


Dear Author,

Please, note that changes made to the HTML content will be added to the article before publication, but are not reflected in this PDF.

Note also that this file should not be used for submitting corrections.

AUTHOR QUERY FORM

 ELSEVIER	Journal: STOTEN Article Number: 17670	Please e-mail your responses and any corrections to: E-mail: Corrections.ESCH@elsevier.spitech.com
---	--	--

Dear Author,

Please check your proof carefully and mark all corrections at the appropriate place in the proof (e.g., by using on-screen annotation in the PDF file) or compile them in a separate list. Note: if you opt to annotate the file with software other than Adobe Reader then please also highlight the appropriate place in the PDF file. To ensure fast publication of your paper please return your corrections within 48 hours.

For correction or revision of any artwork, please consult <http://www.elsevier.com/artworkinstructions>.

We were unable to process your file(s) fully electronically and have proceeded by

Scanning (parts of) your article

Rekeying (parts of) your article

Scanning the artwork

Any queries or remarks that have arisen during the processing of your manuscript are listed below and highlighted by flags in the proof. Click on the 'Q' link to go to the location in the proof.

Location in article	Query / Remark: click on the Q link to go Please insert your reply or correction at the corresponding line in the proof
Q1	Your article is registered as a regular item and is being processed for inclusion in a regular issue of the journal. If this is NOT correct and your article belongs to a Special Issue/Collection please contact a.louis@elsevier.com immediately prior to returning your corrections.
Q2	Please confirm that given names and surnames have been identified correctly.
Q3	Please check the hierarchy of the section headings and confirm if correct.
Q4	Please check the insertion of the word "River" if appropriate and amend if necessary.
Q5	Supplementary caption was not provided. Please check suggested data if appropriate and correct if necessary. <div data-bbox="643 1465 1133 1583" style="border: 1px solid black; padding: 5px; margin: 10px auto; width: fit-content;"> Please check this box if you have no corrections to make to the PDF file. <input type="checkbox"/> </div>

Thank you for your assistance.

Q5 Supplementary material.



ELSEVIER

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Q1 Recognizing different impacts of human and natural sources on the
2 spatial distribution and temporal trends of PAHs and PCBs
3 (including PCB-11) in sediments of the Nador Lagoon (Morocco)

Q2 Silvia Giuliani^{a,*}, Rossano Piazza^{b,c}, Luca Giorgio Bellucci^a, Fabio Paolo Polo^{b,c}, Marco Vecchiato^{c,d},
5 Stefania Romano^a, Stefano Zambon^b, Mauro Frignani^a, Bouchta El Moumni^{e,f}

6 ^a CNR-Institute of Marine Sciences, Via Gobetti 101, Bologna, Italy

7 ^b Dept. of Environmental Sciences, Informatics and Statistics, Ca' Foscari Univ. of Venice, Dorsoduro 2137, Venice, Italy

8 ^c CNR-Institute for the Dynamics of Environmental Processes, Dorsoduro 2137, Venice, Italy

9 ^d Dept. of Physical Sciences, Earth and Environment, Univ. of Siena, Via Laterina 8, Siena, Italy

10 ^e Dept. of Earth Sciences and Oceanography, Univ. of Tangier, Tangier, Morocco

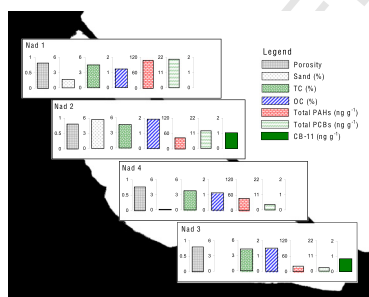
11 ^f Polydisciplinary Faculty of Larache, BP 745 Route de Rabat, Larache, Morocco

12

HIGHLIGHTS

- PAH inputs in sediments of the Nador Lagoon are generally petrogenic.
- PAH pyrogenic inputs characterise the period 1930–1960 near Nador city.
- PCB Aroclor mixtures are well recognizable in surface non-degraded sediments.
- PCB microbial anaerobic degradation is recorded from 1950 to 1990 in the SW lagoon.
- Different land uses control PAH and PCB levels and compositions in lagoon sediments.

GRAPHICAL ABSTRACT



39

ARTICLE INFO

Article history:

41 Received 15 January 2015

42 Received in revised form 15 April 2015

43 Accepted 15 April 2015

44 Available online xxxx

45 Editor: Eddy Y. Zeng

Keywords:

46 PCBs

47 PAHs

48 Contamination sources

49 Nador Lagoon

60

ABSTRACT

The Nador Lagoon holds a major interest in present-day Moroccan socioeconomic development. This environment is exposed to a number of potential polluting sources, such as mine tailings, urban and industrial dumping, and untreated wastewater inputs from surrounding cities. The aim of this study was to assess concentrations and trends of persistent contaminants such as PCBs and PAHs and to identify their origin. The non-Aroclor PCB-11 was determined for the first time in the lagoon sediments. 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 South-Western part of the lagoon where agricultural inputs are dominant. The presence of PCB-11 is linked to specific productions and might be affected by degradation processes. Presently, 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. Total PAH and PCB levels are low (from 21.6 to 108 ng g⁻¹ and from 2.50 to 20.7 ng g⁻¹, respectively) but recent increasing values and the potential threat to humans and biota require continuous and constant monitoring.

© 2015 Published by Elsevier B.V. 68

* Corresponding author.

Q3 1. Introduction

Fast increasing economic development brings about the risk of environmental pollution by inorganic and organic chemicals. For this reason, several regulations were developed to achieve or maintain a Good Environmental Status of marine ecosystems 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). To do so, an increasing scientific knowledge of levels, behaviour, fate of chemicals, and related processes in the marine environment is required.

The Nador Lagoon (North-East Morocco) is a place of great social and economical interest. Indeed, its location and environmental features have favoured the settling of important urban sites and production activities around and within its borders, increasing also the touristic interest (Hamoumi and Benssaou, 2001; Chalouan et al., 2001; González et al., 2007). Potential sources of environmental pollution are expected to be strongly related to the following activities that can be roughly geographically separated in: i) agriculture (specifically intensive cereal production) in the south; ii) metallurgic industry in the west; iii) fishery, fish farming, and food conservation in the north; and iv) tourism in the southeast (Quaranta et al., 2004). Recently, other environmental pressures were linked to the disposal of untreated or partially treated wastewaters in the lagoon, mainly resulting from urban areas and villages (Bloundi et al., 2009). In addition, this study identified the link between mining industry and trace metal enrichments in lagoon sediments, in accordance with previous similar researches (Bellucci et al., 2003; Águila et al., 2004; González et al., 2007). This link was further confirmed by the negative impact observed on bioindicators (Ruiz et al., 2005, 2006).

Studies focusing on the lagoon contamination by organic pollutants are scarce. The few available were based 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), but all agree in evidencing a situation of increasing contamination linked to anthropogenic activities.

As final repositories of materials coming from land, atmosphere, and overlaying water masses, sediments deposited under low-energy conditions are important in environmental studies as they give a trustworthy picture of both present and past situations (e.g., Frignani et al., 2004; Giuliani et al., 2011a; Bellucci et al., 2012). In addition, they provide information on the chronology of contaminant inputs when conditions of low sediment perturbation are met.

The principal aim of this paper was then to partially fill the gap relative to organic contamination in the Nador Lagoon, and to recognize different impacts affecting spatial and temporal distributions of chemicals in its sediments. The attention was focused on polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), as they are highly persistent in the environment and can represent a serious threat to human health and aquatic organisms.

2. Study area

The Nador Lagoon (Fig. 1) is the only lagoon ecosystem in the Moroccan coast facing the Mediterranean Sea. It covers an area of 115 km² with water depths from 3 to 8 m. It is separated into two basins by the Attalayoum peninsula, and is connected to the sea through the artificial Bokhaha Inlet.

The lagoon is fed mainly by marine waters (Ruiz et al., 2006). Secondly, it receives groundwaters from the Bou Areg Plain and by

