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The French Mussel Watch Program reveals the attenuation of coastal lead contamination over four decades

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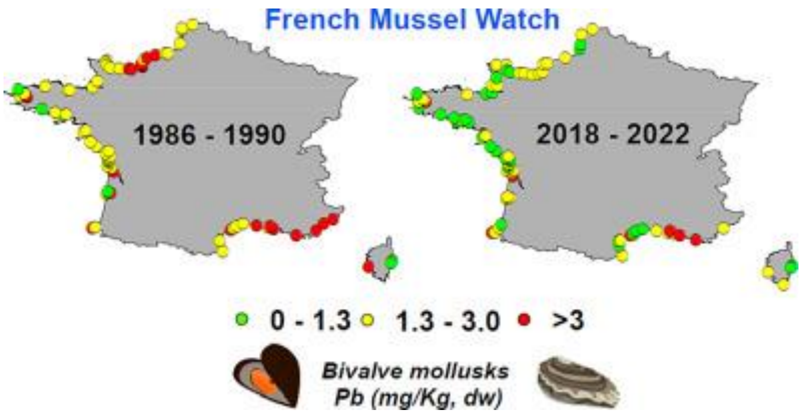
Abstract :

The mid-20th century industrial peak caused severe global lead (Pb) marine contamination. Although Europe initiated Pb emission reduction regulations in the 1980s, the short- and long-term impacts remain unclear. This study investigates the evolution of Pb contamination on the French coast through elemental and isotope analysis in oysters and mussels from the French "Mussel Watch" Program. Observations at 114 monitoring stations over four decades have shown decreasing Pb levels in these bivalve mollusks. In 1988, 95 % exceeded the background reference values; this level had dropped to 39 % by 2021. The Pb isotope ratios in bivalves from eight target sites revealed a reduction in bioaccumulated anthropogenic Pb, albeit without complete elimination. The long residence time of legacy Pb combined with inputs from diffuse urban sources likely explains the persistent presence of anthropogenic Pb on the French coast. This study endorses the importance of continuous biomonitoring to evaluate environmental regulations and policies.

Graphical abstract



Highlights

► In 1988, Pb in bivalves exceeded background reference values at 95 % of stations. ► In 2021, only 39 % of stations exceeded background reference values. ► Isotope analysis revealed reduced bioaccumulated anthropogenic Pb over four decades. ► Pb data demonstrated the effectiveness of implemented Pb regulatory measures. ► Persisting legacy Pb and diffuse urban Pb sources require continuous biomonitoring.

Keywords : Metal contamination, Pb source, Anthropogenic metal, Biomonitoring Pb, contamination

Lead (Pb) and its compounds have been used by humans for centuries in various activities, from paint production to crafting pottery and modern technological applications (e.g., in automotive batteries). However, it is now evident that its widespread use is associated with adverse health effects, such as an elevated risk of detrimental cardiovascular outcomes, a decline in renal function, and neurotoxic effects on cognitive function in children (saturnism; U.S. Environmental Protection Agency [EPA], 2006). Pb is now thought to be responsible for 1 million, or half, of the world's deaths due to chemical exposure (World Health Organization [WHO], 2021). In the 20th century, the amount of Pb that entered the surface compartments (soils, water, and sediments) increased more than tenfold due to industrial activities, including the introduction of alkyl-leaded gasoline in the 1940s (National Research Council [NRC], 2001). Public awareness of elevated Pb pollution levels reached its zenith during the 1970s, leading to regulatory measures to curb escalating emissions. First, in 1981 the European Union (EU) set a Pb limit in gasoline of 0.4 g Pb/L (Council Directive 78/611/EEC). By 1985, an EU mandate (Council Directive 85/210/EEC) required the availability of super unleaded gasoline by 1989. In 1989, France was mandated by an EU regulation to phase out leaded gasoline (von Storch et al., 2003). Unleaded gasoline adoption in France reached around 30% by 1995 (Löfgren and Hammar, 2000). The Aarhus Treaty in 1998 mandated the exclusive use of unleaded gasoline by 2005 in most European countries (Consulting Engineers and Planners [COWI] and Danish Technological Institute [DTI], 1998).

