	3.32	1.29	<d.l.	3.32	3.35	0.820	1.46
Nad 3	0-1	0.070	2.49	1.50	9.68	0.03	1.15	1.19	0.080	0.542	0.276	3.46	0.564	0.102	0.237	0.235	1.18
	1-2	0.248	3.34	1.75	16.1	<d.l.	2.82	3.05	0.911	2.91	1.50	1.70	1.33	1.18	2.04	0.528	2.34
	4-5	0.174	3.25	1.77	16.6	<d.l.	2.51	2.48	0.729	2.15	1.14	1.19	1.18	0.866	1.56	0.352	1.90
	8-10	0.152	5.47	0.93	8.32	<d.l.	1.59	1.98	0.418	1.13	0.594	0.581	0.811	0.525	2.06	0.135	1.26
	16-18	0.152	2.30	2.03	15.3	<d.l.	3.02	2.52	0.662	1.86	1.34	1.51	1.19	1.01	1.40	0.365	1.93
	22-24	0.269	9.11	1.41	11.7	<d.l.	2.52	2.62	0.643	2.26	1.33	1.59	1.17	1.13	2.05	0.406	2.02
Nad 2	0-1	0.308	3.15	2.37	19.0	<d.l.	2.53	2.46	0.835	2.46	2.26	0.742	1.27	2.13	2.88	0.880	2.62
Nad 4	0-1	0.133	4.49	1.92	14.6	0.29	4.30	4.17	1.93	4.14	2.30	0.961	2.24	2.08	2.90	0.893	3.74

Ac = acenaphthylene; Ace = acenaphthene; F = fluorene; Phe = phenanthrene; An = anthracene; Flu = fluoranthene; Py = pyrene; BaAn = benzo(a)anthracene; Ch = chrysene; BbFlu = benzo(b)fluoranthene; BkFlu = benzo(k)fluoranthene; BaPy = benzo(a)pyrene; BghiPe = benzo(g,h,i)perylene; IPy = indeno(1,2,3-cd)pyrene; DahAn = dibenzo(a,h)anthracene

[a] sum of BaAn, Ch,, BbFlu, BkFlu, BaPy, IPy, and DahAn, each multiplied for their respective toxicity equivalence factors (US EPA, 1993)

<d.l. = lower than detection limit.

PAH concentrations as Toxic Equivalents (TEQs) were calculated as specified in Table 1, using toxicity equivalence factors reported by US-EPA (1993). Values for TEQs are 1.46–8.41 ng g^{-1} in core Nad 1, 1.18–2.34 ng g^{-1} in core Nad 3, 2.67 ng g^{-1} at site Nad 2 and 3.74 ng g^{-1} at site Nad 4, with higher values at site Nad 1.

4.3 PCBs

Total PCB concentrations (ng g^{-1}) are shown in Fig. 2 for surficial samples and in Fig. 3 for cores Nad 1 and Nad 3. As for PAHs, values measured in surficial samples are higher at Nad 1 (21 ng g^{-1}) then decrease southeastward, passing from 13 ng g^{-1} at Nad 2 to 4.0 ng g^{-1} at Nad 4 and 2.5 ng g^{-1} at Nad 3 (Fig. 2). Also downcore values follow trends similar to PAHs, in that core Nad 1 shows the maximum concentration at the surface, whereas core Nad 3 has its highest value in the subsurficial layer, between 1 and 5 cm (8.5-9.4 ng g^{-1}, Fig. 3). No increase at depths between 22 and 42 cm of core Nad 1 is evidenced by total PCBs (Fig. 3).

Table 2 reports the concentration of PCB homologues (grouped as chlorination classes) in pg g^{-1}. Cl-3s are the most important for site Nad 2 and core Nad 1 (with the exception of layers 22-24 and 45-48 where Cl-4 congeners are dominant). Core Nad 3 is characterized by a higher contribution of Cl-2s, while Cl-6 congeners are the highest at Nad 4.

PCB concentrations as Toxic Equivalents (TEQs) were calculated as specified in Table 2, using toxicity equivalence factors reported by Van den Berg et al. (2006). Values for TEQs span the interval 0.0045–15.8 pg g^{-1} in core Nad 1, 0–0.582 pg g^{-1} in core Nad 3, and are 1.59 and 0.212 pg g^{-1} at Nad 2 and Nad 4, respectively, with average higher values at the northernmost sites Nad 1 and Nad 2.

The molar dechlorination product ratio (MDPR) was calculated in order to detect possible PCB dechlorination processes active in the sediments, as described in Liang et al. (2014). The ratio could not be calculated for most core levels in Nad 1 and at sites Nad 2 and Nad 4 because the concentrations of the selected PCBs were all below detection limits (Table 2 and Supplementary Material). On the contrary, values for core Nad 3 varied from 0.002 to 0.357 (Table 2).

Table 2. Concentrations of PCB homologues and TEQs (pg g^{-1}) in both surficial and downcore sediment samples from the Nador Lagoon. Estimates of MDPR (Molar Dechlorination Product Ratio) and percent contributions by the non-Aroclor CB-11 are also presented.

core	level (cm)	Cl-1	Cl-2	Cl-3	Cl-4	Cl-5	Cl-6	Cl-7	Cl-8	Cl-9	Cl-10	TEQ[a]	MDPR[b]	CB-11
Nad 1	0-1	<d.l.	<d.l.	10154	7082	1421	1304	734	24.3	<d.l.	<d.l.	0.0113	/	<d.l.
	1-2	<d.l.	1696	7911	3743	1046	1251	654	94.5	<d.l.	<d.l.	0.358	/	10.3
	4-5	<d.l.	501	8983	6404	851	1207	701	119	<d.l.	<d.l.	1.90	/	<d.l.
	7-8	<d.l.	644	8276	3440	926	1769	680	47.7	<d.l.	<d.l.	15.8	0.011	0.785
	14-16	<d.l.	1894	5813	2515	750	1948	911	359	<d.l.	<d.l.	0.0075	0.008	8.08
	22-24	<d.l.	977	4275	4416	3885	1649	503	72.5	<d.l.	<d.l.	0.750	/	3.94
	30-33	<d.l.	868	3420	2389	897	337	72.8	104	<d.l.	<d.l.	0.0054	/	10.7
	39-42	<d.l.	1255	3845	2161	641	195	18.6	53.1	<d.l.	<d.l.	0.0053	/	15.4
	45-48	<d.l.	1190	1173	1532	438	132	25.0	<d.l.	<d.l.	<d.l.	0.0045	/	26.5
Nad 3	0-1	<d.l.	963	610	819	58.6	33.5	12.1	<d.l.	<d.l.	<d.l.	0.0000	0.016	33.8
	1-2	<d.l.	1898	1131	1382	678	1781	1297	223	41.0	<d.l.	0.0073	0.006	<d.l.
	4-5	<d.l.	5229	1056	753	418	1048	690	154	<d.l.	<d.l.	0.582	0.244	7.53
	8-10	<d.l.	1360	641	643	181	276	87.7	25.8	<d.l.	<d.l.	0.119	0.313	9.07
	16-18	<d.l.	2696	1222	1181	282	329	107	20.4	<d.l.	<d.l.	0.148	0.357	8.88
	22-24	<d.l.	4040	1154	1251	531	991	673	162	<d.l.	<d.l.	0.483	0.002	20.1
Nad 2	0-1	<d.l.	1031	8077	1779	427	712	664	80.6	<d.l.	<d.l.	1.59	/	8.07
Nad 4	0-1	14.1	<d.l.	552	289	373	1429	1098	207	<d.l.	<d.l.	0.212	/	<d.l.

[a] sum of CB-77, -81, -105, -114, -118, -123, -126, -156, -157, -167, -169, and -189, each multiplied for their respective toxicity equivalence factors, as re-evaluated by the WHO in 2005 (Van den Berg et al., 2006)

[b] ratio of the sum of CB-1, -4, -8, -10, -19, and -54 over total PCBs (Liang et al., 2014)

<d.l. = lower than detection limit.

Among non-Aroclor PCBs (CB-11, CB-206, CB-207, CB-208 and CB-209; Hu et al., 2011), only CB-11 was detected at significant levels (Tables S2-4 in the Supplementary Material). Percent CB-11 contributions to the total concentrations range from <d.l. to 26 % in core Nad 1, from <d.l. to 34 % in core Nad 3, and are 8% and <d.l at Nad 2 and. Nad 4, respectively (Table 2). Concentrations vary from <d.l. to 1.70 ng g^{-1} at Nad 1, from <d.l. to 1.77 ng g^{-1} at Nad 3, and are 1.03 and <d.l ng g^{-1} at Nad 2 .and Nad 4, respectively (Figs. 2 and 3). No specific spatial and downcore trends are evidenced.