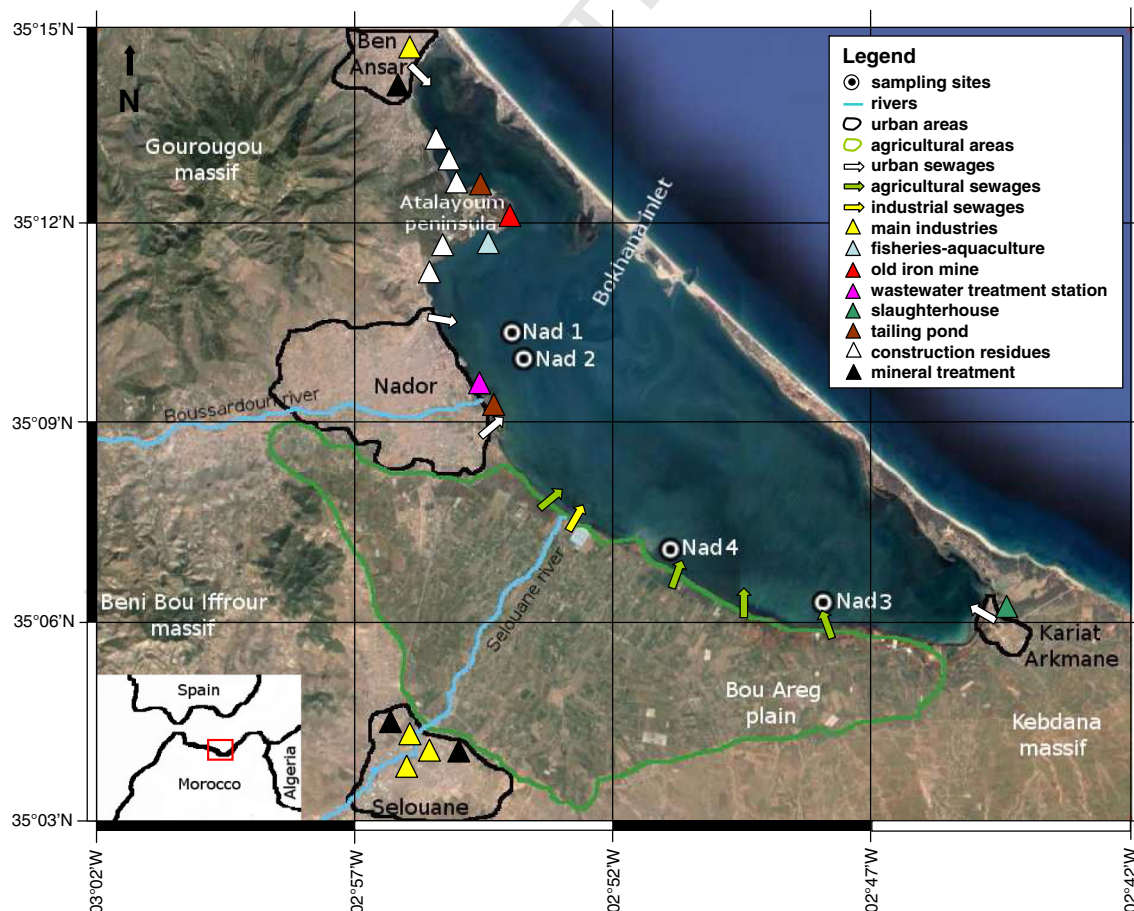


Fig. 1. Sampling sites in the Nador Lagoon. The most important human activities are indicated (Ruiz et al., 2006; González et al., 2007).

Q4 intermittent flows from inland areas. The Selouane River is the most notable river and delivers large amounts of raw sewage (González et al., 2007). Irrigation canals come from Nador, Ben Ansar and Kariat Arkmane (Fig. 1). Once in the lagoon, internal currents move water inputs in an hourly sense (Ruiz et al., 2006).

Many anthropogenic point and diffuse active sources are present along its shores. Their locations and typologies are reported in Fig. 1. Further details can be found in the Supporting material.

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. The four locations (Fig. 1) were selected on the basis of water depths (Table S1 in the Supplementary material) and the surficial grain size distribution was reported by El-Alami et al. (1998). In this way the sampling of fine sediment was favoured, as silt and clay fractions are acknowledged to interact preferentially with contaminants (Frignani et al., 2001; Ünlü and Alpar, 2006; Bellucci et al., 2012; Gibbs et al., 2014). In addition, fine-grained materials deposited under low-energy conditions do not favour mixing and resuspension and are more suited for retaining chronological information (Cochran et al., 2005; Mendes et al., 2010; Bellucci et al., 2012).

The cores were extruded and sectioned into 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 S3–6 in the Supplementary material, 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 and the formula reported by Berner (1971).

Grain size analyses were carried out by wet sieving at 63 µm, to separate sands, after a pre-treatment with H₂O₂. Fine contents (silt and clay) were determined as weight difference between total and sand.

Percent total carbon (TC) and organic carbon (OC) were measured by a Shimadzu TOC-5050A Analyzer, coupled with a Solid Sample Module (SSM-5000A). OC was determined after elimination of carbonates by treatment with HCl in a glass capsule. Samples were then heated at 120 °C for 2 h and left overnight in an oven at 100 °C. The analyses were performed after the samples spent one day in a dryer.

3.3. Radiotracers

²¹⁰Pb was analysed via alpha spectrometry of its granddaughter ²¹⁰Po, assuming secular equilibrium. 1.5–3 g of dry sediments was leached twice with hot 8 N HNO₃ and H₂O₂. Extracts were brought to near dryness and treated with concentrated HCl to eliminate nitric ions. Finally, the residues were diluted with 1.5 N HCl, the iron was reduced with ascorbic acid and Po spontaneously plated overnight on silver disks. ²⁰⁹Po was added to the sediments at the beginning of the procedure, as internal standard and to account for all efficiencies (extraction, deposition and counting). Supported ²¹⁰Pb (in equilibrium with ²²⁶Ra naturally present in sediments) was obtained from gamma counted activities of ²¹⁴Pb. The excess ²¹⁰Pb (²¹⁰Pb_{ex}) was calculated by subtracting the supported fraction from the total (Bellucci et al., 2007).

For ¹³⁷Cs determinations, 5–10 g of dry sediments was put in standard geometries and gamma counted. The accuracy was tested with respect to the IAEA river sediment certified standard and yielded ¹³⁷Cs activities within 4.1% of certified value.

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, based on ²¹⁰Pb results. A higher resolution was selected at the top core, thus favouring the identification

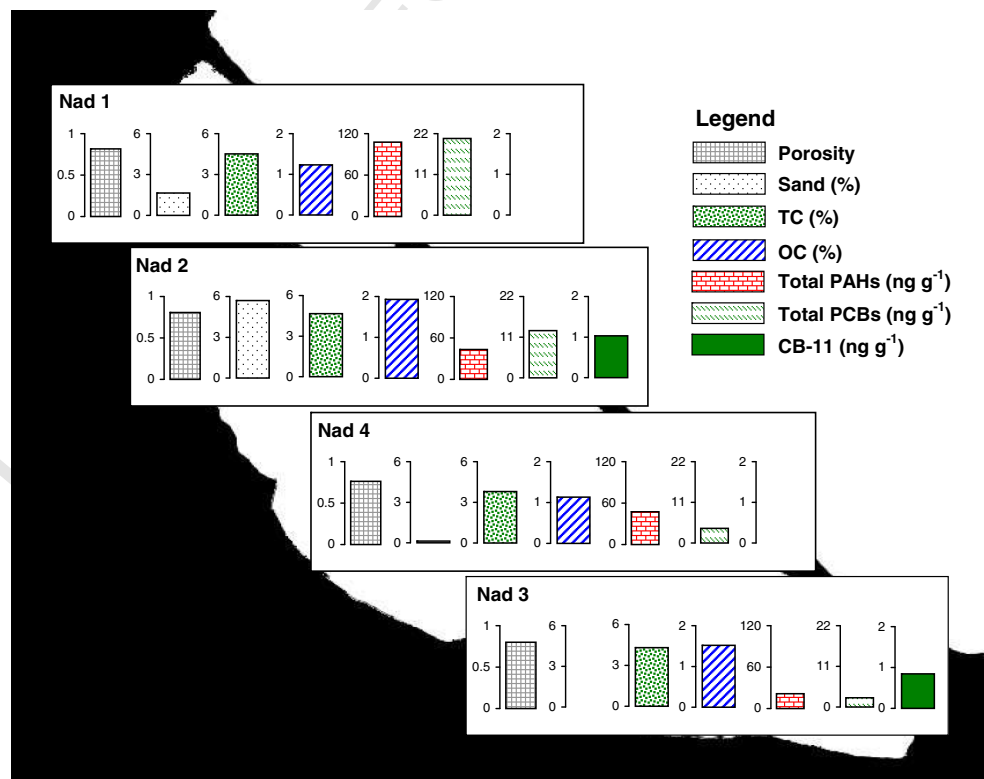


Fig. 2. Surficial distribution of porosity, sand content, TC, OC, total PAHs, total PCBs, and CB-11 in cores Nad 1, Nad 2, Nad 4 and Nad 3.

