
Evidencing the Impact of Coastal Contaminated Sediments on Mussels Through Pb Stable Isotopes Composition

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Abstract :

Heavily contaminated sediments are a serious concern for ecosystem quality, especially in coastal areas, where vulnerability is high due to intense anthropogenic pressure. Surface sediments (54 stations), 50 cm interface cores (five specific stations), river particles, coal and bulk Pb plate from past French Navy activities, seawater and mussels were collected in Toulon Bay (NW Mediterranean Sea). Lead content and Pb stable isotope composition have evidenced the direct impact of sediment pollution stock on both the water column quality and the living organisms, through the specific Pb isotopic signature in these considered compartments. The history of pollution events including past and present contaminant dispersion in Toulon Bay were also demonstrated by historical records of Pb content and Pb isotope ratios in sediment profiles. The sediment resuspension events, as simulated by batch experiments, could be a major factor contributing to the high Pb mobility in the considered ecosystem. A survey of Pb concentrations in surface seawater at 40 stations has revealed poor seawater quality, affecting both the dissolved fraction and suspended particles and points to marina/harbors as additional diffuse sources of dissolved Pb.

Graphical abstract



37 1. INTRODUCTION

38 Sources of trace metals in the environment are numerous, either natural or anthropogenic. The
39 principal natural source of metals is crust weathering/erosion while a multitude of
40 anthropogenic emissions occur in the environment (mining/smelting/metal manufacturing,
41 fossil-fuel combustion, urban waste, sewage sludge, etc. ¹). Among these metals, Pb has been
42 widely used for thousands of years (during Etruscan-Greek-Roman, medieval and modern
43 periods ²) due to its low melting point and corrosion resistance. Lead geochemical affinity is
44 chalcophilic, resulting in the predominance of galena (PbS) as the main mineral of economic
45 importance ¹. The four main Pb stable isotopes are ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb with average
46 proportions of 1:17:15:37 ^{3,4}. Except ²⁰⁴Pb which is not radiogenic, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb are the
47 radioactive decay products of ²³⁸U, ²³⁵U and ²³²Th, respectively. The Pb stable isotope ratios
48 are widely used as a source tracking tool in environmental samples ^{2,5,6} as well as in
49 organisms ⁷⁻⁹. Among these organisms, bivalve molluscs and particularly mussels are
50 consensually used as biological monitor organisms of coastal pollution due to their
51 advantageous properties of sedentarity, large spatial distribution, easy sampling and pollutants
52 bioaccumulation ⁷. Several "mussel watch programs" (MWP) have been worldwide active for
53 decades (France: RNO/ROCCH ^{8,10}, Spain ⁷, USA ¹¹, ect.). The most important Pb sources
54 assessed by Pb isotope signatures are coal combustion, leaded gasoline, metal smelting,
55 battery factories, sewage sludge and waste incineration ^{1,2}. Another recent source of metals,
56 including Pb, could be their growing use in antifouling paints ^{12,13}. In coastal ecosystems,
57 sediments accumulate settling contaminated particles, providing historical archives of
58 pollution ¹⁴. Such sediments could also be a serious concern for the ecosystem quality ¹⁵ due
59 to numerous biogeochemical processes within sediments and at the sediment/water interface
60 (SWI) ¹⁶⁻¹⁹. However, it remains a complex issue to interlink sediment contamination with the
61 degradation of water quality and the living organisms' exposure to pollutants, as a
62 prerequisite for an adapted environmental policy.

63 Toulon Bay (NW Mediterranean sea) sediments are extremely contaminated by a multitude of
64 metals/metalloids/organo-metallics ^{17,20-22} and organic contaminants (unpublished data). Such
65 status originated both from historic (bombardments, warship scuttling and -raising during and
66 after the 2nd World War ²¹) and more recent activities (main French Navy harbor, nautical
67 traffic, release of sewage from the Toulon urban area, industries, tourism...), coupled with its

68 characteristics (semi-closed area, low tidal amplitude, long water/particle residence time ²³).
69 Analysing data from the MWP, Andral et al. ²⁴ have observed that Toulon Bay mussels had,
70 by far, the highest Pb concentrations over 1800 km of the French Mediterranean coast (~5.4
71 $\mu\text{g g}^{-1}$, dry weight, in comparison to an average value of 1.0 (n = 91)), together with huge
72 anomalies in other pollutants (DDT, CB153, Hg, ...). Trace metals concentrations monitoring
73 both in water and mussel samples from Toulon Bay has shown clear co-variations ²⁵, even if
74 the origins of high Pb and Hg levels still remain unclear. All these observations, associated
75 with the presence of aquaculture activities (fish and mussel farming) inside the bay, raise
76 numerous questions about the potential mobility of such pollutants and further risks for the
77 surrounding environment, making this site a model environment to study such processes
78 which also act in many other areas.

79 The present study reports on Pb levels and isotope signatures in sediments, seawater and
80 mussels of the Toulon Bay, focussing on its origins and pathways between these
81 compartments. The objective was to investigate whether the historical sediment Pb pollution
82 together with resuspension cycles may explain the exceptionally high Pb contamination in
83 both farmed and wild mussels. Lead concentrations and isotope ratios were measured in (i)
84 total and 1 M-HCl extracts of surface sediments (0-5 cm) and 50-cm interface sediment cores,
85 (ii) farmed mussels from the RNO/ROCCH sample bank covering the 1979-2012 period and
86 wild mussels collected in the most contaminated area, (iii) particles issued from small
87 tributaries and hazardous material (coal block and battleship's bulk Pb plate from French
88 Navy) and (iv) surface seawater samples around the Toulon Bay. Finally, resuspension
89 experiments with surface/deep sediments covering a wide range of Pb contamination levels
90 aimed at studying Pb behaviour and remobilisation kinetics.

91

92 2. MATERIALS AND METHODS

93

94 2.1. Study site and sampling

95 The Toulon Bay hosts a large urban area on the French NW Mediterranean coast where
96 various anthropogenic activities (Navy/civil harbours, aquaculture, urban sewage release,
97 industries...) have resulted in severe multi-contamination of the ecosystem, especially in
98 sediments ^{17,20-22}. The bay is divided by a seawall (N-S straight line, Fig. 1) in two non-

99 equivalent parts (Small and Large Bay). Two urban river outlets (Las and Eygoutier Rivers)
100 represent the main freshwater inputs to the bay, located on the north shore, whereas the main
101 anthropogenic activities cover large areas around the Toulon Bay (Fig. 1). In these two
102 tributaries (Las and Eygoutier Rivers), particle traps ^{26,27} were installed by IRSN
103 (Radioprotection and Nuclear Safety Institute) to assess the terrestrial contribution to the
104 coastal system. Five particles samples were collected in each tributary using 2 weeks
105 collection periods from October 2012 and May 2013, mostly during rain events ²⁸.
106 The studied sediments were collected at 54 stations covering the whole bay (Fig. 1) using an
107 interface corer (10-cm diameter and 1-m long Plexiglass[®] tube) with the support of the French
108 Navy (boats, materials, divers), as detailed elsewhere ^{16,18,20,28}. Briefly, for each site, duplicate
109 cores were sliced for surface sediments (0-5 cm) and slices were pooled, homogenized in
110 HDPE 1-L bottles and deep-frozen (-18°C). Moreover, interface sediment cores (~50 cm)
111 were sampled at five specific stations (MIS, 3B, 12, 15 and 23, Fig. 1). Only cores with well-
112 preserved SWI were analysed. The stations MIS and 3B are located in the Navy area, the
113 station 12 is close to a former Navy submarine base and the station 15 is in the aquaculture
114 area. Finally, the station 23 is situated in the Large Bay, in front of the Eygoutier River outlet.
115 The interface cores were sliced with 2 cm resolution under inert atmosphere (N₂). Slices were
116 then centrifuged (4000 rpm, 15 min, Sigma 3-18K). Porewater was recovered in a glove-box
117 by filtration (0.2-µm on-line syringe filters, cellulose nitrate, Sartorius) and stored in the
118 adapted vessels, more details in Dang et al. ¹⁷. The solid fraction was deep-frozen in HDPE
119 bottles, freeze-dried, 2-mm sieved and kept deep-frozen (-18°C) until analysis.
120 To evaluate the surface (0.5 m) distribution of Pb concentrations in the water column of
121 Toulon Bay, water samples were collected at 40 stations covering the whole bay in early
122 summer (June 24th, 2013) and winter (February 17th, 2014). For each station, raw (unfiltered)
123 and on-field filtered (0.2 µm cellulose nitrate syringe filter, Sartorius) seawater samples were
124 stored in 125-mL FEP bottles (Nalgene), previously acid-cleaned (10% HNO₃, pro analysis),
125 thoroughly rinsed with mQ water (18.2 MΩ, Millipore) and acid-conditioned (0.1% HNO₃,
126 s.p., Merck) before being rinsed with raw/filtered water from the site. Raw and filtered
127 samples were then acidified (0.2%, HNO₃, s.p., Merck) and digested for 24h under UV
128 irradiation (150W ²⁹) to assess the dissolved and total acid-leachable (hereafter considered as
129 "total") concentrations, respectively. Additional surface water (0.5 m) was sampled in 2-L

130 HDPE pre-cleaned bottles at 6 stations the 21st of October 2013 (Fig. 1) to analyse Pb isotopic
131 signature.

132 Farmed mussels (35-65 mm, *Mytilus galloprovincialis*) were sampled in the aquaculture area
133 close to the station 15 within the framework of the RNO/ROCCH program since 1979
134 (seasonally until 2002 and twice a year (February and November) since 2003). Wild mussels
135 were sampled in 2014 at station MIS, 12 and close to Milhaud dock (Fig. 1). The mussels (at
136 least 50) were depurated for 24 h in a polyethylene aquarium filled with filtered seawater
137 from the station. The soft tissues were separated from shells, pooled, freeze-dried and deep-
138 frozen (-20°C).

139 During the dredging operations started in 2013 in the area around the station 3B, huge
140 quantity of coal blocks were discovered in sediments. The inscribed signs ("Anzin, 1912",
141 Fig. S1) illustrated its origin (North of France) and the period. An aliquot was crushed and
142 burned out at 550 °C. The powder was digested on a hot plate with HCl/HNO₃ solution at 110
143 °C until complete acid evaporation before dilution with HNO₃ (s.p, Merck) for Pb
144 concentration and Pb isotopes analysis.

145 Finally, a bulk Pb plate (~0.5 m², Fig. S1) originating from the French Navy battleship
146 "Magenta", sunk in 1876 in the North of Toulon Bay, was collected by Navy divers in April
147 2015 from the battleship's beaching area (at 15 m depth, near the Toulon Navy harbour
148 entrance). Aliquots were cut up, and then submitted to the same protocol as coal powder for
149 Pb isotope analysis.

150

151 2.2. Sediment and mussel samples analysis

152 Pseudo-total element contents in sediments and tributaries particles were measured after aqua
153 regia/microwave digestion according to a previously described protocol ^{21,29} and validated
154 using PACS-2 certified materials (National Research Council of Canada; accuracy between
155 0.9 and 7% according to the considered element ^{21,29}. HCl extraction (1M HCl, s.p. Merck)
156 was performed to assess the potential bioavailability and mobility of major and trace elements
157 ^{17,29,31}.

158 Farmed mussels (dried powder of *Mytilus galloprovincialis*) were taken from the French
159 national mussel watch programme sample bank (RNO/ROCCH; IFREMER). Aliquots (150 –
160 200 mg) were digested with 8 mL of HNO₃ (ultrapure), in a microwave oven (MARS-5, CEM

161 Corporation), equipped with a carousel holding 12 Teflon vessels and under temperature and
162 pressure control. After cooling, digests were diluted to 50 mL with mQ water.
163 Lead concentrations in semi-total and 1M-HCl extracts of sediments (108 from surface
164 cartography, 184 from interface cores, 10 tributary particles) were analyzed by High
165 Resolution Inductively Coupled Plasma Mass Spectrometer at RBI-Zagreb laboratory (HR
166 ICP-MS, Element 2, Thermo Finnigan, more details in Lenoble et al. ³²).
167 Stable Pb isotopes (²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb) were measured by quadrupole ICP-MS on (1) a
168 representative set of sediments samples (34 surface sediments, 70 from interface cores (53
169 semi-total and 17 1M-HCl extracts), 10 tributary particles) at EPOC laboratory-Bordeaux
170 (XSeries 2, ThermoScientific, more details are presented by Petit et al. ³³); and on (2) mussels
171 extracts at LBCP-IFREMER laboratory (Element X series, Thermo Electron Corporation).
172 Mass bias and instrumental drift were corrected with a standard bracketing method by
173 analyzing NIST SRM-981 standard reference material. The ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb
174 internal relative standard deviation were in the range of 0.16-0.24% (n = 192) and 0.10-0.16%
175 (n = 10) for sediments and mussels analysis, respectively.