5. DISCUSSION

5.1 Chronological framework and inputs of PAHs and PCBs to the Nador Lagoon

Under costant flux-constant sedimentation (CF-CS) assumptions (Robbins, 1978; Oldfield and Appleby, 1984), the linear regressions calculated for ln^{210}Pb$_{ex}$ vs depth profiles of cores Nad 1 and Nad 3 (Fig. 4) allow the calculation of sediment accumulation rates of 0.541 and 0.320 cm y^{-1}, respectively, in accordance with the Constant Rate of Supply (CRS) average sedimentation rate of 0.50 cm y^{-1} determined by Flower et al. (2009) in a sediment core collected near site Nad 1. With these rates, ^{137}Cs peaks in cores Nad 1 and Nad 3 are located in sediment layers deposited in the early 1960s, in good accordance with maximum fallout timing. In addition, the bases of ^{137}Cs profiles date back to the mid 1940s, when nuclear bomb testings began. With these ^{137}Cs independent confirmation, ^{210}Pb-based chronology was applied to the profiles of porosity, sand content, TC, OC, total PAHs and total PCBs (Fig. 3).

The porosity decrease observed in core Nad 1 approximately between 20 and 40 cm depth (Fig. 3) is relative to a time period spanning from the early 1930s to the mid 1960s. In the same period, relative lower values of OC and relative higher values of total PAHs can be observed, while sand contents and TC values remain quite constant. Contemporary total PCBs are low and start to increase just at the end of this time window, thus recording a period of maximum PCB use that peaked in the late 1960s (Aguilar and Borrell, 2005; Mugnai et al., 2011). The most recent sediment layers of core Nad 1 (approximately from the beginning of the 21st century, Fig. 3) are characterized by constant increases of both PAH and PCB total concentrations with no evident correlation to grain size and carbon content (Table 3). The recent PCB increase appears in contrast to the production bans and use restrictions in 1970-1980s. Further recommendations were promoted in 2001 by the Stockholm Convention on Persistent Organic Pollutants, ratified also by Morocco in 2004 (http://www.pops.int/documents/ convtext/convtext_en.pdf). The observed increase could be associated to PCB mobility from reservoirs or unconfined wastes that are expected to cause continuous release in aquatic environments for several more decades (Tanabe, 1988). Furthermore, it is known that landfills can be considered one of the most important present sources, with the uncontrolled disposal of old electrical appliances (Giuliani et al., 2011b). On the contrary, the increase of PAH concentrations can be associated to natural or anthropogenic causes that will be discussed in the following section.

A previous research in the lagoon (Piazza et al., 2009) reported a total PCB surficial sediment value of 6.13 ng g^{-1}. Rather surprisingly, the surficial value measured in core Nad 1 is higher than those determined in the ports of Larache and Kenitra (Piazza et al., 2009) that, in turn, are similar to the concentration found at site Nad 2.

Core Nad 3 shows an abrupt change of sedimentary conditions in the early 1980s: materials deposited from that time onward are significantly finer than older ones and are comparable to those found at Nad 1. This means that the hydrodynamics in the area has decreased in recent times, thus allowing the accumulation of finer sediments. In support to this hypothesis, Lefebvre et al. (1997) reported a progressive siltation of the Bokhana inlet (from the first dredging activities in 1910 until its complete closure in 1977) that might have reinforced local water circulation in the southern sector of the lagoon. The present-day hydrodynamic setting is the result of a storm in 1981 (Lefebvre et al., 1997) that reopened the inlet and might have favoured fine sediment deposition all over the lagoon. Neither carbon content nor contaminant inputs seem to have been considerably affected by these changes (Fig. 3). Both total PAH and total PCB concentrations peaked in late 1990s–early 2000s and are presently decreasing.

5.2 Sources of PAHs and PCBs to the Nador Lagoon

Both PAH and PCB surficial values are higher at Nad 1 with respect to all other sampled locations (Fig. 2). This pattern is clearly due to the vicinity of this site to the most important anthropogenic activities: according to Fig. 1, Nad 1 might be influenced by many different anthropogenic sources, such as urban sewage, wastewaters, mining and fisheries-aquaculture activities. In addition, the higher water depth at this location (ca. 5 m, Table S1 in the Supporting Material) might favour the accumulation of both sediment and chemicals, thus partly explaining the lower concentrations measured in the nearby shallower site Nad 2.

5.2.1. PAHs

PAHs are regarded as priority pollutants because many of them show mutagenic and carcinogenic properties (Nielsen et al., 1995).

Diagnostic ratios for selected PAH groups are used to determine their origin (Tobiszewski and Namiesnik, 2012). For example, petrogenic PAHs (mainly from oil or carbon spills) are characterized by a predominance of low molecular weight (i.e,. those with 2-3 benzene rings) and alkylated congeners, whereas heavier PAHs originate from high- or low-temperature pyrogenic inputs from natural or anthropogenic sources. The ΣLMW/ΣHMW and ΣCOMB/ΣPAH ratios (Fig. 5a) can then be used to discriminate what is the main contribution to PAHs in the samples. Further information relative to PAH sources can be derived by diagnostic ratios between pairs of congeners with the same molecular mass but with different thermodynamic stability (Tobiszewski and Namiesnik, 2012). Flu and Py, for example, both have a molecular mass of 202 but very different stability and therefore may discriminate between different pyrogenic sources (Fig. 5a). Similarly, IPy and BghiPe (molecular mass 276) can be used to identify the same processes (Fig. 5a).

PAHs in most samples originate from petrogenic sources (Fig. 5a). The few exceptions are represented by the surficial sediment at Nad 4 and the layer between 22 and 42 cm depth in core Nad 1 that are characterized by PAH assemblages mostly due to combustion.