Recent studies have revealed the effectiveness of phasing out leaded gasoline in reducing global atmospheric dispersion of Pb in open waters (e.g., Hong et al., 1994; Boyle, 2001; Gallon et al., 2011; Boyle et al., 2014; Olivelli et al., 2023). However, predicting Pb levels, behavior, and trends in coastal regions presents a greater challenge owing to the interplay between numerous Pb sources and biogeochemical pathways. Moreover, the pathways related to Pb from its sources in the drainage basin to its eventual presence in coastal environments involve complex interactions within many reservoirs and variable residence times, leading to uncertain legacy Pb burdens and dynamics. Within coastal areas, both legacy and contemporary contamination may form hotspots and pose risks to the ecosystem and human health, primarily through the consumption of seafood (Pan and Wang, 2012; Wang et al., 2013; Jahan and Strezov, 2019; Suami et al., 2019; Pinzon-Bedoya et al., 2020; Dehghani et al., 2021). Substantial population and industrial activities are concentrated within the watersheds of the main fluvio-estuarine systems along the French coastline, namely the Seine, Loire, Gironde, and Rhône. These activities result in polymetallic contamination of the Atlantic (Dhivert et al., 2016;

Masson et al., 2006; Larrose et al., 2010; Grosbois et al., 2012), Mediterranean Sea (Bethoux et al., 1990; Danovaro, 2003), and English Channel (Chiffoleau et al., 1994; Dauvin, 2008) coastal zones. For example, the Gironde Estuary is emblematic of legacy metal contamination, stemming from metallurgy incidents that have been documented since 1979 (e.g., Masson et al., 2006; Larrose et al., 2010), while the Seine Estuary stands out as one of Europe's most metal-contaminated regions due to extensive industrial and urban activities (Dauvin, 2008). Smaller coastal ecosystems, such as the Arcachon Bay (Araújo et al., 2021b) and the Toulon Bay (Araújo et al., 2019), also grapple with significant anthropogenic pressure, primarily driven by tourism and naval activities, respectively. Both bays support shellfish production. Despite the prevalence of coastal metallic contamination in France, the persistence of this contamination and its transfer to the trophic chain remain inadequately understood.

It is notable that Pb exhibits hydrophobic behavior (i.e., reactive particles) in aquatic environments, thus making particulate matter the dominant reservoir of Pb in most natural waters. Bivalve mollusks uptake trace metals by filtering substantial water volumes and bioaccumulating metals in their tissues over their whole lifespan. As these organisms are sessile, exhibit a cosmopolitan distribution, and are easy to collect and process, they are regarded as excellent sentinel organisms for monitoring the bioavailability of trace metals in the so-called "Mussel Watch Programs" (MWPs; Goldberg, 1986; Boening, 1999; Gupta and Singh, 2011; Waykar and Deshmukh; 2012). Conceived to monitor the chemical contamination of coastal and estuarine environments, these programs were initially established in the United States and France, and are currently implemented worldwide (Farrington et al., 2016; Yap et al., 2021), including China (Lu et al., 2017), South Korea (Jeong et al., 2021), Canada (Cossa and Tabard; 2020), Argentina (Buzzi and Marcovecchio; 2018), and Italy (Tavaloni et al., 2021). The French MWP has operated continuously since the late 1970s, acquiring samples from a total of 260 sites over time. Data from these samples have been published, revealing the spatial distributions of silver (Ag) levels along the French coastline (Chiffoleau et al., 2005) and the temporal evolution of zinc (Zn) levels and isotopes in the Loire Estuary (Araújo et al., 2021b). Claisse (1989) assessed the spatiotemporal evolution of Pb levels from 1979 to 1988 on the French coast, but data gaps for Pb levels have remained since then.

MWPs can now benefit from isotope analysis to complement trace metal level information with source tracking, enhancing environmental pollution analysis. There has been growing attention and successful application of numerous isotope systems, including copper (Cu; Araújo et al., 2021a, 2023), Zn (Shiel et al., 2012; 2013; Araújo et al., 2017, 2021a; Jeong et al., 2021), cadmium (Cd; Shiel et al., 2012; 2013), and lithium (Li; Thibon et al., 2021), as source tracers within bivalves. In particular, Pb is part of a radiogenic isotope system that is influenced by the radioactive decay of uranium (U) and thorium (Th) isotopes. Environmental samples present distinct Pb isotopic compositions based on their initial Pb, U, and Th contents, as well as their age. Sphalerite minerals lack U within their crystal lattice, resulting in consistent stable isotope compositions over time. Consequently, anthropogenic Pb, ultimately derived from these minerals, typically exhibits low $^{206}Pb/^{207}Pb$ isotope ratios, making it "less radiogenic" compared with rocks containing U and Th. This distinction enables tracing the origins of Pb in various natural matrices (Komárek et al., 2008), including bivalve samples (Shiel et al., 2012, 2013; Jeong et al., 2023). Today, quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS) allows for fast and reliable analysis of Pb isotopes, at a lower cost than high-resolution mass spectrometers like thermal ionization mass spectrometry (TIMS) and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS), albeit with slightly lower precision. Therefore, it constitutes a preferable instrument to identify anthropogenic Pb in monitoring programs.

