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Environmental Science & Technology

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Article

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Environ. Sci. Technol., **Just Accepted Manuscript** • DOI: 10.1021/acs.est.7b04614 • Publication Date (Web): 20 Oct 2017

ACS Publications

Environmental Science & Technology is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Occurrence, loading and exposure of atmospheric particle-bound POPs at the African and European edges of the western Mediterranean Sea

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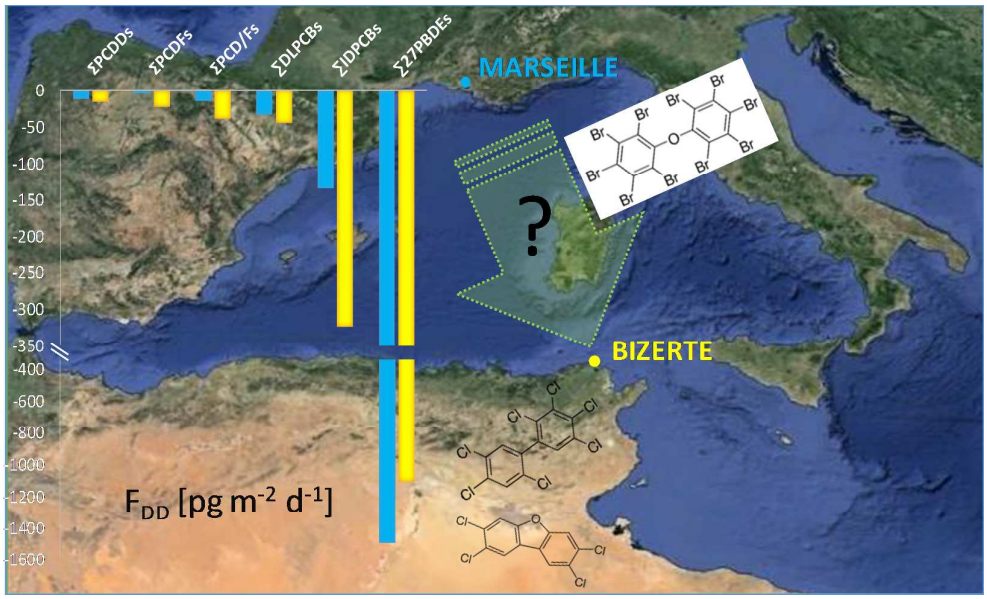
Abstract

A comparative study for 62 toxic chemicals based on the monthly collection of aerosol samples during 2015-2016 in two coastal cities at both the African (Bizerte, Tunisia) and European (Marseille, France) edges of the W Mediterranean basin is presented. Legacy polychlorinated biphenyls (Σ_{18}PCBs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (Σ_{17}PCDD/Fs) show generally higher median levels at the African edge (2.1 and 0.2 pg m^{-3}, respectively) compared to the European coastal site (1.0 and 0.08 pg m^{-3}, respectively). Contrary, the "emerging" polybrominated diphenyl ethers (Σ_{27}PBDEs) median concentrations were higher in Marseille (~ 9.0 pg m^{-3}) compared to Bizerte (~ 6.0 pg m^{-3}). Different past usage and current emission patterns were found at both edges of the W Mediterranean, most probably linked to the respective different regulatory frameworks for toxic chemicals. Our results indicate that the total organic carbon (TOC) and/or the elemental carbon (EC) contents in the atmospheric aerosol may have a stronger effect than the total suspended particle (TSP) content as a whole on the spatial-temporal variability and the long-range atmospheric transport potential of the studied POPs. A "jumping" of the PBDE local atmospheric stocks from the NW European Mediterranean edge to the NW African coast seems to be possible under favorable conditions at present. While a higher PBDE median loading is estimated for Marseille area (~ 550 ng m^{-2} y^{-1}) compared to Bizerte (~400 ng m^{-2} y^{-1}), the median PCB and PCDD/F dry deposition fluxes were higher at the African site, resulting in a 3-fold higher toxic equivalent (TEQ) loading of dioxin-like pollutants (400 pg TEQ m^{-2} y^{-1}) compared to Marseille (~140 pg TEQ m^{-2} y^{-1}) with potential implications for the aquatic organisms. However, the inhalation exposure assessment points to a minimum risk for human health at both sites.

Keywords:

PCB, flame retardant, dioxin, marine pollution, environmental risk

TOC art



Introduction

Atmospheric particulate matter has been recognized as a major environmental airborne pollutant impacting human health and ecosystems.[1] A recent study performed in the Mediterranean Sea supports the hypothesis that atmospheric aerosols can elicit a number of toxic effects in marine organisms due to the presence of hydrophobic contaminants intimately associated to the atmospheric particle phase.[2] High molecular weight (HMW) polycyclic aromatic hydrocarbons (PAHs) and generally persistent organic pollutants (POPs) such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are among the contaminants suspected to produce these hazardous effects.[2] In addition, POPs associated to the atmospheric particle phase can be more resistant to atmospheric degradation processes (e.g. photodegradation) increasing therefore their atmospheric residence times, subsequent long-range atmospheric transport (LRAT) and potential expossure.[2] A first step in order to elucidate the potential role of particle-bound POPs in toxic pathways and to estimate their atmospheric dry deposition, considered as the main vector for the introduction of the most hydrophobic contaminants in aquatic ecosystems, is their accurate qualitative (congener specific distribution) and quantitative (environmental concentration) determinations in the atmospheric aerosol. The legacy PCDD/Fs and PCBs may lead to complex mixtures in the environment. However, the seventeen 2,3,7,8-chlorine substituted PCDD/Fs (i.e. seven PCDDs or "dioxins" + ten PCDFs or "furans") and the twelve dioxin-like PCBs ($_{DL}$PCBs) named CBs-81, -77, -105, -114, -118, -123, -126, -156, -157, -167, -169, -189, jointly considered as dioxin-like pollutants, have received most of the attention due to their accumulation and toxic effects in biota and humans.[3-6] In addition, a set of non-dioxin-like PCBs, commonly

referred as indicator PCBs ($_{ID}$PCBs), containing CBs-28, -52, -101, -138, -153 and -180 are often monitored due to their higher environmental concentrations and potential toxic effects by different mechanisms of action.[7-9] Other POPs with recognized toxicity too, such as polybrominated diphenyl ethers (PBDEs) can add up to the "contaminant-aerosol cocktail".[10,11] These pollutants have different sources in the environment. PCDD/Fs can occur as unintentional by-products in a number of industrial processes and domestic heating,[12,13] while current emissions of PCBs are urban/industrial centers, open burning of products containing PCBs, waste incinerations, accidental fires and re-volatilization from environmental reservoirs.[14,15] PBDE were mostly used (and still used in some regions) as flame retardants and, contrary to PCDD/Fs and PCBs, are considered as a first generation of "emerging contaminants" (only recently restricted). Three PBDE commercial formulations were extensively used worldwide: the penta-formulation (with predominance of BDE-47 and -99), the octa-BDE (with PBDE-183 as one of the major components) and the deca-BDE (with BDE-209 predominating).[16]

These contaminants are globally banned by the Stockholm Convention of POPs (including all PBDE formulations) and regulated by the Water and Marine Strategy Framework Directives at European level (except for the octa- and deca-PBDE formulations). However, still very little or no information exists on current base line levels and stocks for many marine areas, even in environments under important anthropogenic pressure like the Mediterranean Sea. This semi-enclosed environment of high ecological and socio-economic relevance is largely impacted by POPs and related contaminants.[17,18,19] PCDD/Fs, PCBs and PBDEs are among the POPs found in the atmospheric compartment from various NW Mediterranean coastal environments (from rural to large cities),[20-26] and the central/Eastern basin[27-33], but also farther from the coast in the entire Mediterranean Sea.[34-36] The European Mediterranean coast is by far

the most studied and only few measurements (focussing in the SE Mediterranean) have been carried out in the African Mediterranean edge. [37,38]. The atmospheric occurrence of POPs over the NW Mediterranean African coast still largely unknown. In addition, parallel observations at both the African and European margins of the Mediterranean Sea have never been attempted to the best of our knowledge.