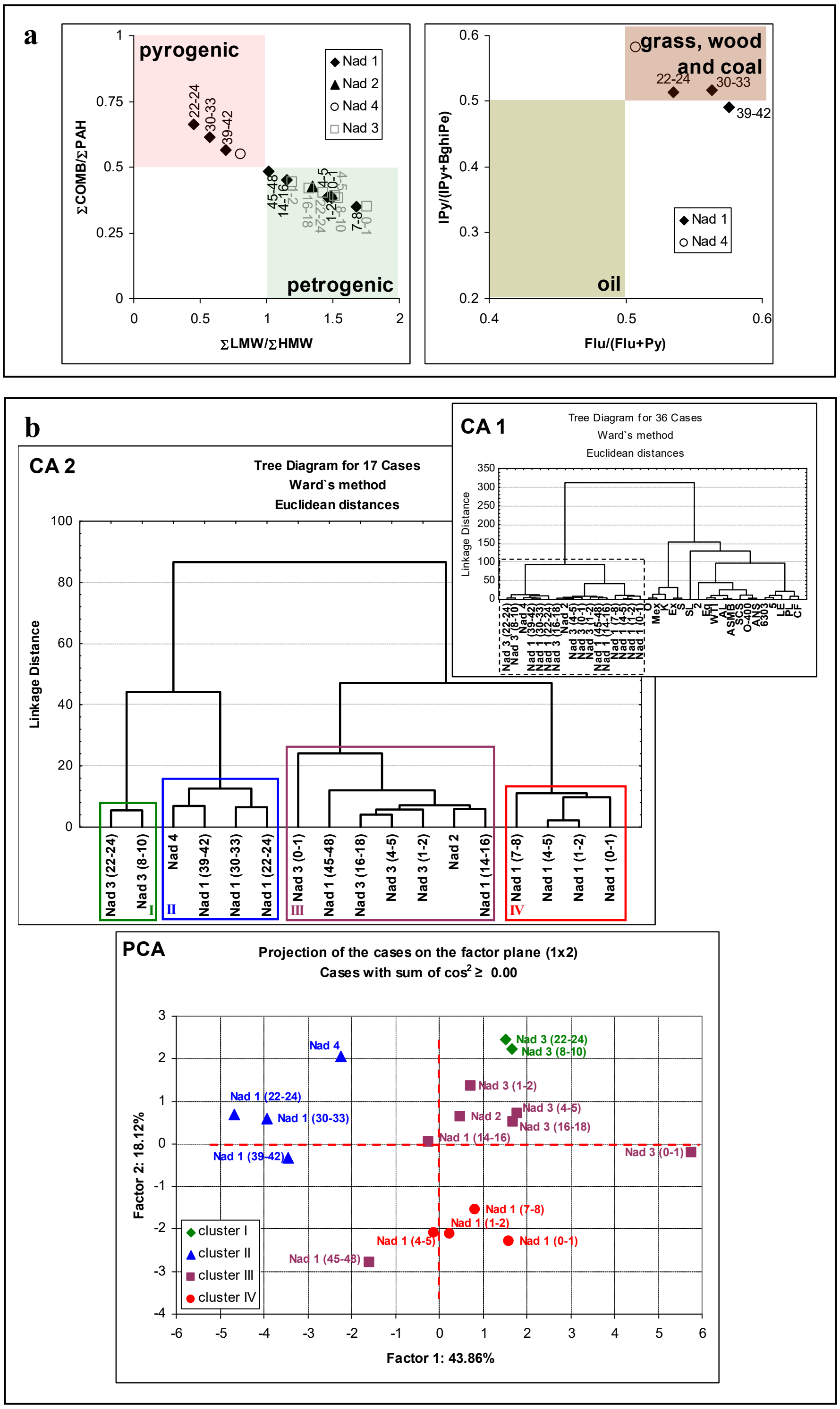


Fig. 5. Origin and sources of PAHs to the Nador Lagoon: (a) diagnostic ratios based on concentrations of congeners: ΣLMW=sum of low molecular weight (2-3 rings) congeners (Ac, Ace, F, Phe, An); ΣHMW=sum of high molecular weight (4-6 rings) congeners (Flu, Py, BAn, Ch, BbFlu, BkFlu BaPy, BPe, IPy, DahAn); ΣCOMB= sum of 9 non-alkylated PAHs (Py, Flu, BaAn, Ch, BFluos, BaPy, BghiPe, IPy); ΣPAH=sum of all measured PAHs; (b) Cluster Analysis (CA) and Principal Component Analysis (PCA) performed on percent contribution of each PAH congener to the total. CA 1 considers all sediment samples collected in the Nador Lagoon and crude oils from various parts of the world (see the Supplementary Material for details). CA 2 was run only on Nador Lagoon sediment samples. Clusters identified by the CAs are reported on the PCA.

This means that in the period early 1930s–mid 1960s, PAHs reaching site Nad 1 originated mainly by high-temperature pyrogenic inputs, prevalently from grass, wood and coal matrices, as diagnosed by Flu/(Flu+Py) and IPy/(IPy+BghiPe) ratios (Fig. 5a). This input was not irrelevant, since resulted in PAH concentrations that were similar to those detected in the recentmost sediment layer that has been linked to anthropogenic-petrogenic sources (Fig. 3). The combustion of organic matter might be further confirmed by the lower OC content detected in the same period (Fig. 3), even if no significant correlation between total PAHs and OC is generally evidenced (Table 3).

Table 3 Product Moment correlations between sediment parameters (porosity, sand content, TC and OC) and analysed chemicals (total PAHs, total PCBs and CB-11, as ng g^{-1}). Bold values are significant at $p< 0.05$.

	porosity	**sand**	**TC**	**OC**	**PAH**	**PCBs**
sand	**-0.82**					
TC	-0.26	**0.68**				
OC	**0.73**	**-0.56**	-0.12			
PAHs	0.41	-0.45	-0.38	0.38		
PCBs	**0.49**	-0.36	0.06	0.46	**0.65**	
CB-11	-0.23	0.14	-0.04	0.15	-0.04	-0.11

Petrogenic PAH assemblages characterising the other samples (Fig. 5a) do not present any significant resemblance with the average composition of different kinds of oil extracted all over the world (Renzi and Peirong, 1991; Bojakowska and Sokolowska, 2001, Wang et al., 2003): the Cluster Analysis (CA) performed on percent composition of selected PAHs (F, Phe, Flu, Py, BaAn and Ch, see Table S5 in the Supplementary Material) and reported as CA 1 in Fig. 5b, shows a clear separation between the Nador Lagoon sediment samples and reference black oils. Therefore, mixing of different petrogenic sources must be considered as the origin of PAH assemblages in these sediments. In addition, post depositional degradation processes may have significantly changed the patterns with respect to the original composition.

A magnified version of the CA 1 dotted area is reported in Fig. 5b as CA 2 and considers only the sediments from the Nador Lagoon. In this way, similarities among samples could be better resolved. Indeed, CA 2 results agree with diagnostic ratios in evidencing the differences between the Nad 1 sedimentary level between 22 and 42 cm (cluster II, Fig. 5b) and the remainder of the core. Samples belonging to cluster II are characterized by a higher contribution of heavier congeners and present the lowest percentages of Phe (Table 1 and Table S6 in the Supplementary Material). In addition, core Nad 3 and Nad 1 belong in general to two similar but clearly separated clusters (III and IV, Fig. 5b) characterized by different contributions of Ace (1.4-12 % in III, and < d.l. in IV, Table S6 in the Supplementary Material), probably reflecting the varying relevance of anthropogenic impacts over the two sites (i.e. prevalently urban/industrial for Nad 1 and agricultural for Nad 3, Fig. 1). Cluster I (Fig. 5b) is composed by the two sedimentary levels in core Nad 3 that show the highest Ace contributions (22-24%, Table S6 in the Supplementary Material).

Table 4 Variable contribution to PCA factors, based on correlations: (a) PAH congeners; (b) PCB chlorination classes.

(a)	**Factor 1**	**Factor 2**
Ac	0.016174	0.085856
Ace	0.025859	0.213462
F	0.088091	0.003067
Phe	0.039233	0.192304
An	0.055793	0.084009
Flu	0.075899	0.000542
Py	0.033634	0.023147
BaA	0.117100	0.038636
Ch	0.085360	0.074241
BbFlu	0.127259	0.000033
BkFlu	0.047085	0.008859
BaPy	0.011811	0.217922
BghiPe	0.121895	0.019829
IPy	0.075737	0.019971
DahAn	0.079070	0.018123
(b)	**Factor 1**	**Factor 2**
Cl-1	0.000911	0.307625
Cl-2	0.001579	0.339431
Cl-3	0.104604	0.063246
Cl-4	0.114616	0.130720
Cl-5	0.000079	0.118565
Cl-6	0.178841	0.025867
Cl-7	0.221962	0.006923
Cl-8	0.193791	0.004292
Cl-9	0.183617	0.003331

Results of the Principal Component Analysis (PCA) performed on the same dataset of CA 2 (Fig. 5b) agree well with the clustering and provide further confirmation of different sources controlling PAH inputs to sediments of the Nador Lagoon (Table 4): Factor 1 (44 % of observed differences; Fig. 5b), that separates samples of cluster II from the rest, is controlled prevalently by high weight congeners, whereas Ace and Phe variations are crucial for Factor 2 (18 % of observed differences; Fig. 5b) that separates clusters I, III and IV.

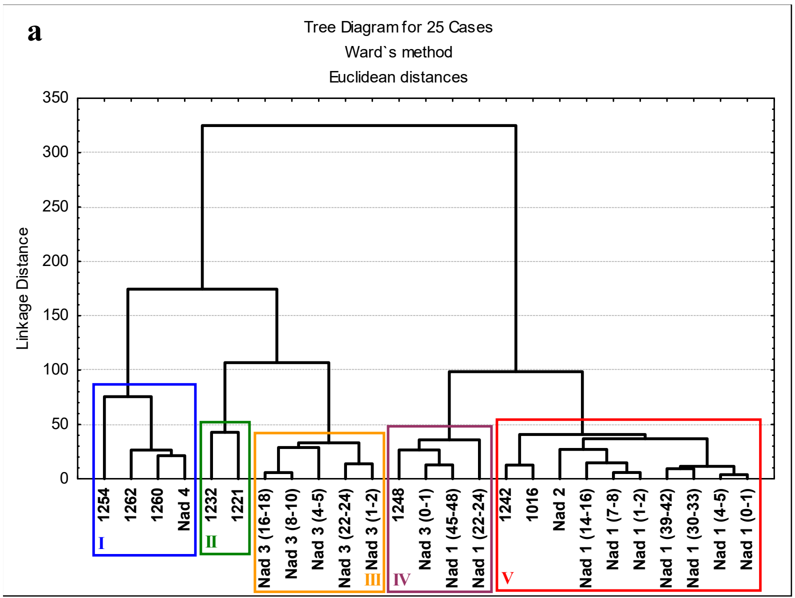
5.2.2. PCBs

PCBs are mixtures of synthetic organic chemicals that were used in the past in hundreds of industrial and commercial applications, due to their flame retardant proprieties, chemical stability, high boiling point and insulating properties. However, their presence has been reported in sediments deposited prior to the onset of production and related also to natural combustion processes (Ruiz-Fernandez et al., 2012 and references therein). These latter are generally evidenced by a strong significant correlation between total PCB concentrations and OC contents (Ruiz-Fernandez et al., 2012). No such correlation is detected in the Nador Lagoon ($r = 0.46$ at $p< 0.05$, Table 3), therefore, coupled to the fact that the PCB depth profile is consistent to the chronology of inputs (see section 5.1), the most plausible source of PCBs in this area is still anthropogenic.