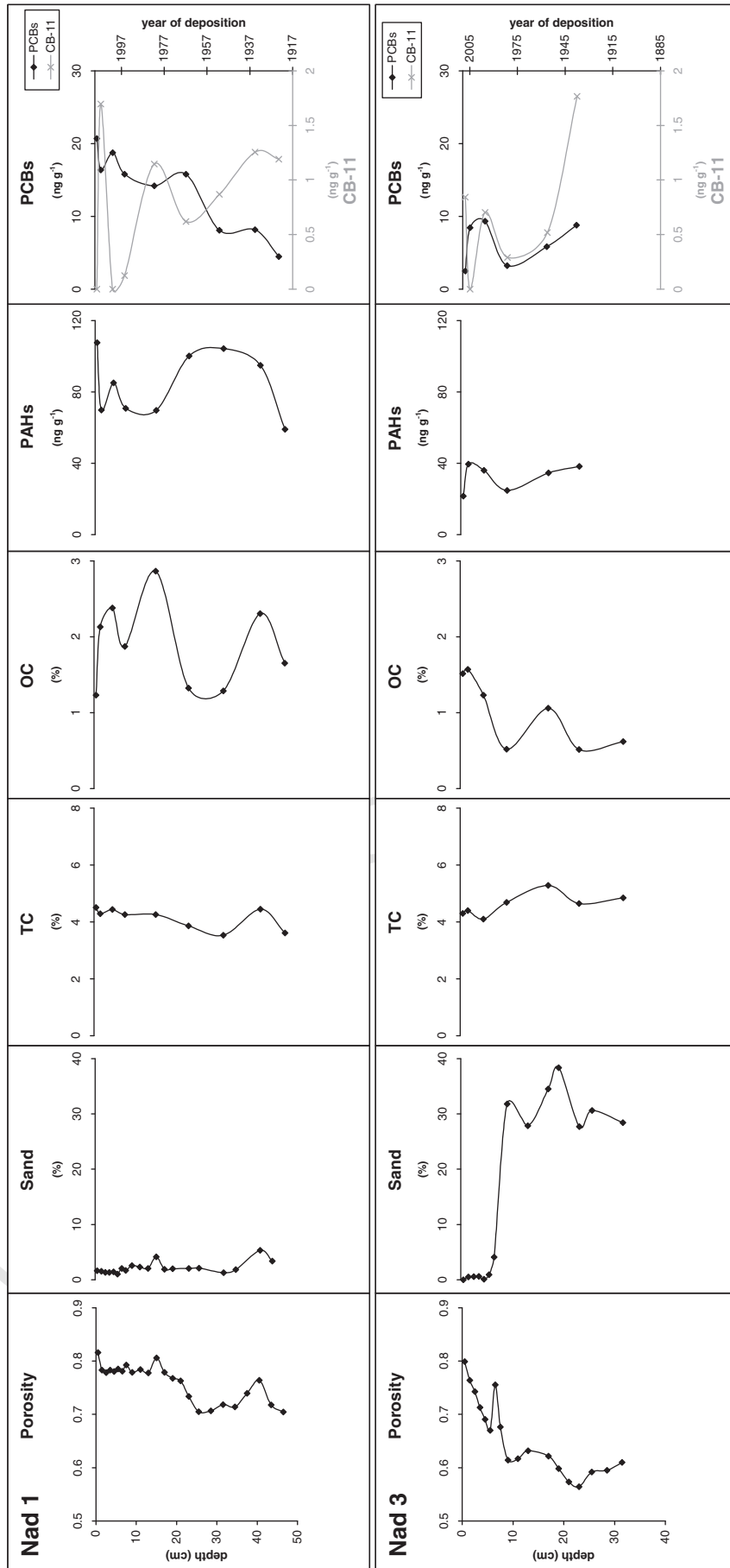


Fig. 3. Depth distribution of porosity, grain size (as sand % content), TC, OC, total PAHs, total PCBs, and CB-11 in cores Nad 1 and Nad 3. Profiles are reported also versus the established year of deposition (see Fig. 4).

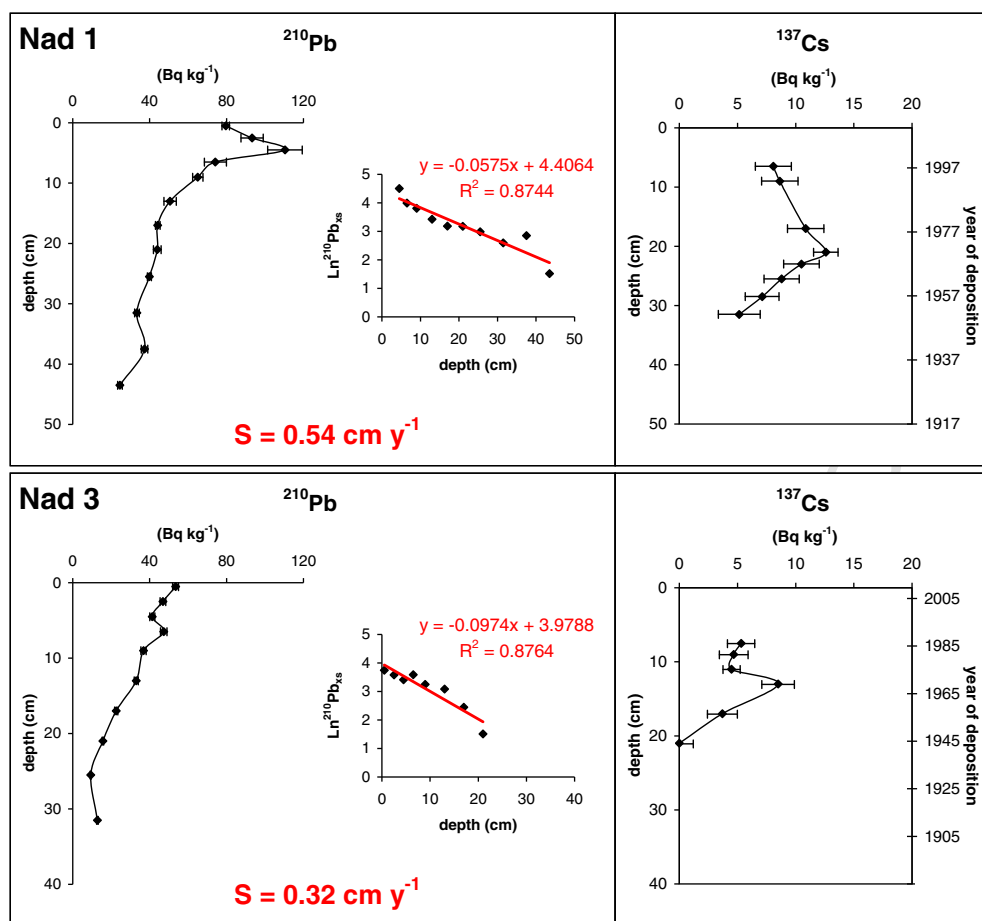


Fig. 4. Activity-depth profiles of ^{210}Pb and semilogarithmic plots of excess ^{210}Pb vs depth in cores Nad 1 and Nad 3. Calculated sediment accumulation rates (S , in cm y^{-1}) are reported, as well as ^{137}Cs profiles vs. depth and time. The first 2 cm of core Nad 1 is excluded from calculation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

of recent conditions and changes. One sample was selected at the base of the ^{210}Pb profile (i.e. where ^{210}Pb activity starts to be in excess with respect to the supported fraction), when an age of ~ 100 years B.P. is reached. For Nad 1, one additional sample was selected at the core bottom (45–48 cm), corresponding to sediments deposited prior to PCB production.

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 $500 \text{ pg } \mu\text{L}^{-1}$ and 21 ^{13}C -labelled PCBs at $40 \text{ pg } \mu\text{L}^{-1}$) as internal standards. 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 the 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 (PowerPrepTM, FMS) and by eluting with 30 ml of *n*-hexane and 30 ml of 1:1 *n*-hexane:dichloromethane, collected in a single fraction. Purified samples were reduced to $100 \mu\text{L}$ 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 $1000 \text{ pg } \mu\text{L}^{-1}$ and ^{13}C -PCB 47 and ^{13}C -PCB 141 at $40 \text{ pg } \mu\text{L}^{-1}$. 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; see Table S2 in the Supplementary material). Quantification was achieved using internal standards and isotopic dilution. ^{13}C -labelled Acenaphthene, Phenanthrene, and Benzo(a)pyrene were used to quantify PAHs, while a mixture containing all indicators and dioxin-like ^{13}C -labelled compounds was used for PCBs. 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), phenanthrene (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 ubiquitous presence (Klotz et al., 2011) leads to very high analytical errors.

PCB total concentrations were calculated as the 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, 248