This study aimed to investigate historical spatiotemporal patterns of Pb contamination along the French coast. Through the comprehensive analysis of both elemental and isotope Pb levels in soft tissues from bivalve mollusks, we sought to elucidate the impact of Pb pollution on coastal ecosystems. Specifically, our objectives included integrating long-term spatiotemporal data, conducting source apportionment assessments for both natural and anthropogenic contributions, and establishing a robust framework for evaluating the evolution of coastal trace metal contamination. The ultimate goal was to gain insights into the temporal dynamics of Pb environmental regulations, discerning the timeframe required for their effects to manifest in the status of coastal ecosystems.

The French MWP is operated by Ifremer (in French: *Institut Français de Recherche pour l'Exploitation de la Mer*; in English: French Research Institute for Exploitation of the Sea) within the French chemical monitoring network (French acronym: ROCCH). The selected bivalve samples comprise oysters (*Crassostrea gigas*) and blue mussels (*Mytilus edulis* and *Mytilus galloprovincialis*), collected between January and March over the past four decades at 114 sampling stations distributed along the French coast (Fig. 1). Shellfishing typically occurs in close proximity to the coast and is subject to anthropogenic influences, posing a risk of contamination from both historical and contemporary sources. A single bivalve species was analyzed for each section of the French coastline: *C. gigas* on the Atlantic coast, *M. edulis* on the English Channel coast, and *M. galloprovincialis* on the Mediterranean coast (Fig. 1). The exception is the Loire/Chemoulin station on the Atlantic coast, which was solely analyzed for Pb isotopes and is represented by *M. edulis*. This study only considered sampling stations that had data for at least 5 years and for at least 3 years in a row. The Pb isotope ratio was determined in a subset of eight sampling stations representing emblematic French coastal sites: on the Atlantic coast, the Vilaine Estuary (Er Fosse), the Loire Estuary (Chemoulin), the Gironde Estuary (La Fosse), and the Arcachon Bay (Cap Ferret and Comprian); on the English Channel coast, the Seine Estuary (Villerville); and on the Mediterranean coast, the Rhône Estuary (Cap Couronne) and Toulon Bay (Lazaret). Published data series for the Seine Estuary and Gironde Estuary (from 1985 to 2005; Couture et al., 2010) were included and completed to more recent years (2005–2020).

Each sample in this study integrates/represents soft tissues pooled from a dozen individuals to account for individual variability. These individuals were depurated for 24 h using local, filtered seawater, frozen, thawed, ground in a blender, and subsequently lyophilized under stringent contamination control conditions to preserve their chemical integrity, according to the methodology of Claisse (1989). Only ~3-year-old individuals with similar shell length were used to reduce body size and age biases. Lyophilized sample aliquots (~200 mg) were digested in nitric acid via microwave digestion (Ethos Up, Thermo Fisher Scientific), and elemental and isotope Pb were determined by ICP-MS analysis (an Xseries or Icap instrument, Thermo Fischer Scientific). All elemental concentrations obtained from bivalve samples were above the detection limit. The Pb concentrations (dry weight) of routinely analyzed certified reference materials (CRMs)—oyster SRM 1566b-NIST®, mussel ERM-CE278k, and mussel NIST2976—deviated from the certified values by less than 5%. The Pb NIST SRM-981 standard was used to correct instrumental mass bias. Precisions of isotope ratio measurements for the unknown samples and CRMs were typically around 0.3% and 0.4%, respectively.

