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

3
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18

19 **Abstract**

20 A comparative study for 62 toxic chemicals based on the monthly collection of aerosol
21 samples during 2015-2016 in two coastal cities at both the African (Bizerte, Tunisia)
22 and European (Marseille, France) edges of the W Mediterranean basin is presented.
23 Legacy polychlorinated biphenyls ($\Sigma_{18}\text{PCBs}$) and polychlorinated dibenzo-p-dioxins
24 and dibenzofurans ($\Sigma_{17}\text{PCDD/Fs}$) show generally higher median levels at the African
25 edge (2.1 and 0.2 pg m^{-3} , respectively) compared to the European coastal site (1.0 and
26 0.08 pg m^{-3} , respectively). Contrary, the “emerging” polybrominated diphenyl ethers
27 ($\Sigma_{27}\text{PBDEs}$) median concentrations were higher in Marseille ($\sim 9.0 \text{ pg m}^{-3}$) compared to
28 Bizerte ($\sim 6.0 \text{ pg m}^{-3}$). Different past usage and current emission patterns were found at
29 both edges of the W Mediterranean, most probably linked to the respective different
30 regulatory frameworks for toxic chemicals. Our results indicate that the total organic
31 carbon (TOC) and/or the elemental carbon (EC) contents in the atmospheric aerosol
32 may have a stronger effect than the total suspended particle (TSP) content as a whole on
33 the spatial-temporal variability and the long-range atmospheric transport potential of the
34 studied POPs. A “jumping” of the PBDE local atmospheric stocks from the NW
35 European Mediterranean edge to the NW African coast seems to be possible under
36 favorable conditions at present. While a higher PBDE median loading is estimated for
37 Marseille area ($\sim 550 \text{ ng m}^{-2} \text{ y}^{-1}$) compared to Bizerte ($\sim 400 \text{ ng m}^{-2} \text{ y}^{-1}$), the median
38 PCB and PCDD/F dry deposition fluxes were higher at the African site, resulting in a 3-
39 fold higher toxic equivalent (TEQ) loading of dioxin-like pollutants ($400 \text{ pg TEQ m}^{-2} \text{ y}^{-1}$)
40 compared to Marseille ($\sim 140 \text{ pg TEQ m}^{-2} \text{ y}^{-1}$) with potential implications for the
41 aquatic organisms. However, the inhalation exposure assessment points to a minimum
42 risk for human health at both sites.