Similarly to total PCBs, CB-11 concentrations in the Nador Lagoon display no significant correlations with sediment features (r values ranging from -0.23 to 0.15 at $p<0.05$, Table 3), therefore its relevant presence in some samples accounts for specific typical sources, linked to local human activities utilizing pigments or dyes (Rodenburg et al., 2010; Romano et al., 2013). The presence of relatively high levels of CB-11 at depths corresponding to the early 1940s in Nad 3 (Fig. 3) could be an indication of consistent direct inputs at that time that should be further investigated. For the rest of PCB congeners, it is a well established practice to compare the PCB composition in environmental samples to commercial mixtures, usually Aroclors, in order to evaluate the most relevant human sources (e.g. Fava et al., 2003; Frignani et al., 2004; Piazza et al., 2009; Liang et al., 2014). For this purpose, the CA shown in Fig. 6a was performed on percent composition of PCB homologues in the analysed samples of the Nador Lagoon and in the most widely used Aroclor mixtures (Frame et al., 1996; see Table S7 in the Supplementary Material). Non-Aroclor CB-11 was excluded from the analysis, since its presence would overestimate the relevance of Cl-2s. Five clusters are well evidenced in Fig. 6a and, with the exception of clusters II and III, each is characterized by resemblances of lagoon sediments to specific Aroclor mixtures: cluster I groups closely together the highly chlorinated Aroclors 1260 and 1262 (more loosely 1254) with Nad 4 surficial sediment, as they are all characterized by the clear prevalence of Cl-6 and -7 (see Table S7 in the Supplementary Material); cluster IV links the surficial level of core Nad 3, and the deepest (45-48 cm) and intermediate (22-24 cm) levels of core Nad 1 to Aroclor 1248 (dominance of Cl-4); while cluster V includes in a close relationship all remaining levels of core Nad 1, Nad 2 surficial sediment, and Aroclors 1016 and 1242, as they are all clearly dominated by Cl-3 (see Table S7 in the Supplementary Material). Sediments from 1 to 24 cm depth in core Nad 3 (cluster III, Fig. 6a) do not display any resemblance to the considered Aroclor mixtures, since they are characterized by the prevalence of Cl-2s (indeed, the closest linkage is a feeble resemblance with cluster II, where Cl-1 and -2 dominated Aroclors 1221 and 1232 are grouped, Fig. 6a). This sedimentary level corresponds to the period spanning from early 1940s to early 2000s (Figures 2 and 3), when PCB production was still allowed all over the world (until 1980s) or not yet restricted in Morocco (from 2004, see section 5.1).

The observed differences between PCB assemblages in these sediments and commercial mixtures might then be explained by a series of factors, linked either to post-depositional processes (such as microbial anaerobic dechlorination) or mixed inputs.

In order to evaluate the magnitude of natural PCB degradation through microbial dechlorination processes in core sediments, the molar dechlorination product ratio (MDPR) was used (Table 2). It is assumed that anaerobic dechlorination often preferentially removes chlorines at para- and meta-positions, resulting in the enrichment of ortho-chlorinated congeners (Fava et al., 2003). Therefore five exclusively ortho-chlorinated PCBs (CB-1, -4, -10, -19, -54) and CB-8 were selected to identify the ultimate dechlorination products, as indicated by Liang et al. (2014). The ratio of the sum of their concentrations (see Tables S2-4 in the Supplementary Material) over total PCB concentrations is named MDPR (Table 2). For the majority of analysed samples, the MDPR either could not be calculated because the selected congeners were all below detection limits or showed low concentrations (Table 2). This is a clear indication that PCB degrading processes are not significant in these sediments, and it is expected in surficial sediments that represent recent not-degraded inputs. It is interesting to notice that downcore samples with no evidence of anaerobic dechlorination are those that show some resemblance to Aroclor commercial mixtures (Table 2 and Fig. 6a).



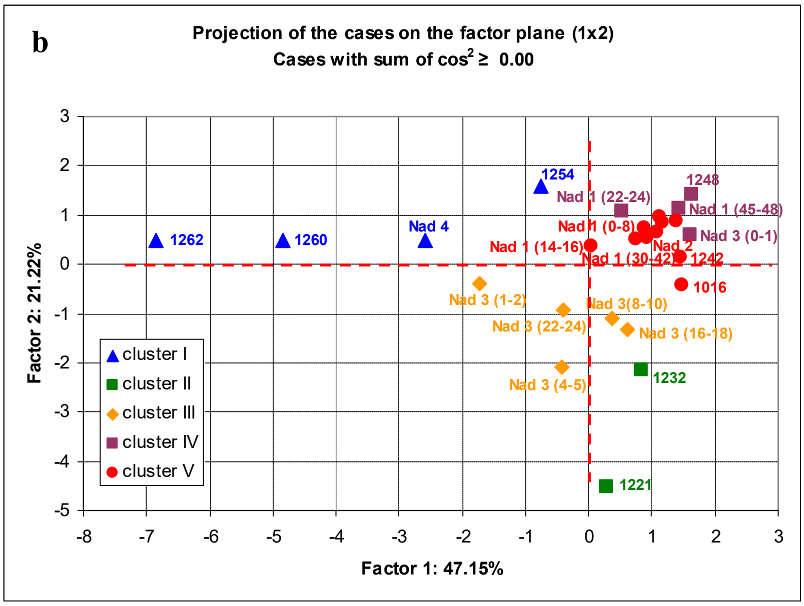


Fig. 6 Origin and sources of PCBs to the Nador Lagoon: (a) CA on percent contribution of each PCB chlorination class to the total (with the exclusion of CB-11). Average composition of the most important commercial Aroclor mixtures was also considered (from Frame et al., 1996); (b) Results of the PCA performed on the same data matrix of the CA. Clusters identified by the CA are reported on the PCA.

The sole indications of anaerobic dechlorination are evidenced by Nad 3 sediments deposited in the period late 1940s-mid 1990s (MDPR ranging from 0.244 to 0.357, Table 2 and Figs. 2 and 3), and are confirmed also by the CA (Fig. 6a). Interestingly, also CB-11 in that period presents a clear decrease from higher concentrations in the late 1940s to lower levels in more recent times (Fig. 3), as if some aerobic degradation (Rodenburg et al., 2010) of this congener had contemporarily occurred. Unfortunately, these results are not sufficient in clarifying whether degrading processes (in that period and at that location) might have been favoured by hydrodynamic changes, evidenced by sand content profiles (see section 5.1), or are linked to other causes. However, they helped in recognizing that the importance of mixed contribution by different PCB inputs is evident only in the deepest/oldest sedimentary level of core Nad 3.

The PCA reported in Fig. 6b was performed on the same dataset used for the CA (see Table S6 in the Supplementary Material) and confirms its results. In addition, the PCA more strikingly evidences that the observed differences between cores Nad 1 and Nad 3 are guided prevalently by varying percentages of Cl-2, that is the major contributor to Factor 2 (Table 3), explaining 20 % of the observed differences (Fig. 6b).

5.3 Potential toxicity of Nador Lagoon sediments due to PAHs and PCBs

PAH levels in the lagoon (21.6-108 ng g^{-1}, average value 51.9 ng g^{-1}, Fig. 3 and Table 1) are rather low when compared with those found all over the world (see Giuliani et al., 2008 and references therein), even when total values are normalized for a completely fine-grained sediment (Fig. 3). PAH concentrations are lower than internationally accepted sediment quality guidelines (e.g., consensus-based TEC and PEC; Ingersoll et al., 2000). In addition, total PAHs as TEQs (Table 1) are similarly low (up to three orders of magnitude lower) when compared to impacted areas (e.g. Aryal et al., 2013; Nekhavhambe et al., 2014; Dong et al., 2014). Therefore, PAHs in the analysed sediments of the Nador Lagoon do not pose any potential threath to humans and biota.

