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Historical Records of Mercury, Lead, and Polycyclic Aromatic Hydrocarbons Depositions in a Dated Sediment Core from the Eastern Mediterranean

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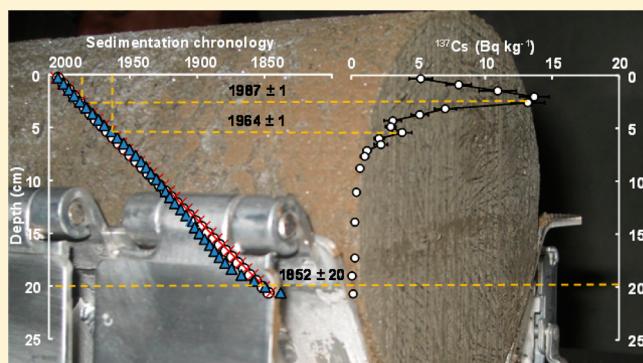
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Supporting Information

ABSTRACT: Depth profiles of mercury, lead and its stable isotopes, and polycyclic aromatic hydrocarbons were determined in a dated sediment core from the Levantine basin. Sedimentary records show that preindustrial fluxes and levels of Hg, Pb, and PAHs remained generally constant in the region before 1850. An almost concurrent uniform increase of both metals and PAHs deposition occurring at the beginning of the Industrial Revolution suggests coal combustion as a main source of these contaminants in the Levantine basin after the 1850s. However, none of the contaminant profiles indicates a decline after 1950–60, the characteristic period of coal use reduction. The modern fluxes of Hg and Pb reveal a 3- to 5-fold increase over preindustrial loads, while the contemporaneous flux of PAHs rises by 4–7 times. On the whole, records in the Eastern Mediterranean suggest atmospheric inputs from relatively distant sources, likely from Central and Eastern Europe.



INTRODUCTION

Mercury (Hg), lead (Pb), and polycyclic aromatic hydrocarbons (PAHs) all have natural and anthropogenic origins in the environment. Anthropogenic sources include biomass and fossil fuel combustion (coal, petroleum, natural gas), and waste incineration, as well as mining and smelting industries.^{1–3} Large quantities of petroleum PAHs also originate from direct discharges, especially in marine environments, such as natural and accidental oil seeps, oil spills, and maritime traffic.⁴ The relative contributions of anthropogenic sources to global emissions of Hg, Pb, and PAHs have considerably varied over time. A number of studies have used archiving media, such as sediment cores from marine and lake environments, Arctic ice and snow, and ombrotrophic peat to evaluate and reconstruct historical records of contaminant inputs in the environment.^{5–12} Emerging trends show a global/regional deposition of these contaminants in various environmental compartments and provide evidence for their transboundary long-range transport to remote locations.^{6,11,13,14} Generally, good correlations have been observed between trends of contaminants in sediment and energy consumption records.^{7,9,15} Determination of Pb stable isotopes in sediment cores allows for further discrimination among different anthropogenic sources, and provides additional information on contaminant environmental inputs and pathways.^{8,15–17}

Nevertheless, a limited number of dated sedimentary records are available for Hg, Pb, and PAHs. This is because, initially, such records require a well-preserved sediment stratification. They also assume a negligible influence of diagenesis and degradation processes, as well as postdepositional bioturbation and mobility on contaminant distributions. Finally, on the one hand, they should cover a time span sufficient to provide preindustrial levels and fluxes of contaminants, which is necessary data for the appraisal of a magnitude of anthropization. On the other hand, they should afford just enough temporal resolution to minimize short-term temporal variations, but also to allow the reconstruction of historical records. All these conditions are rarely fulfilled. Furthermore, most of the available sedimentary records on Hg, Pb, and PAHs have been obtained in Europe and North America. There is a lack of such data from the Eastern Mediterranean Sea.

In this study, we report on depositional fluxes and concentrations of Hg, Pb (including signatures of its stable isotopes ratios), and polycyclic aromatic hydrocarbons in a dated sediment core from the Levantine basin in the Eastern

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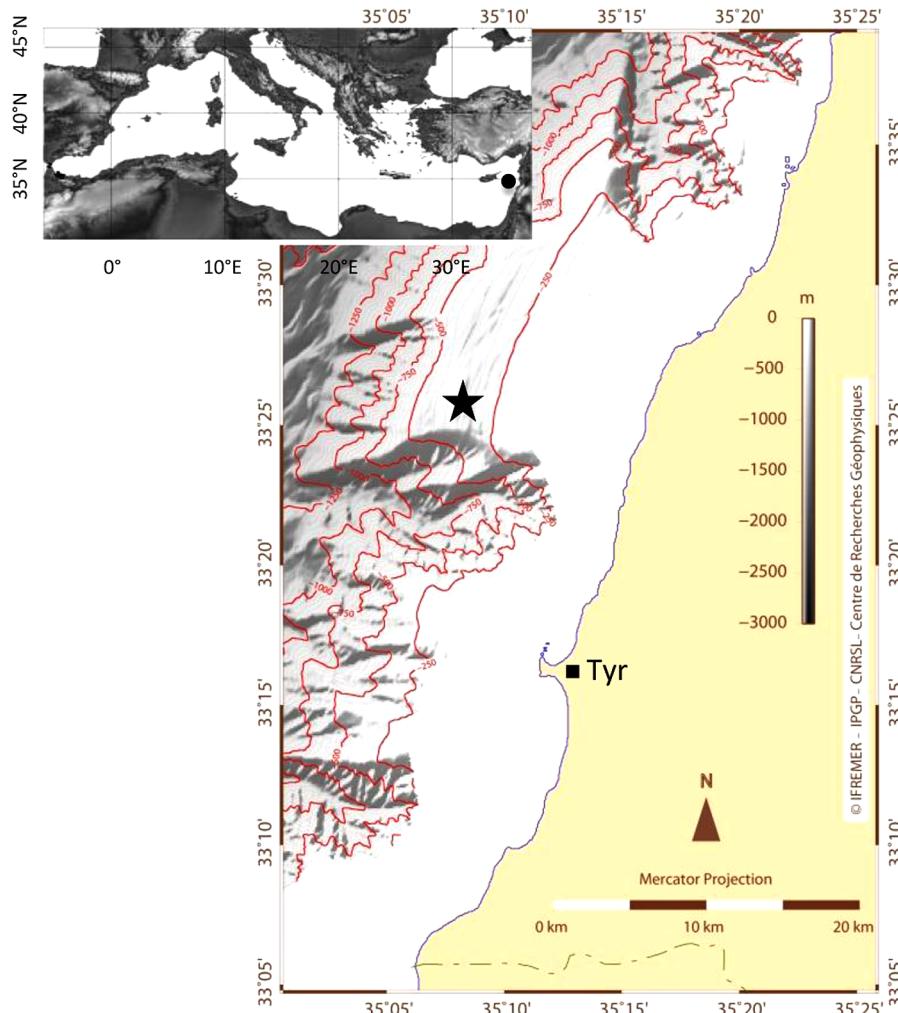