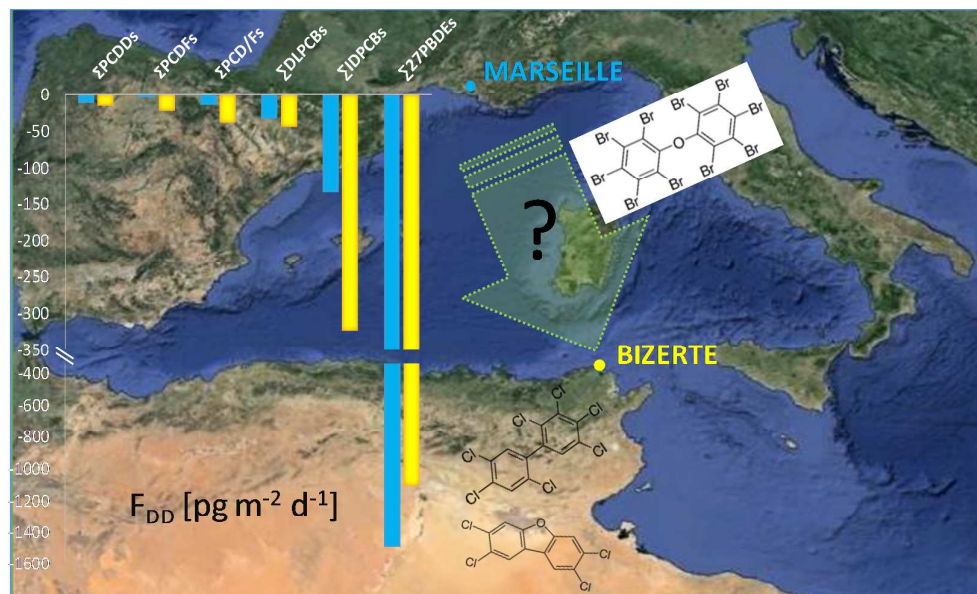
43

44 **Keywords:**

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

46

47 **TOC art**



48

49

50 Introduction

51

52 Atmospheric particulate matter has been recognized as a major environmental airborne
53 pollutant impacting human health and ecosystems.¹ A recent study performed in the
54 Mediterranean Sea supports the hypothesis that atmospheric aerosols can elicit a
55 number of toxic effects in marine organisms due to the presence of hydrophobic
56 contaminants intimately associated to the atmospheric particle phase.² High molecular
57 weight (HMW) polycyclic aromatic hydrocarbons (PAHs) and generally persistent
58 organic pollutants (POPs) such as polychlorinated dibenzo-p-dioxins and dibenzofurans
59 (PCDD/Fs) and polychlorinated biphenyls (PCBs) are among the contaminants
60 suspected to produce these hazardous effects.² In addition, POPs associated to the
61 atmospheric particle phase can be more resistant to atmospheric degradation processes
62 (e.g. photodegradation) increasing therefore their atmospheric residence times,
63 subsequent long-range atmospheric transport (LRAT) and potential exposure.² A first
64 step in order to elucidate the potential role of particle-bound POPs in toxic pathways
65 and to estimate their atmospheric dry deposition, considered as the main vector for the
66 introduction of the most hydrophobic contaminants in aquatic ecosystems, is their
67 accurate qualitative (congener specific distribution) and quantitative (environmental
68 concentration) determinations in the atmospheric aerosol. The legacy PCDD/Fs and
69 PCBs may lead to complex mixtures in the environment. However, the seventeen
70 2,3,7,8-chlorine substituted PCDD/Fs (i.e. seven PCDDs or “dioxins” + ten PCDFs or
71 “furans”) and the twelve dioxin-like PCBs (DLPCBs) named CBs-81, -77, -105, -114, -
72 118, -123, -126, -156, -157, -167, -169, -189, jointly considered as dioxin-like
73 pollutants, have received most of the attention due to their accumulation and toxic
74 effects in biota and humans.³⁻⁶ In addition, a set of non-dioxin-like PCBs, commonly

75 referred as indicator PCBs ($_{ID}PCBs$), containing CBs-28, -52, -101, -138, -153 and -180
76 are often monitored due to their higher environmental concentrations and potential toxic
77 effects by different mechanisms of action.⁷⁻⁹ Other POPs with recognized toxicity too,
78 such as polybrominated diphenyl ethers (PBDEs) can add up to the “contaminant-
79 aerosol cocktail”.^{10,11} These pollutants have different sources in the environment.
80 PCDD/Fs can occur as unintentional by-products in a number of industrial processes
81 and domestic heating,^{12,13} while current emissions of PCBs are urban/industrial centers,
82 open burning of products containing PCBs, waste incinerations, accidental fires and re-
83 volatilization from environmental reservoirs.^{14,15} PBDE were mostly used (and still used
84 in some regions) as flame retardants and, contrary to PCDD/Fs and PCBs, are
85 considered as a first generation of “emerging contaminants” (only recently restricted).
86 Three PBDE commercial formulations were extensively used worldwide: the penta-
87 formulation (with predominance of BDE-47 and -99), the octa-BDE (with PBDE-183 as
88 one of the major components) and the deca-BDE (with BDE-209 predominating).¹⁶
89 These contaminants are globally banned by the Stockholm Convention of POPs
90 (including all PBDE formulations) and regulated by the Water and Marine Strategy
91 Framework Directives at European level (except for the octa- and deca-PBDE
92 formulations). However, still very little or no information exists on current base line
93 levels and stocks for many marine areas, even in environments under important
94 anthropogenic pressure like the Mediterranean Sea. This semi-enclosed environment of
95 high ecological and socio-economic relevance is largely impacted by POPs and related
96 contaminants.^{17,18,19} PCDD/Fs, PCBs and PBDEs are among the POPs found in the
97 atmospheric compartment from various NW Mediterranean coastal environments (from
98 rural to large cities),²⁰⁻²⁶ and the central/Eastern basin²⁷⁻³³, but also farther from the
99 coast in the entire Mediterranean Sea.³⁴⁻³⁶ The European Mediterranean coast is by far

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

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

114

115 **Materials and Methods**

116

117 *Sampling and study areas*

118

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

124 Environmental, Inc, USA). The sampling volume ranged from ~ 1800 to ~ 5000 m³
125 depending on the site and sampling event (Table S1).

126

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

140

141 *Bizerte*: Sampling was conducted on the roof top (~ 8 m AGL) of the Faculty of Science
142 of Bizerte ($37^{\circ} 16' 0.5802''$ N, $9^{\circ} 52' 49.875''$ E) around 1 km far from the city center,
143 close to the Gulf of Bizerte shoreline and Bizerte lagoon water front (Figure S1). A
144 detailed sampling description is offered elsewhere.⁴⁴ Briefly, Bizerte is a medium-size
145 city (~ 127 000 inhabitants), located in the north of Tunisia, between the Mediterranean
146 Sea and the Bizerte lagoon. Even if agriculture and fishery activities are important in the
147 area, a considerable number of light and heavy industries (i.e., cement, plastic, textile,
148 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 ¹³C-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 ¹³C-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-substituted), 18 PCBs (12
171 DLPCBs+6IDPCBs) and 27 PBDEs (Text S1). Quantification was carried out by isotopic
172 dilution according to 1613 US EPA method⁴⁵ on a gas chromatograph (Trace GC ultra,