PCB total values in the lagoon ranging from 2.50 and 20.7 ng g^{-1} (average value 9.17 ng g^{-1}, Fig. 3 and Table 2) can be similarly considered rather low when compared to impacted places and similar to average concentrations of other coastal lagoons (Giuliani et al., 2011b) even when total values are normalized for a completely fine-grained sediment (Fig. 3). As for PAHs, the maximum PCB value is well below the consensus-based TEC of 59.8 ng g^{-1} (Ingersoll et al., 2000). TEQ values (<d.l.-15.8 pgTEQ g^{-1}, average 1.29 pgTEQ g^{-1}, Table 2) are similar to those characteristic of low-impacted areas (Kumar et al., 2013; Dodoo et al., 2012). Therefore also PCBs cannot be considered dangerous neither to biota nor to the local population. Relatively little is known about the toxicity of CB-11: because it is not substituted in the ortho positions, it may exhibit dioxin-like toxicity (Rodenburg et al., 2010). However, measured concentrations in the Nador Lagoon are similar to those detected in other low impacted areas (Romano et al., 2013; Guo et al., 2014) and well below the limit of 50 ng g^{-1} set by the EU Directive 89/677/EEC for PCBs in pigments.

CONCLUSIONS

The results of this work agree with previous studies on Moroccan coastal areas and testify a low degree of contamination by PAHs and PCBs in sediments of the Nador Lagoon, consequently defining also their very low toxicity. However, total concentrations (both as ng g^{-1} and TEQs) are higher in the sites located near the city of Nador and are presently increasing, confirming the potential higher impact of urban areas and the surrounding industrial sites with respect to agricultural activities located in the southwestern part of the lagoon. Indeed, the different activities present along the lagoon borders (i.e urban and industrial sites vs agricultural and touristic areas) seem to control the level and composition of PAH and PCB assemblages measured in the sediment.

The combined study of sediment chronology and source apportionment evidences the different inputs and post-depositional processes controlling the two classes of contaminants: i) PAHs show a predominant petrogenic origin from mixed sources in recent times all over the lagoon, whereas they are characterized by important pyrogenic inputs in sediments deposited between the early 1930s and the mid 1960s near the city of Nador. The combustion was prevalently of natural matrices (i.e. grass, wood and coal) defining the relevance of natural or man-made fires impacting the area at that time; ii) PCBs show higher similarities to commercial Aroclor mixtures in recent sediments or near the most important industrial sites, while some evident signs of microbial anaerobical degradation are present in the location where agricultural inputs are prevalent. Indeed, PCB degradation is detected in sediments dating from the mid 1950s to the mid 1990s, likely linked also to hydrodynamic changes relative to the period, with the progressive closure and successive abrupt opening of the Bokhana inlet. The effect of selective fractionation and long-range atmospheric transport can not be ruled out, either.

CB-11 has been analysed for the first time in the Nador Lagoon and results suggest the relevance of specific input sources likely connected to pigment use and production.

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Supplementary Material to the paper:

Recognizing the different impacts of human and natural sources to PAH and PCB (including PCB-11) spatial distribution and temporal trends in sediments of the Nador Lagoon (Morocco)

Silvia Giuliani[1], Rossano Piazza[2,3], Luca Giorgio Bellucci[1], Fabio Paolo Polo[2,3], Marco Vecchiato[3,4], Stefania Romano[1], Stefano Zambon[2], Mauro Frignani[1], Bouchta El Moumni[5,6]

[1]CNR-Institute of Marine Sciences, Via Gobetti 101, Bologna, Italy
[2]Dept. of Environmental Sciences, Informatics and Statistics, Univ. of Venice, Dorsoduro 2137, Venice, Italy
[3]CNR-Institute for the dynamics of Environmental processes, Dorsoduro 2137, Venice, Italy
[4] Univ. of Siena
[5]Dept. of Earth Sciences and Oceanography, University of Tangier, Morocco
[6]Polydisciplinary Faculty of Larache, BP 745 Route de Rabat, Larache, Tangier region, Morocco

Table S1. Sampling date, water depths, lengths, and coordinates of sediment cores collected in the Nador Lagoon.

site	date	water depth (m)	length (cm)	Lat.	Long.
Nad 1	23/06/09	5	50	35º 10.833' N	02º 53.928’ W
Nad 2	23/06/09	3.5	36	35º 10.421’ N	02º 53.701’ W
Nad 4	23/06/09	3.5	35	35º 07.415’ N	02 º 50.878’ W
Nad 3	23/06/09	4	38	35º 06.579’ N	02º 47.939’ W

Table S2. Concentrations (in pg g^{-1}) of PCB congeners in the selected sediment layers (cm) of core Nad 1. The asterisk identifies the 21 congeners present in the ^{13}C-labelled mixtures spiked as internal standards. A double asterisk identifies the two labeled ^{13}C congeners (PCB-47 and -141) used for recovery measurements.

PCB #	**Chlorination class**	**Sediment layer**								
		0-1	**1-2**	**4-5**	**7-8**	**14-16**	**22-24**	**30-33**	**39-42**	**45-48**
1	1	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
2	1	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
3*	1	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
10.4	2	<d.l.	<d.l.	<d.l.	<d.l.	79.5	<d.l.	<d.l.	<d.l.	<d.l.
7.9	2	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
6	2	<d.l.	<d.l.	<d.l.	<d.l.	32.2	<d.l.	<d.l.	<d.l.	<d.l.
5+8	2	<d.l.	<d.l.	<d.l.	168	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
11	2	<d.l.	1696	<d.l.	124	1147	621	868	1255	1190
12	2	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
15*	2	<d.l.	<d.l.	501	353	635	356	<d.l.	<d.l.	<d.l.
19	3	<d.l.	<d.l.	<d.l.	<d.l.	36.4	<d.l.	<d.l.	<d.l.	<d.l.
18	3	1607	692	1019	847	596	205	548	<d.l.	239
17	3	2083	755	1081	730	623	215	123	1091	<d.l.
24.27	3	<d.l.	301	<d.l.	<d.l.	72.3	<d.l.	<d.l.	73.3	<d.l.
16.32	3	796	378	584	588	430	358	364	240	103
34	3	<d.l.	<d.l.	<d.l.	433	124	<d.l.	<d.l.	366	<d.l.
29	3	<d.l.	<d.l.	<d.l.	508	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
26	3	<d.l.	<d.l.	467	664	279	222	191	198	<d.l.
25	3	<d.l.	1059	<d.l.	<d.l.	101	<d.l.	<d.l.	<d.l.	100.1
31	3	<d.l.	918	1252	1068	825	778	586	426	222
28*	3	1966	1545	2035	1464	1063	1096	750	543	258
20.33	3	2290	1094	1676	1335	877	930	573	640	251
22	3	1411	1169	871	639	408	470	285	267	<d.l.
37	3	<d.l.	<d.l.	<d.l.	<d.l.	378	<d.l.	<d.l.	<d.l.	<d.l.
45	4	<d.l.	62.4	<d.l.	43.6	<d.l.	47.7	<d.l.	29.3	<d.l.
46	4	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
69	4	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
52*	4	1993	<d.l.	1281	823	434	800	724	571	374
49	4	409	269	429	248	270	266	133	124	79.7
47**.48	4	634	367	554	239	498	297	194	170	104
44	4	634	375	441	323	231	418	256	238	157
59.42	4	463	290	367	73.6	61.1	76.3	183	149	123
71.41.64	4	949	544	749	473	338.9	511	317	271	202
40	4	<d.l.	131	185	98.8	38.6	117	<d.l.	<d.l.	<d.l.
67	4	<d.l.	24.7	101	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
63	4	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
74	4	300	240	240	123	106	293	110	126	101
70	4	532	433	442	291	228	673	177	182	145