176

177 2.3. Seawater sample analysis

178 Total and dissolved Pb concentrations in seawater samples were determined by Differential
179 Pulse Anodic Stripping Voltammetry (DPASV). More details on instruments and analytical
180 procedure are described elsewhere ³⁴. Iron and Mn concentrations in water samples from
181 sediment resuspension experiments (see part 2.4) were measured by HR ICP-MS (RBI
182 laboratory).

183 Seawater samples for Pb isotopes analysis were filtered (0.45 µm, polycarbonate, Nucleopore)
184 under nitrogen pressure. Filtrates were acidified (0.1% HNO₃ s.p.) and stored in polyethylene
185 double-bags protected bottles. Quantitative Pb extraction from the seawater matrix was
186 performed by dithiocarbamate chelation, extraction into an immiscible organic solution and
187 back-extraction with diluted HNO₃ following an adapted protocol of Danielsson et al. ³⁵, as
188 described by Chiffoleau et al. ³⁶. In brief, a sample aliquot (400 - 500 g) was buffered to pH
189 5.5 with ammonium acetate (s.p.) solution. APDC/DDDC chelating solution was then added
190 and shaken to homogenize. Freon was added next and vigorously shaken. After phase
191 separation, the Freon phase was carefully collected. This Freon extraction step was repeated

192 twice. The collected organic phase was then treated with 0.5 mL HNO₃ (s.p.) and 2 mL mQ
193 water to degrade the dithiocarbamate chelates. After vigorous shaking and phase separation,
194 the aqueous phase was collected. 1 mL of the extract was diluted to 5 mL with mQ water.
195 Stable Pb isotope ratios were measured according to the same procedure as mussel samples.
196 In addition, ICP measurements of the procedural blanks was verified to reach values around
197 500 cps (²⁰⁸Pb), when samples were adjusted (by dilution) to ~100 000 cps. The blank signal
198 only accounted for less than 1% of the sample signal.

199

200 2.4. Sediment resuspension experiments

201 In order to assess the potential of Pb mobilization during sediment resuspension events (e.g.
202 storm, boat traffic, dredging ...), laboratory experiments were performed using sediments
203 from various sites presenting a large range of contamination. Sediment cores from stations
204 MIS, 3B, 12 and 15 were sliced under N₂ conditions, and aliquots of surface/suboxic (0-2 cm,
205 stations MIS, 3B, 12 and 15) and deep/anoxic (20-22 and 30-32 cm for stations 3B and MIS,
206 respectively) sediments were kept under inert atmosphere until the start of resuspension
207 experiments. To ensure close replication of natural conditions no pre-treatment (e.g. seawater
208 filtering or UF irradiation, autoclaving, poisoning, ...) of the sediment or seawater was
209 performed. However, more detailed experimentation would be necessary to delineate the roles
210 of the various components (e.g., microbes, DOM, minerals, ...).

211 The solid/liquid (S/L) ratio was setup to ~1 g L⁻¹ (expressed in dry weight), a value close to
212 in-situ levels of SPM measured during surface sediment reworking (personal data). Sediment
213 aliquots were then transferred into pre-cleaned 2 L FEP bottles (Nalgene), and filled with the
214 corresponding unfiltered surface (0.5 m below the surface) seawater from each sampling
215 station. FEP bottles were then immediately submitted to overhead shaking (15 rpm, Heidolph
216 Reax 20) for 2 weeks. After 10 different contact times (5, 15, 30 min, 1, 3, 7 h, 1, 2 days and
217 1, 2 weeks), agitation was stopped for few minutes to allow particles settling, then 50 mL
218 aliquots (or 250 mL at 1 h, 7 h and 2 w) were sampled from the surface of the supernatant
219 using pre-cleaned syringes and FEP tube, immediately filtered through 0.45 µm filters
220 (hydrophilic PTFE, Millex LCR, Millipore), stored in 60 mL FEP bottles, acidified (0.2%
221 HNO₃, s.p., Merck) and UV-digested as previously described, before dissolved Pb, Mn, Fe
222 concentrations measurement. Lead isotope analysis was performed on aliquots collected at 0,

223 1, 7 h and 2 weeks of contact time following the procedure described in section 2.3. To
224 minimize S/L ratio variations, 50 mL (or 250 mL at 1 and 7 h) of unfiltered seawater were
225 injected at each sampling time. To maintain stable oxic conditions (i.e. as encountered in the
226 bay water column during sediment resuspension due to dredging or boat traffic), FEP bottles
227 were opened every day for a few minutes during the whole experiment. Parallel resuspension
228 batches were performed in separate HDPE bottles to monitor the daily variations of physico-
229 chemical parameters (T, pH, Eh, dissolved O₂) using multi-probes (Hach Lange).

230

231 3. RESULTS AND DISCUSSION

232

233 3.1. Lead distribution and isotopic composition in sediments

234 Previous studies^{17,20-22,29} have evidenced the huge stock of contaminants (inorganic,
235 organometallic and organic) in the northern Small bay and non-negligible levels in the rest of
236 the bay (Fig. 1). Within the broad Pb content range (15-470 µg g⁻¹), the ²⁰⁶Pb/²⁰⁷Pb ratio
237 variation was unexpectedly low (1.156-1.180), with an average value of 1.168±0.005 (n = 34).
238 The lowest ²⁰⁶Pb/²⁰⁷Pb ratios (1.156-1.167) occurred in the most contaminated zones (Navy
239 area, former shipyard, La Seyne s/Mer harbour) and the highest ²⁰⁶Pb/²⁰⁷Pb ratios (~1.174-
240 1.180) occurred in the less contaminated area. Similar results were obtained using ²⁰⁶Pb/²⁰⁸Pb,
241 with an average value and variation range of 0.475±0.001 (n = 34) and 0.474-0.478,
242 respectively (Table 1). The Pb 1M-HCl extractability was similar, close to 64±6 % (n=50), for
243 all the stations²⁹ and the Pb isotopic composition of 1M-HCl extracts was identical to that of
244 Pb in total digestions (n=10).

245 Total Pb, HCl-extracted Pb content and Pb stable isotopes depth profiles from 5 stations
246 (MIS, 3B, 12, 15 and 23) are shown in Fig. 2 and A.1 and compared to previously published
247 Pb depth profiles from stations 3B, 12 and 15^{21,29}. At stations MIS and 3B, the observed Pb
248 contents were extremely high all down the cores (380-1300 and 201±29 µg g⁻¹, respectively)
249 with the majority in the HCl-extracted fraction (~80±8 % at station 3B). Such deep extension
250 of Pb contamination, corresponding to an incoherent period of time if considering a stable
251 sedimentation rate estimated around 0.2 cm yr⁻¹ for the whole bay²¹ are probably the
252 consequence of sediment disturbance due to past (raising of scuttled warships) and present
253 (e.g. harbour extension) activities. In these sediments, the ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁸Pb ratios,

254 either in the total or the HCl-extracted fraction, were stable and close to the values
255 encountered in surface sediments (Fig. 2, Fig. S2, Table 1). Both high Pb contamination and
256 specific Pb isotope ratios in different parts of the Toulon Bay support the idea that the Pb
257 sedimentary contamination at the scale of the bay mainly originates from a main source,
258 situated in the military area, mainly linked to past events (2nd World War) and resulting from
259 the multiplicity of Pb uses by Navy (e.g. weapons, batteries, hull protection, weights,
260 antifouling, explosive, ...). Hereafter, the Pb stock with ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁸Pb values
261 (1.165±0.004 and 0.475±0.001 (n = 14), respectively) is called ^{anthropogenic}Pb (Table 1).

262 At station 12, a strong contamination peak occurred for many pollutants (Ag, Cd, Cu, Hg, Pb,
263 Zn, Sn, ΣBT) at -11 cm ^{20,21,29} (Fig. 2). Deeper, smaller peaks at -25, -40 and -50 cm were
264 hypothetically attributed to a partial burying of contaminated sediment due to nautical/harbour
265 activities ²¹. The present Pb isotope signatures undoubtedly confirm these hypotheses: the
266 main multi-contamination peak has the typical ^{anthropogenic}Pb signature, similar to that of deeper
267 peaks. Between these small peaks, the non-negligible Pb burdens (70-110 µg g⁻¹, Fig. 2) in
268 deeper sediment layers show slightly higher ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁸Pb ratios, i.e. values
269 closer to the natural signature (^{natural}Pb, 1.195±0.014 and 0.483±0.003 (n = 16), respectively,
270 Table 1 and A.1). Concerning the HCl-extracted fraction, a similar ²⁰⁶Pb/²⁰⁷Pb ratio and a
271 slightly lower ²⁰⁶Pb/²⁰⁸Pb ratio were recorded in surface sediments compared to deep
272 sediments. In parallel, the HCl-extracted Pb percentage increased from ~22±6 % (n=7) in the
273 surface sediments to ~45±3 % (n= 18) below -15 cm.

274 Stations 15 and 23 showed similar depth profiles of Pb content and isotope ratios (Fig. 2 and
275 Fig. S2). Surface layers (0-15 cm) had quasi-constant Pb contents (92±6.9 and 65±5.4 µg g⁻¹,
276 respectively), along with the ^{anthropogenic}Pb signature. Deeper, both cores displayed decreasing
277 Pb concentrations along with increasing ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁸Pb ratios, reaching the local
278 background of Toulon Bay (~13.6 µg g⁻¹, ²¹) and typical signature of ^{natural}Pb. Contrarily to the
279 station 12, the Pb acid extractability was significantly higher for the surface sediments (~76±4
280 %). A similar ²⁰⁶Pb/²⁰⁷Pb ratio and a slightly higher ²⁰⁶Pb/²⁰⁸Pb ratio were observed.

281 The accumulation of ^{anthropogenic}Pb in the first 10-12 cm (corresponding to the past 50-70 years
282 ²¹) at stations 12, 15 and 23 suggests a main common historical pollution event. The
283 dispersion of these Pb contaminated particles (and associated pollutants ²⁰⁻²²) is probably still
284 a major pollution source for the more distal parts of the bay. This ongoing pollution spreading

285 is most probably activated by natural (storm, waves, etc.) or anthropogenic (large boat traffic,
286 harbour activities, etc.) resuspension of the contaminated sediments in the north part of
287 Toulon Bay, followed by particles transport-settling-resuspension processes driven by bottom
288 water hydrodynamics^{23,37}.

289

290 3.2. Pb content and source in mussels

291 The Pb contents ranged from 2.2 to 18.7 $\mu\text{g g}^{-1}$ in farmed mussels (1979-2012) and from 14.7
292 to 27.8 $\mu\text{g g}^{-1}$ in wild mussels (Fig. 3). These values were much higher than those measured in
293 the same species along the French Mediterranean coast ($\sim 1.0 \mu\text{g g}^{-1}$ ²⁴), Italian coast (0.07 to
294 4.2 $\mu\text{g g}^{-1}$ ³⁸) or American coast (low: 0-3 $\mu\text{g}_{\text{Pb}} \text{g}^{-1}$; medium: 4-6 $\mu\text{g}_{\text{Pb}} \text{g}^{-1}$; high: 7-13 $\mu\text{g}_{\text{Pb}} \text{g}^{-1}$
295 ¹¹). Except the 1985-1991 period, it appeared that Pb concentrations in mussels were
296 systematically higher in winter/spring period than summer/fall due to biological dilution
297 during reproduction cycles⁸. Apart from such intra-annual variation, the long-term Pb
298 accumulation in mussels seemed to slightly decrease, inversely to the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio which
299 tended to increase, still being in the range of ^{anthropogenic}Pb values (Fig. 3). A similar trend was
300 observed for mussels (*Mytilus edulis*) from other sites along the French Atlantic coast⁸. The
301 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in Toulon Bay mussels ($\sim 1.163 \pm 0.004$, $n = 31$) was close to that reported in
302 the literature (~ 1.167 in the Norman-Breton Gulf, ~ 1.161 in the Seine Estuary⁸). Labonne et
303 al.³⁹ have evidenced 3 isotopic domains in Thau Lagoon mussels, corresponding to 3 spatial
304 areas: sea ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.170-1.176$), harbour ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.162-1.169$) and coastal
305 runoff/chemical-impacted zones ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.158-1.161$). This last specific signature
306 corresponded to the ^{anthropogenic}Pb signal measured in both Toulon Bay sediments and mussels,
307 suggesting that mussels are exposed to similar Pb source.