Fig. 2 summarizes the temporal evolution of the average Pb concentrations in bivalves from the Atlantic, English Channel, and Mediterranean coastal regions. The shaded ranges in this figure were determined by using the background assessment concentration (BAC, 1.3 mg/kg, dry weight; OSPAR, 2009) and the maximum permissible concentration (MPC; European Commission, 2006). The BAC guideline establishes the threshold value to consider concentrations near the natural background (OSPAR, 2009). The MPC indicates the maximum permissible concentration in seafood to ensure the product is safe for human consumption. The MPC dry weight reference values are 8.3, 9.1, and 7.9 mg/kg for *C. gigas*, *M. edulis*, and *M. galloprovincialis*, respectively. These values are based on the wet weight reference value of 1.5 mg/kg (European Commission, 2006), which is converted to dry weight by using the percentage of the dry weight average in soft tissue for each species (Database on the Marine Environment [DOME], 2022). In the present study, the BAC and MPC reference values are mentioned for environmental and sanitary references, respectively.

Over the last four decades, the data revealed a synchronized pattern of declining average Pb concentrations in bivalve samples from the three coastal systems. There was a substantial decrease in the concentrations during the 1990s, followed by a period of stable concentrations that has persisted into the 2000s and beyond (Fig. 2). We also noted a temporal decrease in the frequency of outlier values, indicating a convergence to more homogenous ranges of Pb concentrations. Snapshots of average Pb concentrations in the bivalve sampling stations for two intervals (1986–1990 and 2018–2022) for the Atlantic, English Channel, and Mediterranean coasts are shown in Figs. 3, 4, and 5, respectively. These maps enable better visualization of the spatiotemporal evolution of Pb data. The selected Pb concentration ranges (0–1.3, 1.3–3, and > 3 mg/kg, dry weight) encompass the background reference value of 1.3 mg/kg (OSPAR, 2009). We strategically chose these ranges to accentuate the most noteworthy variations along the French coast.

Fig. 6 illustrates how the percentage of sampling stations registering different levels of Pb concentrations has changed over time. Notably, across all three coastal systems, there has been a significant increase in the percentage of sampling sites with Pb concentrations below the background reference value of 1.3 mg/kg (OSPAR, 2009), rising from 5% in 1988 to 60% in 2021. This change has been most substantial in the English Channel. Additionally, there has been a decline in the frequency of sampling stations exceeding the sanitary reference values (as established by the European Commission in 2006), decreasing from 9% in 1993 to 0% since 2020 (Fig. 6).

The Atlantic coast generally exhibits the lowest historical Pb concentrations in bivalve samples (Fig. 2). This phenomenon is likely the result of coastal flushing by oceanic waters, a phenomenon that facilitates the dispersion of contaminants and less anthropogenic Pb release toward the continental shelf. The highest average Pb concentration on the Atlantic coast was recorded in 1995, peaking at 2.4 mg/kg, with around 81% of the sampling stations registering Pb concentrations above the background reference value (1.3 mg/kg; OSPAR, 2009). These values were mainly the result of data from stations near the historically contaminated Gironde Estuary (metallurgical contamination). In 1996, Pb concentrations in bivalves peaked along the Atlantic coast, with 9.6 mg/kg at the Hendaye station, situated within the Bidasoa Estuary near the Spanish border. This is the only station along the Atlantic coast to present Pb concentrations above the sanitary reference value of 8.3 mg/kg (dry weight, *C. gigas*; corrected from the wet weight reference value from the European Commission, 2006). This surge in Pb levels can be predominantly attributed to inputs from an industrially polluted tributary, the Jaizubia River (Saiz-Salinas et al., 1996). Pb concentrations along the Atlantic coast have gradually decreased over time: By 2022, 61% of the sampling stations had Pb concentrations below the background reference value (1.3 mg/kg; OSPAR, 2009; Fig. 2). Notably, the Aulne River station (see map in Fig. 1), which has a historical association with tributaries draining former silver-bearing lead mining areas (Rivière d'Argent and Poullaouen Stream), displayed the highest Pb concentrations (3.9 mg/kg) in 2022. Additionally, two stations presented significantly higher concentrations than the background reference value of 1.3 mg/kg (OSPAR, 2009): the Hendaye station (2.7 mg/kg) in the Bidasoa Estuary and the La Fosse station (2.5 mg/kg) in the Gironde Estuary. Since 1997, no station has presented Pb concentrations above the sanitary reference value (8.3 mg/kg, dry weight, for *C. gigas*; European Commission, 2006).