continue…

...continue

PCB #	Chlorination class	Sediment layer								
		0-1	1-2	4-5	7-8	14-16	22-24	30-33	39-42	45-48
66	4	658	589	708	416	162	459	138	168	130
56.60	4	510	375	377	247	147	401	156	110	100
81*	4	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
77*	4	<d.l.	42.3	530	40.5	<d.l.	56.8	<d.l.	24.9	16.4
104	5	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
103	5	<d.l.	<d.l.	13.6	30.1	<d.l.	<d.l.	<d.l.	19.6	<d.l.
93.95	5	10.2	128	117	103	105	425	141	109	80.8
91	5	51.1	29.7	35.2	34.9	30.5	71.2	27.0	24.6	24.9
92	5	37.1	18.5	23.4	<d.l.	33.1	89.3	21.2	22.6	26.1
84.101.90	5	344	218	142	205	180	865	326	103	64.4
99	5	120	102	146	184	153	313	45.4	34.8	19.1
119	5	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
83	5	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
97	5	79.5	39.1	50.8	37.2	29.0	178	35.3	37.9	24.4
87.115	5	105	85.0	29.1	40.4	33.2	257	43.0	64.3	26.5
85	5	60.3	30.3	40.4	27.8	27.6	133	<d.l.	31.3	11.3
110	5	277	141	89.9	90.2	65.2	644	76.8	89.0	65.5
82	5	27.3	15.0	<d.l.	<d.l.	<d.l.	35.8	<d.l.	9.8	<d.l.
107	5	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	21.1	<d.l.	<d.l.	<d.l.
123*	5	62.2	6<d.l.	31.0	26.6	<d.l.	73.5	45.7	40.1	56.8
118*	5	162	127	77.4	104	67.7	551	111	27.1	23.4
114*	5	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	12.3	<d.l.
105*	5	84.7	53.3	55.1	43.2	25.7	228	25.1	15.3	15.1
126*	5	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
136	6	52.7	34.2	23.8	27.5	42.8	49.9	14.1	17.5	11.4
151	6	73.4	70.8	62.0	58.8	109	88.3	<d.l.	24.0	14.1
135.144	6	36.8	36.9	36.9	32.4	49.6	59.0	<d.l.	23.4	<d.l.
147	6	<d.l.	<d.l.	26.9	23.6	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
149	6	214	169	141	216	254	303	55.8	52.0	43.3
134	6	<d.l.	9.8	<d.l.	<d.l.	<d.l.	19.2	<d.l.	<d.l.	<d.l.
131	6	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
146	6	46.3	48.2	61.6	73.3	77.4	51.9	<d.l.	<d.l.	<d.l.
153*	6	317	353	412	439	680	369	95.2	26.0	10.1
132	6	89.1	52.8	31.5	34.4	59.4	118	28.0	10.9	16.9
141**	6	39.0	24.2	16.2	17.1	15.5	59.7	<d.l.	11.7	<d.l.
137	6	<d.l.	47.9	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
164.138	6	353	310	284	279	505	411	144	29.2	36.3
158	6	16.3	11.8	<d.l.	<d.l.	17.4	30.4	<d.l.	<d.l.	<d.l.
129	6	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
128.167*	6	44.3	40.9	28.6	40.1	122	47.9	<d.l.	<d.l.	<d.l.
156*	6	16.6	17.4	20.9	<d.l.	16.2	17.8	<d.l.	<d.l.	<d.l.

continue…

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PCB #	Chlorination class	Sediment layer								
		0-1	**1-2**	**4-5**	**7-8**	**14-16**	**22-24**	**30-33**	**39-42**	**45-48**
157*	6	5.6	12.2	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
169*	6	<d.l.	11.5	61.4	527	<d.l.	23.9	<d.l.	<d.l.	<d.l.
179	7	50.9	38.2	42.0	58.2	<d.l.	36.1	<d.l.	<d.l.	<d.l.
176	7	9.4	17.6	<d.l.	<d.l.	<d.l.	15.3	<d.l.	<d.l.	<d.l.
178	7	30.3	20.2	47.8	29.1	42.9	24.8	<d.l.	<d.l.	<d.l.
187	7	143	149	191	219	245	123	<d.l.	<d.l.	<d.l.
183	7	57.3	33.5	29.3	33.8	57.8	28.1	<d.l.	<d.l.	<d.l.
185	7	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
174	7	61.1	56.7	48.9	31.7	60.3	38.3	<d.l.	<d.l.	<d.l.
177	7	66.0	54.8	74.1	76.5	110	43.8	<d.l.	<d.l.	<d.l.
171	7	13.2	14.9	<d.l.	<d.l.	26.6	29.9	<d.l.	<d.l.	<d.l.
173	7	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
172	7	19.9	<d.l.	<d.l.	<d.l.	18.8	<d.l.	<d.l.	<d.l.	<d.l.
180*	7	161	172	150	122	211	110	72.8	18.6	25.0
193	7	14.2	<d.l.	18.7	18.3	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
191	7	<d.l.	<d.l.	4.7	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
170.190	7	108	96.2	94.3	92.0	120	53.8	<d.l.	<d.l.	<d.l.
189*	7	<d.l.	<d.l.	<d.l.	<d.l.	17.3	<d.l.	<d.l.	<d.l.	<d.l.
197	8	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	104.1	<d.l.	<d.l.
199	8	<d.l.	31.8	55.6	<d.l.	44.8	<d.l.	<d.l.	<d.l.	<d.l.
196.203	8	<d.l.	23.7	25.1	<d.l.	40.8	38.4	<d.l.	32.7	<d.l.
195	8	<d.l.	<d.l.	<d.l.	<d.l.	229	<d.l.	<d.l.	<d.l.	<d.l.
194*	8	24.3	39.1	38.7	47.7	44.3	34.0	<d.l.	<d.l.	<d.l.
205	8	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	20.4	<d.l.
208*	9	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
207	9	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
206	9	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
209*	10	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.

<d.l. = lower than detection limit

Table S3. Concentrations (in pg g^{-1}) of PCB congeners in selected sediment layers (cm) of core Nad 3. The asterisk identifies the 21 congeners present in the ^{13}C-labelled mixtures spiked as internal standards. A double asterisk identifies the two labeled ^{13}C congeners (PCB-47 and -141) used for recovery measurements.

PCB #	Chlorination class	Sediment layer					
		0-1	1-2	4-5	8-10	16-18	22-24
1	1	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
2	1	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
3*	1	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
10.4	2	39.9	54.1	<d.l.	<d.l.	32.9	19.7
7.9	2	<d.l.	934	1908	<d.l.	1.86	2155
6	2	<d.l.	<d.l.	<d.l.	10.4	<d.l.	<d.l.
5+8	2	<d.l.	<d.l.	2279	1006	2053	<d.l.
11	2	843	<d.l.	704	291	519	1767
12	2	<d.l.	673	338	<d.l.	<d.l.	<d.l.
15*	2	80.2	237	<d.l.	51.9	89.5	99.3
19	3	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
18	3	125	<d.l.	<d.l.	94.7	170	151
17	3	111	124	155	63.2	191	84
24.27	3	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
16.32	3	<d.l.	77.0	<d.l.	38.7	85.9	66.9
34	3	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
29	3	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	23.9
26	3	68.8	94.6	<d.l.	41.9	<d.l.	93.4
25	3	<d.l.	37.6	<d.l.	41.3	16.1	40.1
31	3	141	200	236	69.6	213	<d.l.
28*	3	164	240	297	103	240	197
20.33	3	<d.l.	237	241	127	193	231
22	3	<d.l.	121	126	61.0	114	135
37	3	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	131
45	4	<d.l.	<d.l.	<d.l.	<d.l.	24.6	25.7
46	4	<d.l.	<d.l.	78.0	131	80.6	80.7
69	4	<d.l.	<d.l.	<d.l.	92.4	<d.l.	<d.l.
52*	4	205	433	201	<d.l.	281	183
49	4	64.2	104	<d.l.	43.5	72.9	60.5
47**.48	4	91.0	<d.l.	<d.l.	72.0	115	117
44	4	78.4	125	<d.l.	65.1	105	93.3
59.42	4	<d.l.	<d.l.	<d.l.	<d.l.	15.4	55.4
71.41.64	4	90.8	203	171	106	111	116
40	4	52.8	<d.l.	<d.l.	<d.l.	26.8	22.9
67	4	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
63	4	<d.l.	92.3	<d.l.	<d.l.	49.7	73.1
74	4	41.8	83.0	74.3	39.4	57.5	90.3
70	4	89.3	161	147	<d.l.	110	164