308 The observed very high levels of ^{anthropogenic}Pb in mussels, which equalled or even exceeded
309 the average ($\sim 1.4 \pm 0.1 \mu\text{g g}^{-1}$) and the highest levels ($\sim 8.3 \mu\text{g g}^{-1}$) recorded on a large scale
310 survey of the Western Mediterranean coastal waters⁴⁰, could be of serious concern. The
311 observed Pb levels often surpassed the French limit for mussel consumption ($7.5 \mu\text{g g}^{-1}$ ^{41,42}).
312 The common evolution of Pb isotope signatures encountered in both sediments and mussels
313 from Toulon Bay clearly suggests a close link between these compartments.

314

315 3.3. Tracing Pb sources and Pb remobilization mechanisms

316 Different source-specific Pb isotope signatures from the literature were plotted to define the
 317 domains of variations for the main Pb sources (Table S1; Fig. S3) and the results obtained for
 318 Toulon Bay sediments, tributary river particles, coal, battleship's Pb plate, mussels and
 319 surface seawater were then compared to these various sources (Fig. 4). The deeper layers at
 320 stations 12, 15 and 23 showed ^{natural}Pb signatures. All the other sediment samples had typical
 321 ^{anthropogenic}Pb signatures. When compared to literature data (Fig. 4A), this quite characteristic
 322 signature (²⁰⁶Pb/²⁰⁷Pb ~ 1.166±0.003 and ²⁰⁶Pb/²⁰⁸Pb ~ 0.475±0.001, n = 56, Table 1) is
 323 common to the domains of industries (metal refinery), European coal and urban wastes. Such
 324 Pb isotopic ratios were also close to those of ore deposits in Italia (²⁰⁶Pb/²⁰⁷Pb ~ 1.161;
 325 ²⁰⁶Pb/²⁰⁸Pb ~ 0.474) and Spain (²⁰⁶Pb/²⁰⁷Pb ~ 1.167; ²⁰⁶Pb/²⁰⁸Pb ~ 0.472)⁴. The "Anzin" coal
 326 (total Pb content ~300 µg g⁻¹) presented a Pb isotope signature significantly different from
 327 ^{anthropogenic}Pb, either as bulk or ash, probably contributing only slightly to the overall Pb
 328 contamination.

329 As the ^{anthropogenic}Pb signature appeared to significantly differ from that of ^{natural}Pb, it was
 330 possible to estimate the contribution of the Pb contamination in sediments, using a binary
 331 mixing model⁴³, according to the following equation:

$$X_i = \frac{i(^{206}Pb/^{207}Pb) - natural(^{206}Pb/^{207}Pb)}{anthropogenic(^{206}Pb/^{207}Pb) - natural(^{206}Pb/^{207}Pb)}$$

(Eq. 1)

333 where X_i is the percentage contribution of ^{anthropogenic}Pb source in sample i ; $i(^{206}Pb/^{207}Pb)$,
 334 ^{anthropogenic}(²⁰⁶Pb/²⁰⁷Pb) and ^{natural}(²⁰⁶Pb/²⁰⁷Pb) are the isotopic signatures in the sample i and the
 335 main identified Pb sources in Toulon Bay, respectively.

336 The spatial distribution of X_i values in surface sediments of the Toulon Bay (Fig. S5) clearly
 337 showed the generally dominant contribution of the ^{anthropogenic}Pb source, being at least of 43%
 338 in the Large Bay and >99% in the Small Bay.

340 The Pb concentrations in particles transported by the Las and Eygoutier Rivers ranged from 8-
 341 40 and 24-123 µg g⁻¹ (n=10), respectively. In the most contaminated particles, the Pb isotope
 342 signature was close to that of ^{anthropogenic}Pb. However, the regression line's slope of ²⁰⁶Pb/²⁰⁸Pb
 343 over ²⁰⁶Pb/²⁰⁷Pb ratio in particles was higher than that obtained for sediments (Fig. 4A). This
 344 observation, in addition to the lower Pb content in Las particles compared to the Small Bay

345 sediments suggests that present river-borne continental inputs only partially contribute to the
346 poor quality of Toulon Bay sediments, mainly influenced by past nautical activities. Indeed,
347 Pb isotope signature of the "Magenta" French Navy battleship's Pb plate was close to that of
348 anthropogenicPb (Fig. 4A). Even if the contamination of Toulon bay sediments cannot be induced
349 by bulk Pb originating from a unique battleship sunk in the 19th century, it illustrates the
350 signature of the Pb which was used by the French Navy and had mostly contributed to the
351 excessive contamination of the bay during the 2nd World War.

352 The slight increase in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in farmed mussels to reach anthropogenicPb value since
353 the 1990s, (Fig. 3) could partly reflect the withdrawal of the contribution of leaded gasoline
354 ($^{\text{gasoline}}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb} = 1.084 \pm 0.010$ and $^{206}\text{Pb}/^{208}\text{Pb} = 0.458 \pm 0.002$ ($n = 9$)⁴³, Table 1, A.1)
355 due to the progressive substitution of leaded gasoline in France since the 1990s and its total
356 prohibition in 2000. However, the historical record of Pb isotope ratios in farmed mussels
357 suggests that the contribution (from atmosphere and tributaries inputs) of $^{\text{gasoline}}\text{Pb}$ (compared
358 to anthropogenicPb using a binary mixing model equation similar to Eq.1) has decreased from
359 18% in 1980s to an extremely low level (<0.5%) since 2004. Accordingly, the observed Pb
360 isotope signals provided clear evidence that the local anthropogenicPb contamination has always
361 been greatly dominant, even during the period of maximum leaded gasoline use. The
362 extremely high Pb content (up to $28.8 \mu\text{g g}^{-1}$) and anthropogenicPb isotopic composition (Fig. 3)
363 in wild mussels in the most polluted area highlights the strong exposure and response of filter
364 feeders to sediment contamination. However, the exact pathway between contaminated
365 sediments and mussels did not become obvious, considering the various mechanisms
366 controlling metal absorption by mussels and other bivalves, which can involve (i) direct
367 assimilation of dissolved metals^{9,44,45}, (ii) ingestion of metal-contaminated phytoplankton⁴⁶,
368 (iii) ingestion of contaminated particles (e.g. sediments)⁴⁷ or (iv) mixed mechanisms⁴⁸⁻⁵⁰.

369 The two mapping campaigns provided a view on the spatial distribution of dissolved Pb levels
370 in surface water of the Toulon Bay. The dissolved Pb concentrations measured in Winter 2014
371 were up to 29 times greater than those in unpolluted Mediterranean waters ($\sim 0.085 \text{ nM}^{51}$) and
372 confirmed previous observations^{25,52} showing that Toulon Bay water is strongly contaminated
373 by Pb (Fig. 5A). The highest Pb concentrations in surface water occurred in harbour/marina
374 areas (Fig. 5A), coinciding with higher Pb contents in sediments (Fig. 1). Results obtained in
375 summer 2013 (data not shown) displayed similar trends. The total vs. dissolved Pb

376 concentrations (slope = 1.97, $r^2 = 0.86$, $n = 80$, Fig. S6) showed an equi-repartition of this
377 trace metal between dissolved and particulate fractions (K_d value $\sim 5 \times 10^5$ L kg^{-1} , considering
378 an average SPM concentration of 2 mg L^{-1}), confirming its high affinity for particles^{53,54}. The
379 6 surface seawater samples collected at various places of the Toulon Bay (Fig. 1) to assess
380 seawater Pb isotopic signature covered a representative range of concentrations (0.2-1.8 nM).
381 Their corresponding Pb isotopic signature ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.166 \pm 0.002$ and $^{206}\text{Pb}/^{208}\text{Pb} \sim$
382 0.475 ± 0.001 , $n = 6$) appeared to fall exactly in that of anthropogenic Pb (Fig. 4B). Even if these
383 results did not enable the preferred mussel pathway of Pb assimilation from dissolved and
384 particulate fractions to be distinguished, common spatial distribution and isotope signals
385 strongly support the existence of a direct link between the Pb contamination of Toulon Bay's
386 water column and contaminated sediments, which could originate both from trace metals
387 diffusive flux through the SWI^{29,55} or remobilisation during sediment resuspension⁵⁶.
388 The obtained kinetics of Pb remobilisation during simulated resuspension of different Toulon
389 Bay sediments reveal both common points and sediment-specific responses (Fig. 5B). As
390 expected, the measured physico-chemical parameters (pH, Eh, O_2 ...) remained stable all along
391 the experiments (data not shown), maintaining oxic conditions, even if a slight acidification
392 was noticeable after a few days (e.g. surface sediment from stations 3B and MIS, Fig. S4).
393 Confirming previous results, Pb concentrations initially measured at each site (time of 0.01 h,
394 Fig. 5B) reflected the contamination pattern in Toulon Bay's waters as observed during the
395 mapping campaign, following a South-North gradient from 0.40 to 1.65 nM (station 15 and
396 MIS, respectively). From this initial status, resuspension of surface/suboxic sediments (0-2
397 cm layer from the 4 stations, characterized by Eh values ranging from -105 to -2 mV_{/ENH})
398 systematically induced significant Pb remobilisation, reaching maximal values after a few
399 hours of contact time, probably due to desorption processes⁵⁷. The Pb release from sediment
400 increased the initial Pb concentration by up to 5-13 fold, reaching levels as high as 9.9 nM
401 (i.e. 120 fold the level in unpolluted Mediterranean waters⁵¹), although the maximal
402 proportion of mobilized Pb from the solid fraction remained low (0.15 to 0.5%, $n = 6$). Deep
403 sediment (20-22 cm) from station 3B showed quasi-similar behaviour as surface sediments
404 from the same site (Fig. 5B). As previously discussed (section 3.1.), sediments from this area
405 were submitted to reworking and partial mixing, resulting in a burying of the contamination
406 (Fig. S2), and modifying the diagenesis processes, with a sulfidic layer appearing as deep as -

407 30 cm¹⁷. For all these sediments, the rapid Pb remobilisation was systematically followed by
408 Pb removal after days to weeks of contact time (Fig. 5B), a behaviour already observed
409 elsewhere¹³. Contrarily, resuspension of the deep/anoxic sediment layer (30-32 cm) from
410 station MIS induced a first rapid removal until 1h of contact time, followed by a continuous
411 remobilisation reaching the highest recorded Pb level (22 nM). This succession of Pb
412 remobilisation/removal steps reflects adsorption/desorption and/or co-precipitation/dissolution
413 processes at different scales, which can partly be explained by the variations of the other
414 parameters. For example, the Fig. S4 represents the temporal variations of pH and dissolved
415 Pb, Fe and Mn concentrations for the surface sediment (0-2 cm) slurries from stations 3B and
416 MIS. The expected, nearly immediate increase in dissolved metal concentrations due to
417 porewater dilution was calculated from measured concentrations in porewater^{17,28} and from
418 sediment porosity. The experimental data support important porewater contribution to the
419 measured dissolved Fe and Mn concentrations in the batch experiment, as suboxic porewater
420 was enriched in Fe^{II} and Mn^{II}, due to reactive Fe and Mn (oxy)hydroxides reduction by early
421 diagenesis¹⁷. If Fe is rapidly scavenged (~15 min) due to known fast kinetics of reoxydation
422 and precipitation in oxygenated seawater, Mn remained in dissolved phase for a longer time
423 (~7 h) before being removed following the same processes. Such differences in Fe and Mn
424 precipitation kinetics have already been observed in previous studies^{58,59}. Concerning Pb
425 remobilisation kinetics, the rapid release within 5 min, noticeable in most of the performed
426 experiments (Fig. 5B and A.3), was not due to porewater contribution but could be attributed
427 to a fast solid/liquid repartitioning, describable by a K_d partition coefficient⁶⁰. This weakly-
428 bound Pb fraction was assumed as the "labile" fraction whose release mechanism was related
429 to cation exchange reactions⁶¹. Then, Pb appeared to be continuously released, probably from
430 a more strongly particle-bound fraction⁶¹ until ~7 h, after which Mn oxides started to
431 precipitate. As Mn oxides are known to be efficient Pb carrying phases in sediments⁶², Pb
432 adsorption onto freshly precipitated Mn oxyhydroxides could explain the systematic Pb
433 removal⁶³ observed for the longest contact times with all the studied surface sediments (Fig.
434 5B). The noticeable discrepancy observed for the deep/anoxic sediments from station MIS
435 (Fig. 5B) could be attributed to the involvement of sulfidic phases, acting as binding phases
436 prior to be reoxydized within minutes to hours^{61,62}. This scenario suggests that Pb

437 precipitated and definitively fixed as diagenetic sulphides in anoxic sediments, could be
438 partially released into the oxic water column within hours or days of resuspension.