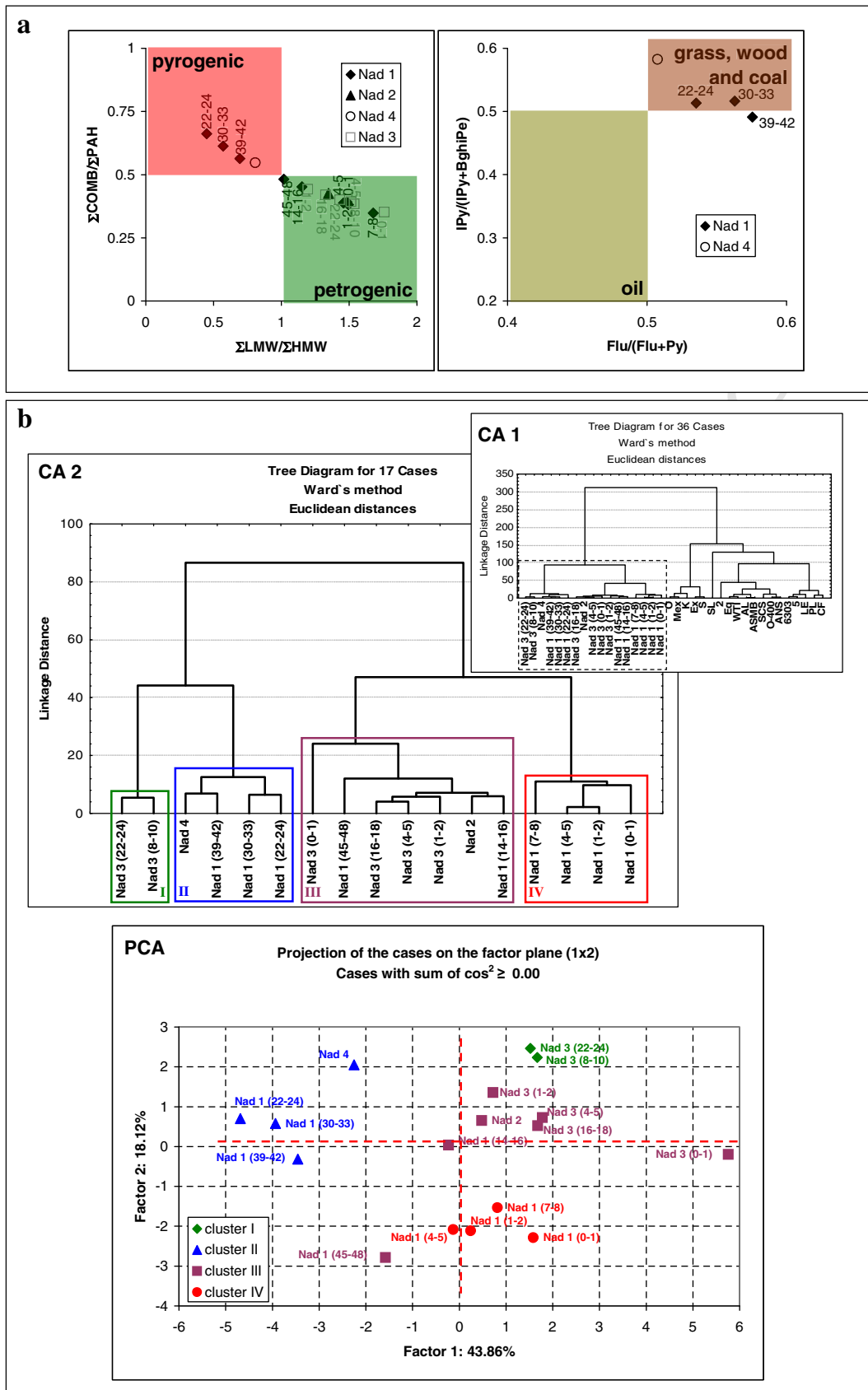


Fig. 5. Origin and sources of PAHs to the Nador Lagoon: (a) diagnostic ratios: ΣLMW = sum of low molecular weight congeners (Ac, Ace, F, Phe, An); ΣHMW = sum of high molecular weight congeners (Flu, Py, BaA, Ch, BbFlu, BkFlu, BaPy, BPe, IPy, DahAn); ΣCOMB = sum of 9 non-alkylated PAHs (Py, Flu, BaA, 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 (Table S7 in the Supplementary material). CA 2 was run only on Nador Lagoon sediment samples (Table S8 in the Supplementary material). Clusters identified by the CAs are reported on the PCA.

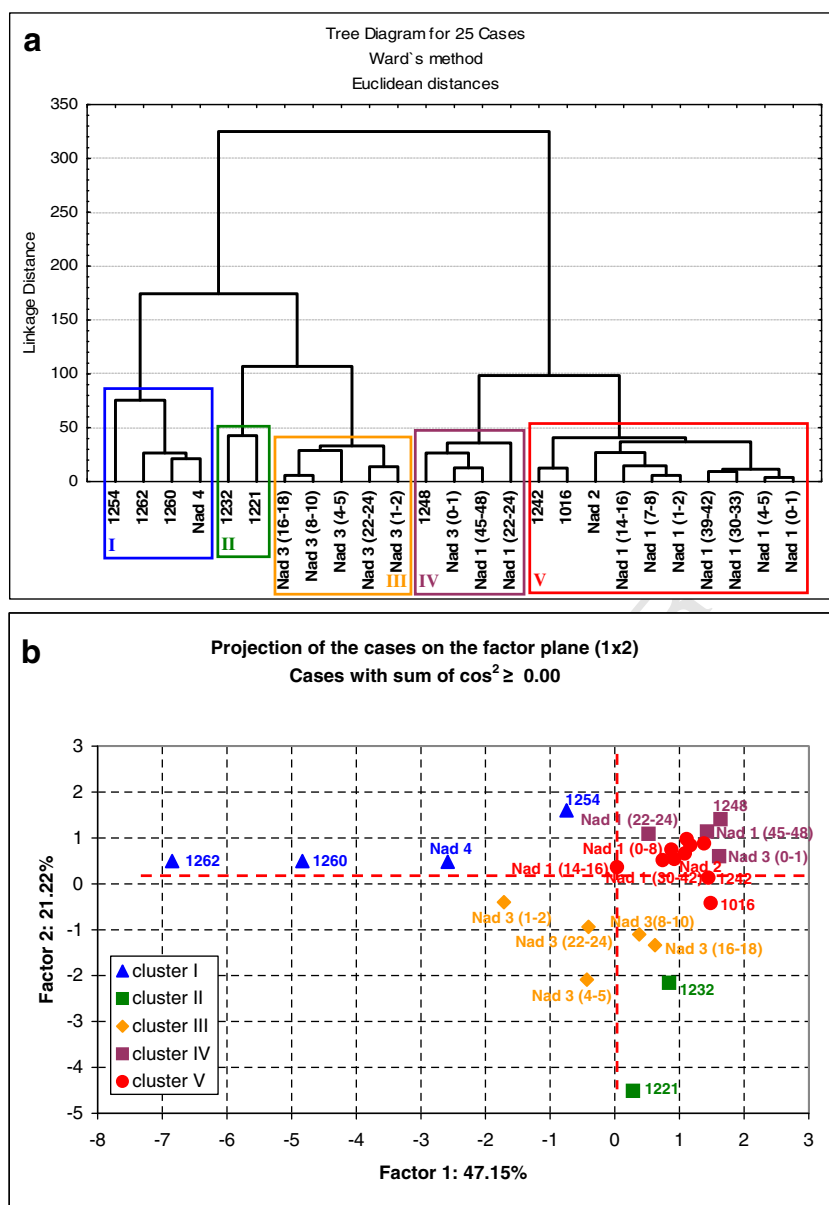


Fig. 6. Origin and sources of PCBs to the Nador Lagoon: (a) CA on percent contribution of each PCB chlorination class to the total (with the exclusion of CB-11). Average composition of the most important commercial Aroclor mixtures was also considered (from Frame et al., 1996); (b) results of the PCA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

249 -82, -107, -123, -118, -114, -105, -126), 22 hexachlorobiphenyls (CB-
 250 136, -151, -135 + 144, -147, -149, -134, -131, -146, -153, -132, -141,
 251 -137, -138 + 164, -158, -129, -128 + 167, -156, -157, -169), 17
 252 heptachlorobiphenyls (CB-179, -176, -178, -187, -183, -185, -174,
 253 -177, -171, -173, -172, -180, -193, -191, -170 + 190, -189),
 254 7 octachlorobiphenyls (CB-197, -199, -196 + 203, -195, -194, -205),
 255 3 nonachlorobiphenyls (CB-208, -207, -206) and CB-209. Calculated
 256 concentrations for all congeners are reported in the Supporting
 257 material.

258 Precision, measured as the standard deviation of replicated analyses
 259 of the same sample, was always below 10% for total PAHs and total PCBs.
 260 It ranged from 7% to 21% for the PCB groups and from 0.4% (CB-183) to
 261 25% (CB-84 + 101 + 90) when every single PCB congener was consid-
 262 ered. Accuracy was estimated through repeated analyses of NIST 1941b
 263 Reference Standard Material. Results were always within the certified
 264 analytical uncertainty. For PAHs, 54% of the values were accurate within
 265 1σ , 87% within 2σ . Procedural average recoveries were respectively
 266 $70 \pm 11\%$ for PCBs and $50 \pm 8\%$ for PAHs. Three procedural blanks

were conducted during the analyses. Resulting detection limits, calcu- 267
 268 lated as three times the standard deviations of the background signal,
 269 were comprised between 0.11 ng (benzo(k)fluoranthene) and 7.7 ng
 270 (phenanthrene) for PAHs and 0.025 pg (PCB-12) and 136 pg (PCBs
 271 $84 + 101 + 90$) for PCBs.

4. Results 272

4.1. Sediment features 273

Sediment porosities range from 0.56 to 0.81 (Figs. 2 and 3). Core 274
 275 trends for Nad 1 and Nad 3 show higher values at surface, as generally
 276 observed in recent unconsolidated layers. Values in Nad 1 remain
 277 quite constant (~ 0.77) between 1 and 22 cm depth, then decrease to
 278 ~ 0.72 down to the core bottom, with an isolated peak of 0.76 at 39 cm
 279 depth (Fig. 3). Porosity trend along the sediment record of Nad 3 pre-
 280 sents a constant decrease from surface to 6 cm depth. Then values

increase up to 0.76 at 7 cm depth, and remain constant around 0.60 from that depth down to the core bottom (Fig. 3).

The analysed sediments are predominantly fine grained (sand content varies from 0 to 38%, Figs. 2 and 3), in agreement with previous measurements (El-Alami et al., 1998). Nad 1 presents constant sand contents around 2%, 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 ($\geq 96\%$, Fig. 3), whereas the deeper layers are characterised by sand contents averaging 31% (Fig. 3).

TC varies from 3.53 to 5.28% and trends along the core record of 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 minima both at the surface and at 22–33 cm depth in core Nad 1, whereas the surficial 2 cm of core Nad 3 shows the highest 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}), whereas Nad 1 displays its maximum at 5 cm depth (110 Bq kg^{-1}). This is probably due to post-depositional processes (such as bioturbation or physical mixing) that 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.