We report here results from 22 aerosol samples (total suspended particles, TSP) simultaneously collected (once per month) in two urban coastal sites at both the African and European edges of the W Mediterranean. The samples have been analysed for 62 toxic chemicals associated to the atmospheric aerosol. The main objectives of this study are: (1) to establish base line atmospheric levels of three of the most toxic POPs families (i.e. PCDD/Fs, PCBs, and PBDEs) in two reference urban coastal sites in the European and African W Mediterranean and (2) to compare the status of pollution, to estimate the atmospheric loading and potential exposure of those chemicals at both edges of the W Mediterranean coast.

Materials and Methods

Sampling and study areas

Atmospheric aerosols samples (TSP) were simultaneously collected from March 2015 to January 2016 in two representative coastal locations under strong anthropogenic pressure at both the African and European W Mediterranean Sea edges: the cities of Bizerte (Tunisia) and Marseille (France) (Figure S1). The air was drawn through pre-combusted quartz fiber filters (QFFs) placed in high volume air samplers (Tisch

Environmental, Inc, USA). The sampling volume raged from ~ 1800 to ~5000 m^3 depending on the site and sampling event (Table S1).

Marseille: Samples were collected at the roof (~10m AGL) of the Endoume Marine Research Station (43° 16' 49.90" N, 5° 20' 57.32" E) located at the water front and around 4 km from the city center and the Marseille maritime terminal. Marseille can be considered as a NW large coastal city of the Mediterranean basin (~1 million inhabitants), inducing important car traffic and biomass burning. A detailed area description has been reported elsewhere. [39-41] Briefly, Marseille hosts one of the most important ports of the Mediterranean Sea (~88 million tonnes of goods handled per year) and stands in the vicinity (40 km SE) of the large petrochemical and industrial complex of Fos-Berre area (e.g. petroleum refining, cement factory, waste combustion units, metallurgical industries). The region is well known for its intense photo-oxidative pollution episode[42,43] and several characteristic wind patterns, generally below 5m s^{-1}, except during the Mistral events (NW strong wind, 20-30 m s^{-1}) which are frequent in the area (100 days/year) (Figure S1)

Bizerte: Sampling was conducted on the roof top (~8 m AGL) of the Faculty of Science of Bizerte (37° 16' 0.5802" N, 9° 52' 49.875" E) around 1 km far from the city center, close to the Gulf of Bizerte shoreline and Bizerte lagoon water front (Figure S1). A detailed sampling description is offered elsewhere. [44] Briefly, Bizerte is a medium-size city (~127 000 inhabitants), located in the north of Tunisia, between the Mediterranean Sea and the Bizerte lagoon. Even if agriculture and fishery activities are important in the area, a considerable number of light and heavy industries (i.e., cement, plastic, textile, mechanic and electronic, iron and steel metallurgy, petroleum refining and lubricants)

149 are present in the area. [44] Average temperature of 22 °C, with hot summer and mild
150 spring, frequent (200 days per year) NW winds (average speed of 6–8 m s^{-1}) and
151 precipitation episodes mostly in fall and winter months, characterized the climate of
152 Bizerte area. [44]

153

154 *Sample processing*

155 QFFs were lyophilized, weighed, and spiked with a suit of PCDD/Fs, PCBs, and PBDEs
156 ^{13}C-labeled standards prior to Soxhlet extraction (24h) with a n-hexane: DCM (9:1)
157 mixture. Extracts were rota-evaporated and cleaned-up by using the "Dioxin Prep
158 System-Florisil Version" (Supelco, Bellefonte, PA, USA). PCBs and PBDEs were
159 collected in a first fraction by elution (100 mL of n-hexane) of the multilayer silica gel
160 column coupled to a florisil column and a subsequent elution (40 mL of DCM) of only
161 the multilayer silica gel column (prior removal of the florisil column). PCDD/Fs were
162 obtained in a second fraction by elution of the florisil column with 50 mL of DCM.
163 Final extracts were rota-evaporated to ~ 1 mL, transferred to vials, and dried under a
164 gentle nitrogen steam. Fractions were reconstituted in a few microliters of the respective
165 PCDD/F, PCB, and PBDE ^{13}C-labeled injection standards prior to instrumental analysis
166 (Text S1).

167

168 *Instrumental Analysis*

169

170 Samples were analysed for 17 PCDD/Fs (congeners 2,3,7,8-susbtituted), 18 PCBs (12
171 $_{DL}$PCBs+6$_{ID}$PCBs) and 27 PBDEs (Text S1). Quantification was carried out by isotopic
172 dilution according to 1613 US EPA method[45] on a gas chromatograph (Trace GC ultra,

Thermo Fisher Scientific, Milan, Italy) coupled to a high resolution mass spectrometer (DFS, Thermo Fisher Scientific, Bremen, Germany). The injection temperature was 260 ºC and 1 µL of extract was injected (splitless mode). GC separation of PCBs and PCDD/Fs was achieved using a 60 m × 0.25 mm × 0.25 µm DB-5MS column (Agilent J&W, USA), while a 15 m × 0.25 mm × 0.10 µm Rxi®-5Sil MS column (Restek, USA) was used for PBDEs. Different oven temperature programs were used for each family of analytes (Table S2). Positive electron ionization (EI+) was used operating in selected ion monitoring (SIM) mode at 10,000 resolving power.