439 The Pb isotopic composition of seawater during MIS sediment resuspension experiments
440 corresponded to that of sedimentary Pb (Fig. 5B). This observation supports mobility of the
441 sedimentary ^{anthropogenic}Pb stock being desorbed from particles and the consecutive impact on
442 the ecosystem quality.

443 Therefore, any scenario inducing resuspension of Pb contaminated surface sediments will lead
444 to a non-negligible Pb remobilisation, resulting in both increased particulate and dissolved Pb
445 concentrations in the water column, which can further be transferred to and bio-accumulated
446 by filter feeder organisms such as mussels. In coastal systems such as the Toulon Bay, which
447 are constantly submitted to various forcing and sediment perturbation (e.g. storm/waves, tidal
448 current, bioturbation, ship traffic/trawling, dredging, harbour infrastructure building, ...), such
449 processes are more than probable to play an important role on surface water quality, although
450 it remains difficult to quantify their respective contributions. It is, however, evident from
451 sediment contamination mapping and hydrodynamic studies that resuspension processes
452 actually participate to the export of contaminants to the open sea ^{20,23}, probably inducing
453 noticeable toxicological/ecological impacts on various marine organisms ⁶⁴⁻⁶⁶.

454 The obtained results on Pb distribution in sediments, water and stable Pb isotopic signatures
455 clearly evidenced the impact of historical pollution and the dispersion of this pollutant stock
456 over the whole bay, together with other accompanying pollutants (e.g. Hg). A specific
457 ^{anthropogenic}Pb isotopic signature in the Toulon Bay was revealed (²⁰⁶Pb/²⁰⁷Pb ~ 1.166±0.003
458 and ²⁰⁶Pb/²⁰⁸Pb ~ 0.475±0.001), probably resulting from the multiplicity of Pb sources used
459 by Navy in the last century. Different factors, either natural (storms, waves, bioturbation) or
460 anthropogenic (ship movement, dredging) most probably explain Pb export (i) to the more
461 distal surface sediments of the bay and also (ii) to other compartments such as water column
462 through remobilisation (as illustrated by sediment resuspension experiments) and biota. The
463 combination of the spatial distribution of Pb concentrations in surface water and sediments of
464 the Toulon Bay, isotope signatures in water, sediment and mussels and our observations on Pb
465 release during sediment resuspension clearly supports Pb transfer between these
466 compartments. This study confirmed the vulnerability of the Toulon Bay ecosystems in
467 particular, and those of many coastal areas worldwide, where Pb contamination may affect

468 both ecosystem and Human health, given that Toulon Bay mussels are still consumed,
469 although their Pb levels equal or exceed European safety thresholds.

470

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483

484 SUPPORTING INFORMATION

485

486 Table S1: The Pb stable isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$) of different Pb sources

487 Figure S1: Photos of coal block and bulk Pb plate from the "Magenta" French Navy battleship

488 Figure S2: Pb stable isotope ratios and Pb content depth profiles at stations 3B and 23

489 Figure S3: $^{206}\text{Pb}/^{208}\text{Pb}$ ratio as a function of $^{206}\text{Pb}/^{207}\text{Pb}$ for various Pb sources

490 Figure S4: Time variation of pH, dissolved Pb, Fe and Mn concentrations released during
491 sediment resuspension

492 Figure S5: Contribution of anthropogenic Pb source of Toulon Bay's surface sediments

493 Figure S6: Relationship observed between the total and dissolved Pb at 40 stations around
494 Toulon bay

495 This information is available free of charge via the Internet at <http://pubs.acs.org/>

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TABLE

Table 1: Summary of Pb contents, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios in semi-total extracts expressed in average (number of sample) and the variation range (min-max) in surface and cored sediments. The specific Pb isotope compositions of lead issued from anthropogenic, natural and gasoline sources are presented as $^{\text{anthropogenic}}\text{Pb}$, $^{\text{natural}}\text{Pb}$ and $^{\text{gasoline}}\text{Pb}$. The $^{\text{natural}}\text{Pb}$ and $^{\text{gasoline}}\text{Pb}$ signatures are gathered from literature, see Table S1 for detailed values and citations.

		Pb content ($\mu\text{g g}^{-1}$)	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{208}\text{Pb}$
Surface sediments	Average	107 (n = 54)	1.168 (n = 34)	0.475 (n = 34)
	Range (min-max)	15-467	1.156-1.180	0.474-0.478
St. MIS	Average	907 (n = 28)	1.164 (n = 7)	0.475 (n = 7)
	Range (min-max)	377-1310	1.156-1.172	0.474-0.476
St. 3B	Average	201 (n = 23)	1.166 (n = 7)	0.475 (n = 7)
	Range (min-max)	146-265	1.162-1.1700	0.474-0.476
St. 12	Average	179 (n = 29)	1.174 (n = 29)	0.476 (n = 29)
	Range (min-max)	70-423	1.165-1.180	0.475-0.479
St. 15	Average	50 (n = 28)	1.179 (n = 14)	0.478 (n = 14)
	Range (min-max)	14-118	1.164-1.197	0.475-0.482
St. 23	Average	41.9 (n = 20)	1.175 (n = 7)	0.476 (n = 7)
	Range (min-max)	15-78	1.165-1.189	0.473-0.478
$^{\text{anthropogenic}}\text{Pb}$	n = 14		1.165±0.004	0.475±0.001
$^{\text{natural}}\text{Pb}$	n = 16		1.195±0.014	0.483±0.003
$^{\text{gasoline}}\text{Pb}^{43}$	n = 9		1.084±0.010	0.458±0.002

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FIGURES

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Figure 1: Map of the studied site with the main anthropogenic activities and location of the 54 sampled surface (0-5 cm) sediments (open square), 5 50-cm interface sediment cores (circle) and 6 seawater samples collected for Pb isotopes analysis (open diamond). The contour plot represents the total Pb content in surface sediments.

Figure 2: Pb stable isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$, circle and square, respectively) and Pb content depth profiles (diamond) from 50-cm interface core collected at stations MIS, 12 and 15. The full and open symbols respectively represent total and HCl-extracted fractions. The filled areas with increasing grey scale indicate specific signature of industrial Pb, leaded gasoline and natural Pb, respectively. The full and dashed lines represent the variation range and the average value of the Pb isotopes ratios recorded in surface sediments ($n = 54$) of Toulon Bay, respectively.

Figure 3: Pb content in farmed mussels sampled in summer/fall and winter/spring periods (close and open triangle, respectively). The grey diamond, circle and square symbols represent wild mussels sampled in 2014 at stations MIS, 12 and Milhaud dock, respectively. The filled areas represent guideline levels in mussels from American coast¹¹. The dotted line represents the range of Pb content in Mediterranean mussels^{24,39}. $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (grey symbols) in mussels is compared to the average and range of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio variation in surface sediments (full and dashed lines). The calculated contribution of $f^{\text{anthropogenic}}$ Pb signature in mussel is shown (red line).

Figure 4: $^{206}\text{Pb}/^{208}\text{Pb}$ ratio as a function $^{206}\text{Pb}/^{207}\text{Pb}$ ratio for (A) Toulon Bay sediments (circles and squares illustrating interface sediment cores and surface sediments, respectively), tributaries particles (cross, symbol size as a function of Pb total content), "Anzin" coal block (star) and "Magenta" French Navy battleship's Pb plate (hexagone), (B) seawater (blue triangles), mussels (reverse triangles, grey square, circle and diamond) samples in comparison to the range of variation of various Pb sources from literature (Table S1 and Figure S2).

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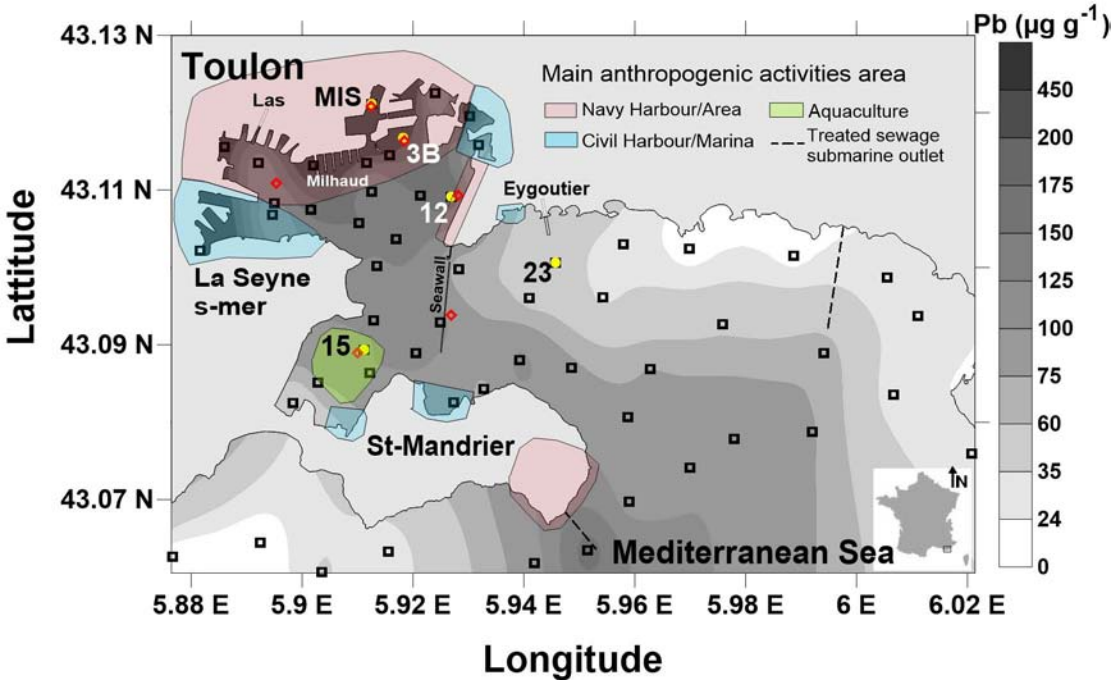
742 **Figure 5:** (A) Dissolved Pb concentration in surface seawater at 40 stations of Toulon Bay
743 (February 2014). A contour map was generated by kriging method and the scale layers
744 represent the statistical distribution (centiles) of the concentration range. (B) Dissolved Pb
745 concentration (and $^{206}\text{Pb}/^{207}\text{Pb}$ ratio) remobilized during sediments resuspension simulation
746 experiments using sediments from stations MIS, 3B, 12 and 15 as a function of time. Open
747 and close symbols represent surface and deep sediments, respectively (see text for more
748 details).