173 Thermo Fisher Scientific, Milan, Italy) coupled to a high resolution mass spectrometer
174 (DFS, Thermo Fisher Scientific, Bremen, Germany). The injection temperature was 260
175 °C and 1 µL of extract was injected (splitless mode). GC separation of PCBs and
176 PCDD/Fs was achieved using a 60 m × 0.25 mm × 0.25 µm DB-5MS column (Agilent
177 J&W, USA), while a 15 m × 0.25 mm × 0.10 µm Rxi®-5Sil MS column (Restek, USA)
178 was used for PBDEs. Different oven temperature programs were used for each family of
179 analytes (Table S2). Positive electron ionization (EI+) was used operating in selected
180 ion monitoring (SIM) mode at 10,000 resolving power.

181

182 *Quality assurance / quality control (QA/QC)*

183

184 Clean QFFs were individually wrapped in aluminum foil, baked at 450 °C overnight,
185 weighted and then stored at -20 °C in double sealed plastic bags until used. Field blanks,
186 consisting on baked QFFs transported to the sampling area, mounted in the sampler, and
187 dismantled, were collected at both sites, stored and analysed concurrently with the
188 samples. After sampling, QFFs were wrapped in aluminium foil again and stored in the
189 dark at -20°C. Blank levels were generally low for the three POP classes compared to
190 their concentrations in the samples, ranging from 0.02 to 3.5 pg (PCDD/Fs), from not
191 detected (n.d.) to 150 pg (PCBs), and from n.d. to 530 pg (PBDEs) depending on the
192 congener and sample (Table S3). Laboratory blanks (1 blank per five-sample batch)
193 showed lower or similar levels to field blanks, so no contamination during sampling,
194 storage and analysis occurred. Results were blank corrected. Chromatographic peaks
195 were only considered when the ratio between the two monitored ions was within ±15%
196 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 $S/N \geq 10$. 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 flow⁴⁷ 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 $\Sigma 2,3,7,8$ -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

222 months of April, July and September 2015 (3, 11, ~5-fold higher levels in Bizerte,
223 respectively). However, these values were not significantly different (Mann-Whitney
224 test, $p=0.28$) for the sum of 2,3,7,8-PCDD/Fs most probably due to the high annual
225 variability, in particular in Bizerte site, and the limited number of samples analysed.
226 Significant differences were only found for two furan congeners (i.e. 2,3,4,6,7,8-
227 HxCDF and 1,2,3,4,6,7,8-HpCDF) (Mann-Whitney test, $p=0.04$) (Figure S2, Table S6).
228 A general trend showing higher PCDD/F levels in the coldest months of the year was
229 observed at both sites. This effect has been previously reported in other Mediterranean
230 coastal areas and has been attributed to the combined effect of the increase of diffusive
231 combustion sources (e.g. domestic heating and road traffic) and a less efficient
232 dispersion of the local emissions during cold conditions.²³
233 The Σ 2,3,7,8-PCDD/F was clearly dominated by the contribution of PCDDs in
234 Marseille whereas a more even contribution of PCDDs and PCDFs was found for the
235 aerosols of Bizerte area (Figure 1A), pointing to different PCDD/F sources at both sites.
236 This is the first time that PCDD/Fs have been measured in atmospheric aerosols from
237 the Marseille area and in a coastal site at the African Mediterranean edge. The
238 concentrations found at both sites are within the range of those previously reported for a
239 coastal area in the Gulf of Lion ($50\text{-}1500\text{ fg m}^{-3}$)²³, urban/industrial sites from
240 Barcelona area ($570\text{-}1162\text{ fg m}^{-3}$)²⁴ and in the open NW Mediterranean ($94\text{-}990\text{ fg m}^{-3}$).
241 ³⁵ Reported values from a cruise transect close to the NW Mediterranean African coast
242 (38 fg m^{-3}) are lower than those measured in Bizerte coastal area. ³⁵ Concentrations
243 measured in a background site in Barcelona area (230 fg m^{-3}) are lower too than those in
244 Marseille²⁴. No data for comparison was found in the central/eastern Mediterranean Sea.
245 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