Figure 1. Map showing the location of the C1 core sampling station (star).

Mediterranean. ^{210}Pb and ^{137}Cs depth-profiles are used to assess sedimentation dynamics and to determine depositional chronology. These records are used to (i) determine the detailed down-core flux and concentration profiles of contaminants and their chronological changes, (ii) quantify temporal trends and highlight distinct periods, (iii) investigate potential sources of Pb and PAHs revealed by their specific chemical signatures, and (iv) estimate their pre- and post-industrial fluxes and appraise the extent of anthropogenic inputs of contaminants in the area. Well-resolved historical sedimentary records of Hg, Pb, and PAHs presented here might be representative for the Eastern Mediterranean basin.

■ EXPERIMENTAL SECTION

Sampling. Sediment cores were collected aboard the R/V *Europe* (Genavir/Ifermer) at 300 m depth from the southern Lebanese continental margin in the Eastern Levantine Basin ($33^{\circ}26,373'$ N and $35^{\circ}8,211'$ E) in July 2007 (Figure 1). Sampling was done with a modified dual gravity stainless steel corer. The cores were frozen at $-40\text{ }^{\circ}\text{C}$ and were transported to the laboratory. Frozen sediment cores were extruded and sliced in the cold clean laboratory ($T = -5\text{ }^{\circ}\text{C}$), using a band saw (0.63 mm blade width) mounted on a clean stainless steel table. Sediment slices (0.5 and 1 cm) were stored at $-20\text{ }^{\circ}\text{C}$, then freeze-dried and ground, using agate mortar.

Pb-210 and Cs-137 Analysis and Dating. Dry sediment aliquots (1–5 g) were measured for ^{210}Pb , ^{226}Ra , and ^{137}Cs by direct gamma counting, using a low-background, well-type germanium detector (Canberra, Ge volume 280 cm^3).¹⁸ The unsupported ^{210}Pb was calculated by subtracting the ^{226}Ra activity, corresponding to the supported ^{210}Pb , from total ^{210}Pb . Counting errors for ^{210}Pb total and ^{226}Ra were propagated to excess ^{210}Pb ($^{210}\text{Pb}_{\text{xs}}$) and ranged from 4.6 to 23%.

Grain Size Distribution and Porosity Determination. Sediment-particle size distribution analyses were done by laser diffraction with a Beckman–Coulter LS-200. Water content was determined by weighing sediment samples before and after drying at $105\text{ }^{\circ}\text{C}$, and porosity was subsequently calculated, assuming a mineral density of 2.6 g cm^{-3} .

Lead and Stable Isotopes (^{206}Pb , ^{207}Pb , ^{204}Pb , and ^{208}Pb) Analyses. Analyses were performed on an inductively coupled plasma quadrupole mass spectrometer ICP-MS (Thermo Electron XSeries) after digestion of approximately 200 mg of dry sediment in Teflon bombs by $\text{HCl}/\text{HNO}_3/\text{HF}$ mixture.¹⁹ Analytical accuracy of Pb determination was checked by analyzing a reagent blank and replicates of a certified reference material (MESS-3) within each 25-sample batch. Blank concentrations were below detection limit. Accuracy and reproducibility were determined by the analysis of Certified Reference Material (CRM, MESS-3, NRC). Accuracy check