continue…

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PCB #	Chlorination class	Sediment layer					
		0-1	**1-2**	**4-5**	**8-10**	**16-18**	**22-24**
66	4	51.7	78.5	81.2	45.6	55.0	71.1
56.60	4	53.8	93.3	<d.l.	48.5	70.2	87.9
81*	4	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
77*	4	<d.l.	9.47	<d.l.	<d.l.	6.29	10.3
104	5	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
103	5	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
93.95	5	29.2	111	58.6	<d.l.	48.3	67.9
91	5	<d.l.	25.8	<d.l.	<d.l.	13.3	18.7
92	5	<d.l.	30.2	<d.l.	<d.l.	6.53	16.8
84.101.90	5	<d.l.	205	111	60.5	74.6	129
99	5	13.8	62.0	34.1	26.9	30.0	39.3
119	5	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	4.15
83	5	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
97	5	<d.l.	33.6	17.7	17.0	15.5	20.9
87.115	5	<d.l.	41.3	24.3	15.9	19.2	<d.l.
85	5	<d.l.	42.7	20.4	19.0	24.4	30.0
110	5	16	98.3	55.0	19.7	27.8	66.4
82	5	<d.l.	<d.l.	<d.l.	<d.l.	2.17	<d.l.
107	5	<d.l.	<d.l.	<d.l.	5.37	3.65	9.02
123*	5	<d.l.	<d.l.	65.1	<d.l.	<d.l.	58.9
118*	5	<d.l.	<d.l.	31.3	8	13.8	38.3
114*	5	<d.l.	6.86	<d.l.	<d.l.	2.64	10.4
105*	5	<d.l.	21.6	<d.l.	8.14	<d.l.	21.1
126*	5	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
136	6	<d.l.	39.9	27.3	11.4	<d.l.	27.8
151	6	<d.l.	86.7	57.3	36.0	20.1	52.0
135.144	6	<d.l.	54.8	35.9	10.7	15.2	32.1
147	6	<d.l.	<d.l.	<d.l.	2.90	<d.l.	<d.l.
149	6	33.5	262	173	44.6	54.4	158
134	6	<d.l.	26.6	<d.l.	7.94	<d.l.	<d.l.
131	6	<d.l.	<d.l.	<d.l.	4.08	<d.l.	<d.l.
146	6	<d.l.	63.0	29.2	12.7	15.1	38.1
153*	6	<d.l.	447	265	52.5	79.7	243
132	6	<d.l.	103	66.8	15.6	18.0	59.5
141**	6	<d.l.	68.0	42.7	6.39	9.89	41.5
137	6	<d.l.	14.5	<d.l.	<d.l.	<d.l.	<d.l.
164.138	6	<d.l.	455	286	67.0	89.6	270
158	6	<d.l.	33.5	<d.l.	<d.l.	<d.l.	<d.l.
129	6	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
128.167*	6	<d.l.	94.9	45.8	<d.l.	14.3	33.8
156*	6	<d.l.	32.8	<d.l.	<d.l.	7.63	19.3

continue…

...continue

PCB #	Chlorination class	Sediment layer					
		0-1	**1-2**	**4-5**	**8-10**	**16-18**	**22-24**
157*	6	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
169*	6	<d.l.	<d.l.	19.2	4.0	4.9	15.9
179	7	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
176	7	<d.l.	24.8	12.0	<d.l.	<d.l.	16.3
178	7	<d.l.	35.0	19.3	3.28	<d.l.	17.0
187	7	<d.l.	189	111	26.3	30.4	<d.l.
183	7	<d.l.	82.0	48.0	<d.l.	4.66	41.9
185	7	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
174	7	<d.l.	129	<d.l.	13.2	13.3	87.3
177	7	<d.l.	110	67.1	14.9	20.6	80.1
171	7	<d.l.	39.2	41.8	<d.l.	<d.l.	28.6
173	7	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
172	7	<d.l.	31.3	21.6	<d.l.	7.58	22.2
180*	7	12.1	349	238	30.0	30.4	225.6
193	7	<d.l.	24.8	<d.l.	<d.l.	<d.l.	11.8
191	7	<d.l.	12.1	<d.l.	<d.l.	<d.l.	<d.l.
170.190	7	<d.l.	217	131	<d.l.	<d.l.	143
189*	7	<d.l.	54.1	<d.l.	<d.l.	<d.l.	<d.l.
197	8	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
199	8	<d.l.	56.7	45.2	<d.l.	10.1	40.1
196.203	8	<d.l.	62.9	56.3	14.1	<d.l.	46.5
195	8	<d.l.	29.0	<d.l.	<d.l.	<d.l.	20.3
194*	8	<d.l.	74.0	52.4	11.7	10.4	55.5
205	8	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
208*	9	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
207	9	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
206	9	<d.l.	41.0	<d.l.	<d.l.	<d.l.	<d.l.
209*	10	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.

<d.l. = lower than detection limit

Table S4. Concentrations (in pg g^{-1}) of PCB congeners in the surficial sediment layers (0-1 cm) of cores Nad 2 and 4. The asterisk identifies the 21 congeners present in the ^{13}C-labelled mixtures spiked as internal standards. A double asterisk identifies the two labeled ^{13}C congeners (PCB-47 and -141) used for recovery measurements.

PCB #	Chlorination class	Nad 2	Nad 4
1	1	<d.l.	<d.l.
2	1	<d.l.	<d.l.
3*	1	<d.l.	14.1
10.4	2	<d.l.	<d.l.
7.9	2	<d.l.	<d.l.
6	2	<d.l.	<d.l.
5+8	2	<d.l.	<d.l.
11	2	1031	<d.l.
12	2	<d.l.	<d.l.
15*	2	<d.l.	<d.l.
19	3	<d.l.	<d.l.
18	3	<d.l.	193
17	3	299	<d.l.
24.27	3	<d.l.	<d.l.
16.32	3	116	<d.l.
34	3	<d.l.	<d.l.
29	3	<d.l.	<d.l.
26	3	132	<d.l.
25	3	<d.l.	<d.l.
31	3	2253	136
28*	3	2492	223
20.33	3	2638	<d.l.
22	3	146	<d.l.
37	3	<d.l.	<d.l.
45	4	<d.l.	<d.l.
46	4	<d.l.	62.4
69	4	<d.l.	<d.l.
52*	4	636	<d.l.
49	4	48.6	<d.l.
47**.48	4	80.0	87.0
44	4	172	<d.l.
59.42	4	76.8	<d.l.
71.41.64	4	136	34.9
40	4	<d.l.	<d.l.
67	4	<d.l.	<d.l.
63	4	<d.l.	57.6
74	4	100	<d.l.
70	4	88.6	<d.l.

continue…

...continue

PCB #	Chlorination class	Nad 2	Nad 4
66	4	261	<d.l.
56.60	4	86.6	46.7
81*	4	<d.l.	<d.l.
77*	4	92.7	<d.l.
104	5	<d.l.	<d.l.
103	5	17.9	<d.l.
93.95	5	56.2	84.7
91	5	<d.l.	13.7
92	5	<d.l.	<d.l.
84.101.90	5	124	174
99	5	55.0	<d.l.
119	5	<d.l.	<d.l.
83	5	<d.l.	<d.l.
97	5	19.3	<d.l.
87.115	5	22.6	<d.l.
85	5	11.8	24.0
110	5	38.9	<d.l.
82	5	<d.l.	<d.l.
107	5	<d.l.	<d.l.
123*	5	29.4	<d.l.
118*	5	37.0	57.6
114*	5	<d.l.	<d.l.
105*	5	14.5	18.2
126*	5	<d.l.	<d.l.
136	6	19.0	33.0
151	6	38.1	68.1
135.144	6	23.7	41.5
147	6	10.3	<d.l.
149	6	106	232
134	6	<d.l.	9.84
131	6	<d.l.	<d.l.
146	6	<d.l.	46.7
153*	6	227	393
132	6	<d.l.	82.4
141**	6	<d.l.	51.4
137	6	<d.l.	<d.l.
164.138	6	195	415
158	6	<d.l.	23.5
129	6	<d.l.	<d.l.
128.167*	6	31.7	<d.l.
156*	6	7.99	25.9

continue…

...continue

PCB #	Chlorination class	Nad 2	Nad 4
157*	6	<d.l.	<d.l.
169*	6	52.6	6.95
179	7	26.6	<d.l.
176	7	39.9	24.3
178	7	157	22.0
187	7	113	161
183	7	22.2	52.6
185	7	<d.l.	<d.l.
174	7	31.2	120
177	7	43.7	92.6
171	7	<d.l.	27.9
173	7	<d.l.	<d.l.
172	7	<d.l.	26.1
180*	7	107.5	358
193	7	21.6	15.7
191	7	<d.l.	<d.l.
170.190	7	102.1	198
189*	7	<d.l.	<d.l.
197	8	<d.l.	3.05
199	8	28.8	52.7
196.203	8	22.1	58.3
195	8	<d.l.	24.4
194*	8	29.6	68.4
205	8	<d.l.	<d.l.
208*	9	<d.l.	<d.l.
207	9	<d.l.	<d.l.
206	9	<d.l.	<d.l.
209*	10	<d.l.	<d.l.