Quality assurance / quality control (QA/QC)

Clean QFFs were individually wrapped in aluminum foil, baked at 450 ºC overnight, weighted and then stored at -20 ^{o}C in double sealed plastic bags until used. Field blanks, consisting on baked QFFs transported to the sampling area, mounted in the sampler, and dismounted, were collected at both sites, stored and analysed concurrently with the samples. After sampling, QFFs were wrapped in aluminium foil again and stored in the dark at -20°C. Blank levels were generally low for the three POP classes compared to their concentrations in the samples, ranging from 0.02 to 3.5 pg (PCDD/Fs), from not detected (n.d.) to 150 pg (PCBs), and from n.d. to 530 pg (PBDEs) depending on the congener and sample (Table S3). Laboratory blanks (1 blank per five-sample batch) showed lower or similar levels to field blanks, so no contamination during sampling, storage and analysis occurred. Results were blank corrected. Chromatographic peaks were only considered when the ratio between the two monitored ions was within ±15% of the theoretical value, and the signal-to-noise (S/N) ratio>3 (instrumental limit of

197 detection, LOD). Limits of quantification (LOQs) corresponded to S/N≥10. Calibration
198 curves were daily checked. Median LODs ranged from ~ 0.3 to ~ 1.1 pg (PCDD/Fs),
199 from 2.1 to ~ 8.3 pg (PCBs) and from ~ 1.1 to 32.5 pg (PBDEs) depending on the
200 compound and sample (Table S4). Median method recoveries (extraction-cleanup-
201 analysis) varied from 70 to 97 % (PCDD/Fs), from 83 to 110 % (PCBs) and from 60 to
202 120 % (PBDEs) (Table S5). Results were corrected by recoveries.

203

204 *TOC, EC determinations and statistical analysis*

205

206 Total organic carbon (TOC) content was determined in filter subsamples by high
207 temperature combustion (CHN analyser).[46] For the elemental carbon (EC)
208 determination, additional filter sub-samples were pre-combusted at 340 °C during 2 h
209 under oxygen flow[47] and then analysed as above indicated. STATA/SE 12.1 software
210 was employed for the statistical data analysis.

211

212 **Results and discussion**

213

214 ***Concentrations in the atmospheric aerosol***

215

216 *Dioxin-like POPs*

217

218 ∑2,3,7,8-PCDD/F concentrations in the aerosols over Bizerte area (Tunisia) ranged
219 from 32 to 1100 fg m^{-3} (222 fg m^{-3}, median) along the sampling period and were
220 generally higher than those over Marseille coastal area (France), varying from 31 to
221 1280 fg m^{-3} (83 fg m^{-3}, median) (Figure 1A). The highest differences were found for the

months of April, July and September 2015 (3, 11, ~5-fold higher levels in Bizerte, respectively). However, these values were not significantly different (Mann-Whitney test, *p=0.28*) for the sum of 2,3,7,8-PCDD/Fs most probably due to the high annual variability, in particular in Bizerte site, and the limited number of samples analysed. Significant differences were only found for two furan congeners (i.e. 2,3,4,6,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF) (Mann-Whitney test, *p=0.04*) (Figure S2, Table S6). A general trend showing higher PCDD/F levels in the coldest months of the year was observed at both sites. This effect has been previously reported in other Mediterranean coastal areas and has been attributed to the combined effect of the increase of diffusive combustion sources (e.g. domestic heating and road traffic) and a less efficient dispersion of the local emissions during cold conditions. [23]

The ∑2,3,7,8-PCDD/F was clearly dominated by the contribution of PCDDs in Marseille whereas a more even contribution of PCDDs and PCDFs was found for the aerosols of Bizerte area (Figure 1A), pointing to different PCDD/F sources at both sites.

This is the first time that PCDD/Fs have been measured in atmospheric aerosols from the Marseille area and in a coastal site at the African Mediterranean edge. The concentrations found at both sites are within the range of those previously reported for a coastal area in the Gulf of Lion (50-1500 fg m^{-3})[23], urban/industrial sites from Barcelona area (570-1162 fg m^{-3})[24] and in the open NW Mediterranean (94-990 fg m^{-3}). [35] Reported values from a cruise transect close to the NW Mediterranean African coast (38 fg m^{-3}) are lower than those measured in Bizerte coastal area. [35] Concentrations measured in a background site in Barcelona area (230 fg m^{-3}) are lower too than those in Marseille[24]. No data for comparison was found in the central/eastern Mediterranean Sea. Recent PCDD/F measurements carried out in the atmospheric aerosol over remote areas

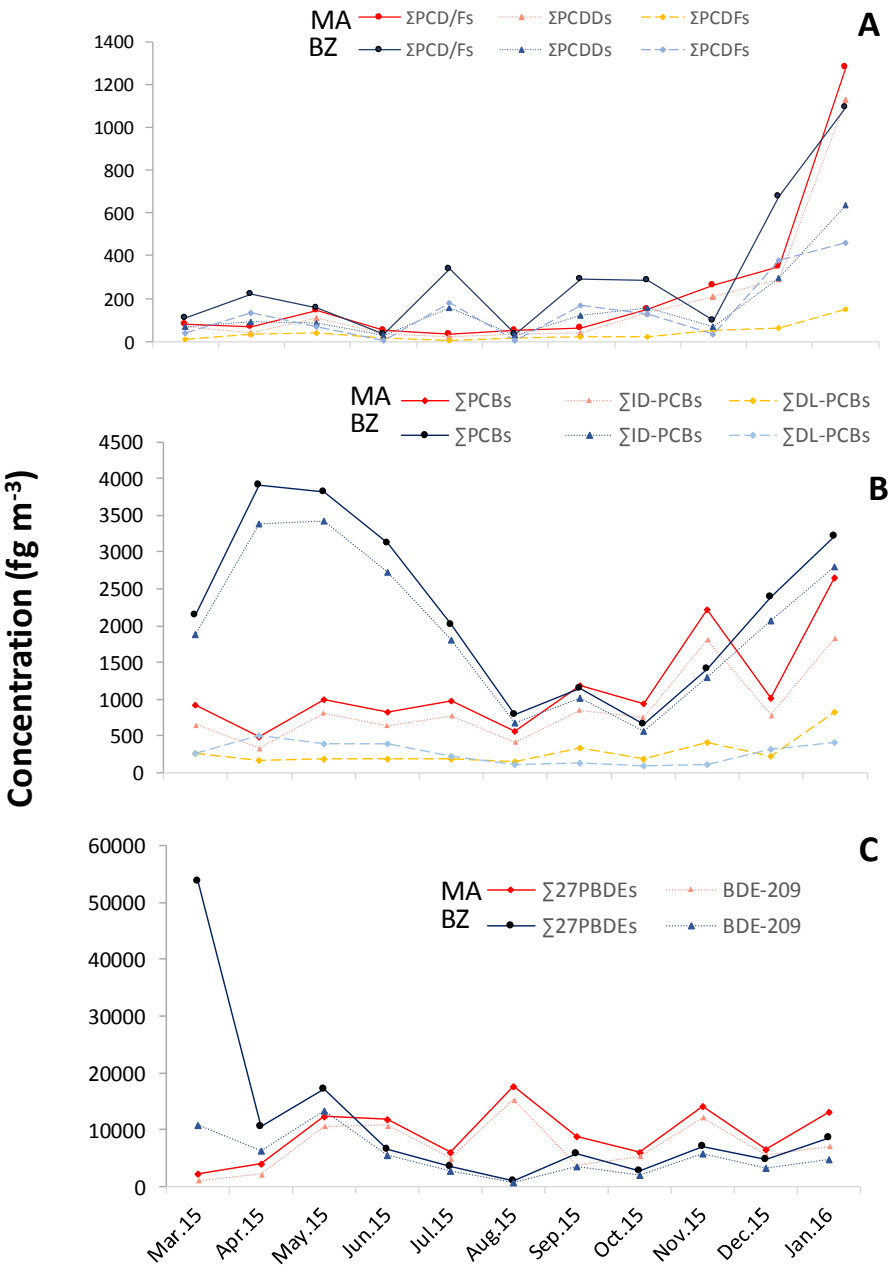
246 from the Atlantic, Pacific and Indian oceans revealed 6 to 11-fold lower background
247 levels (5 to 113 fg m^{-3}).[48]
248
249 The $\sum_{18}$PCB concentrations measured in the aerosols from Bizerte, ranging from 0.7 to
250 ~4.0 pg m^{-3} (2.1 pg m^{-3}, median) were significantly higher (Mann-Whitney test, *p=0.03*)
251 than those measured in the aerosols over Marseille, which varied from 0.5 to 2.7 pg m^{-3}
252 (1.0 pg m^{-3}, median). $_{ID}$PCBs dominated the total levels at both sites with $\sum_{ID}$PCB
253 concentrations significantly higher too in Bizerte (0.6 to 3.4 pg m^{-3}, median value of ~
254 2.0 pg m^{-3}) than in Marseille (0.3 to 1.8 pg m^{-3}, median value of 0.8 pg m^{-3}) (Mann-
255 Whitney test, *p=0.01)* (Figure 1B). $\sum_{DL}$PCB concentrations, which represented a minor
256 contribution to the total PCB atmospheric stock at both sites, were not statistically
257 different (0.1 - 0.5 pg m^{-3} in Bizerte compared to 0.1 - 0.8 pg m^{-3} in Marseille).
258 However, the concentrations of some of the most toxic $_{DL}$PCBs (i.e. CB-81, -126, -169)
259 as well as the CBs-167, -189 were significantly higher in Bizerte than in Marseille
260 coastal area (2-4 fold-higher median values depending on the congener) (Figure S3,
261 Table S7).
262 $\sum_{18}$PCB (and $\sum_{ID}$PCB) concentrations exhibited different annual trends in both sites.
263 While a general increase of concentrations was observed in winter months compared to
264 spring and summer in Marseille, a more pronounced seasonality was observed for
265 Bizerte, showing clearly higher concentrations in spring-early summer and late autumn-
266 winter months, with minimum levels in August, September and October (Figure 1B). As
267 a result, 2 to 8-fold higher $\sum_{18}$PCB levels were measured in Bizerte than in Marseille
268 from March to July while the concentration differences between the two sites in winter
269 months were less important, and in some months (e.g. November) higher for Marseille.
270 Interestingly, higher $\sum_{DL}$PCB concentrations were generally measured from August