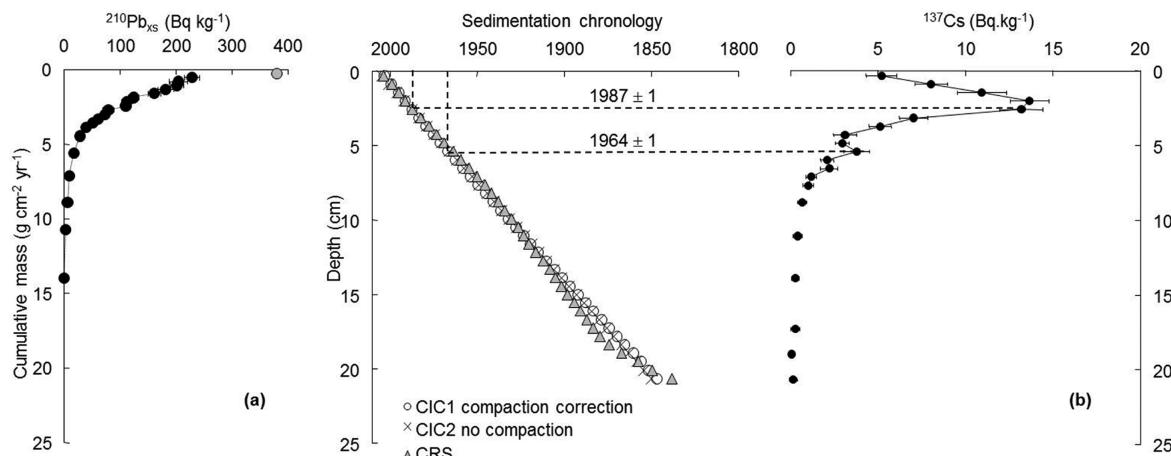


Figure 2. (a) Unsupported $^{210}\text{Pb}_{\text{xs}}$ activity profile plotted against cumulative sediment mass in C1 core; $^{210}\text{Pb}_{\text{xs}}$ activity in superficial sediment (gray circle) not used for sedimentation rate calculation. (b) Sedimentation chronology estimated by ^{210}Pb CIC model (with and without compaction correction) and by CRS model and ^{137}Cs activity profile plotted against sediment depth.

showed that measurements were within the confidence interval of the CRM value. Analytical precision was better than 5% for the Pb determinations in MESS-3 ($n = 9$). NIST-SRM 981 standard was used for a standard bracketing technique that allows correction of instrument drift in Pb isotopes analyses.⁸ Relative standard deviations of isotope determinations varied between 0.2 and 0.6%.

Mercury Analysis. Mercury was determined by atomic absorption spectroscopy after dry mineralization of the sample and preconcentration of the Hg on gold trap with an automatic mercury analyzer, the AMA-254 (Altec).²⁰ Accuracy, checked by running the MESS-3 CRM sediment every 10 samples, was found to be within the range of the certified value ($0.091 \pm 0.009 \mu\text{g g}^{-1}$). Blanks were lower than detection limit ($0.0007 \mu\text{g g}^{-1}$). Analytical precision was better than 5% ($n = 6$ replicates).

PAH Analysis. Dry sediments (5–20 g) were spiked with perdeuterated recovery standards (phenanthrene- d_{10} and benzo[*e*]pyrene- d_{12} refer to fully deuterium labeled compounds) and extracted twice by accelerated solvent extraction (Dionex ASE 200), using dichloromethane.²¹ Fractionation and purification of extracts was done by a two-layer 5% deactivated silica/alumina column. Analysis was performed using an Agilent 7890 gas chromatograph coupled to an Agilent 5975 mass selective detector. Prior to GC-MS analysis, extracts and calibration solutions were each spiked with a deuterated internal standard mixture (acenaphthene- d_{10} , fluorene- d_{10} , pyrene- d_{10} , benz[*a*]antracene- d_{12} , and indeno[1,2,3-*cd*]pyrene- d_{12}). Quantification of individual PAH peak areas was corrected with the correspondent surrogate standard mass and area. Precision and accuracy were assessed by analyses of EC-2 NWRI reference material. Overall accuracy was within 60–93% of certified values ($n = 6$). Relative standard deviation was better than $\pm 11\%$ for all analytes considered in this study except trimethylchrysenes (~30%). Average recovery of standards phenanthrene- d_{10} and benzo[*e*]pyrene- d_{12} was $64.5 \pm 9.3\%$ and $83.0 \pm 10.8\%$, respectively.

RESULTS AND DISCUSSION

Sedimentation Rates and Chronology. Unsupported $^{210}\text{Pb}_{\text{xs}}$ activity decreased exponentially with depth from the surface of the sediment core until negligible concentrations of

$^{210}\text{Pb}_{\text{xs}}$ were attained (at 11 cm depth and at a cumulative dry mass of 5.4 g cm^{-2} ; Figure 2a). Such a profile of $^{210}\text{Pb}_{\text{xs}}$ is a convincing argument for a regular sedimentation rate and an undisturbed sediment sequence with no or little surficial mixing.²² Furthermore, the grain size distribution is nearly homogeneous, exclusively assembled with clayey fine grain sediment over the entire sediment core length ($98.3 \pm 1.2\% < 25 \mu\text{m}$; Supporting Information (SI) Figure S-1). Continuous sediment morphology and absence of biological activity (photos given in SI) also indicate homogeneous composition and lack of bioturbation in the sediments, including those below the depth of $^{210}\text{Pb}_{\text{xs}}$ penetration. These results and observations presume regular, low-energy sediment transport, and deposition processes favorable to good stratigraphic sediment preservation in C1 core.

CIC (constant initial concentration) and CRS (constant rate of supply) models were used to calculate sedimentation and sediment mass accumulation rates. Both models gave very similar results (Table S-1). Estimated mass accumulation rates are 0.064 and $0.065 \text{ g cm}^{-2} \text{ yr}^{-1}$ and sedimentation rates are 0.128 and 0.122 cm yr^{-1} for CIC (with compaction correction) and CRS models, respectively. These data were used for an appraisal of sediment core chronology. The validity of the sediment core dating by different models (CRS and CIC) was also checked against an independent time-stratigraphic marker, the ^{137}Cs activity profile reflecting its historical fallout (Figure 2b). Cs-137 profile exhibits a subsurface peak with maximum activity in 1987 ± 1 consistent with widespread fallout of ^{137}Cs in the Northern Hemisphere after the Chernobyl reactor disaster in 1986.^{23–25} Significant fallout of ^{137}Cs after the Chernobyl accident was also reported in the Eastern Mediterranean seawaters²⁶ and in Syrian soils.²⁷ A smaller peak is detected in deeper layers in C1 core corresponding to 1964 ± 1 and may be related to ^{137}Cs fallout due to maximum nuclear weapon testing in 1962.^{28,29}