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 gradient from the northernmost site Nad 1 (108 ng g^{-1}) to 2–4 ($43\text{--}47 \text{ ng g}^{-1}$) 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 ($95\text{--}104 \text{ ng g}^{-1}$, Fig. 3). Total PAHs in core Nad 3 are highest at 2 cm depth (39.5 ng g^{-1} , Fig. 3).

Table S3 in the Supporting material reports the concentration of PAH congeners (ng g^{-1}) in sediment cores and surficial samples. Phenanthrene shows the highest concentrations in all analysed samples ($8.32\text{--}59.2 \text{ ng g}^{-1}$), followed by fluoranthene and pyrene in core Nad 1 ($<\text{d.l.}\text{--}14.6$ and $1.19\text{--}15.2 \text{ ng g}^{-1}$, respectively) and by acenaphthene in core Nad 3 and sites Nad 2 and Nad 4 ($<\text{d.l.}\text{--}9.11 \text{ ng g}^{-1}$).

PAH concentrations as toxic equivalents (TEQs) were calculated as specified in Table S3 in the Supporting material, using toxicity equivalence factors reported by the United States Environmental Protection Agency (US EPA, 1993). Values for TEQs are $1.46\text{--}8.41 \text{ ng g}^{-1}$ in core Nad 1, $1.18\text{--}2.34 \text{ ng g}^{-1}$ 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. Values measured in surficial samples are higher at Nad 1 (21 ng g^{-1}) then decrease South-Eastward, 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). Core Nad 1 shows the maximum concentration at surface, whereas core Nad 3 presents the highest value in the subsurficial layer, between 1 and 5 cm depth ($8.5\text{--}9.4 \text{ ng g}^{-1}$, Fig. 3).

Tables S4–6 in the Supporting material report the concentration of PCB homologues in pg g^{-1} . Cl-3s are the most important ones for site Nad 2 and core Nad 1 (with the exception of layers 22–24 cm and 45–48 cm where Cl-4 congeners are dominant). Core Nad 3 is characterised by a higher contribution of Cl-2s, while Cl-6 congeners dominate at Nad 4.

PCB concentrations as TEQs were calculated as specified in Tables S4–6 in the Supporting material, using toxicity equivalence factors reported by Van den Berg et al. (2006). Values for TEQs cover the

interval $0.0045\text{--}15.8 \text{ pg g}^{-1}$ in core Nad 1, $0\text{--}0.582 \text{ pg g}^{-1}$ in core Nad 3, and are 1.59 and 0.212 pg g^{-1} at Nad 2 and Nad 4, respectively, with surficial values higher at sites Nad 1 and Nad 2.

The Molar Dechlorination Product Ratio (MDPR) was calculated in order to detect possible PCB dechlorination processes 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 selected PCB concentrations were below detection limits. Values for core Nad 3 varied from 0.002 to 0.357 (Tables S4–6 in the Supplementary material).

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 S4–6 in the Supplementary material). Percent CB-11 contributions to the total concentrations range from $<\text{d.l.}$ to 26% in core Nad 1, from $<\text{d.l.}$ to 34% in core Nad 3, and are 8% and $<\text{d.l.}$ at Nad 2 and Nad 4, respectively. Concentrations vary from $<\text{d.l.}$ to 1.70 ng g^{-1} at Nad 1, from $<\text{d.l.}$ to 1.77 ng g^{-1} at Nad 3, and are 1.03 and $<\text{d.l.}$ 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

Constant flux–constant sedimentation (CF–CS) was assumed (Robbins, 1978; Oldfield and Appleby, 1984) and the semilogarithmic plot of $^{210}\text{Pb}_{\text{ex}}$ activities vs depth allowed the calculation of sediment accumulation rates of 0.54 and 0.32 cm y^{-1} for cores Nad 1 and Nad 3, respectively (Fig. 4). These values are 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. According to these rates, ^{137}Cs peaks in cores Nad 1 and Nad 3 are located in sediment layers deposited in the early 1960s, in 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 confirmations, ^{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 between 20 and 40 cm depth in core Nad 1 (Fig. 3) is then dated from the early 1930s to the mid 1960s. In the same period, lower values of OC and higher values of total PAHs are observed. Contemporary total PCBs are low and start to increase just at the end of this time window, in accordance with the 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 characterised by constant increases of both PAH and PCB total concentrations, with no evident correlation to grain size and carbon content (Fig. 3). The recent PCB increase is apparently in contrast with the production bans and use restrictions of the 1970–1980s (Frignani et al., 2001, 2004), but it must be specified that Morocco ratified the 2001 Stockholm Convention on Persistent Organic Pollutants only in 2004 (http://www.pops.int/documents/convtext/convtext_en.pdf). The observed increase could also be associated to PCB release from reservoirs or unconfined wastes (Tanabe, 1988; Weber et al., 2008). In addition, the uncontrolled disposal of old electrical appliances in landfills is one of the most important current sources (Giuliani et al., 2011b). Other factors such as disturbances in the sediment core and/or delays on the predicted emissions (Breivik et al., 2007) can play a role. A previous research carried out 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) which, in turn, are similar to the concentration found at site Nad 2. The increase of PAH concentrations can be associated with natural or anthropogenic causes that will be discussed in the following section.

Sediment core Nad 3 shows an abrupt change of sedimentary conditions in the early 1980s: materials deposited from that time on are significantly finer than older ones and are comparable to those found at Nad 1. This means that the hydrodynamics in the area have recently decreased, thus enabling the accumulation of finer sediments. The progressive siltation of the Bokhana inlet (from the first dredging activities in 1910 until its complete closure in 1977; Lefebvre et al., 1997) might have reinforced local water circulation in the southern sector of the lagoon, thus promoting the accumulation of coarser sediments prior to 1980s. The present-day low-energy setting is then the result of a storm in 1981 (Lefebvre et al., 1997) that reopened the inlet, favouring 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 the late 1990s–early 2000s and are presently decreasing.

5.2. Sources of PAHs and PCBs in the Nador Lagoon

Surficial values of PAH and PCB are higher at Nad 1 than at all other sampled locations (Fig. 2). This confirms that site Nad 1 is influenced by the numerous different nearby anthropogenic sources (Fig. 1), such as urban sewage, wastewaters, mining and fisheries–aquaculture activities. In addition, the higher water depth at this location (~5 m, see Table S1 in the Supporting material) might have favoured 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

Diagnostic ratios for selected PAH groups are used to determine their origin (Tobiszewski and Namiesnik, 2012). Petrogenic PAHs (mainly from oil or carbon spills) are characterised by a predominance of low molecular weight (i.e., those with 2–3 benzene rings) and alkylated congeners. Conversely, heavier PAHs originate from high- or low-temperature pyrogenic inputs from natural or anthropogenic sources (Nielsen et al., 1995). The $\Sigma\text{LMW}/\Sigma\text{HMW}$ and $\Sigma\text{COMB}/\Sigma\text{PAH}$ ratios (Fig. 5a) can thus indicate the main contribution to PAHs in the samples. Further information relative to PAH sources can be derived from diagnostic ratios between pairs of congeners with the same molecular mass but with different thermodynamic stability (Tobiszewski and Namiesnik, 2012). Fluoranthene and pyrene, for example, both have a molecular mass of 202 but very different stability and therefore may discriminate between different pyrogenic sources (Fig. 5a). Indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene (molecular mass 276) are used to identify the same processes (Tobiszewski and Namiesnik, 2012).

PAHs in most samples originate from petrogenic sources (Fig. 5a). Exceptions are the surficial sediment at Nad 4 and the layer between 22 and 42 cm depth in core Nad 1, where PAH assemblages derive from combustion. This means that between the early 1930s and mid 1960s, PAHs reaching site Nad 1 originated mainly from 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 PAH concentrations were similar to those detected in the most recent sediment layer (Fig. 3). The combustion of organic matrices might be confirmed also by the lower OC content detected in the same period (Fig. 3). Indeed, fires convert continental biomass and detrital carbon mainly to gaseous forms (CO₂ and smaller proportions of CO and CH₄; Preston and Schmidt, 2006), thus reducing OC inputs to aquatic environments. However, the lack of measurements of pyrogenic carbon (mainly represented by solid charred residues and a black carbon fraction that is resistant to laboratory oxidation; Preston and Schmidt, 2006) in sediments, and the absence of a significant correlation between total PAHs and (Table 1) hinder the confirmation of this hypothesis.

Petrogenic PAH assemblages characterise the other samples (Fig. 5a). No significant resemblance with the average composition of

different kinds of oil extracted worldwide is observed: the Cluster Analysis (CA), performed on percent composition of selected PAHs (F, Phe, Flu, Py, BaAn and Ch, see Table S7 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. Refined oil products used in the area (e.g. diesels and gasolines) are probably responsible for PAH petrogenic assemblages in these sediments, but reference data are missing. Moreover, post-depositional degradation processes may have significantly changed the patterns with respect to the original composition.

Fig. 5b reports the results of the CA (CA 2) performed only on sediments from the Nador Lagoon. In this way, similarities/dissimilarities among samples could be better resolved. Indeed, the results of CA 2 agree with diagnostic ratios, and evidence 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 S8 in the Supplementary material). In addition, cores Nad 3 and Nad 1 generally belong to two separate clusters (III and IV, Fig. 5b) characterised by different contributions of Ace (1.4–12% in III, and <d.l. in IV, Table S8 in the Supplementary material). The two clusters probably reflect the different anthropogenic impacts across 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 that show the highest Ace contributions in core Nad 3 (22–24%, Table S8 in the Supplementary material).