2015 to January (except in December) in Marseille. These facts highlight the differential environmental behaviour, seasonality and related exposure of individual PCBs at both sites.

PCB data comparability may be tricky since different number and type of PCBs may be considered. Therefore, for comparative purposes we focus only on $_{ID}$PCBs. Σ_{ID}PCB concentrations measured at both edges of the NW Mediterranean Sea were generally lower than previous coastal measurements performed in the NW Mediterranean in the Gulf of Lion (0.5 to 7.2 pg m^{-3})[23,26] and those carried out close to Barcelona area (9 - 26 pg m^{-3}).[26] Cruise measurements encompassing the Mediterranean Sea and the SW Black Sea in 2006 and 2007 revealed higher concentrations too for Σ_{ID}PCB (0.4-18 pg m^{-3}), but PCB-118 was included in the sums.[36] However, concentrations measured in Bizerte and Marseille were generally higher that those reported for a coastal site (considered as a background location) in the Eastern Mediterranean[27] consistent with previous studies indicating higher PCB levels in the W Mediterranean.[36] Most of the previous studies correspond to measurements performed more than a decade ago (as for PCDD/Fs) so comparison must be done carefully. Particle-bound PCBs have received little attention since then in the Mediterranean basin compared to gas phase PCBs, most probably due to the dominant role of vapor PCBs driving total PCB ambient levels (especially for low MW congeners) and the increasing applications of passive sampling techniques to POP atmospheric measurements. Thus, recent studies in the Mediterranean Sea considered only the gas phase or the assemble gas+particle phases. [32,33] $\sum_{DL}$PCB background measurements in the atmospheric aerosol over remote areas from the Atlantic, Pacific and Indian oceans revealed up to 500-fold lower levels (1 - 2675 fg m^{-3}).[48]

These figures confirmed that the NW Mediterranean Sea is considerably exposed to dioxin-like POPs, and might act in turn as a potential secondary source, in particular of

296 PCBs, for other Mediterranean regions (less exposed) and for the most pristine areas of
297 the major oceans of the Earth. It has been reported that the principal control on the
298 levels of legacy POPs in active circulation in the global environment is currently in a
299 state of transition (from primary to secondary source control).[14] The role of the NW
300 Mediterranean Sea (and other similar impacted marine areas) as potential secondary
301 sources at present remains uncertain and requires further investigation.



302

Figure 1. Temporal variability of PCDD/F (A), PCB (B) and PBDE (C) concentrations in atmospheric aerosols over Marseille (MA) and Bizerte (BZ) coastal areas from March 2015 to January 2016.

PBDEs

Σ_{27}PBDE concentrations were generally higher than dioxin-like POPs (in particular compared to PCDD/Fs) at both sites. Levels in the aerosol from Bizerte ranged from 1.0 to 54.0 pg m^{-3} (~ 6.0 pg m^{-3}, median), while in Marseille varied from 2.2 to 17.6 pg m^{-3} (~ 9.0 pg m^{-3}, median) (Figure 1C). A general trend of higher levels in Marseille area was found, with the exception of the samples collected in spring in Bizerte, in particular the one of March 2015 (which exhibited 3 to ~50-fold higher PBDE levels than the rest of samples collected in Bizerte). This concentration peak can be attributed to an unusual higher concentration of medium-high MW PBDEs in that sample compared to the others, in particular BDE-183 (Table S8), likely due to the combined effect of the air mass back trajectories (BTs) and potential local sources during this sampling event (see discussion below). However, the concentrations at both sites did not show a statistical difference (Mann-Whitney test, *p>0.05).* Still, some individual congeners exhibited statistical differences but with contrasting trends, like BDE-47 with 3-fold higher median concentrations in Marseille than Bizerte (Mann-Whitney test, *p=0.01)*, while BDE-3, -7, -71, -77, -126, and -156 showing higher levels in the aerosols from Bizerte ($p<0.01 – 0.04$) (Figure S4, Table S8). PBDE-209 was the major contributor to the total Σ_{27}PBDE for most of the samples at both sites (Figure 1C).