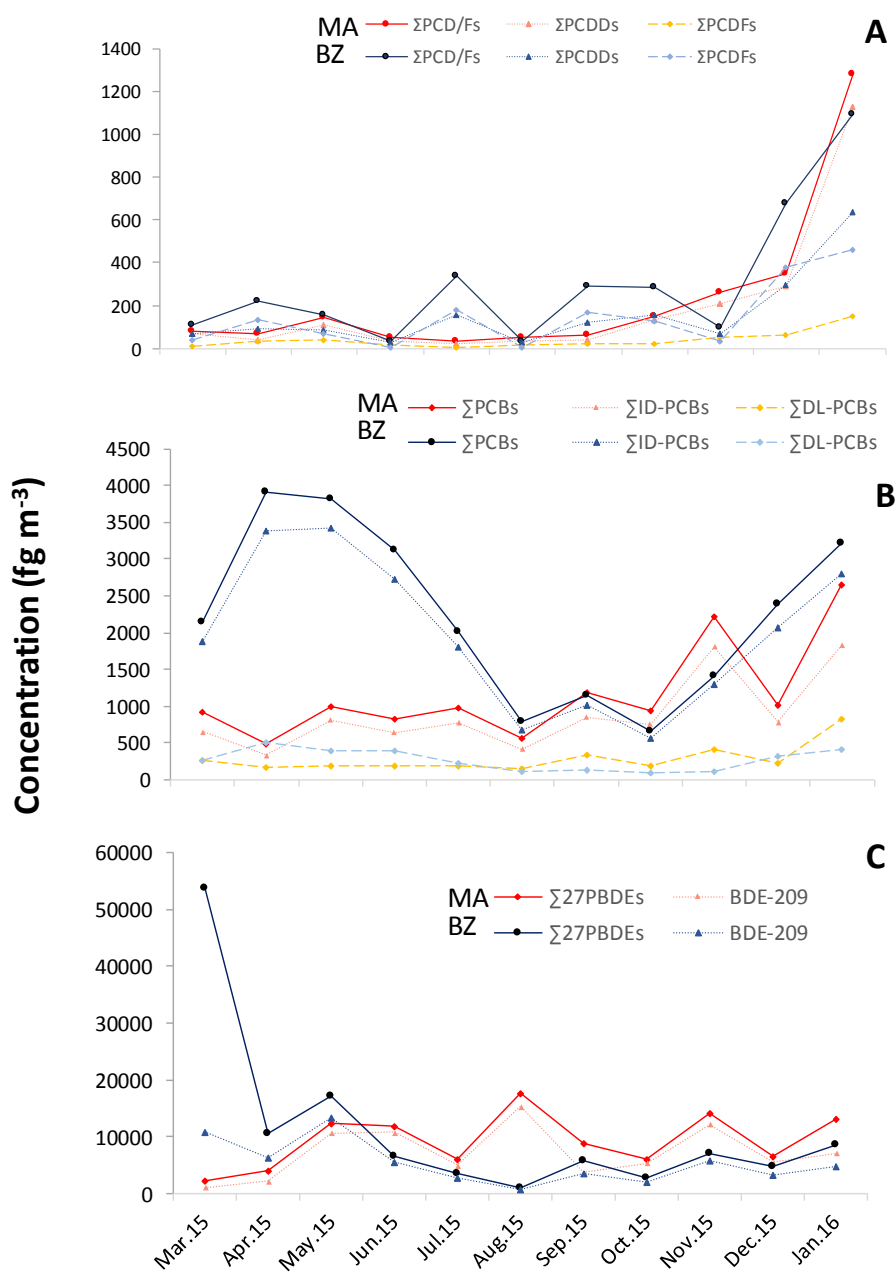
249 The $\sum_{18}\text{PCB}$ concentrations measured in the aerosols from Bizerte, ranging from 0.7 to
250 ~ 4.0 pg m⁻³ (2.1 pg m⁻³, median) were significantly higher (Mann-Whitney test, $p=0.03$)
251 than those measured in the aerosols over Marseille, which varied from 0.5 to 2.7 pg m⁻³
252 (1.0 pg m⁻³, median). IDPCBs dominated the total levels at both sites with $\sum_{\text{ID}}\text{PCB}$
253 concentrations significantly higher too in Bizerte (0.6 to 3.4 pg m⁻³, median value of \sim
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). $\sum_{\text{DL}}\text{PCB}$ 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 DLPCBs (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 $\sum_{18}\text{PCB}$ (and $\sum_{\text{ID}}\text{PCB}$) 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 $\sum_{18}\text{PCB}$ 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 $\sum_{\text{DL}}\text{PCB}$ concentrations were generally measured from August

271 2015 to January (except in December) in Marseille. These facts highlight the differential
272 environmental behaviour, seasonality and related exposure of individual PCBs at both
273 sites.