Results of the Principal Component Analysis (PCA) performed on the same dataset of CA 2 (Fig. 5b) agree with the clustering and provide details relative to factors controlling PAH inputs to sediments of the Nador Lagoon (Table S10 in the Supplementary material): i) Factor 1 (44% of observed differences; Fig. 5b) separates samples of cluster II from the rest and is controlled prevalently by high weight congeners, ii) 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 were used in the past in hundreds of industrial and commercial applications (Frame et al., 1996). Regarding not-industrial sources, significant PCB emissions were measured from domestic combustion (Gullett et al., 2003), while natural combustion processes were considered responsible for PCB presence in sediments deposited prior to the onset of production (Ruiz-Fernández et al., 2012). In this case, a strong significant correlation between total PCB concentrations and OC contents was observed (Ruiz-Fernández et al., 2012). No such correlation is detected in the Nador Lagoon ($r = 0.46$ at $p < 0.05$, Table 1), and, more notably, the depth profile is consistent to the chronology of inputs (see Section 5.1). Therefore, the most plausible source of PCBs in this area is still anthropogenic and related to industrial production.

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 1). Its presence is then to be linked to specific anthropogenic sources, such as those using pigments or dyes (Rodenburg et al., 2010; Romano et al., 2013). Relatively

Table 1

Product moment correlations between standardized^a 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	
CBn11	-0.23	0.14	-0.04	0.15	-0.04	-0.11

^a Computed as Std. Score = (raw score - mean) / Std. deviation.

high levels of CB-11 at depths corresponding to the early 1940s in Nad 3 (Fig. 3) could identify consistent direct inputs at that time that should be further investigated. As for the remaining 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). The CA shown in Fig. 6a was then 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 S9 in the Supplementary material). Fenoclor mixtures produced in France were similar to Aroclors (Erickson, 1997), therefore they are associated in Table S9 in the Supplementary material. Non-Aroclor CB-11 was excluded from the analysis, since its presence would lead to an overestimation of the relevance of Cl-2s. Five clusters are well evidenced in Fig. 6a and, with the exception of clusters II and III, each is characterised by the resemblance between lagoon sediments and specific Aroclor mixtures: cluster I groups closely together the highly chlorinated Aroclors 1260 and 1262 with Nad 4 surficial sediment (prevalence of Cl-6 and -7, Table S9 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); cluster V includes all remaining levels of core Nad 1, Nad 2 surficial sediment, and Aroclors 1016 and 1242 (majority of Cl-3). 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 (Fig. 6a). This sedimentary level corresponds to the period spanning from early 1940s to early 2000s (Figs. 2 and 3), when PCB production was still allowed all over the world (until 1980s) or not yet restricted in Morocco (from 2004, Aguilar and Borrell, 2005).

Differences with commercial mixtures might be explained by a series of factors, likely linked to multiple inputs, selective fractionation from long-range atmospheric transport, and post-depositional processes (such as microbial anaerobic dechlorination). Indeed, selective transport and enhanced degradation would act in modifying the original PCB assemblage, and information about sources would be progressively lost. In order to evaluate the magnitude of natural PCB degradation through microbial dechlorination processes in core sediments, the MDPDR was used (Tables S4–6 in the Supplementary material) as indicated by Liang et al. (2014). It is assumed that anaerobic dechlorination 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 (Liang et al., 2014). The ratio of the sum of their concentrations over total PCB concentrations is named MDPDR. For the majority of analysed samples, the MDPDR could not be calculated because the selected congeners were below detection limits or showed low concentrations (Tables S4–6 in the Supplementary material). This proves that PCB degrading processes are not significant in these sediments, as expected in surficial sediments that represent recent not-degraded inputs. It is interesting to notice that deeper samples with no evidence of anaerobic dechlorination show some resemblance with Aroclor commercial mixtures (Fig. 6a). For these samples, the effect of selective atmospheric transport (that favours the accumulation of lighter congeners in sediments; Giuliani et al., 2011b) can be important.

The only indications of anaerobic dechlorination are evidenced by Nad 3 sediments deposited in the period ranging between the late 1940s and the mid 1990s (MDPDR ranging from 0.244 to 0.357, Tables 4–6 in the Supplementary material), grouped in cluster III by the CA (Fig. 6a). Interestingly, in that period CB-11 also 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 to clarify whether degrading processes (in that period and at that location) might have

been triggered by hydrodynamic changes, evidenced by sand content profiles (see Section 5.1), or are linked to other causes. However, they helped us recognize 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 S9 in the Supplementary material) and confirms its results. In addition, the PCA presents more prominent 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 S10 in the Supplementary material), 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, Table 2) are rather low when compared with those found elsewhere (Table 2). They are also 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 S2 in the Supplementary material) are much lower (up to three orders of magnitude) when compared to impacted areas (e.g. Aryal et al., 2013; Nekhavhambe et al., 2014; Dong et al., 2014).

PCB total values in the lagoon ranging from 2.50 to 20.7 ng g⁻¹ (average value 9.17 ng g⁻¹, Table 2) can be similarly considered rather low when compared to impacted places and similar to average concentrations of other coastal lagoons. 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, Tables S3–5 in the Supplementary material) are comparable to those characteristic of low-impacted areas (Kumar et al., 2013; Dodoo et al., 2012). Relatively little is known about the toxicity of CB-11: as 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.

These data are consistent with the idea that PAH and PCB concentrations measured in sediments of the Nador Lagoon are safe for humans and biota. However, these contaminants present high persistence in the environment, liposolubility, and carcinogenic characteristics (Nielsen et al., 1995; Erickson, 1997) that require a constant and continuous monitoring. In addition, PAHs and PCBs can also biomagnificate and adverse effects related to co-contaminated sediments are poorly known.

6. Conclusions

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. Total concentrations (both as ng g⁻¹ and TEQs) are higher in sites located near the city of Nador and are

Table 2

Comparison of PAH and PCB maximum, minimum and average values measured in sediments of the Nador Lagoon with similar estimates in other parts of the world (Giuliani et al., 2008, 2011b). Values are in ng g⁻¹. Total PAHs are calculated as the sum of 16 US-EPA priority pollutants. Total PCBs are defined by different assemblages, from 3 to 8 Cl-substituted congeners. Details relative to sampling locations are reported in the Supplementary material.

	PAHs			PCBs		
	Max	Min	Avg	Max	Min	Avg
This paper	108	21.6	51.9	20.7	2.50	9.17
Lagoons	1009	84.4	389	31.8	1.80	15.0
Coastal areas	1311	50.0	475	244	2.20	78.7
Polluted areas	271,801	4300	103,676	7690	200	2343

presently increasing. These factors account for the higher impact of urban areas and surrounding industrial sites compared to agricultural activities located in the South-Western 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 different inputs and post-depositional processes controlling the two classes of contaminants: i) PAHs show a predominant petrogenic origin all over the lagoon, with the exception of sediments deposited between the early 1930s and the mid 1960s near the city of Nador, when important pyrogenic inputs are observed. 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 greater 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 to hydrodynamic changes triggered by the progressive closure and successive abrupt opening of the Bokhana inlet. The effect of selective fractionation from long-range atmospheric transport can also not be ruled out.

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.

Results of this research represent a good starting point for the study of contaminants' origin and levels in the Nador Lagoon, but future monitoring programmes should include more sampling sites and the analysis of specific materials that could represent well defined inputs. In addition, other classes of contaminants have to be considered (i.e. pesticides used in agriculture).

Acknowledgements

The authors wish to thank B. Lahoucine for his assistance in sampling and sample handling. We are indebted to three anonymous reviewers for their valuable contributions. The research was carried out in the framework of a bilateral programme between the Italian CNR and the Moroccan CNRST. This is contribution No. XXXX from the Institute of Marine Sciences, Bologna, Italy.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2015.04.057>.