An overestimation of sedimentary fluxes may occur in sites where sediment focusing takes place. The focusing factor is calculated as the ratio of the seabed $^{210}\text{Pb}_{\text{xs}}$ flux, calculated from the sediment inventory ($14 \text{ mBq cm}^{-2} \text{ yr}^{-1}$), to the expected $^{210}\text{Pb}_{\text{xs}}$ flux, due to atmospheric fallout plus the $^{210}\text{Pb}_{\text{xs}}$ production in the water column from decay of ^{226}Ra .¹⁸ The production rate through the water column was estimated to 1–

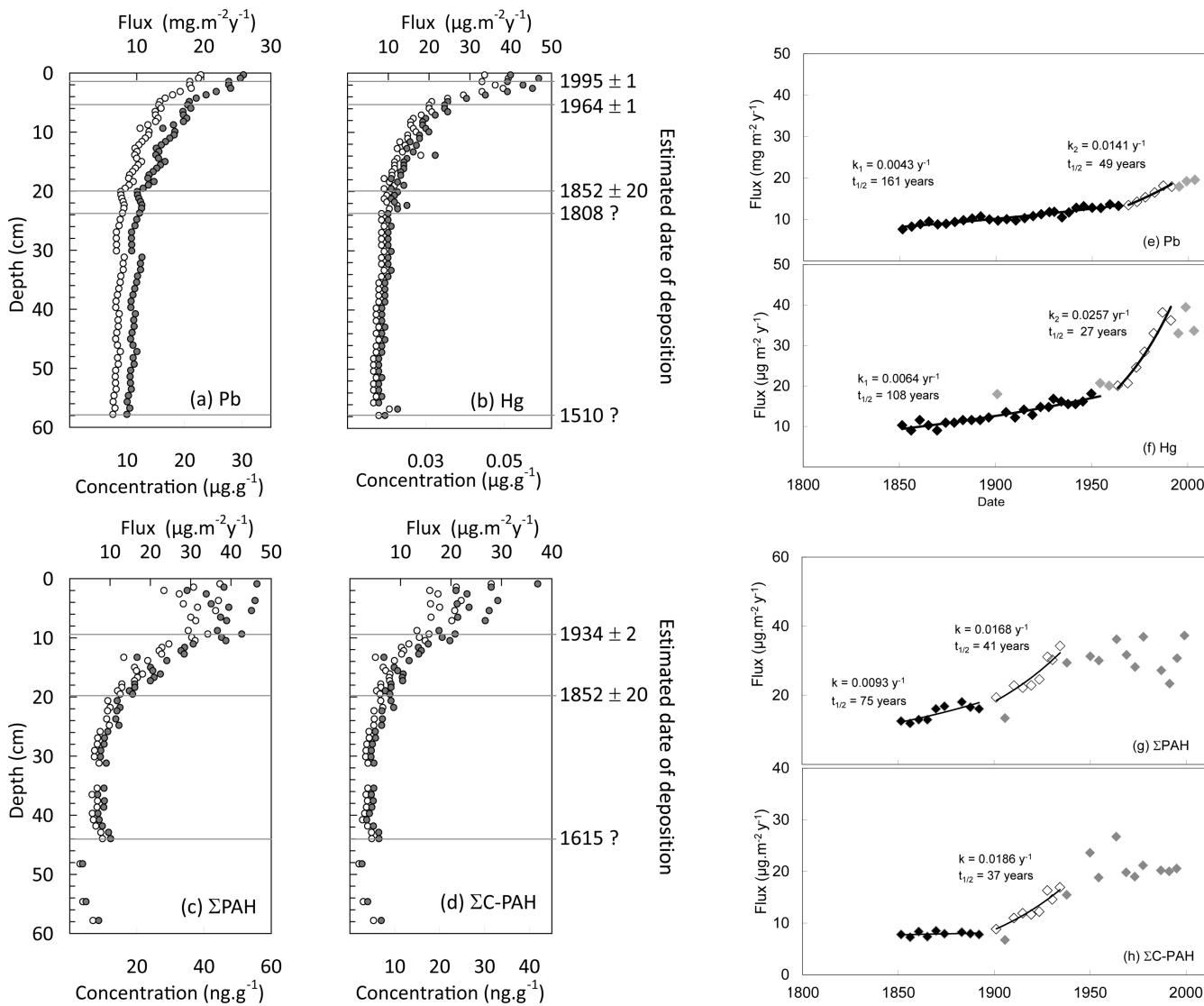


Figure 3. Down-core depth profiles of fluxes (open circles) and concentrations (closed circles) of Pb (a), Hg (b), parent Σ PAH (c), and alkylated homologues Σ C-PAH (d). Flux changes over distinct time intervals: closed diamonds post-1852 to 1964 for Pb (e), to 1950 for Hg (f), to 1892 for Σ PAH (g), and Σ C-PAH (h). Gray diamonds: data excluded from calculation of first-order rate of flux increase. See SI for summed concentrations of Σ PAH and Σ C-PAH accounts.

2 mBq $\text{cm}^{-2} \text{ y}^{-1}$ using ^{226}Ra activities in Mediterranean waters.³⁰ The focusing factor of C1 core ranges between 0.85 and 1.55, considering the uncertainties on atmospheric fallout (8–15 mBq $\text{cm}^{-2} \text{ y}^{-1}$).^{31–34} Because of these uncertainties the calculated fluxes and inventories reported in this paper will, however, not be corrected for relatively low focusing factor.