Σ_{27}PBDE concentrations measured in Marseille and Bizerte were generally within the range of those reported for a coastal site in the NW Mediterranean (2-18 pg m^{-3}, Σ_8PBDE)[23], higher than levels in a coastal background site in central/E Mediterranean (0.5-2 pg m^{-3}, Σ_{15}PBDE)[30] but in the lower end of values reported for aerosols collected over large cities in the E Mediterranean like Athens (Greece) (15-23 pg m^{-3}, Σ_{12}PBDE)[29] and Izmir (Turkey) (27-62 pg m^{-3}, Σ_7PBDE). [38]

POPs patterns in the atmospheric aerosol

The PCDD/F atmospheric pattern (congener relative contribution) for most of Bizerte samples showed an important contribution of furans, with 1,2,3,4,6,7,8-HpCDF and OCDF accounting for the 16.3±3.7 % and 12.2±7.3 % of the ∑2,3,7,8-PCDD/F, values almost reaching the relative contribution of 1,2,3,4,6,7,8-HpCDD (17.0±4.0 %) and OCDD (25.5±4.5 %) which are the two most abundant PCDDs (Figure 2A-1). However, the PCDD/F pattern in samples from Marseille was dominated by a higher contribution of 1,2,3,4,6,7,8-HpCDD (21.2±6.8 %) and OCDD (53.0±4.0 %) and lower contribution of 1,2,3,4,6,7,8-HpCDF and OCDF accounting for the 5.8±3.0 % and 6.0±2.8 % of the ∑2,3,7,8-PCDD/F, respectively (Figure 2A-2). A higher contribution of PCDFs in the PCDD/F atmospheric pattern compared to PCDDs has been associated in previous studies to 'fresh' emissions (sources). A situation in which the lower chlorinated congeners, in particular PCDFs, have insufficient time to experience significant atmospheric degradation / depletion processes.[23,35,49,50] Contrary, a predominance of higher chlorinated PCDDs and little contribution of PCDFs is considered as a 'sink' signal where the lighter congeners were 'weathered' in their travel from the source to the sampling sites due to atmospheric processes (e.g. photodegradation).

These patterns suggest current local PCDD/F emission in Bizerte in combination with a minor contribution of long/medium-range atmospheric transport of PCDD/Fs to the area. Contrary, the long/medium range atmospheric transport seems to drive the atmospheric occurrence of PCDD/Fs in Marseille area with a minor contribution of local sources. The possibility of short-range atmospheric transport from the adjacent industrial areas (Fos-Berre) to Marseille with known sources of PCDD/Fs (e.g. from incinerators, metallurgical and petrochemical facilities) is not excluded. Nevertheless, because of the surrounding topography of Marseille, bordered by the Mediterranean from the SW and enclosed from N, E and S by mountain ranges up to ~700m ASL, direct transport from the Fos-Berre area to Marseille is rarely observed. Such transport could occur when the wind is a composition of land/sea breeze and light Mistral but the air mass will go towards the sea before to come back to Marseille which corresponds to a half-range atmospheric transport. Furthermore, these wind conditions correspond generally to sunny period inducing strong photochemical processes. [39-41,43]

The PCB atmospheric pattern was dominated in general by the HMW $_{ID}$PCBs at both sites. A clear predominance of PCB-180 in Bizerte (accounting for the 35.0±8.7 % of the $\sum_{18}$PCBs) was observed compared to Marseille area (19.2±5.1 % of the $\sum_{18}$PCBs). A similar pattern was observed in the two sites for $_{DL}$PCB, but PCB-118 and -105 predominated in Marseille (12.6±3.2% and 5.7±1.8%, respectively) compared to Bizerte (4.6±2.0% and 1.9±0.5%, respectively). The different abundance of these three major PCBs may be either the reflect of different past usage of PCB commercial mixtures at both sites or distinct emissions rates to the environment at present. For example, PCB-180 is one of the major constituent of Aroclor 1260 and 1262, while CB-105, 118 were relatively more abundant in the Aroclor 1254 formulation. One of the major uses of

these Aroclor formulations was as industrial oils destined to transformers. [51] It has been very recently reported that a large number of transformers containing PCBs are still used or stored in unsatisfactory conditions in Bizerte area with high probability of oil leaks. [44] This could explain the higher contribution of PCB-180 in Bizerte compared to Marseille.

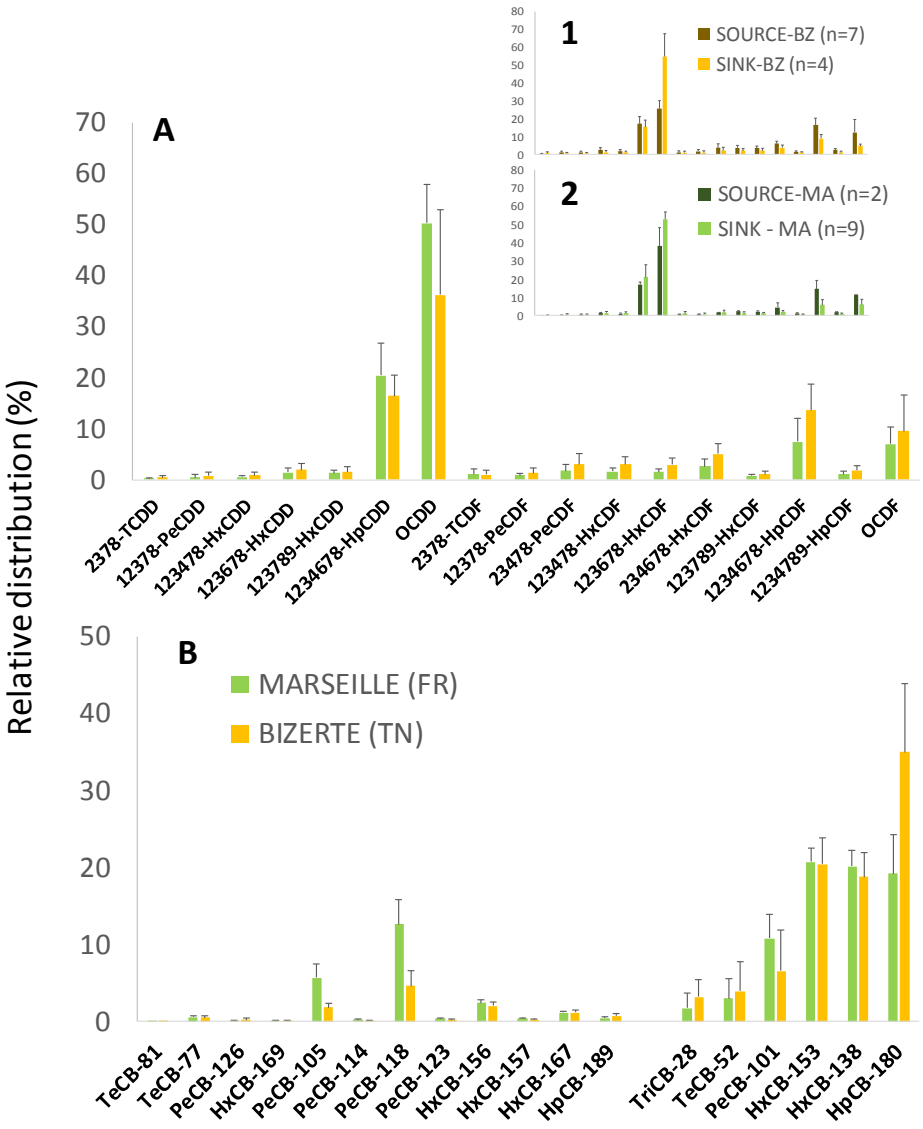
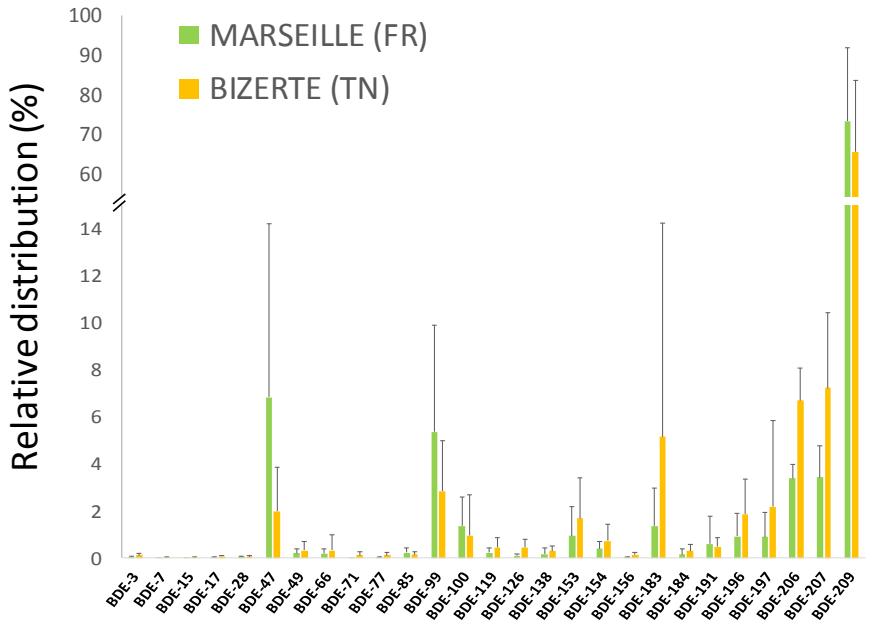