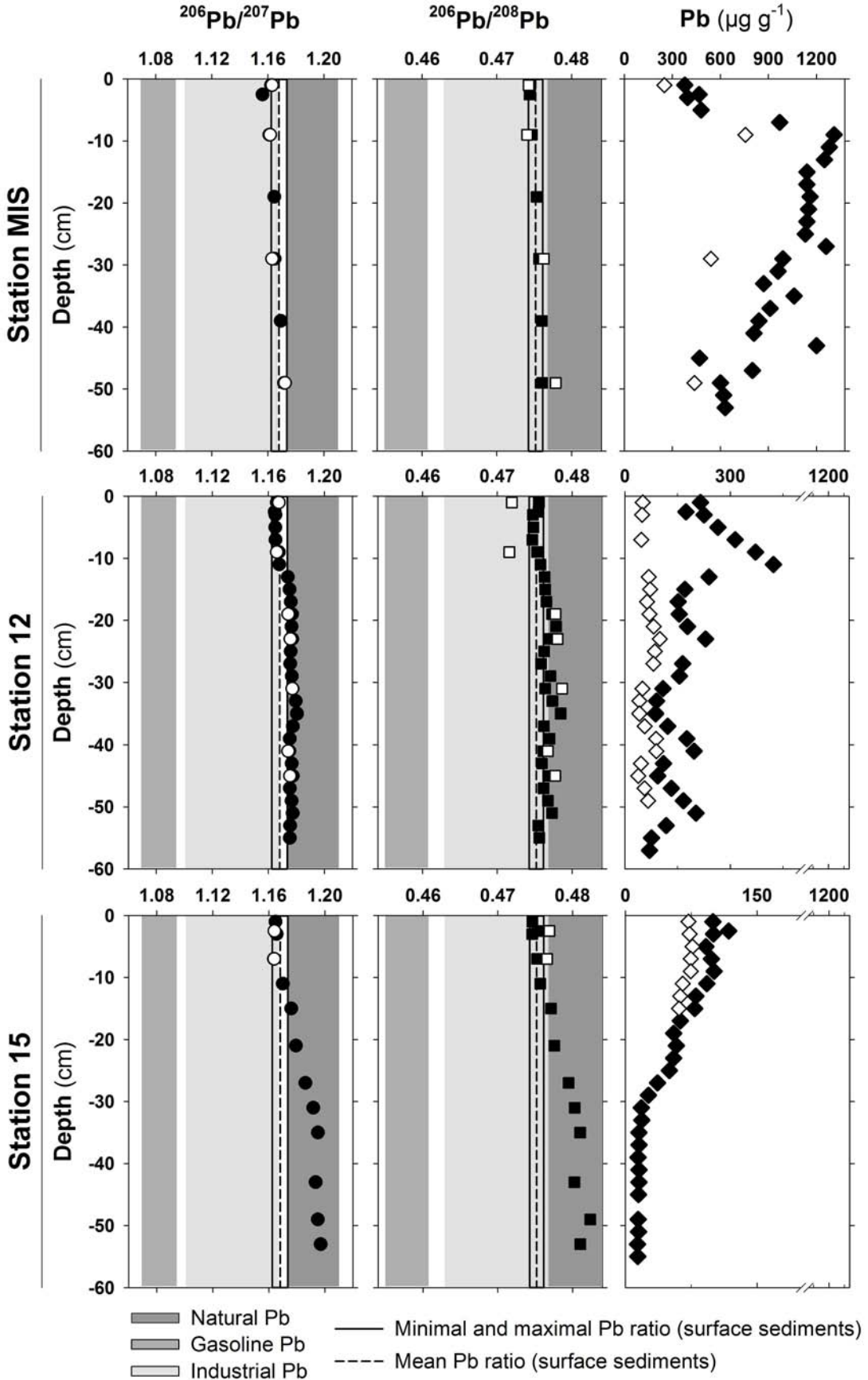
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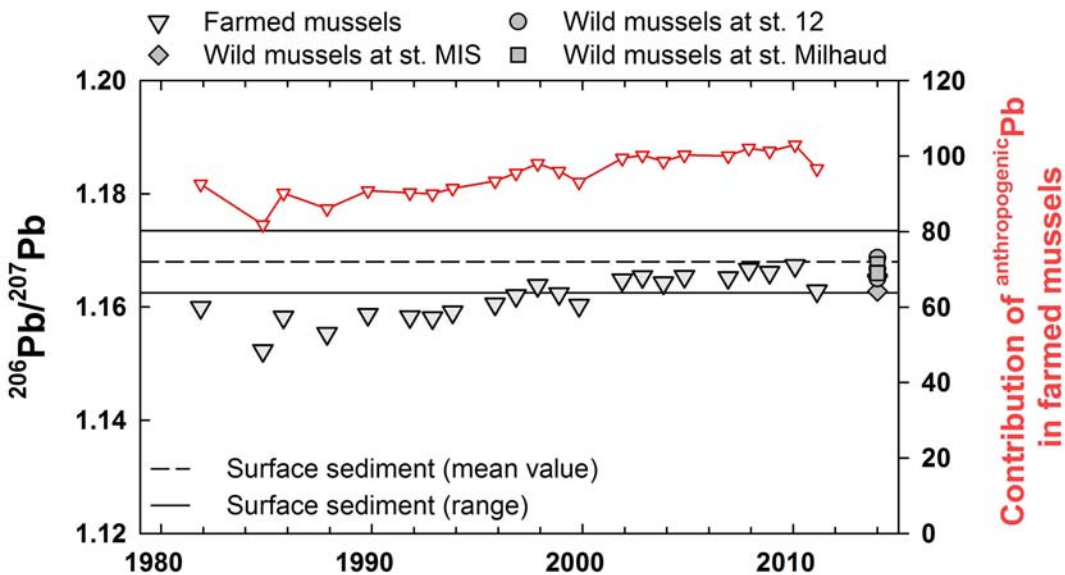
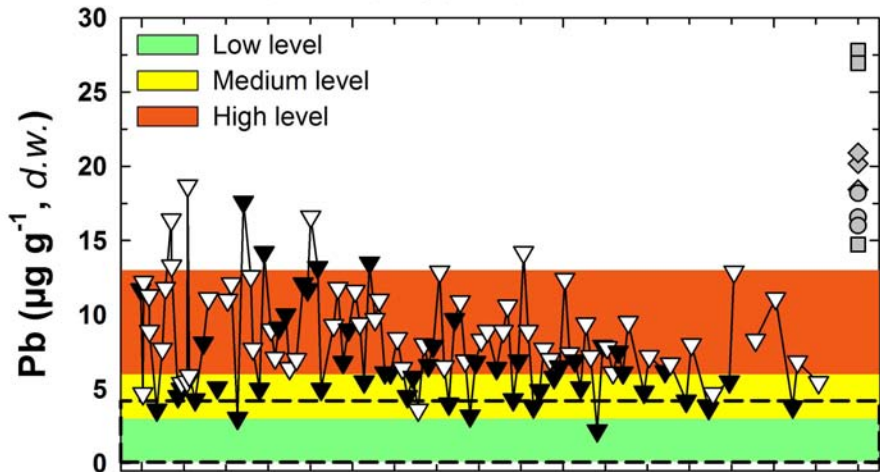
Table 1:

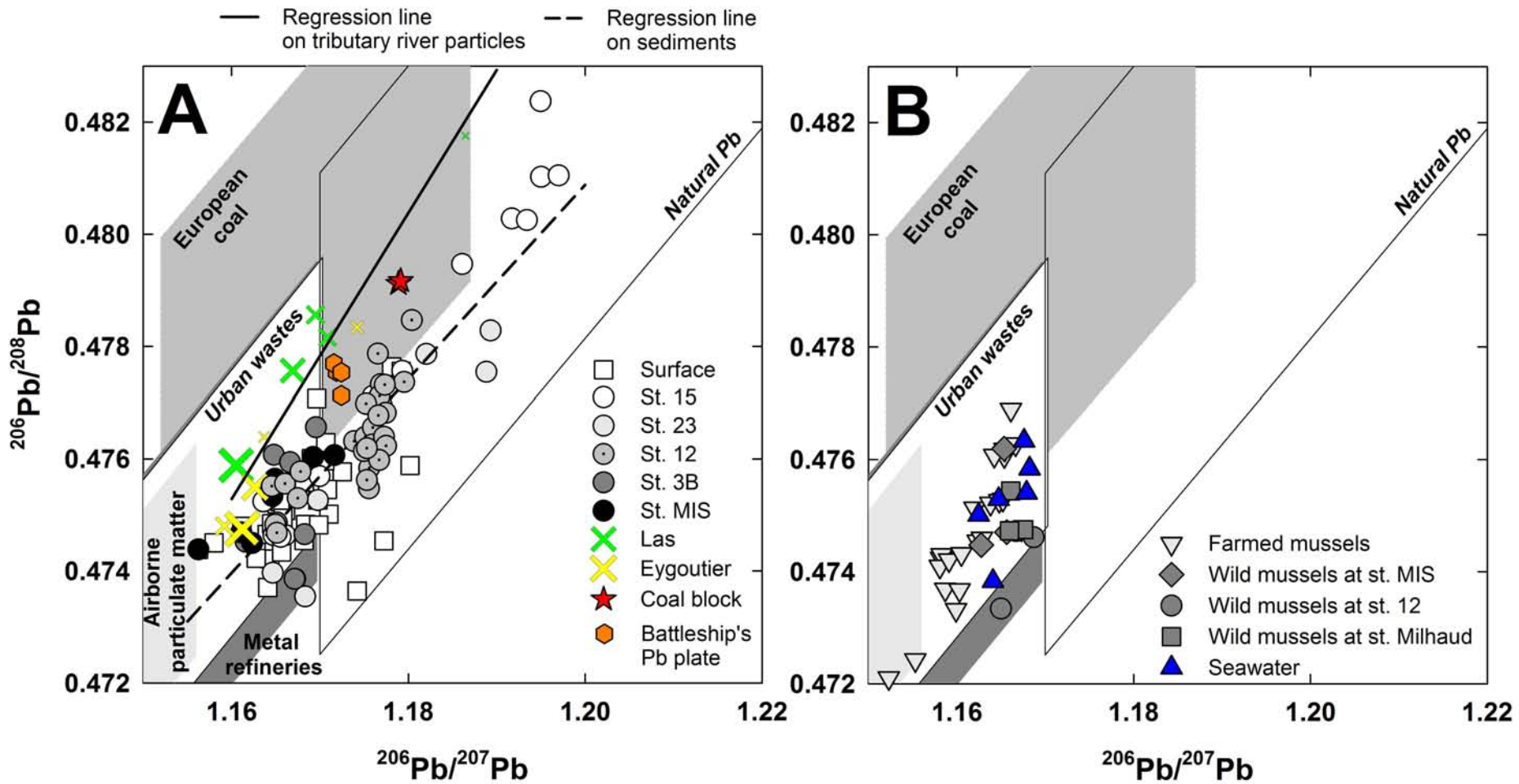
		Pb content ($\mu\text{g g}^{-1}$)	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{208}\text{Pb}$
Surface sediments	Average (sample number)	107 (34)	1.168 (34)	0.475 (34)
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	Range (min-max)	377-1310	1.156-1.172	0.474-0.476
St. 3B	Average	201 (23)	1.166 (7)	0.475 (7)
	Range (min-max)	146-265	1.162-1.1700	0.474-0.476
St. 12	Average	179 (29)	1.174 (29)	0.476 (29)
	Range (min-max)	70-423	1.165-1.180	0.475-0.479
St. 15	Average	50 (28)	1.179 (14)	0.478 (14)
	Range (min-max)	14-118	1.164-1.197	0.475-0.482
St. 23	Average	41.9 (20)	1.175 (7)	0.476 (7)
	Range (min-max)	15-78	1.165-1.189	0.473-0.478
anthropogenic Pb	n = 14		1.165 \pm 0.004	0.475 \pm 0.001
natural Pb	n = 16		1.195 \pm 0.014	0.483 \pm 0.003
gasoline Pb ⁴³	n = 9		1.084 \pm 0.010	0.458 \pm 0.002