274 PCB data comparability may be tricky since different number and type of PCBs may be
275 considered. Therefore, for comparative purposes we focus only on $\Sigma_{ID}PCB$
276 concentrations measured at both edges of the NW Mediterranean Sea were generally
277 lower than previous coastal measurements performed in the NW Mediterranean in the
278 Gulf of Lion (0.5 to 7.2 pg m^{-3})^{23,26} and those carried out close to Barcelona area (9 - 26
279 pg m^{-3}).²⁶ Cruise measurements encompassing the Mediterranean Sea and the SW Black
280 Sea in 2006 and 2007 revealed higher concentrations too for $\Sigma_{ID}PCB$ (0.4 - 18 pg m^{-3}),
281 but PCB-118 was included in the sums.³⁶ However, concentrations measured in Bizerte
282 and Marseille were generally higher than those reported for a coastal site (considered as
283 a background location) in the Eastern Mediterranean²⁷ consistent with previous studies
284 indicating higher PCB levels in the W Mediterranean.³⁶ Most of the previous studies
285 correspond to measurements performed more than a decade ago (as for PCDD/Fs) so
286 comparison must be done carefully. Particle-bound PCBs have received little attention
287 since then in the Mediterranean basin compared to gas phase PCBs, most probably due
288 to the dominant role of vapor PCBs driving total PCB ambient levels (especially for low
289 MW congeners) and the increasing applications of passive sampling techniques to POP
290 atmospheric measurements. Thus, recent studies in the Mediterranean Sea considered
291 only the gas phase or the assemble gas+particle phases.^{32,33} $\Sigma_{DL}PCB$ background
292 measurements in the atmospheric aerosol over remote areas from the Atlantic, Pacific
293 and Indian oceans revealed up to 500-fold lower levels (1 - 2675 fg m^{-3}).⁴⁸
294 These figures confirmed that the NW Mediterranean Sea is considerably exposed to
295 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

303 **Figure 1.** Temporal variability of PCDD/F (A), PCB (B) and PBDE (C) concentrations
304 in atmospheric aerosols over Marseille (MA) and Bizerte (BZ) coastal areas from March
305 2015 to January 2016.

306

307 *PBDEs*

308

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

326

327 Σ_{27} PBDE concentrations measured in Marseille and Bizerte were generally within the
328 range of those reported for a coastal site in the NW Mediterranean (2-18 pg m^{-3} ,
329 Σ_8 PBDE)²³, higher than levels in a coastal background site in central/E Mediterranean
330 (0.5-2 pg m^{-3} , Σ_{15} PBDE)³⁰ but in the lower end of values reported for aerosols collected
331 over large cities in the E Mediterranean like Athens (Greece) (15-23 pg m^{-3} ,
332 Σ_{12} PBDE)²⁹ and Izmir (Turkey) (27-62 pg m^{-3} , Σ_7 PBDE).³⁸

333

334 *POPs patterns in the atmospheric aerosol*

335

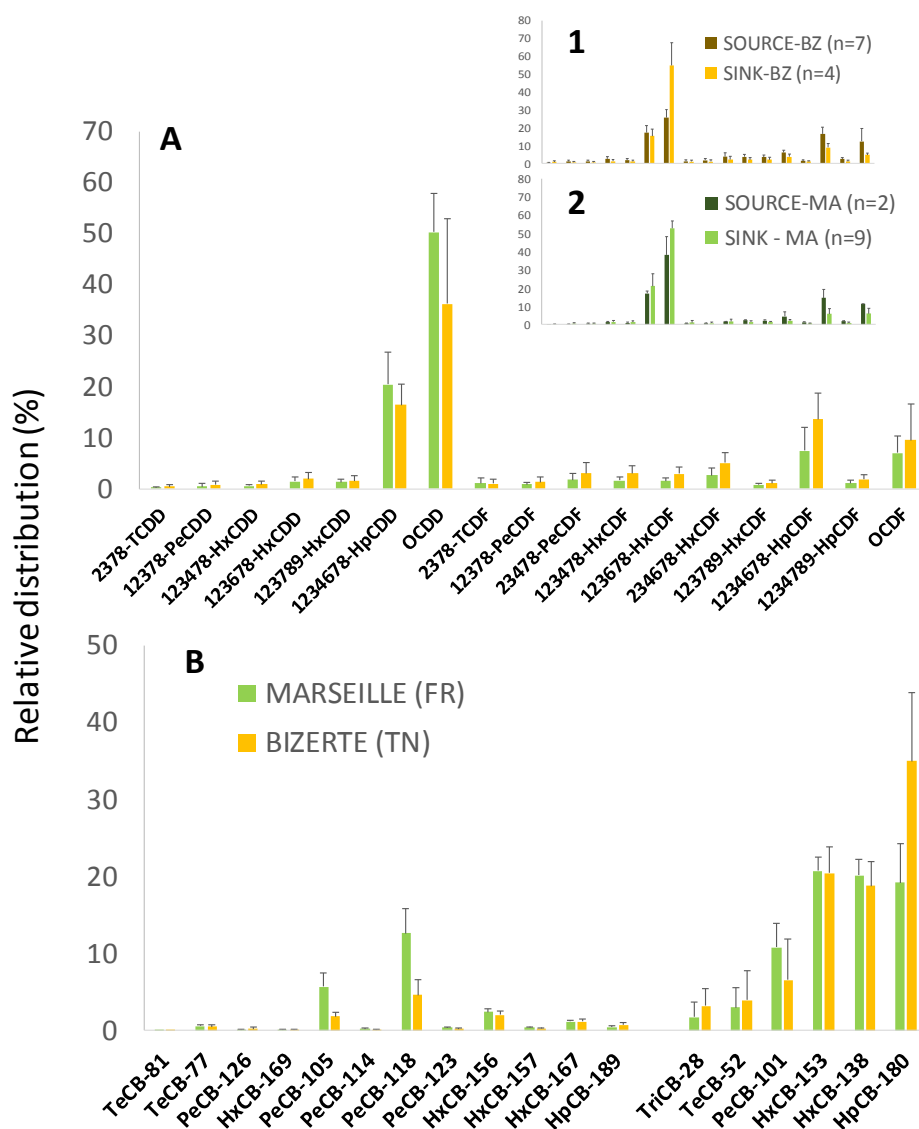
336 The PCDD/F atmospheric pattern (congener relative contribution) for most of Bizerte
337 samples showed an important contribution of furans, with 1,2,3,4,6,7,8-HpCDF and
338 OCDF accounting for the 16.3±3.7 % and 12.2±7.3 % of the $\Sigma_{2,3,7,8}$ -PCDD/F, values
339 almost reaching the relative contribution of 1,2,3,4,6,7,8-HpCDD (17.0±4.0 %) and
340 OCDD (25.5±4.5 %) which are the two most abundant PCDDs (Figure 2A-1). However,
341 the PCDD/F pattern in samples from Marseille was dominated by a higher contribution
342 of 1,2,3,4,6,7,8-HpCDD (21.2±6.8 %) and OCDD (53.0±4.0 %) and lower contribution
343 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
344 $\Sigma_{2,3,7,8}$ -PCDD/F, respectively (Figure 2A-2). A higher contribution of PCDFs in the
345 PCDD/F atmospheric pattern compared to PCDDs has been associated in previous
346 studies to ‘fresh’ emissions (sources). A situation in which the lower chlorinated
347 congeners, in particular PCDFs, have insufficient time to experience significant
348 atmospheric degradation / depletion processes.^{23,35,49,50} Contrary, a predominance of
349 higher chlorinated PCDDs and little contribution of PCDFs is considered as a ‘sink’
350 signal where the lighter congeners were ‘weathered’ in their travel from the source to
351 the sampling sites due to atmospheric processes (e.g. photodegradation).