References

- Águila, E., González, I., Galán, E., Hamoumi, N., Labraimi, M., Blouidi, M.K., 2004. Distribucion de elementos traza en los sedimentos de la laguna de Nador (Marruecos) - Estudio preliminar. *Geotemas* 6, 195–198.
- Aguilar, A., Borrell, A., 2005. DDT and PCB reduction in the western Mediterranean from 1987 to 2002, as shown by levels in striped dolphins (*Stenella coeruleoalba*). *Mar. Environ. Res.* 59, 391–404. <http://dx.doi.org/10.1016/j.marenvres.2004.06.004>.
- Aryal, R., Beecham, S., Vigneswaran, S., Kandasamy, J., Naidu, R., 2013. Spatial variation of polycyclic aromatic hydrocarbons and equivalent toxicity in Sydney Harbour, Australia. *J. Water Clim. Chang.* 4, 364–372. <http://dx.doi.org/10.2166/wcc.2013.059>.
- Azdi, M., Moukrim, A., Burgeot, T., Budzinski, H., Chiffolleau, J.F., Kaaya, A., Zekhnini, A., Narbonne, J.F., Guarrigues, P., 2006. Hydrocarbon pollution along Moroccan coasts and BPH activity in the mussel *Perna perna*. *Polycycl. Aromat. Compd.* 26, 265–282. <http://dx.doi.org/10.1080/10406630600904059>.
- Bellucci, L.G., El Moumni, B., Collavini, F., Frignani, M., Albertazzi, S., 2003. Heavy metals in Morocco lagoon and river sediments. *J. Phys. IV* 107, 139–142. <http://dx.doi.org/10.1051/jp4:20030262>.
- Bellucci, L.G., Frignani, M., Cochran, J.K., Albertazzi, S., Zaggia, L., Cecconi, G., Hopkins, H., 2007. ²¹⁰Pb and ¹³⁷Cs as chronometers for salt marsh accretion in the Venice Lagoon: links to flooding frequency and climate change. *J. Environ. Radioact.* 97, 85–102. <http://dx.doi.org/10.1016/j.jenvrad.2007.03.005>.
- Bellucci, L.G., Giuliani, S., Romano, S., Albertazzi, S., Mugnai, C., Frignani, M., 2012. An integrated approach to the assessment of pollutant delivery chronologies to impacted areas: Hg in the Augusta Bay (Italy). *Environ. Sci. Technol.* 46, 2040–2046. <http://dx.doi.org/10.1021/es203054c>.
- Berner, R.A., 1971. *Principles of Chemical Sedimentology*. McGraw-Hill, New York.
- Blouidi, M.K., Faure, P., Duplay, J., 2008. Organic contamination identification in sediments from a Mediterranean coastal ecosystem: the case of the Nador lagoon (Eastern Morocco). *C. R. Geosci.* 340, 840–849. <http://dx.doi.org/10.1016/j.crte.2008.08.007>.
- Blouidi, M.K., Duplay, J., Quaranta, G., 2009. Heavy metal contamination of coastal lagoon sediments by anthropogenic activities: the case of Nador (East Morocco). *Environ. Geol.* 56, 833–843. <http://dx.doi.org/10.1007/s00254-007-1184-x>.
- Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2002. Towards a global historical emission inventory for selected PCB congeners – a mass balance approach – 3. An update. *Sci. Total Environ.* 377, 296–307. <http://dx.doi.org/10.1016/j.scitotenv.2007.02.026>.
- Chalouan, A., Michard, A., Feinberg, H., Montigny, R., Saddiqi, O., 2001. The Rif mountain building (Morocco): a new tectonic scenario. *Bull. Soc. Geol. Fr.* 172, 603–616.
- Cochran, U.A., Berryman, K.R., Mildenhall, D.C., Hayward, B.W., Southall, K., Hollis, C.J., 2005. Towards a record of Holocene tsunami and storms for northern Hawke's Bay, New Zealand. *N. Z. J. Geol. Geophys.* 48, 507–515. <http://dx.doi.org/10.1080/00288306.2005.9515129>.
- Dodoo, D.K., Essumang, D.K., Jonathan, J.W.A., Bentum, J.K., 2012. Polychlorinated biphenyls in coastal tropical ecosystems: distribution, fate and risk assessment. *Environ. Res.* 118, 16–24. <http://dx.doi.org/10.1016/j.envres.2012.07.011>.
- Dong, C., Chen, C., 2014. Vertical profile, sources, and equivalent toxicity of polycyclic aromatic hydrocarbons in sediment cores from the river mouths of Kaohsiung Harbor, Taiwan. *Mar. Pollut. Bull.* 85, 665–671. <http://dx.doi.org/10.1016/j.marpolbul.2013.09.037>.
- El-Alami, M., Mahjoubi, R., Damnati, B., Kamel, S., Icole, M., Taieb, M., 1998. Sédimentologie et géochimie organique des sédiments superficiels de la lagune de Nador (Maroc nord-oriental). *J. Afr. Earth Sci.* 26, 249–259. [http://dx.doi.org/10.1016/S0899-5362\(98\)00008-6](http://dx.doi.org/10.1016/S0899-5362(98)00008-6).
- Erickson, M.D., 1997. *Analytical Chemistry of PCBs*. second edition. Lewis Publisher, Boca Raton – New York (688 pp.).
- Er-Raioufi, H., Bouzid, S., Marhraoui, M., Saliot, A., 2009. Hydrocarbon pollution of the Mediterranean coastline of Morocco. *Ocean Coast. Manag.* 52, 124–129. <http://dx.doi.org/10.1016/j.ocecoaman.2008.10.006>.
- Fava, F., Gentilucci, S., Zanolli, G., 2003. Anaerobic biodegradation of weathered polychlorinated biphenyls (PCBs) in contaminated sediments of Porto Marghera (Venice Lagoon, Italy). *Chemosphere* 53, 101–109. [http://dx.doi.org/10.1016/S0045-6535\(03\)00438-7](http://dx.doi.org/10.1016/S0045-6535(03)00438-7).
- Flower, R.J., Appleby, P.G., Thompson, J.R., Ahmed, M.H., Ramdani, M., Chouba, L., Rose, N., Rochester, R., Ayache, F., Kraiem, M.M., Elkhiati, N., El Kafrawy, S., Yang, H., Rasmussen, E.K., 2009. Sediment distribution and accumulation in lagoons of the Southern Mediterranean Region (the MELMARINA Project) with special reference to environmental change and aquatic ecosystems. *Hydrobiologia* 622, 85–112. <http://dx.doi.org/10.1007/s10750-008-9677-5>.
- Frame, G.M., Cochran, J.W., Bøwadt, S.S., 1996. Complete PCB congener distributions for 17 aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. *J. High Resolut. Chromatogr.* 19, 657–668. <http://dx.doi.org/10.1002/jhrc.1240191202>.
- Frignani, M., Bellucci, L.G., Carraro, C., Raccanelli, S., 2001. Polychlorinated biphenyls in sediments of the Venice Lagoon. *Chemosphere* 43, 567–575. [http://dx.doi.org/10.1016/S0045-6535\(00\)00408-2](http://dx.doi.org/10.1016/S0045-6535(00)00408-2).
- Frignani, M., Bellucci, L.G., Carraro, C., Favotto, M., 2004. Accumulation of polychlorinated biphenyls in sediments of the Venice Lagoon and the industrial area of Porto Marghera. *Chemosphere* 54, 1563–1572. [http://dx.doi.org/10.1016/S0045-6535\(03\)00552-6](http://dx.doi.org/10.1016/S0045-6535(03)00552-6).
- Gibbs, H.M., Gurnell, A.M., Heppell, C.M., Spencer, K.L., 2014. The role of vegetation in the retention of fine sediment and associated metal contaminants in London's rivers. *Earth Surf. Process. Landf.* 39, 1115–1127. <http://dx.doi.org/10.1002/esp.3575>.
- Giuliani, S., Sprovieri, M., Frignani, M., Cu, N.H., Mugnai, C., Bellucci, L.G., Albertazzi, S., Romano, S., Feo, M.L., Marsella, E., Nhon, D.H., 2008. Presence and origin of polycyclic aromatic hydrocarbon in sediments of nine coastal lagoons in central Vietnam. *Mar. Pollut. Bull.* 56, 1486–1512. <http://dx.doi.org/10.1016/j.marpolbul.2008.04.013>.
- Giuliani, S., Romano, S., Turetta, C., Cu, N.H., Bellucci, L.G., Capodaglio, G., Mugnai, C., Nhon, D.H., Frignani, M., 2011a. Soils and sediments of the Thua Thien-Hue Province (central Vietnam): recognizing trace element sources and the likely influence of natural events. *J. Environ. Monit.* 13, 1383–1392. <http://dx.doi.org/10.1039/c0em00706d>.
- Giuliani, S., Piazza, R., Bellucci, L.G., Cu, N.H., Vecchiato, M., Romano, S., Mugnai, C., Nhon, D.H., Frignani, M., 2011b. PCBs in Central Vietnam coastal lagoons: levels and trends in dynamic environments. *Mar. Pollut. Bull.* 62, 1013–1024. <http://dx.doi.org/10.1016/j.marpolbul.2011.02.035>.
- González, I., Águila, E., Galán, E., 2007. Partitioning, bioavailability and origin of heavy metals from the Nador Lagoon sediments (Morocco) as a basis for their management. *Environ. Geol.* 52, 1581–1593. <http://dx.doi.org/10.1007/s00254-006-0602-9>.
- Gullett, B.K., Touati, A., Hays, M.D., 2003. PCDD/F, PCB, HxCBz, PAH, and PM emission factors for fireplace and woodstove combustion in the San Francisco Bay Region. *Environ. Sci. Technol.* 37, 1758–1765. <http://dx.doi.org/10.1021/es026373c>.
- Guo, J., Capozzi, S.L., Kraeutler, T.M., Rodenburg, L.A., 2014. Global distribution and local impacts of inadvertently generated polychlorinated biphenyls in pigments. *Environ. Sci. Technol.* 48, 8573–8580. <http://dx.doi.org/10.1021/es502291b>.
- Hamoumi, N., Benssaou, M., 2001. The western Anti-Atlas of Morocco: sedimentological and palaeogeographical formation studies in the Early Cambrian. *J. Afr. Earth Sci.* 32, 351–372. [http://dx.doi.org/10.1016/S0899-5362\(01\)90102-2](http://dx.doi.org/10.1016/S0899-5362(01)90102-2).