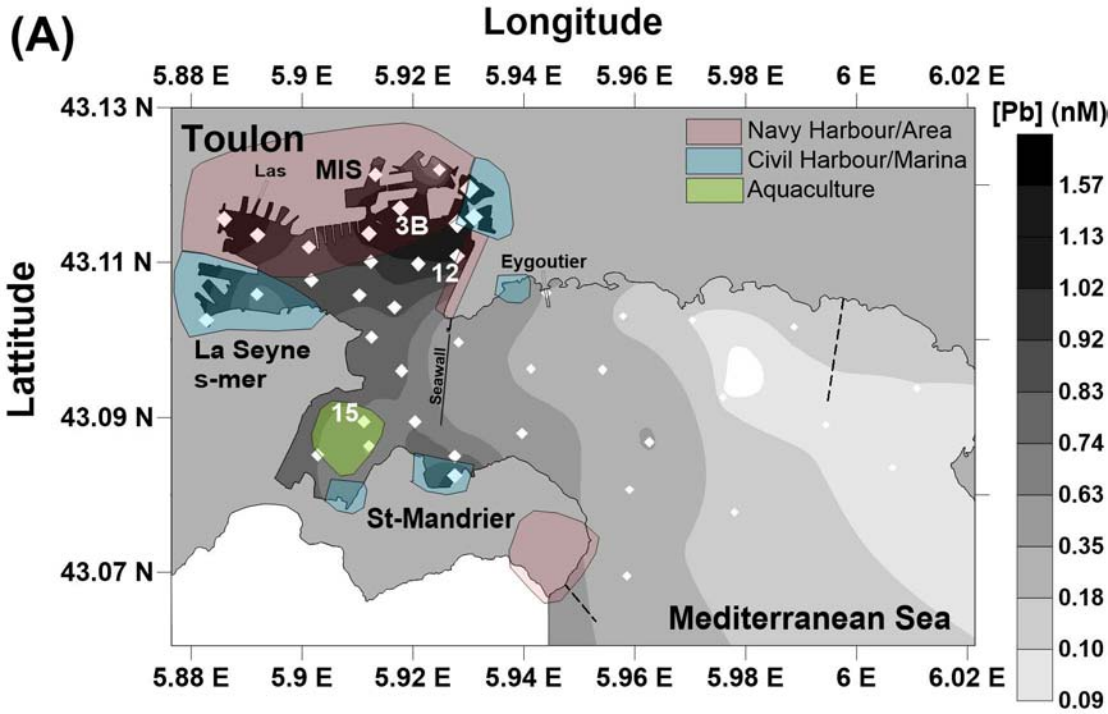


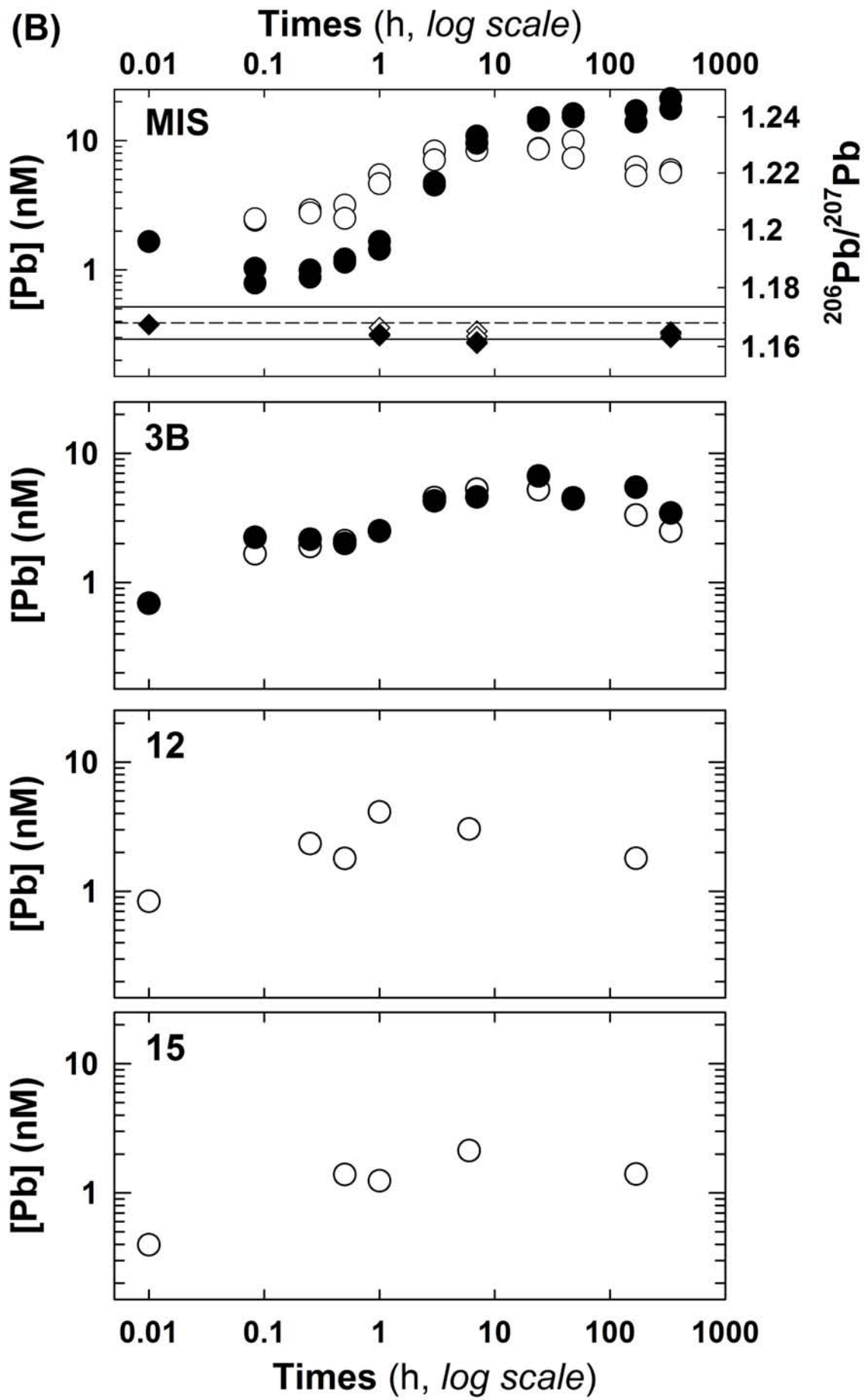


- Pb content range in Mediterranean mussels
- ▼ Farmed mussels (Summer/fall period)
- ▽ Farmed mussels (Winter/spring period)
- ◇ Wild mussels at st. MIS
- Wild mussels at st. 12
- Wild mussels at st. Milhaud









SUPPORTING INFORMATION

Manuscript Title: Evidencing the impact of coastal contaminated sediments on mussels through Pb stable isotopes composition

Authors Duc Huy Dang, Jörg Schäfer, Christophe Brach-Papa, Véronique Lenoble, Gaël Durrieu, Lionel Dutruch, Jean-Francois Chiffolleau, Jean-Louis Gonzalez, Gérard Blanc, Jean-Ulrich Mullot, Stéphane Mounier, Cédric Garnier*

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Number of pages: 11

Table S1: The Pb stable isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$) of different Pb sources

		$^{206}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{208}\text{Pb}$	Sample type	Reference
Natural		1.1730	0.4780	Sediment pre 1870	1
		1.1770	0.4810	Sediment pre 1870	1
		1.1970	0.4840	Pre/early industrial sediments	2
		1.2100	0.4864	Inland whole soil	3
		1.1900	0.4840	Emission pre1992	3
		1.2002	0.4833	Miocene rock and soil	4
		1.1783	0.4768	Pelagic sediments	5
		1.2028	0.4869	Miocene carbonate	6
		1.2046	0.4868	Palaeocene carbonate	6
		1.2019	0.4856	Soil carbonate	6
		1.2219	0.4872	Miocene silicate	6
		1.2043	0.4840	Palaeocene silicate	6
		1.2034	0.4848	Soil silicate.	6
		Mean	1.1947	0.4832	
	Minimal	1.1730	0.4768		
	Maximal	1.2219	0.4872		
Industrial emission		1.1158	0.4665	Airbone Particulate matter	2
		1.1219	0.4680	Airbone Particulate matter	2
		1.1094	0.4647	Airbone Particulate matter	2
		1.1091	0.4649	Airbone Particulate matter	2
		1.1123	0.4653	Airbone Particulate matter	2
		1.1124	0.4658	Airbone Particulate matter	2
		1.1212	0.4676	Airbone Particulate matter	2
		1.1219	0.4680	Airbone Particulate matter	2
		1.1211	0.4681	Airbone Particulate matter	2
		1.1159	0.4668	Airbone Particulate matter	2
		1.1181	0.4672	Airbone Particulate matter	2
		1.1069	0.4643	Airbone Particulate matter	2
		1.1008	0.4629	Airbone Particulate matter	2
		1.1221	0.4681	Airbone Particulate matter	2
		1.1342	0.4709	Airbone Particulate matter	2
		1.1319	0.4706	Airbone Particulate matter	2
		1.1042	0.4638	Airbone Particulate matter	2
		1.1453	0.4721	Airbone Particulate matter	2
		1.1150	0.4662	Emission post1992	3
		1.1530	0.4744	Emission Cairo	3
	1.1230	0.4671	Emission Turkey	3	
	Mean	1.1196	0.4673		
	Minimal	1.1008	0.4629		
	Maximal	1.1530	0.4744		
Metal refineries		1.1549	0.4736	impacted soil-Pb, Zn refinery	7
		1.1576	0.4738	impacted soil-Pb, Zn refinery	7
		1.1569	0.4737	impacted soil-Pb, Zn refinery	7
		1.1563	0.4735	impacted soil-Pb, Zn refinery	7
		1.1565	0.4737	impacted soil-Pb, Zn refinery	7
		1.1579	0.4741	impacted soil-Pb, Zn refinery	7
		1.1565	0.4737	impacted soil-Pb, Zn refinery	7
		1.1574	0.4739	impacted soil-Pb, Zn refinery	7
		1.1583	0.4743	impacted soil-Pb, Zn refinery	7
		1.1575	0.4741	impacted soil-Pb, Zn refinery	7
		1.1584	0.4743	impacted soil-Pb, Zn refinery	7
		1.1667	0.4767	impacted soil-Pb, Zn refinery	7
		1.1633	0.4755	impacted soil-Pb, Zn refinery	7
		1.1040	0.4638	Slag-Pb, Zn refinery	7
	1.1305	0.4712	dust-Pb, Zn refinery	7	

		1.1273	0.4706	dust-Pb, Zn refinery	7	
		1.1176	0.4672	Fe-Mn metallurgy plant	8	
		1.1064	0.4635	Fe-Mn metallurgy plant	8	
		1.1099	0.4643	Fe-Mn metallurgy plant	8	
		1.1336	0.4703	Lead smelter	8	
		1.1323	0.4700	Lead smelter	8	
		Mean	1.1438	0.4717		
		Minimal	1.1040	0.4635		
Maximal	1.1667	0.4767				
Gasoline		1.0693	0.4550		2	
		1.0806	0.4580		2	
		1.0942	0.4604		2	
		1.0942	0.4607		2	
		1.0753	0.4565		2	
		1.0878	0.4592		2	
		1.0736	0.4563		2	
		1.0856	0.4588		2	
		1.0943	0.4602		2	
		Mean	1.0839	0.4584		
Minimal	1.0693	0.4550				
Maximal	1.0943	0.4607				
European coal		1.1840	0.4799		9	
		1.1809	0.4786		10	
		1.1675	0.4778		11	
		1.1700	0.4776		12	
		1.1550	0.4779		13	
		1.1800	0.4830		14	
		1.1740	0.4820		14	
		1.1810	0.4820		14	
		1.1710	0.4800		14	
		1.1710	0.4790		14	
		1.1770	0.4820		14	
		1.1820	0.4830		14	
			1.1800	0.4830		14
			1.1840	0.4830		14
			1.1820	0.4840		14
Mean	1.1760	0.4808				
Minimal	1.1550	0.4776				
Maximal	1.1840	0.4840				
Steel metallurgy plant		1.2226	0.4991		8	
		1.2064	0.4953		8	
		1.1944	0.4922		8	
		1.1829	0.4886		8	
		1.1786	0.4869		8	
		1.1897	0.4904		8	
		Mean	1.1958	0.4921		
		Minimal	1.1786	0.4869		
Maximal	1.2226	0.4991				
Urban wastes		1.1540	0.4742	French southern cities/villages	6	
		1.1620	0.4755	French southern cities/villages	6	
		1.1552	0.4772	French southern cities/villages	6	
		1.1543	0.4734	French southern cities/villages	6	
		1.1673	0.4766	French southern cities/villages	6	
		1.1600	0.4741	French southern cities/villages	4	
		1.1609	0.4738	French southern cities/villages	4	
		1.1600	0.4743	French southern cities/villages	4	
		1.1613	0.4752	French southern cities/villages	4	
		1.1547	0.4741	French southern cities/villages	4	