<d.l. = lower than detection limit

Table S5. PAH data matrix (as % contribution of each congener class to the total) used for statistic on Nador Lagoon sediment samples and different kinds of petroleum..

	F	Phe	Flu	Py	BaAn	Ch
CF	17	57	2.6	6.1	1.9	15
PL	21	52	1.0	5.0	0.7	20
LE	9	62		5.5		23
ANS	32	59	0.072	0.21	0.12	7.7
ASMB	26	64	0.075	0.56	0.090	8.7
AL	26	65	0.014	0.21	0.025	8.4
S	14	81	0.092	0.38	0.24	4.6
SL	6.8	17	0.031	0.073	0.044	76
WTI	25	70	0.11	0.36	0.067	5.4
2	52	48	0.14	0.64	0.005	0.002
5	12	56	0.20	1.4	1.4	29
6303	15	57	0.22	1.2	1.1	26
O-400	30	60	0.13	0.32	0.16	10
K	3.8	84	0.60			11
Eq	22	70				8.0
Ex	15	78	1.3		0.21	5.9
SCS	36	62			0.19	1.7
Mex	2.3	93	1.2			3.0
O	2.4	92				5.8
Nad 1 (0-1)	5.1	62	9.5	16	1.6	5.6
Nad 1 (1-2)	3.5	71	8.7	9.1	2.0	6.0
Nad 1 (4-5)	3.7	69	9.1	11	1.9	5.2
Nad 1 (7-8)	6.6	75		10	2.3	5.9
Nad 1 (14-16)	4.3	61	12	11	3.1	8.1
Nad 1 (22-24)	3.6	39	21	19	5.4	12
Nad 1 (30-33)	4.1	46	18	14	5.6	11
Nad 1 (39-42)	5.2	50	18	13	4.4	10
Nad 1 (45-48)	4.8	57	16	11	3.2	7.7
Nad 3 (0-1)	11	68	8.1	8.4	0.57	3.8
Nad 3 (1-2)	6.4	59	10	11	3.3	11
Nad 3 (4-5)	6.7	63	10	9.4	2.8	8.2
Nad 3 (8-10)	6.5	58	11	14	2.9	7.9
Nad 3 (16-18)	8.0	60	12	10	2.6	7.3
Nad 3 (22-24)	6.7	55	12	12	3.0	11
Nad 2 (0-1)	8.0	64	8.5	8.3	2.8	8.3
Nad 4 (0-1)	6.2	47	14	13	6.2	13

CF = Carpathians Foredeep (PL); PL = Polish Lowlands; LE = Leba Elevation (PL); ANS = Alaska North Slope; ASMB = Alberta Sweet Mixed Blend; AL = Arabian Light; S = Sockeye; SL= South Louisiana; WTI = West Texas Intermediate; 2 = No. 2 (ON, CA); 5 = No. 5 (NJ, USA); 6303 = Heavy fuel oil 6303 (NS, CA); O-400 = Orimulsion 400 (Venezuela); K = Daqing (China); Eq = Jianhan (China); Ex = Jianhan (China); SCS = South China Sea; Mex = Mexico; O = Giuzhou (China)

Table S6. PAH data matrix (as % contribution of each congener to the total) used for statistic on Nador Lagoon sediment samples.

	Ac	Ace	F	Phe	An	Flu	Py	BaAn	Ch	BbFlu	BkFlu	BaPy	BghiPe	IPy	DAn
Nad 1 (0-1)	0.276		4.52	55.0		8.43	14.1	1.41	4.91	1.98	0.777	1.51	2.64	3.40	1.06
Nad 1 (1-2)	0.589		2.69	54.6	2.01	6.69	7.06	1.54	4.62	4.05	1.82	2.27	4.51	5.56	1.98
Nad 1 (4-5)	0.419		2.91	55.2	0.851	7.22	8.55	1.53	4.12	3.57	1.45	2.10	4.60	5.61	1.92
Nad 1 (7-8)	0.381		5.07	57.2			7.91	1.72	4.54	4.08	1.61	2.75	5.65	6.58	2.51
Nad 1 (14-16)	0.407	4.30	3.23	45.6		8.64	8.52	2.27	6.05	4.64	1.96	2.86	3.70	6.55	1.29
Nad 1 (22-24)	0.552	0.715	2.46	26.1	1.11	14.5	12.6	3.67	8.19	6.49	2.79	3.69	6.94	7.32	2.81
Nad 1 (30-33)	0.244	0.854	2.75	31.4	1.10	12.5	9.69	3.77	7.71	6.69	3.29	4.30	6.50	6.94	2.29
Nad 1 (39-42)		6.21	3.20	30.3	1.24	11.0	8.12	2.66	5.83	7.19	2.76	3.57	7.74	7.47	2.66
Nad 1 (45-48)		1.42	3.66	43.5	1.82	12.1	8.66	2.41	5.90	5.62	2.18		5.63	5.68	1.39
Nad 3 (0-1)	0.323	11.5	6.96	44.8	0.128	5.31	5.49	0.371	2.51	1.28	16.0	2.61	0.473	1.10	1.09
Nad 3 (1-2)	0.628	8.47	4.44	40.9		7.15	7.72	2.31	7.39	3.80	4.31	3.37	3.00	5.16	1.34
Nad 3 (4-5)	0.484	9.03	4.92	46.2		6.99	6.89	2.03	5.99	3.17	3.30	3.29	2.41	4.35	0.978
Nad 3 (8-10)	0.614	22.2	3.77	33.7		6.44	8.01	1.69	4.57	2.41	2.35	3.29	2.12	8.34	0.546
Nad 3 (16-18)	0.440	6.65	5.86	44.1		8.73	7.29	1.91	5.37	3.88	4.35	3.43	2.93	4.06	1.06
Nad 3 (22-24)	0.703	23.9	3.70	30.6		6.60	6.85	1.69	5.92	3.48	4.16	3.07	2.95	5.37	1.06
Nad 2 (0-1)	0.712	7.28	5.48	43.9		5.85	5.67	1.93	5.68	5.22	1.71	2.92	4.93	6.66	2.03
Nad 4 (0-1)	0.280	9.47	4.04	30.9	0.616	9.07	8.80	4.08	8.74	4.86	2.03	4.74	4.38	6.12	1.89

Table S7. PCB data matrix (as % contribution of each chlorination class to the total) used for statistic.

	Cl-1	Cl-2	Cl-3	Cl-4	Cl-5	Cl-6	Cl-7	Cl-8	Cl-9	Cl-10
Nad 1 (0-1)			49.0	34.2	6.86	6.29	3.54	0.117		
Nad 1 (1-2)			53.8	25.5	7.12	8.51	4.45	0.643		
Nad 1 (4-5)		2.67	47.9	34.1	4.54	6.43	3.73	0.636		
Nad 1 (7-8)		3.32	52.9	22.0	5.92	11.3	4.34	0.305		
Nad 1 (14-16)		5.73	44.6	19.3	5.75	14.9	6.98	2.75		
Nad 1 (22-24)		2.35	28.2	29.1	25.6	10.9	3.32	0.478		
Nad 1 (30-33)			47.4	33.1	12.4	4.67	1.01	1.44		
Nad 1 (39-42)			55.6	31.3	9.27	2.82	0.270	0.768		
Nad 1 (45-48)			35.5	46.4	13.3	4.00	0.759			
Nad 3 (0-1)		7.26	36.9	49.5	3.55	2.03	0.733			
Nad 3 (1-2)		22.5	13.4	16.4	8.04	21.1	15.4	2.64	0.487	
Nad 3 (4-5)		52.4	12.2	8.7	4.83	12.1	7.99	1.78		
Nad 3 (8-10)		36.6	21.9	22.0	6.18	9.44	3.00	0.882		
Nad 3 (16-18)		40.9	23.0	22.2	5.30	6.18	2.01	0.384		
Nad 3 (22-24)		32.3	16.4	17.8	7.55	14.1	9.57	2.31		
Nad 2 (0-1)			68.8	15.2	3.64	6.06	5.66	0.687		
Nad 4 (0-1)	0.355		13.9	7.29	9.41	36.1	27.7	5.22		
1221	65.5	29.7	4.80							
1232	31.4	23.7	23.4	15.7	5.80					
1016		21.2	51.5	27.3	0					
1242		14.7	46.0	30.6	8.70					
1248			20.9	60.2	18.1	0.800				
1254			1.80	17.1	49.4	27.8	3.90			
1260					9.20	46.9	36.9	6.30	0.700	
1262					4.20	30.9	45.9	17.7	1.30	