Figure 2. Average atmospheric pattern (n=11) of PCDD/F (A) and PCBs (B) in Marseille (MA) and Bizerte (BZ) coastal areas. The small figures (1) and (2) show a

386 focus on the differences in the atmospheric pattern found in Bizerte (dominated by a
387 characteristic "source pattern", n=7) and in Marseille (dominated by a characteristic
388 "sink" pattern, n=9).
389
390 The predominance of BDE209 was reflected also in the atmospheric congener pattern
391 (Figure 3) accounting for the 72.3±18.6% and 65.5±18.0% of the Σ_{27}PBDE in Marseille
392 and Bizerte, respectively. The important abundance of this BDE denotes the past and
393 maybe current usage of deca-PBDE formulations at both edges of the NW
394 Mediterranean Sea.[16] In addition, the predominance of BDE-47 and BDE-99 in the
395 pattern from Marseille samples too, together with their higher abundance (6.8±7.3% and
396 5.3±4.5% for BDE-47 and -99, respectively) compared to the pattern in Bizerte (2.0
397 ±1.9 % and 2.8±2.5 % for BDE-47 and -99, respectively), point first to a major usage of
398 penta-PBDE compared to the octa-PBDE formulations in Marseille. Second, to a
399 different emission and usage pattern compared to Bizerte, where a major usage of octa-
400 PBDE formulations may be the most likely scenario represented by a higher BDE-183, -
401 206, -207 predominance in Bizerte reaching up to 31.6, 9.1 and 13.8% of the Σ_{27}PBDE,
402 respectively.
403



404

405 **Figure 3**. Average atmospheric pattern (n=11) of PBDEs in Marseille and Bizerte
406 coastal areas.

407

408 ***Factors affecting temporal and spatial variability***

409

410 The finest fractions of the atmospheric TSP, like TOC and EC, have been reported to
411 efficiently sorb POPs-like contaminants.[29,52-53] Generally higher median concentrations
412 of TSP (66.0 ug m^{-3}), TOC (7.5 ug m^{-3}) and EC (2.0 ug m^{-3}) were measured in the
413 aerosols over Bizerte compared to Marseille area, exhibiting 48.0, 6.4 and 0.9 ug m^{-3} of
414 TSP, TOC and EC, respectively. However, only significant differences (Mann-Whitney
415 test, *p=0.03-0.006)* were found for the TSP and EC (Figure S5). No correlations were
416 found for PCDD/F concentrations and TSP levels in any of the sites and only $\sum_{18}$PCB,
417 $\sum_{ID}$PCBs and one PCB congener correlated (*p=0.01-0.04*) with TSP concentration in
418 Bizerte (Figure S6). $\sum$PCDD/F and $\sum_{DL}$PCB (as well as most of PCDD/Fs and a certain
419 number of $_{DL}$PCBs) concentrations positively correlated with TOC concentration

(*p=0.004-0.03*) but not with EC levels in Marseille. Only 2,3,7,4-TCDD positively correlated with TOC concentrations in Bizerte and no correlations were observed for $_{DL}$PCBs and TOC in Bizerte. Interestingly, PCDD/F concentrations were not correlated with EC levels in any of the sites, while $\sum_{DL}$PCBs, $\sum_{18}$PCB and $\sum_{ID}$PCBs were correlated with EC mostly in Bizerte (*p=0.002-0.01*), most probably due to the higher EC levels in this site. Σ_{27}PBDE concentrations did not significantly correlate with TSP, TOC or EC in any of the sites. However, while only two individual PBDEs correlated with TSP levels (Bizerte) a considerable number of PBDE congeners were correlated with TOC concentrations in Marseille and with EC levels in Bizerte (Figure S7). The fact that PCDD/Fs did not correlate with EC is somehow unexpected since this correlation has been suggested in other atmospheric studies. [54,55] The narrow range of variation of EC concentrations in the samples analysed could have resulted in this lack of correlation. Regarding TOC, the correlations mostly observed for Marseille could be the result of different TOC sources (different sorption properties) in both sites (e.g. more related to urban activities in Marseille and predominantly industrial activities in Bizerte).