		1.1585	0.4737	French southern cities/villages	4
		1.1476	0.4722	French southern cities/villages	4
		1.1494	0.4724	French southern cities/villages	4
		1.1479	0.4734	French southern cities/villages	4
		1.1578	0.4741	French southern cities/villages	4
		1.1577	0.4745	French southern cities/villages	4
	Mean	1.1587	0.4743		
	Minimal	1.1476	0.4722		
	Maximal	1.1673	0.4772		

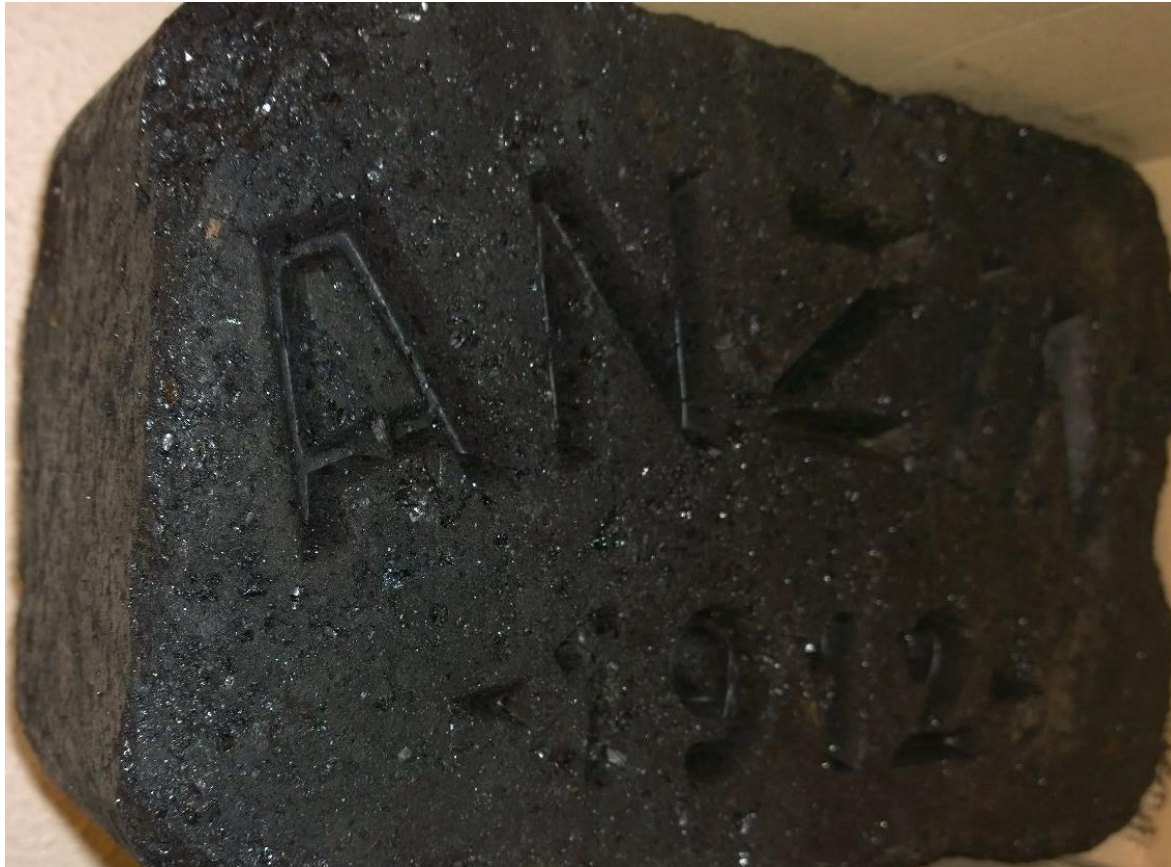


Figure S1: (Left) Coal block found at station 3B during dredging operations (2014) where “Anzin 1912” was inscribed, illustrating its origin (Anzin, North of France) and period. Indeed, blocks of coal were stored and used by the French Navy for its fleets. Up to 400 tons of such blocks were discovered in the area, as it was used as a coal loading dock for French Navy fleet. (Right) Lead plate from the "Magenta" French Navy battleship, sunk in 1876 in the entrance of Toulon Navy harbour.

Figure S2: Pb stable isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$, circle and square, respectively) and Pb content depth profiles (diamond) from 50-cm interface core collected at stations 3B and 23. The full and open symbols respectively represent total and HCl-extracted fractions. The filled areas with increasing grey scale indicate specific signature of industrial Pb, leaded gasoline and natural Pb, respectively. The full and dashed lines represent the variation range and the average value of the Pb isotopes ratios recorded in surface sediments ($n = 54$) of Toulon bay, respectively.

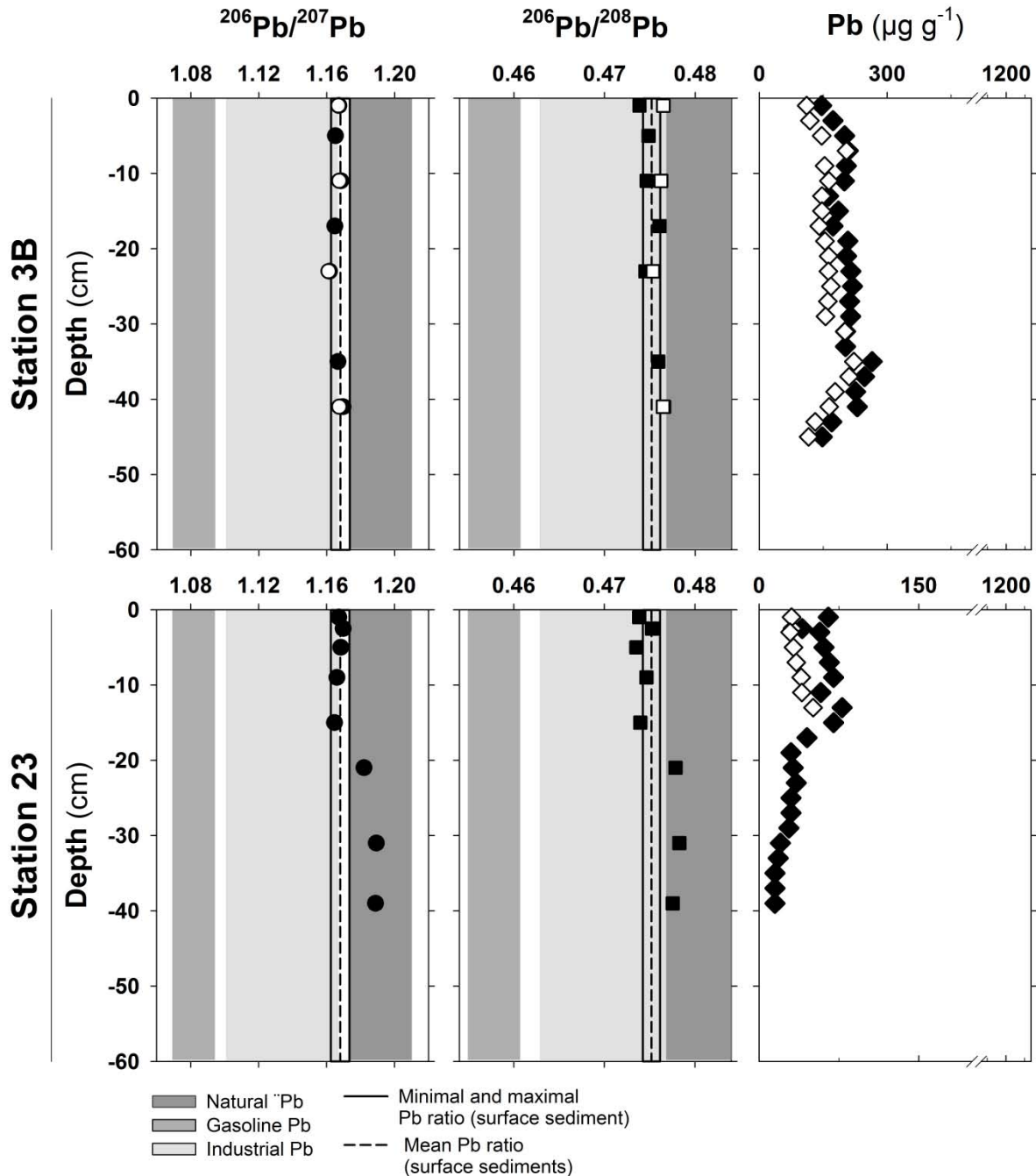


Figure S3: $^{206}\text{Pb}/^{208}\text{Pb}$ ratio as a function of $^{206}\text{Pb}/^{207}\text{Pb}$ for various Pb sources observed in the environment (Table A.1). Only the lines limiting the variation of Pb sources are shown in Figure 4 in comparison to samples from Toulon Bay.

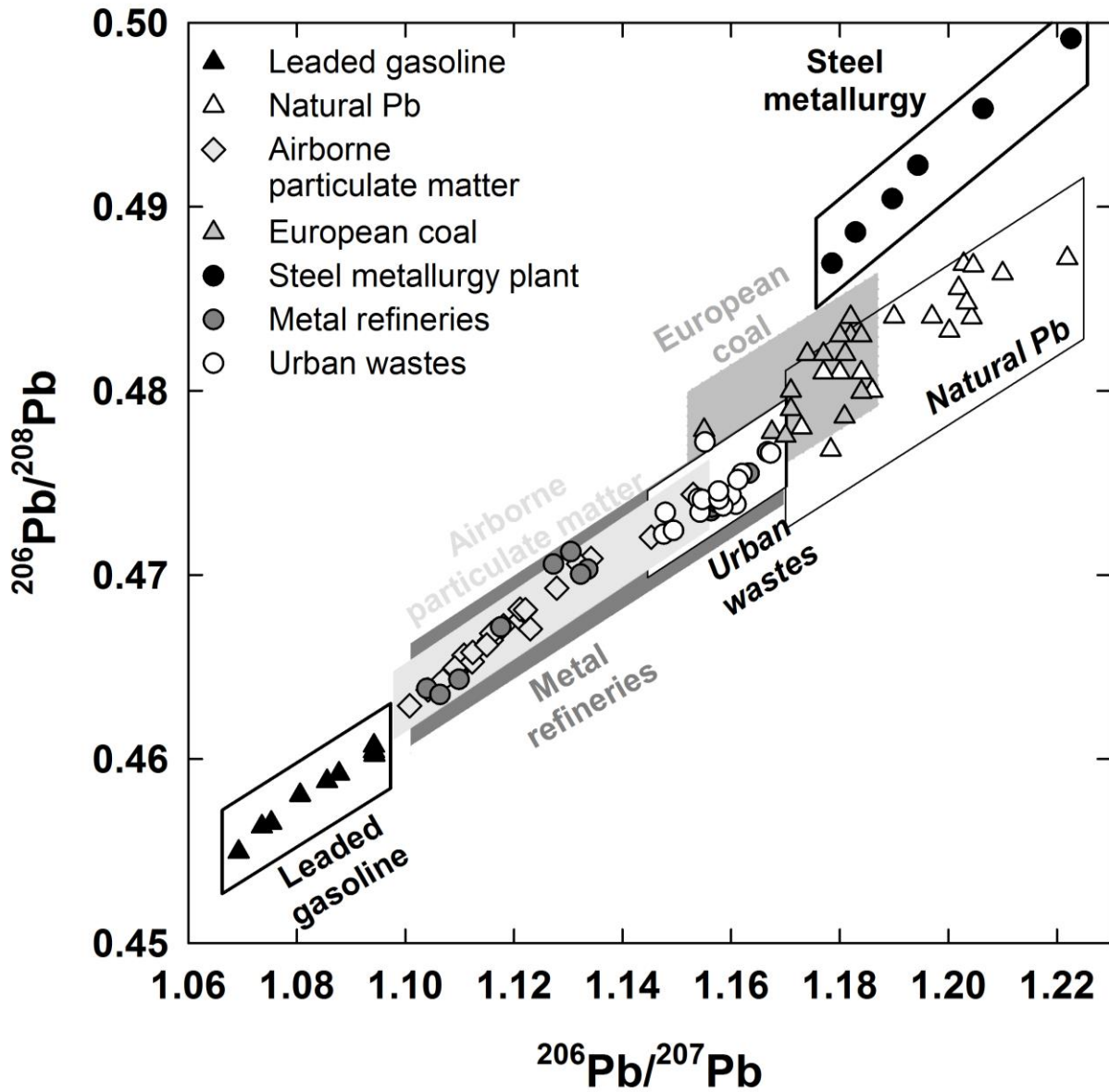


Figure S4: Time variation of pH, dissolved Pb, Fe and Mn concentrations released during sediment resuspension simulation using sediments from stations 3B and MIS (surface sediments, $\sim 1g_{dw} L^{-1}$). The open circles illustrate the initial values measured in seawater. The grey circles represent the contribution of porewater dilution and the black circles represent the measured values at 10 contact times.