- Hu, D., Martinez, A., Hornbuckle, K.C., 2011. Sedimentary records of non-Aroclor and Aroclor PCB mixtures in the Great Lakes. *J. Great Lakes Res.* 37, 359–364. <http://dx.doi.org/10.1016/j.jglr.2011.03.001>.
- Ingersoll, C.G., MacDonald, D.D., Wang, N., Crane, J.L., Field, L.J., Haverland, P.S., Kemple, N.E., Lindskoog, R.A., Severn, C., Smorong, D.E., 2000. Prediction of sediment toxicity using consensus-based freshwater sediment quality guidelines, EPA 905/R-00/007 (33 pp.).
- Klotz, K., Schindler, B.K., Angerer, J., 2011. 1,2-Dihydroxynaphthalene as biomarker for a naphthalene exposure in humans. *Int. J. Hyg. Environ. Health* 214, 110–114. <http://dx.doi.org/10.1016/j.ijheh.2010.11.003>.
- Kumar, B., Kumar, S., Sharma, C.S., 2013. Ecotoxicological risk assessment of polychlorinated biphenyls (PCBs) in bank sediments from along the Yamuna River in Delhi, India. *Hum. Ecol. Risk Assess.* Int. J. 19, 1477–1487. <http://dx.doi.org/10.1080/10807039.2012.723181>.
- Lefebvre, A., Guelorget, O., Perthuisot, J.P., Dafir, J.E., 1997. Evolution biogéologique de la lagune de Nador (Maroc) au cours de la période 1982–1993. *Oceanol. Acta* 20, 371–385 (doi:).
- Liang, Y., Martinez, A., Hornbuckle, K.C., Mattes, T.E., 2014. Potential for polychlorinated biphenyl biodegradation in sediments from Indiana Harbor and Ship Canal. *Int. Biodeterior. Biodegrad.* 89 (2014), 50–57. <http://dx.doi.org/10.1016/j.ibiod.2014.01.005>.
- Mendes, I., Rosa, F., Dias, J.A., Schönfeld, J., Ferreira, T., Pinheiro, J., 2010. Inner shelf paleoenvironmental evolution as a function of land-ocean interactions in the vicinity of the Guadiana River, SW Iberia. *Quat. Int.* 221, 58–67. <http://dx.doi.org/10.1016/j.quaint.2009.10.037>.
- Mugnai, C., Giuliani, S., Bellucci, L.G., Carraro, C., Favotto, M., Frignani, M., 2011. Polychlorinated biphenyls in two salt marsh sediments of the Venice Lagoon. *Environ. Monit. Assess.* 181, 243–254. <http://dx.doi.org/10.1007/s10661-010-1826-4>.
- Nekhahambe, T.J., van Ree, T., Fatoki, O.S., 2014. Determination and distribution of polycyclic aromatic hydrocarbons in rivers, surface runoff, and sediments in and around Thohoyandou, Limpopo Province, South Africa. *Water SA* 40, 415–424. <http://dx.doi.org/10.4314/wsa.v40i3.4>.
- Nielsen, T., Jørgensen, H.E., Larsen, J.C., Poulsen, M., 1995. City air pollution of polycyclic aromatic hydrocarbons and other mutagens: occurrence, sources and health effects. *Sci. Total Environ.* 189/190, 41–49. [http://dx.doi.org/10.1016/0048-9697\(96\)05189-3](http://dx.doi.org/10.1016/0048-9697(96)05189-3).
- Oldfield, F., Appleby, P.G., 1984. Empirical testing of ²¹⁰Pb-dating models for lake sediments. In: Haworth, E.Y., Lund, J.W.G. (Eds.), *Lake Sediments and Environmental History*. University of Minnesota, Minneapolis, pp. 93–124.
- Piazza, R., El Moumni, B., Bellucci, L.G., Frignani, M., Vecchiato, M., Giuliani, S., Romano, S., Zangrando, R., Gambaro, A., 2009. Polychlorinated biphenyls in sediments of selected coastal environments in Northern Morocco. *Mar. Pollut. Bull.* 58, 431–438. <http://dx.doi.org/10.1016/j.marpolbul.2008.11.020>.
- Piazza, R., Gambaro, A., Argiriadis, E., Vecchiato, M., Zambon, S., Cescon, P., Barbante, C., 2013. Development of a method for simultaneous analysis of PCDDs, PCDFs, PCBs, PBDEs, PCNs and PAHs in Antarctic air. *Anal. Bioanal. Chem.* 405, 917–932. <http://dx.doi.org/10.1007/s00216-012-6464-y>.
- Preston, C.M., Schmidt, M.W.I., 2006. Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions. *Biogeosciences* 3, 397–420 (doi:).
- Quaranta, G., Blouidi, K., Duplay, J., Irzi, Z., 2004. L'Analyse du cycle de Vie: un outil pour la gestion intégrée des zones côtières (Cas de la lagune de Nador- Maroc). Proceedings to the International Congress "Gestion Intégrée du Littoral et des Ecosystèmes Associés pour le Développement Durable", Oujda 27–29 May.
- Robbins, J.A., 1978. Geochemical and geophysical applications of radioactive lead isotopes. In: Nriago, J.P. (Ed.), *Biogeochemistry of Lead*. North Holland, Amsterdam, pp. 285–393.
- Rodenburg, L.A., Guo, J., Du, S., Cavallo, G.J., 2010. Evidence for unique and ubiquitous environmental sources of 3,3'-dichlorobiphenyl (PCB 11). *Environ. Sci. Technol.* 44, 2816–2821. <http://dx.doi.org/10.1021/es901155h>.
- Romano, S., Piazza, R., Mugnai, C., Giuliani, S., Bellucci, L.G., Cu, N.H., Vecchiato, M., Zambon, S., Nhon, D.H., Frignani, M., 2013. PBDEs and PCBs in sediments of the Thi Nai Lagoon (Central Vietnam) and soils from its mainland. *Chemosphere* 90, 2396–2402. <http://dx.doi.org/10.1016/j.chemosphere.2012.10.067>.
- Ruiz, F., Abad, M., Bodergat, A.M., Carbonel, P., Rodríguez-Lázaro, J., Yasuhara, M., 2005. Marine and brackish-water ostracods as sentinels of anthropogenic impacts. *Earth Sci. Rev.* 72, 89–111. <http://dx.doi.org/10.1016/j.earscirev.2005.04.003>.
- Ruiz, F., Abad, M., Ollas, M., Galán, E., González, I., Águila, E., Hamoumi, N., Pulido, I., Cantano, M., 2006. The present environmental scenario of the Nador Lagoon (Morocco). *Environ. Res.* 102, 215–229. <http://dx.doi.org/10.1016/j.envres.2006.03.001>.
- Ruiz-Fernández, A.C., Sprovieri, M., Piazza, R., Frignani, M., Sanchez-Cabeza, J., Feo, M.L., Bellucci, L.G., Vecchiato, M., Pérez-Bernal, L.H., Páez-Osuna, F., 2012. ²¹⁰Pb-derived history of PAH and PCB accumulation in sediments of a tropical inner lagoon (Las Matas, Gulf of Mexico) near a major oil refinery. *Geochim. Cosmochim. Acta* 82, 136–153. <http://dx.doi.org/10.1016/j.gca.2011.02.041>.
- Scarpato, A., Romanelli, G., Galgani, F., Andral, B., Amici, M., Giordano, P., Caixach, J., Calvo, M., Campillo, J.A., Albadalejo, J.B., Cento, A., BenBrahim, S., Sammari, C., Deudero, S., Boulahdid, M., Giovanardi, F., 2010. Western Mediterranean coastal waters monitoring PCBs and pesticides accumulation in *Mytilus galloprovincialis* by active mussel watching: the Mytilos project. *J. Environ. Monit.* 12, 924–935. <http://dx.doi.org/10.1039/b920455e>.
- Tanabe, S., 1988. PCB problems in the future: foresight from current knowledge. *Environ. Pollut.* 50, 5–28. [http://dx.doi.org/10.1016/0269-7491\(88\)90183-2](http://dx.doi.org/10.1016/0269-7491(88)90183-2).
- Tobiszewski, M., Namiesnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. *Environ. Pollut.* 162, 110–119. <http://dx.doi.org/10.1016/j.envpol.2011.10.025>.
- Ünlü, S., Alpar, B., 2006. Distribution and sources of hydrocarbons in surface sediments of Gemlik Bay (Marmara Sea, Turkey). *Chemosphere* 64, 764–777. <http://dx.doi.org/10.1016/j.chemosphere.2005.10.064>.
- US EPA, 1993. Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. EPA/600/R-93/089, Washington, DC.
- Van den Berg, M., Birnbaum, L.S., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N., Peterson, R.E., 2006. The 2005 World Health Organization re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicol. Sci.* 93, 223–241. <http://dx.doi.org/10.1093/toxsci/kfl055>.
- Weber, R., Gaus, C., Tysklind, M., Johnston, P., Forter, M., Hollert, H., Heinisch, E., Holoubek, I., Lloyd-Smith, M., Masunaga, S., Moccarelli, P., Santillo, D., Seike, N., Symons, R., Torres, J.P.M., Verta, M., Varbelow, G., Vijgen, J., Watson, A., Costner, P., Woelz, J., Wycisk, P., Zennegg, M., 2008. Dioxin- and POP-contaminated sites – contemporary and future relevance and challenges: overview on background, aims and scope of the series. *Environ. Sci. Pollut. Res.* 15, 363–393. <http://dx.doi.org/10.1007/s11356-008-0024-1>.