Vertical Distributions of Lead, Mercury, and PAHs. The depth profiles of total sedimentary lead and mercury concentrations and depositional fluxes show a very similar shape throughout the entire C1 core. Parent PAHs (Σ PAH) and their alkylated homologues (Σ C-PAH) also display similar depth profiles in C1 core (Figure 3). Because sedimentation rate at the study site did not change over time, profiles of fluxes and concentration are largely same. These records provide also chronology on depositional flux changes and allow us to calculate the rates at which these changes have occurred in the Eastern Levantine Basin (Figure 3). In general, low concentrations and depositional fluxes of Pb, Hg, and PAHs remained constant below 20 cm depth, i.e. until the onset of

their exponential increase at the beginning of the Industrial Revolution (ca. after 1850). A slow and uniform increase in accumulation of both metals starts after 1852 and stretches to the early 1950s for Hg and to the 1960s for Pb (Figure 3). Low but statistically significant first order rates of increase in Hg flux (0.0064 yr^{-1} , $n = 24$, $r^2 = 0.88$) and in Pb flux (0.0043 yr^{-1} , $n = 27$, $r^2 = 0.90$) were determined for these periods (Figure 3). This is followed by abrupt increase in Hg and Pb deposition which occurred between the mid-1960s and the 1990s. During this 25-year period, Hg and Pb fluxes rose by 55% and 33% (relative to 1852–1950/1964 means) and at 3–4 times faster rates (0.0257 yr^{-1} , $n = 7$, $r^2 = 0.95$ and 0.0141 yr^{-1} , $n = 6$, $r^2 = 0.96$), respectively. In the topmost layers of C1 (i.e., after the 1990s), profiles show more variable concentrations and fluxes for Hg and slightly increasing values for Pb.

The increase of parent Σ PAH levels and fluxes begin also after 1852, i.e. at the same time as for Hg and Pb. However, Σ PAH deposition already leveled off in C1 core as early as the mid-1930s, whereas Pb and Hg continued to increase until the

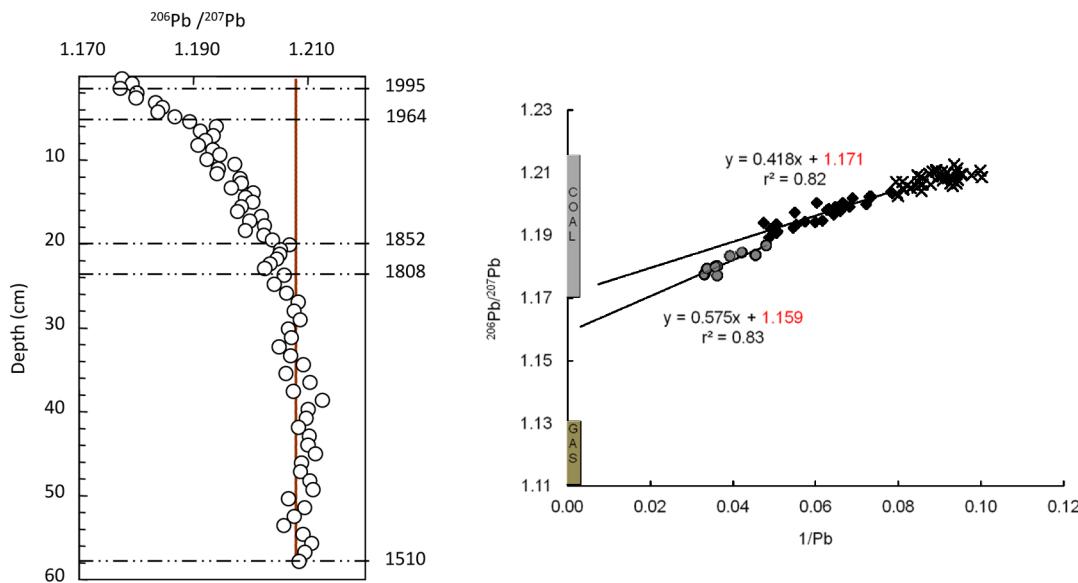


Figure 4. Left panel: down-core depth profiles of $^{206}/^{207}\text{Pb}$ ratio; vertical line indicates mean ($n = 38$) of preindustrial background before 1852 ± 20 . Right panel: $^{206}/^{207}\text{Pb}$ ratio versus $1/\text{Pb}$; symbols represent the following periods: pre-1852 (star), 1852–1964 (diamond), and 1969–2003 (circles) respectively; $^{206}/^{207}\text{Pb}$ signatures of coal and gasoline from Europe are represented on the y axis.

1990s (Figure 3). Indeed, $\sum\text{PAH}$ fluxes show an increase characterized by a first-order rate of $0.0093 \text{ years}^{-1}$ ($n = 9$, $r^2 = 0.72$) between 1852 and the end of the 19th century followed by an increase twice as fast ($0.0168 \text{ years}^{-1}$, $n = 8$, $r^2 = 0.88$) occurring between 1901 and 1932. The rise of alkylated $\sum\text{C-PAHs}$ started later than for their parent homologues, only since the beginning of the 20th century, but with a similar first-order rate of increase ($0.0186 \text{ years}^{-1}$, $n = 8$, $r^2 = 0.90$). Variable concentrations and fluxes, with no clear trend, were determined for both alkylated and parent PAHs in the upper 10 cm of the core (i.e., after the 1930s).