Our results indicate that the TOC and/or EC contents in the atmospheric aerosol may have a stronger effect than the TSP as a whole on the spatial-temporal variability of the studied POPs. Concentrations normalized by TOC slightly decreased the ∑2,3,7,8-PCDD/F, $\sum_{18}$PCB $\sum_{ID}$PCBs and $\sum_{27}$PBDE annual variability at both sites (except for the month of January 2016) and confirmed the similar spatial variability with no significant differences for PCDD/Fs (p=0.67) and PBDEs (p=0.66) and higher levels of $\sum_{18}$PCB (although not significant, p=0.07) and $\sum_{ID}$PCBs (p=0.03) in Bizerte (Figure S8). The higher concentrations in January 2016 resulted in 4 to 9-fold higher levels in

445 Bizerte (412, 1050, 154 and 3210 ng g_{TOC}^{-1}) compared to Marseille (80,113, 51 and 811
446 ng g_{TOC}^{-1}) for ∑2,3,7,8-PCDD/F, $\sum_{ID}$PCB, $_{DL}$PCBs and $\sum_{27}$PBDE, respectively. In
447 addition, an increase of the concentration differences (normalized by TOC) compared to
448 their respective volumetric concentrations was found for $\sum_{DL}$PCBs in March 2015.
449
450 Concentrations normalized by EC (Figure S9) showed predominant levels of ∑2,3,7,8-
451 PCDD/F for Marseille in March 2015 and January 2016 (where the lowest
452 concentration of EC were measured) and confirmed the $\sum_{18}$PCB and $\sum_{ID}$PCB higher
453 levels in Bizerte during spring-early summer compared to Marseille, but pointed to
454 generally higher concentrations in Marseille from September to winter. Interestingly, a
455 statistically significant ($p<0.01$) predominance of $\sum_{DL}$PCB levels in Marseille resulted
456 from the normalization by EC, which was not verified as volumetric or TOC normalized
457 concentrations. The same effect ($p<0.001$) was observed for the $\sum_{27}$PBDE, exhibiting
458 higher levels in Marseille for all months (7.4 ug g_{EC}^{-1}, median value) than in Bizerte
459 (3.0 ug g_{EC}^{-1}, median value) with clear peak differences in August and September.
460
461 Four-day BTs were calculated (50, 500 and 1000m AGL) by using the HYSPLIT
462 model[56] (Figure S10). The lowest ∑2,3,7,8-PCDD/F levels were registered in the
463 months of June, July and August 2015 in Marseille, where air masses had a clear
464 Atlantic influence, while the highest level was measured in the month of January 2016
465 with air masses showing continental influence (Figure S9). A similar min-max temporal
466 pattern was observed in Bizerte, with lower levels in summer months (except for July)
467 than in January. However, the BTs in July revealed a more important continental
468 influence for Bizerte compared to Marseille. $\sum_{18}$PCB concentrations had minimum level
469 in April 2015 over Marseille, with air masses mostly circulating over the W

Mediterranean waters and peaked also in January 2016. The lowest $\sum_{18}$PCB concentrations were measured in October in Bizerte, whereas the higher levels correspond to April 2015 (with air masses circulating over the Bizerte area and the African continent) consistent with suspected current local PCB emissions.

Interestingly, $\sum_{27}$PBDE exhibited the lowest concentrations in the months of March 2015 over Marseille, with air masses showing an important component coming from the N African coast, while the highest concentrations were measured in the same month in Bizerte, with air masses showing the 50m height component coming from the Gulf of Lion area. Recent reports have shown evidences of the North to South atmospheric particle transport over some regions in the NW and E Mediterranean Sea[57,58]. In addition, PBDEs have been described to be mostly associated to the finest particles of the atmospheric aerosol[29], consistent with the correlations found with the TOC and/or EC contents (more abundant and stronger) compared to the TSP as discussed above. This will result in higher atmospheric residence times and a higher potential of LRAT. These facts may support the hypothesis of the potential "jumping" of PBDE local atmospheric stocks from the NW European Mediterranean edge to the NW African coast (where lower PBDE ambient levels has been generally measured) under favorable conditions. Indeed, the two sites are relatively close (around 780 km straight line). However, this hypothesis requires further confirmation with more sites at both edges of the NW Mediterranean. In addition, a better characterization of PBDE local sources (emission inventory) at the African edge is needed. The BT analysis reveals too other potential hot spots farther west in the N African coast which find their way to Bizerte area passing through the Gibraltar strait and along the African cost, as observed in the month of May 2015. The three POP families exhibited higher levels in Bizerte area compared to Marseille (with a different air mass circulation pattern) in this month. This

situation has been previously described for PCDD/Fs[35] and PAHs[18] in the same region. BTs could only explain part of the annual and spatial variability for the studied POPs, most probably due to their different environmental sources and current local emissions patterns (mostly for legacy POPs) at the studied sites as discussed above, which may prevail over the BT influence at a local/regional scale in different seasons of the year. In addition, other parameters affecting the atmospheric gas-particle partitioning of POPs (e.g. temperature, relative humidity) may have an important influence at local scale.

Atmospheric dry deposition and exposure

Dry deposition fluxes ($F_{DD,}$ pg m^{-2} d^{-1}) of PCDD/Fs, PCBs and PBDEs were calculated as:

$$F_{DD} = v_d C_A \quad [1]$$

where C_A is the POP volumetric concentration in the aerosol (pg m^{-3}) and v_d (cm s^{-1}) is the particle deposition velocity. A reference value of 0.2 cm s^{-1} for v_d was adopted for both sites. This value is within the range of v_d experimentally measured[59] or previously used in coastal NW Mediterranean Sea[23,35,36] for the estimation of dry deposition fluxes of POPs. However, a degree of uncertainty is associated to this calculation due to the lack of v_d measurements during the sampling events.

Overall, the atmospheric loading at both coastal areas is dominated by PBDEs, ranging from 70 to ~ 3400 ng m^{-2} y^{-1}, followed by PCBs (30 to ~ 250 ng m^{-2} y^{-1}) and PCDD/Fs (2 to 80 ng m^{-2} y^{-1}) as expected from their relative atmospheric concentrations and the assumptions considered in these calculations (Table 1, S9-S11). These fluxes were

520 generally within the range of previously reported dry deposition estimations in the
521 Mediterranean and SW Black Sea for the same POPs[23,28,35]. However, some differences
522 were found in the atmospheric loading at both edges of the Mediterranean Sea. While a
523 higher PBDE median loading is estimated for Marseille area (~ 550 ng m^{-2} y^{-1})
524 compared to Bizerte (~400 ng m^{-2} y^{-1}), the median dry deposition fluxes of PCBs (135
525 ng m^{-2} y^{-1}, and PCDD/Fs (14 ng m^{-2} y^{-1}) in Bizerte were higher than those of Marseille,
526 ~60 and 5 ng m^{-2} y^{-1}, respectively. Indeed, a 3-fold higher loading of dioxin-like
527 pollutants was estimated for Bizerte as toxic equivalents (TEQ)[60] (400 pg TEQ m^{-2} y^{-1},
528 median) compared to Marseille (137 pg TEQ m^{-2} y^{-1}, median) due to a higher
529 contribution of PCDFs and $_{DL}$PCBs in Bizerte (Table 1). These figures indicate a higher
530 potential exposure to these toxic chemical at the African edge of the W Mediterranean.
531 Considering 1.6 x10^{10} m^2 as the surface of the Gulf of Lion[61] and an equivalent surface
532 in the surroundings of Bizerte in the African coast, from 9 to 10 kg of POPs can be
533 annually loaded (median value) to surface waters at both edges of the Mediterranean
534 associated to the atmospheric aerosol. The sensitive environment of Bizerte coastal
535 lagoon (1.28 x10^8 m^2)[62] could receive up to 0.5 kg of POPs yearly. This loading of toxic
536 chemicals may have implications for the aquatic organisms but this evaluation cannot
537 be performed with the present data. However, it should be further investigated.
538
539 A human health risk assessment for the whole set of dioxin-like POPs was performed
540 based on the inhalation exposure. We follow here a similar approach as a very recent
541 assessment based on only two dioxin-like PCBs performed in Bizerte area[44]. Briefly,
542 concentrations expressed as WHO_{05} TEQ were calculated using the latest available
543 toxic equivalency factors (TEFs).[60] A daily air inhalation volume of 15 m^3 for an adult
544 of 60 kg was assumed.[63] The ∑2,3,7,8-PCDD/F and Σ_{DL}PCB concentrations in the