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

366

367 The PCB atmospheric pattern was dominated in general by the HMW _{ID}PCBs at both
368 sites. A clear predominance of PCB-180 in Bizerte (accounting for the 35.0±8.7 % of
369 the \sum_{18} PCBs) was observed compared to Marseille area (19.2±5.1 % of the \sum_{18} PCBs).
370 A similar pattern was observed in the two sites for _{DL}PCB, but PCB-118 and -105
371 predominated in Marseille (12.6±3.2% and 5.7±1.8%, respectively) compared to Bizerte
372 (4.6±2.0% and 1.9±0.5%, respectively). The different abundance of these three major
373 PCBs may be either the reflect of different past usage of PCB commercial mixtures at
374 both sites or distinct emissions rates to the environment at present. For example, PCB-
375 180 is one of the major constituent of Aroclor 1260 and 1262, while CB-105, 118 were
376 relatively more abundant in the Aroclor 1254 formulation. One of the major uses of

377 these Aroclor formulations was as industrial oils destined to transformers.⁵¹ It has been
 378 very recently reported that a large number of transformers containing PCBs are still
 379 used or stored in unsatisfactory conditions in Bizerte area with high probability of oil
 380 leaks.⁴⁴ This could explain the higher contribution of PCB-180 in Bizerte compared to
 381 Marseille.
 382



383

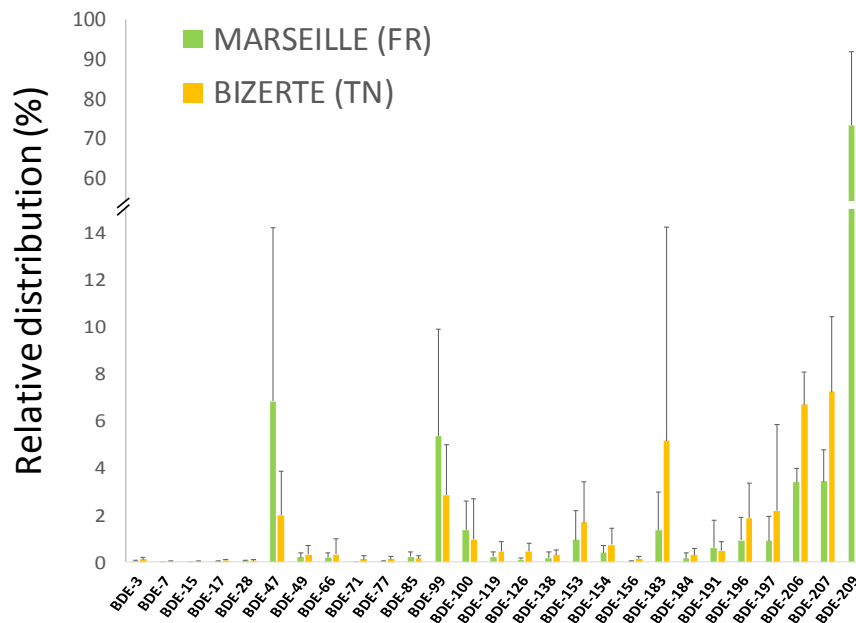
384 **Figure 2.** Average atmospheric pattern (n=11) of PCDD/F (A) and PCBs (B) in
 385 Marseille (MA) and Bizerte (BZ) coastal areas. The small figures (1) and (2) show a