The chronology for the lower portion of C1 profiles agrees well with sedimentary records of Pb and Hg reported in the Eastern and Western Mediterranean Sea,^{15,16,32,35–37} as well as in lake sediments, ombrotrophic peat bogs, and snow in many locations worldwide.^{8,10–12,14} In these studies, the reported increasing trends are related to the growing use of coal as a main source of energy from the mid-19th century until the mid-20th century, when petroleum and natural gas gradually replaced coal-based fuels.^{8,11,15} The influence of coal combustion on PAH emissions is also relatively well demonstrated by several historical records in marine and lake sediments in North America and in Western Europe.^{6–9,38–41} Furthermore, a general agreement between the trends of Pb and PAHs derived from coal was shown in lake sediments in Canada.⁸ Many of the PAH records demonstrate indeed maximum levels between 1940 and 1960, coinciding with the period of the highest coal consumption, in the U.S., Canada, and Western Europe.^{7–9,41} However, in the present study, PAH profiles in the Levantine basin sediments reveal no decreasing levels after 1940–1960, i.e. after a significant reduction in coal consumption in Western Europe.

Regarding the more recent deposits of Pb and Hg, it is difficult to discern a clear picture of actual trends from sediment records reported in published data. Some studies have reported significant decreasing concentrations of lead and mercury in sediments since the 1970s, in relation to regulatory measures on Pb and Hg emissions.^{8,15,32} Other reports show increasing and variable concentrations of lead and mercury in

recent deposits.^{11,16,37} Pb and Hg profiles in the present study show a sharp increase of concentrations over three decades (between 1960 and 1990) and more variable levels in the most recent sediment sections. Similar profiles of Hg in sediments of remote Nova Scotia lakes were reported as representative of the Northern Hemisphere.¹¹ Nevertheless, emission control in the 1970s and 1980s, such as vehicles with catalytic converters and measures for phasing out leaded gasoline, are not reflected in C1 core. It may be possible that this signal, which was well established in other locations in Europe and North America,^{8,15,42} is overwhelmed by recent inputs of anthropogenic lead in the studied region.

An appraisal of the sources of contaminants in Levantine basin sediments is further examined using changes of lead isotopic ratios and of PAH compositional signatures.

Variation of Stable Isotopic Ratios of Lead. The depth profile of the distribution of $^{206}\text{Pb}/^{207}\text{Pb}$ is shown in Figure 4 ($^{206}\text{Pb}/^{208}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios are given in Table S-2). The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio depth-profile mirrors that of lead and mercury concentrations. Lead concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratio are negatively correlated ($r^2 = 0.95$, $p < 0.05$) over the entire core length. The average isotopic composition of lead determined below 20 cm depth, i.e. prior to 1852 ± 20 (1.208 ± 0.0023 and 0.487 ± 0.0008 , $n = 38$, for $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$, respectively) is close to that reported for natural rock residue in Israeli soils (1.210 and 0.488, respectively⁴³). The distinct preindustrial $^{206}\text{Pb}/^{207}\text{Pb}$ signature at our sampling site is also comparable to those generally found in deep sections of sediment cores, or remote sites in the Western and Eastern Mediterranean (1.199–1.220).^{16,35,37,42,44,45} Recently, an average of 1.2011 ± 0.0015 ($n = 24$) for the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio was reported in ancient sediments (prior to 650 BC) in a Mediterranean lagoon, and was considered as the local natural lead signature.¹⁵ Thus, it reasonably appears that preindustrial background lead was determined in the deepest sections of C1 core. No signal of ancient local activities such as ore smelting or preindustrial mining may be revealed in C1 core, perhaps because of the too-short temporal span covered by our sampling.^{15,35,45} The concomitant decrease of the $^{206}\text{Pb}/^{207}\text{Pb}$

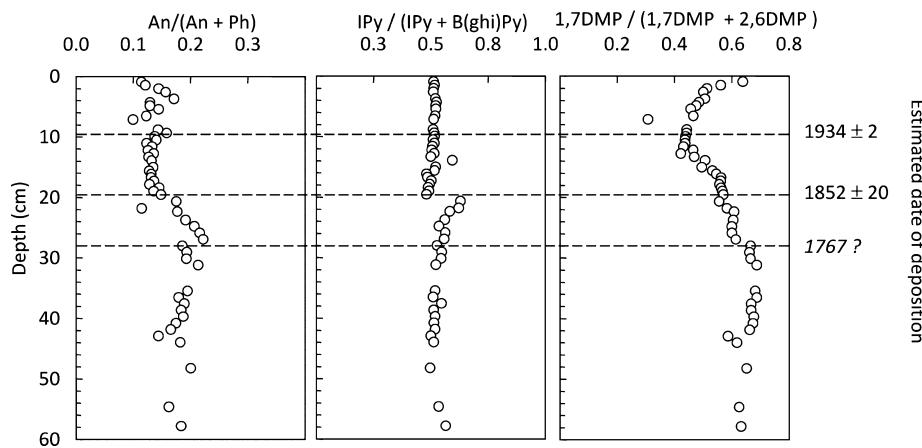


Figure 5. Down-core profiles of selected PAH ratios.

ratio and increase of Pb concentrations from background to the present is thus best explained by an additional flux of anthropogenic lead (i.e., less radiogenic) during the mid-19th and 20th centuries.