aerosols over Bizerte area, ranged from 0.7 – 70.2 and 0.07 - 2.2 WHO_{05} TEQ fg m^{-3}, respectively, whereas in Marseille levels varied from 0.4 – 23.0 and 0.03 to 0.3 WHO_{06} TEQ fg m^{-3}, respectively. Median TEQ values (for all dioxin-like congeners) of 6.3 and 2.2 WHO_{05} TEQ fg m^{-3} (Bizerte and Marseille) would result to potential intakes of 0.002 and 0.001 pg TEQ kg^{-1} day^{-1}, respectively. Both levels are three orders of magnitude lower than the daily intake threshold of 1-4 pg TEQ kg^{-1} day^{-1} propose by WHO[64]. The atmospheric particle phase PCDD/F concentration can be considered as a good descriptor of the total atmospheric concentration due to their general predominance in this compartment after their emissions to the environment.[22,23,35,49] Contrary, PCBs show a general preferential partitioning (mostly low MW congeners) to the vapour phase.[36,48] However, according to filed measurements performed in various urban, coastal and remote Mediterranean environments and inland aquatic ecosystems the Σ_{DL}PCB gas phase concentrations are not expected to exceed more than 100 fold the measured particulate phase concentrations. [23,27,36,63,65] Therefore, the worst case Σ_{DL}PCB TEQ concentration could be estimated as 100 fold the TEQ calculated considering only the particle-bound PCB concentrations, resulting in a corrected daily intake (for all dioxin-like congeners) of 0.01 and 0.004 pg TEQ kg^{-1} day^{-1} in Bizerte and Marseille areas, respectively. This new value stills far below the daily intake threshold proposed by WHO and therefore a risk by the inhalation route is excluded at present in the studied areas. It should be noted thought that the daily intake threshold proposed by WHO is based on toxicity studies evaluating dose-response through oral exposure. However, absorption and tissue partitioning could be different via the inhalation route and the local toxicity effect to lungs is not considered, so there is still an uncertainty degree in this assessment.

There are no TEFs associated to PBDEs and according to the European Chemicals Agency, the risks of deca-BDE and lower brominated transformation products to the humans via the environment cannot be adequately addressed in a quantitative way due to the high uncertainties regarding long-term exposure and effects.[66] Similarly to PCDD/Fs, PBDE particle-bound atmospheric concentrations can be a good indicator of the total atmospheric levels, particularly considering that one of the most abundant PBDEs is the HMW PBDE-209 (almost exclusively in the particle phase). For example, the PBDE particle-bound fraction in a large Mediterranean city (Athens, Greece) exhibiting similar atmospheric TSP concentration as Marseille and Bizerte accounted from more than the 70% of the total airborne PBDE concentrations.[29] Following the above calculations, median intakes of 1.6 and 2.2 pg kg^{-1} day^{-1} were estimated for Bizerte and Marseille, respectively. As a reference, three order of magnitude higher (~7.0 ng kg^{-1} day^{-1}) PBDE intakes has been reported for American adults.[67] However, the exposure to PBDE has been mostly associated to indoors environments (mainly dust ingestion and dermal contact)[67] and inhalation is not considered as the main route of concern for these substances.

586 **Acknowledgement**s

587

588 This work was funded by the Labex OT-Med (no. ANR-11-LABX-0061) – MEDPOP,
589 funded by the French Government "Investissements d'Avenir" (ANR) through the
590 A*MIDEX project (no ANR-11-IDEX-0001-02) and takes place in the
591 MERMEX/MISTRALS program. It also received the financial support from the IRD
592 French-Tunisian International Joint Laboratory (LMI) "COSYS-Med", the MIO-IRD
593 Action Sud project "AEROBIZ" and the PACA region project "Particule". Catherine
594 Guigue is acknowledged for her help on the sample preparation for the TOC/EC
595 determinations. We thank Patrick Raimbault for the TOC analyses, Xavier Mari and
596 Benjamin Guinot for the preparation of samples for EC determinations and Genevieve
597 Deviller (DERAC) for her contribution in the chemical risk assessment section.

598

599 **Supporting information available**

600

601 Additional data on the sampling and analytical procedures, QA/QC, compound-by-
602 compound atmospheric levels and spatial distribution (box-plots) and deposition fluxes
603 are presented in this section. This information is available free of charge via the Internet
604 at http://pubs.acs.org/

605

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Table 1. Atmospheric dry deposition fluxes of PCDD/Fs, PCBs and PBDEs in Marseille and Bizerte coastal areas

	Flux (ng m^{-2} y^{-1})						TEQ[a] (pg m^{-2} y^{-1})					
	Marseille (FR)			Bizerte (TN)			Marseille (FR)			Bizerte (TN)		
	Median	Mean	Range	Median	Mean	Range	Median	Mean	Range	Median	Mean	Range
Σ_7PCDDs	4.4	12.1	1.5 - 71.2	5.8	10.0	1.7 - 40.1	60.9	179.7	9.7 - 941.0	122.5	421.2	28.2 - 1955.8
Σ_{10}PCDFs	1.5	2.5	0.5 - 9.6	8.0	9.2	0.3 - 29.0	84.0	139.9	16.9 - 507.8	214.2	602.9	16.5 - 2473.1
Σ_{17}PCD/Fs	5.2	14.6	2.0 - 80.8	14	19.2	2.0 - 69.2	128.6	319.7	26.5 - 1448.8	375.3	1024.1	45.0 - 4428.9
$\sum_{12DL}$PCBs	12.1	17.7	8.7 - 52.2	16.1	16.9	5.4 - 32.2	8.40	10.10	2.0 - 21.6	23.7	37.8	4.1 - 136.7
$\sum_{6ID}$PCBs	49.0	55.3	20.81- 115.2	118.7	124.1	35.9 - 216.1				/		
$\sum_{18}$PCBs	61.1	73.0	30.8 - 167.4	134.8	141.0	41.3 - 246.2				/		
$\sum_{27}$PBDEs	547.90	586.90	141.0 - 1110.3	405.00	695.80	69.4 - 3386.0				/		
$\sum$POPs	**614.2**[b]	**674.5**[b]	**173.8 - 1358.5**[b]	**553.9**[b]	**855.9**[b]	**112.7 - 3701.4**[b]	**137.1**[c]	**329.8**[c]	**28.5 - 1470.4**[c]	**399.0**[c]	**1061.9**[c]	**49.2 - 4565.4**[c]

[a]TEQ values are calculated using WHO-TEF 2005; [b]$\sum_{62}$POPs; [c]$\sum_{29}$POPs (dioxin-like POPs)

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