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 $72.3 \pm 18.6\%$ and $65.5 \pm 18.0\%$ of the $\Sigma_{27}\text{PBDE}$ 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 ($6.8 \pm 7.3\%$ and
396 $5.3 \pm 4.5\%$ for BDE-47 and -99, respectively) compared to the pattern in Bizerte (2.0
397 $\pm 1.9\%$ and $2.8 \pm 2.5\%$ 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 $\Sigma_{27}\text{PBDE}$,
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_{10} 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

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

436

437 Our results indicate that the TOC and/or EC contents in the atmospheric aerosol may
438 have a stronger effect than the TSP as a whole on the spatial-temporal variability of the
439 studied POPs. Concentrations normalized by TOC slightly decreased the $\sum_{2,3,7,8}$ -
440 PCDD/F, $\sum_{18}\text{PCB}$ $\sum_{\text{ID}}\text{PCBs}$ and $\sum_{27}\text{PBDE}$ annual variability at both sites (except for
441 the month of January 2016) and confirmed the similar spatial variability with no
442 significant differences for PCDD/Fs ($p=0.67$) and PBDEs ($p=0.66$) and higher levels of
443 $\sum_{18}\text{PCB}$ (although not significant, $p=0.07$) and $\sum_{\text{ID}}\text{PCBs}$ ($p=0.03$) in Bizerte (Figure
444 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 $\sum_{2,3,7,8}$ -PCDD/F, \sum_{ID} PCB, \sum_{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 $\sum_{2,3,7,8}$ -
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 model⁵⁶ (Figure S10). The lowest $\sum_{2,3,7,8}$ -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

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

474 Interestingly, $\sum_{27}\text{PBDE}$ exhibited the lowest concentrations in the months of March
475 2015 over Marseille, with air masses showing an important component coming from the
476 N African coast, while the highest concentrations were measured in the same month in
477 Bizerte, with air masses showing the 50m height component coming from the Gulf of
478 Lion area. Recent reports have shown evidences of the North to South atmospheric
479 particle transport over some regions in the NW and E Mediterranean Sea^{57,58}. In
480 addition, PBDEs have been described to be mostly associated to the finest particles of
481 the atmospheric aerosol²⁹, consistent with the correlations found with the TOC and/or
482 EC contents (more abundant and stronger) compared to the TSP as discussed above.
483 This will result in higher atmospheric residence times and a higher potential of LRAT.
484 These facts may support the hypothesis of the potential “jumping” of PBDE local
485 atmospheric stocks from the NW European Mediterranean edge to the NW African
486 coast (where lower PBDE ambient levels has been generally measured) under favorable
487 conditions. Indeed, the two sites are relatively close (around 780 km straight line).
488 However, this hypothesis requires further confirmation with more sites at both edges of
489 the NW Mediterranean. In addition, a better characterization of PBDE local sources
490 (emission inventory) at the African edge is needed. The BT analysis reveals too other
491 potential hot spots farther west in the N African coast which find their way to Bizerte
492 area passing through the Gibraltar strait and along the African cost, as observed in the
493 month of May 2015. The three POP families exhibited higher levels in Bizerte area
494 compared to Marseille (with a different air mass circulation pattern) in this month. This

495 situation has been previously described for PCDD/Fs³⁵ and PAHs¹⁸ in the same region.
496 BTs could only explain part of the annual and spatial variability for the studied POPs,
497 most probably due to their different environmental sources and current local emissions
498 patterns (mostly for legacy POPs) at the studied sites as discussed above, which may
499 prevail over the BT influence at a local/regional scale in different seasons of the year. In
500 addition, other parameters affecting the atmospheric gas-particle partitioning of POPs
501 (e.g. temperature, relative humidity) may have an important influence at local scale.

502

503 *Atmospheric dry deposition and exposure*

504

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

$$507 \quad F_{DD} = v_d C_A \quad [1]$$

508

509 where C_A is the POP volumetric concentration in the aerosol (pg m^{-3}) and v_d (cm s^{-1}) is
510 the particle deposition velocity. A reference value of 0.2 cm s^{-1} for v_d was adopted for
511 both sites. This value is within the range of v_d experimentally measured⁵⁹ or previously
512 used in coastal NW Mediterranean Sea^{23,35,36} for the estimation of dry deposition fluxes
513 of POPs. However, a degree of uncertainty is associated to this calculation due to the
514 lack of v_d measurements during the sampling events.