The mixing plot of $^{206}\text{Pb}/^{207}\text{Pb}$ versus $1/\text{Pb}$ in sediment samples is illustrated in Figure 4. Two linear regression lines separate samples into two time intervals (1852–1964 and 1969–2003) and further suggest the existence of two isotopically distinct types of anthropogenic lead, apparently admixed with preindustrial lead. The isotopic compositions of anthropogenic source end-members are given by regression intercepts.⁴² Preindustrial lead is also well distinguished by the lowest Pb concentrations and the highest $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (Figure 4). The first type of anthropogenic lead is most likely concurrent with higher worldwide emissions of Pb derived from coal combustion.^{8,11,15} The average $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ (1.197 ± 0.004 and 2.475 ± 0.003 ; respectively; $n = 25$) is consistent with central Europe coal signatures (1.196 ± 0.019 and 2.468 ± 0.011 ;^{46,47} see literature data of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ signatures for lead source end-members SI Table S-3 and Figure S-2). However, such source assignment is uncertain, because of the wide ranges of lead isotopic signatures from different source end-members.^{43,46–48} The presence of a second type of anthropogenic lead at our sampling site corresponds to the sharp increase of lead concentrations. This lead may be ascribed to local sources and may contain additional lead emitted from the combustion of petroleum fuels. Isotopic signatures in the top sediment sections of C1 core (1.178 for $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.458 for $^{208}\text{Pb}/^{207}\text{Pb}$) are in agreement with the end-members of lead in air aerosols in the Eastern Mediterranean region. Furthermore, the recent increase of coal consumption in Israel (between 1980 and 2002⁴⁹) may contribute additionally, as a local source, to a higher Pb emission and its sedimentary burdens. On the other hand, there is a possible contribution of continuing distant sources related to lead emissions from Western, Central, and Eastern Europe and Russia (such atmospheric fallout is ascertained by well-defined ^{137}Cs peak in the C1 indicative of the Chernobyl emissions). Sedimentary lead in our samples is likely composed of a mixture of preindustrial lead and of several sources of anthropogenic lead with variable contributions through time. The assignment of lead end-member/source isotope signatures to our data is thus quite tentative.

PAH Compositional Signature Changes. Alkylated and parent PAHs show very similar profiles in C1 core (Figure 3)

and are highly correlated ($r^2 = 0.95$; $p < 0.05$). Parent compounds predominate over the entire core length (55–73% of the total PAHs) that is commonly associated with combustion-derived pyrogenic PAH source (biomass and fossil fuels combustion).^{13,50–52} Alkylated compounds are formed in lower proportions during combustion, and have frequently been used as indicators of petroleum inputs into the marine environment.^{53–56} Nevertheless, certain homologues (such as retene 1-methyl-7-isopropylphenanthrene and pimanthrene 1,7-dimethylphenanthrene) have been identified as specific markers of biomass burning.^{57,65} Isomer ratios and relative abundances of selected individual PAHs also allow us to evaluate the contribution of PAH sources in the Levantine basin sediments.^{7,9} (Additional information on PAH ratios and individual compound abundances is provided in Figure S-3).

The ratio of ideno(1,2,3-*cd*)pyrene to (ideno(1,2,3-*cd*)pyrene + benzo(*ghi*)perylene), IPy/(IPy + BghiPy) did not vary greatly over the entire sediment core length (Figure 5). Although a slight shift in this ratio from preindustrial values may be seen around 1852. The mean value 0.52 ± 0.031 ($n = 29$) of IPy/(IPy + BghiPy) ratio lies within the range reported for coal combustion (0.48–0.57) and it is far higher than the values reported for combustion of gasoline (0.09–0.22).^{51,58} Ratios of anthracene to (anthracene + phenanthrene), An/(An + Ph) and that of 1,7-dimethylphenanthrene to (1,7-dimethylphenanthrene + 2,6-dimethylphenanthrene), 1,7-DMP/(1,7-DMP + 2,6-DMP) have varied over time respective to the key features of the PAH records in C1 core (Figure 5). The ratio An/(An + Ph) is used to distinguish roughly between petrogenic (inferior to 0.1) and pyrogenic (superior to 0.1) sources, while a higher 1,7-DMP/(1,7-DMP + 2,6-DMP) ratio may be indicative of a soft wood combustion source.^{57–59} After 1852, the mean value of An/(An + Ph) (0.135 ± 0.014 ; $n = 29$) remains higher than the threshold value of 0.1 and suggests combustion-derived PAHs.^{58,59} The 1,7-DMP/(1,7-DMP + 2,6-DMP) ratio declines gradually during maximum PAH concentration increase then shows a rapid rise in the uppermost horizons (Figure 5). However, a significant shift of this ratio is also already noticeable at the 27-cm sediment core depth (i.e., around 70 years before 1852). 1,7-DMP is primarily emitted by coniferous wood burning and higher 1,7-DMP/(1,7-DMP + 2,6-DMP) ratio may be indicative of this PAHs source.^{57–59} Thus, during the early portion of the preindustrial PAHs record (below 27-cm depth, i.e. before ca. 1770) the higher ratios are related to biomass combustion, while the precise explanation of an early

decline in 1,7-DMP/(1,7-DMP + 2,6-DMP) ratio is not known. On the other hand, the regular increase of 1,7-DMP/(1,7-DMP + 2,6-DMP) between the mid-1930s and the 1950s could reasonably come from the main shift in energy sources from coal to petroleum. However, the most recent increase of this ratio might also be related to a higher relative contribution of PAHs derived from wood combustion. This assumption is also supported by a very high fraction of retene (12–37%) determined in the uppermost layers of the C1 core, along with an increase in the abundance of 1,7-DMP since the early 1970s (Figure S-3). These results suggest a probable very recent wood combustion source of PAHs in Levantine basin. High concentrations of retene were also recently found in the surface sediments in Greece and they were related to forest fires.⁶⁰ Furthermore, the mean surface of burned forests in the Mediterranean basin has indeed doubled since 1970.^{61,62}