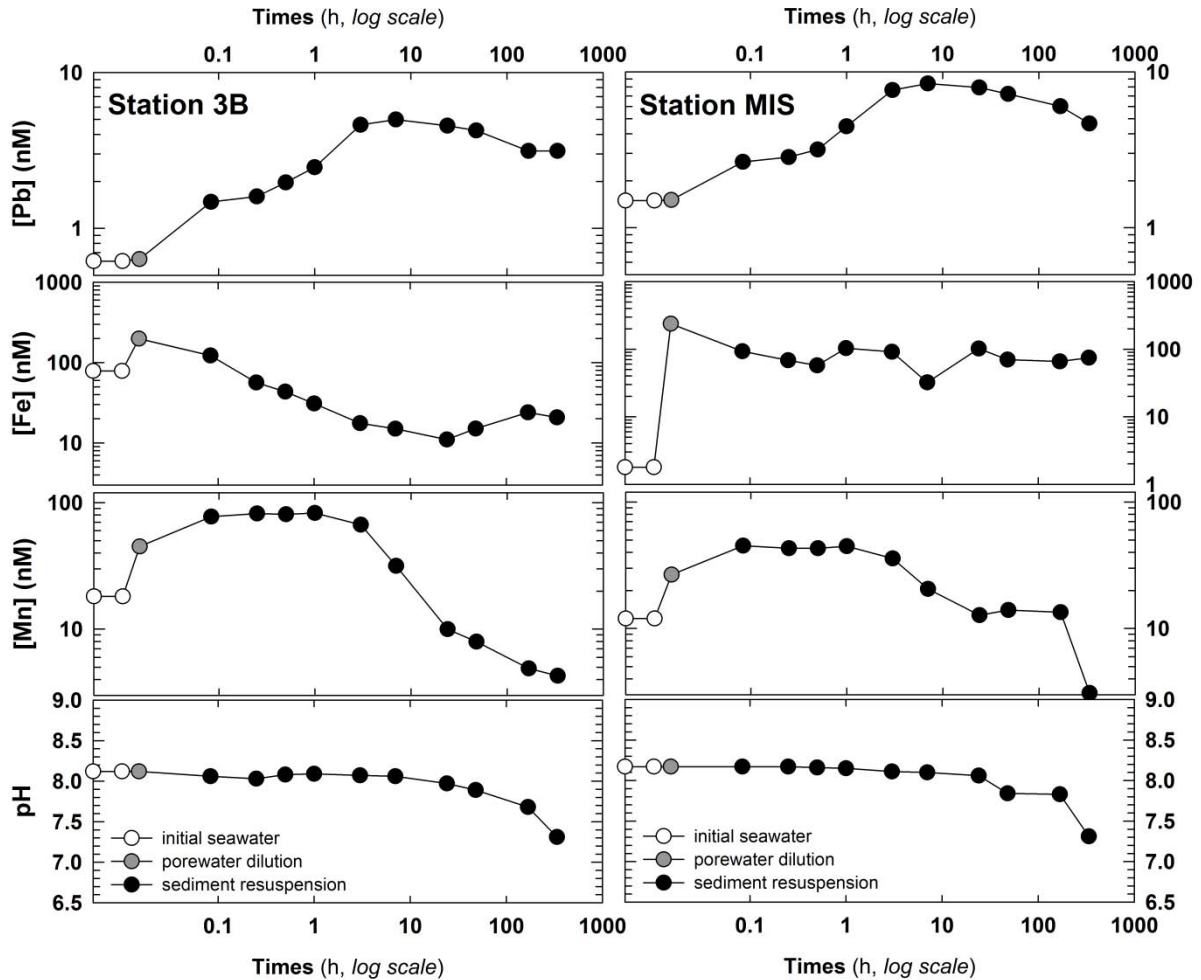


Figure S5: Assessment of the contribution of anthropogenic Pb source in Pb contamination of Toulon Bay's surface sediments (see text for more details).

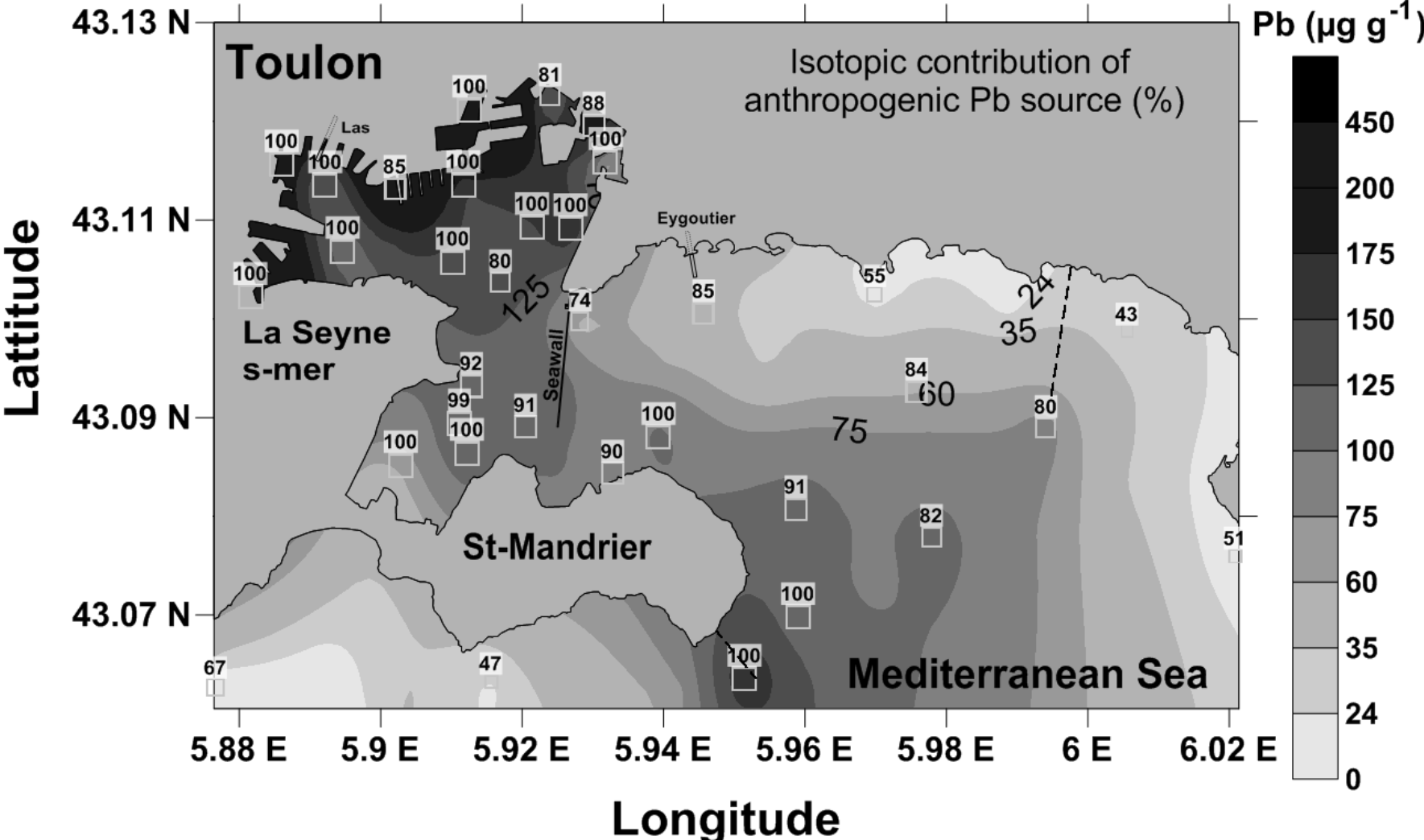
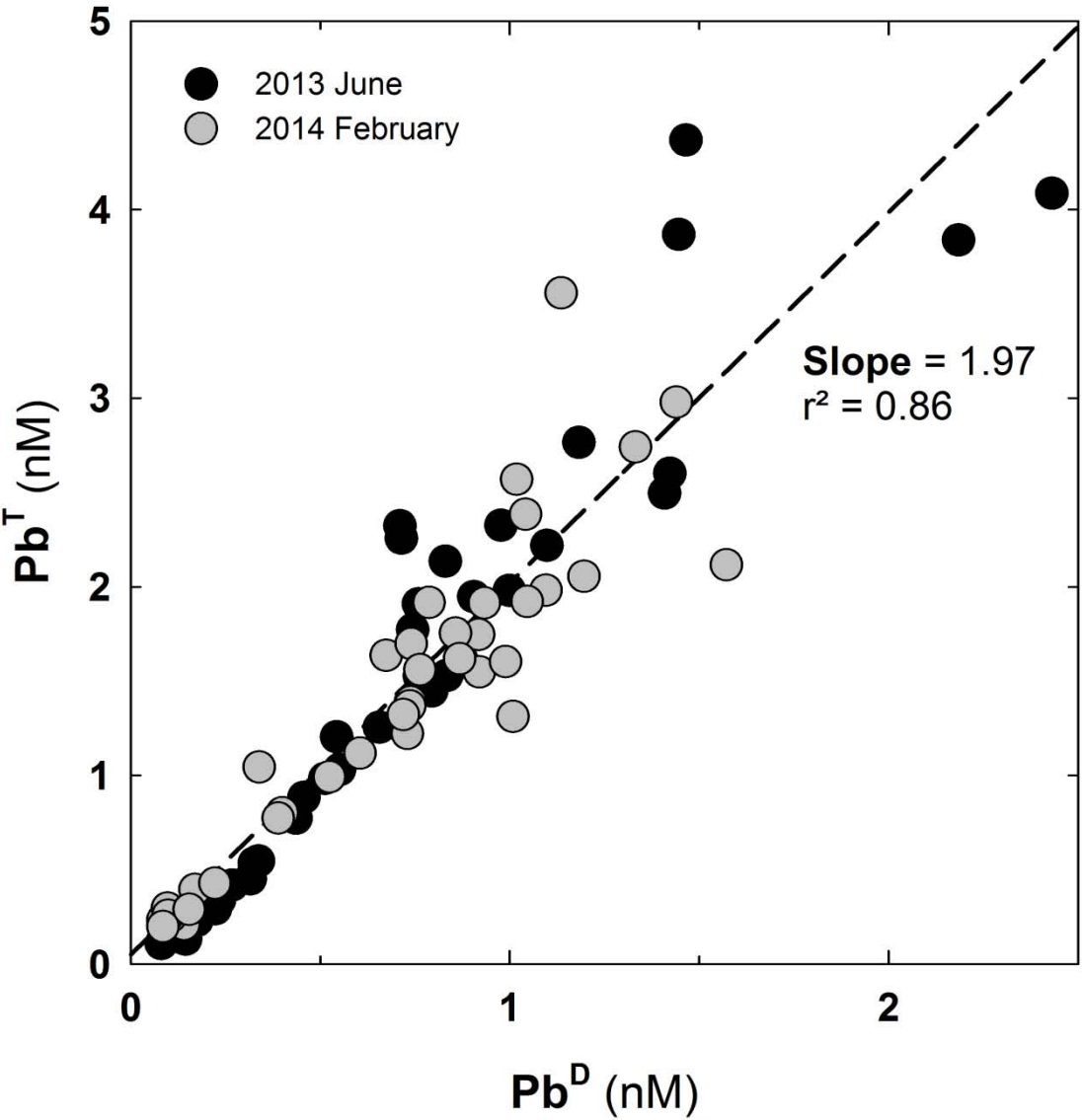


Figure S6: The relationship observed between the total and dissolved Pb at 40 stations around Toulon bay.



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