515

516 Overall, the atmospheric loading at both coastal areas is dominated by PBDEs, ranging
517 from 70 to $\sim 3400 \text{ ng m}^{-2} \text{y}^{-1}$, followed by PCBs (30 to $\sim 250 \text{ ng m}^{-2} \text{y}^{-1}$) and PCDD/Fs
518 (2 to $80 \text{ ng m}^{-2} \text{y}^{-1}$) as expected from their relative atmospheric concentrations and the
519 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 ($\sim 550 \text{ ng m}^{-2} \text{ y}^{-1}$)
524 compared to Bizerte ($\sim 400 \text{ ng m}^{-2} \text{ y}^{-1}$), the median dry deposition fluxes of PCBs (135
525 $\text{ ng m}^{-2} \text{ y}^{-1}$, and PCDD/Fs ($14 \text{ ng m}^{-2} \text{ y}^{-1}$) in Bizerte were higher than those of Marseille,
526 ~ 60 and $5 \text{ ng m}^{-2} \text{ y}^{-1}$, respectively. Indeed, a 3-fold higher loading of dioxin-like
527 pollutants was estimated for Bizerte as toxic equivalents (TEQ)⁶⁰ ($400 \text{ pg TEQ m}^{-2} \text{ y}^{-1}$,
528 median) compared to Marseille ($137 \text{ pg TEQ m}^{-2} \text{ y}^{-1}$, 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 $1.6 \times 10^{10} \text{ m}^2$ as the surface of the Gulf of Lion⁶¹ 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 ($1.28 \times 10^8 \text{ m}^2$)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 area⁴⁴. 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 $\Sigma_{2,3,7,8}\text{-PCDD/F}$ and $\Sigma_{\text{DL}}\text{PCB}$ concentrations in the

545 aerosols over Bizerte area, ranged from 0.7 – 70.2 and 0.07 - 2.2 WHO₀₅ TEQ fg m⁻³,
546 respectively, whereas in Marseille levels varied from 0.4 – 23.0 and 0.03 to 0.3 WHO₀₆
547 TEQ fg m⁻³, respectively. Median TEQ values (for all dioxin-like congeners) of 6.3 and
548 2.2 WHO₀₅ TEQ fg m⁻³ (Bizerte and Marseille) would result to potential intakes of
549 0.002 and 0.001 pg TEQ kg⁻¹ day⁻¹, respectively. Both levels are three orders of
550 magnitude lower than the daily intake threshold of 1-4 pg TEQ kg⁻¹ day⁻¹ propose by
551 WHO⁶⁴. The atmospheric particle phase PCDD/F concentration can be considered as a
552 good descriptor of the total atmospheric concentration due to their general
553 predominance in this compartment after their emissions to the environment.^{22,23,35,49}
554 Contrary, PCBs show a general preferential partitioning (mostly low MW congeners) to
555 the vapour phase.^{36,48} However, according to filed measurements performed in various
556 urban, coastal and remote Mediterranean environments and inland aquatic ecosystems
557 the $\Sigma_{DL}PCB$ gas phase concentrations are not expected to exceed more than 100 fold the
558 measured particulate phase concentrations.^{23,27,36,63,65} Therefore, the worst case $\Sigma_{DL}PCB$
559 TEQ concentration could be estimated as 100 fold the TEQ calculated considering only
560 the particle-bound PCB concentrations, resulting in a corrected daily intake (for all
561 dioxin-like congeners) of 0.01 and 0.004 pg TEQ kg⁻¹ day⁻¹ in Bizerte and Marseille
562 areas, respectively. This new value stills far below the daily intake threshold proposed
563 by WHO and therefore a risk by the inhalation route is excluded at present in the
564 studied areas. It should be noted thought that the daily intake threshold proposed by
565 WHO is based on toxicity studies evaluating dose-response through oral exposure.
566 However, absorption and tissue partitioning could be different via the inhalation route
567 and the local toxicity effect to lungs is not considered, so there is still an uncertainty
568 degree in this assessment.

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

585

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587

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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 ₇ PCDDs	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
Σ _{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
Σ _{6ID} PCBs	49.0	55.3	20.81- 115.2	118.7	124.1	35.9 - 216.1				/		
Σ ₁₈ PCBs	61.1	73.0	30.8 - 167.4	134.8	141.0	41.3 - 246.2				/		
Σ ₂₇ PBDEs	547.90	586.90	141.0 - 1110.3	405.00	695.80	69.4 - 3386.0				/		
ΣPOPs	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

^aTEQ values are calculated using WHO-TEF 2005; ^bΣ₆₂POPs; ^cΣ₂₉POPs (dioxin-like POPs)

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