Isolation of Preindustrial/Background and Anthropogenic Pb, Hg, and PAHs. Below the anthropogenic imprint, concentration levels of both Pb and Hg in the C1 core ($11.3 \pm 0.74 \mu\text{g g}^{-1}$ and $0.013 \pm 0.002 \mu\text{g g}^{-1}$, $n = 39$, respectively) are in the ranges of background/natural or preindustrial concentrations reported in Eastern Mediterranean (11.2–20.0 and $0.01\text{--}0.02 \mu\text{g g}^{-1}$ for Pb and Hg, respectively)^{16,35,36} and in Western Mediterranean sediments (11.0–20.1 and $0.016\text{--}0.018 \mu\text{g g}^{-1}$ for Pb and Hg, respectively).^{15,16,36,37,42} Assuming that pre-1850 samples define constant preindustrial levels in the area (i.e., background), anthropogenic lead and mercury were estimated as the difference between measured values and background values (52–63% and 70–79% for Pb and Hg, respectively, from the 1980s to the present). By taking the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio as an independent index, and by using a simple mixing mass balance model (calculation given in SI), we have also calculated similar percentage of anthropogenic lead in post-1980s sediments (46–59%). The very close results obtained by both calculation methods confirm anthropogenic Pb estimations and argue for a sizable anthropization in the area.⁴⁰ Parent and alkylated PAHs concentrations in horizons below 20-cm depth are also very low (mean 10.4 ± 2.8 and $5.7 \pm 1.6 \text{ ng g}^{-1}$, $n = 23$, respectively) and seem to correspond to the preindustrial background levels. These levels are in the lower ranges of PAHs concentrations reported in deep horizons of sediment cores in European mountain lakes (20–100 ng g^{-1}).⁶ Contribution of anthropogenic fraction of PAHs during the last 25 years of their accumulation is estimated to be between 72 and 83% in sediments in Levantine basin.

Using the preindustrial and contemporary depositional fluxes for both metals and PAHs an estimate of an enrichment ratio may be calculated (additional information in Figure S-4 and flux ranges comparison with literature data Tables S-4 to S-6). Ratios of postindustrial Pb and Hg depositional fluxes to the mean background flux reveal a 4- to 5-fold increase of Hg and an almost 3-fold rise in Pb accumulation in the surface sediments in Levantine basin. Comparably, a 4-fold rise of modern emissions assessed over natural/preindustrial emissions of Hg to global atmosphere has been previously reported.¹¹ Our findings also show that the relative rise in Pb accumulation was lower than that of Hg perhaps because of stricter measures of Pb emission reductions, whereas international Hg regulations are still under discussion.⁶³ The contemporary depositional fluxes of total PAHs rose between 4 and 7 times compared to preindustrial background in the study area (Figure S-4). This increase in PAHs deposition from the background is in agreement with values in the range of 2–6 reported in the

European mountain lakes located in the periphery of Europe and lower than those with increases between 6 and 34 in lakes situated in central regions of Europe and in North America.⁶ However these contemporary/background flux ratios are much lower than ratios of 10^3 found in Pettaquamscutt estuary⁷ (Northeastern U.S.). On the whole, the magnitude and relatively low increase in PAH fluxes in the Levantine basin imply inputs that are characteristic of remote sites, mainly under atmospheric depositional fluxes. The temporal coherence between a rise of Hg, Pb, and PAHs fluxes, accounts of coal usage in Europe,^{15,46,64} and isotopic signatures of sedimentary lead, imply that metal and PAH loads in the Eastern Mediterranean may be associated with their remote atmospheric emissions from industrialized and densely populated areas of Europe. The dominant air masses reaching Levantine basin from the European continent may support such assumptions.^{65,66} In addition, lack of clear trends in recent horizons of C1 core may be related to the fact that in Central and Eastern Europe the technological improvements and regulation efforts for emissions of atmospheric contaminants took place later, only since the 1990s.^{46,67}

Furthermore, stratigraphic sediment preservation in C1 core has allowed us to provide well-resolved temporal sedimentary records for Hg, Pb, and PAHs. The synchronized increase of concentrations and fluxes of both metals and PAHs occurring around the time of the Industrial Revolution in Western countries suggests also that our records provide a picture of more global depositional trends of these contaminants and indicate coal combustion burning as an important source of Hg, Pb, and PAHs in the Levantine basin sediments between the 1850s and 1950s. However, unlike some sedimentary records from Europe and North America,^{7–9,15} surface layers in C1 core indicate no decline in Hg, Pb, and PAH concentrations related to reduction of coal use.^{7–9,15} Modern deposition in our study area may reflect Central and Eastern European atmospheric emissions of contaminants, where shifts among fossil fuels, reduction of coal consumption, and technological industrial improvements took place later.⁶⁷ Local loads seem to be low and not very well constrained in C1 core and combustion-derived contaminants appear to predominate over the entire core length. We emphasize that our findings also provide well-defined preindustrial levels and fluxes of Hg, Pb, and PAHs in the region. Modern fluxes of anthropogenic Hg and Pb reveal a 3- to 5-fold increase over preindustrial loads, while contemporaneous fluxes of PAH rose 4–7 times. We believe also that our findings make a supplementary contribution to compelling data sets on sedimentary historical records of Hg, Pb, and PAHs. Such data are needed in order to better assess and constrain the worldwide contemporary trends and cycles of these contaminants.

ASSOCIATED CONTENT

S Supporting Information

Additional information and data, Pb source model calculation, and references. This information is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interest.

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