The Pb concentrations along the English Channel coast have decreased significantly over the years (Fig. 4). In 1992, the average Pb concentration was 3.4 mg/kg, which decreased to 1.2 mg/kg in 2021 (Fig. 2). All monitoring stations recorded Pb concentrations higher than the background reference value of 1.3 mg/kg (OSPAR, 2009) in 1992 (Fig. 6). This trend was mainly influenced by the proximity of these monitoring stations to the Seine River (see map in Fig. 1 and data in Fig. 4), exemplified by the Pb concentrations in Cap de la Hève, which peaked at 13.7 mg/kg in 1993 (above the sanitary reference of 9.1 mg/kg, dry weight, for *M. edulis*; European Commission, 2006). The historical contamination of the Seine Estuary by trace metals is attributed to intense industrial and urban activities in this watershed (Dauvin, 2008). Indeed, it drains 25%–30% of French industrial activity and 23% of the French population. The subsequent reduction in Pb concentrations resulted in 78% of the stations recording levels below the background reference value (1.3 mg/kg; OSPAR, 2009) in 2021 (Fig. 3). It is important to mention that between 2021 and 2022, the Antifer – Digue and Yport stations witnessed a significant increase in Pb concentrations. The concentrations rose from 1.2 and 1.4 mg/kg (around the background reference values of 1.3 mg/kg) to 3.4 and 3.1 mg/kg, respectively. These twofold fluctuations highlight the importance of continuous monitoring and vigilant environmental management. Since 2003, no station has presented

Pb concentrations above the sanitary reference value (9.1 mg/kg, dry weight, for *M. edulis*; European Commission, 2006).

The highest historical Pb concentrations along the French coastline have been observed in the Mediterranean region, particularly during the late 1980s and early 1990s (Fig. 2) in areas influenced by the discharge of the Rhône River (Fig. 5). The region's characteristic low tidal ranges (< 50 cm) and limited coastal flushing by oceanic waters favor the high residence time of metal contaminants in sediments and waters (e.g., Toulon Bay; Tessier et al., 2011; Dang et al., 2015; Araújo et al., 2019). The average Pb concentrations peaked in the Mediterranean bivalves in 1988, at 7.5 mg/kg, when 88% of the sampling stations exceeded the background reference value (1.3 mg/kg; OSPAR, 2009) in this zone, and 25% surpassed the sanitary reference value (7.9 mg/kg, dry weight, for *M. galloprovincialis*; European Commission, 2006) (Fig. 6). The Mediterranean is the only section of the French coastline that has presented more the one station with Pb concentrations above the sanitary reference value in a single year (up to four stations in 1993 and 1994). Over time, Pb concentrations have steadily declined in this region, reaching a minimum average of 1.8 mg/kg in 2021. In 2022, 60% of the sampling sites recorded Pb concentrations below the background reference value (1.3 mg/kg; OSPAR, 2009; Fig. 6). The highest Pb concentration on the French coast occurred in this zone, in 1992, at 30.0 mg/kg in Nice – La Réserve. Although biomonitoring in this station ceased in 1995, observations from nearby stations such as Golfe de la Napoule, Toulon/Lazaret, and Pomègues Est have demonstrated a significant and synchronized attenuation of Pb levels in the region: decreasing from 14.4 mg/kg in 1988 to 1.4 mg/kg in 2021, from 17.6 mg/kg in 1985 to 5 mg/kg in 2022, and from 27.7 mg/kg in 2000 to 3.6 mg/kg in 2021, respectively. The southeastern coast of France is facing environmental challenges due to extensive industrial and urban activities within the Rhône River watershed. The area is particularly concerning because Pb concentrations in bivalves from popular tourist destinations have consistently exceeded background and sanitary reference values throughout the study period (Figs. 2 and 5).

Pb isotope ratio determinations performed in the subset of eight sampling stations representing emblematic coastal sites allowed us to evaluate decadal changes in Pb isotope ratios ($^{206}Pb/^{207}Pb$) from the 1980s to the 2010s and revealed a shift from lower to higher values (Fig. 7). Anthropogenic sources of Pb typically have a lower $^{206}Pb/^{207}Pb$ ratio compared with natural geological sources because anthropogenic materials, such as leaded gasoline, contain Pb that comes from ore deposits with a lower $^{206}Pb/^{207}Pb$ ratio (Komarek et al., 2008). Therefore, the downward shift in the observed isotope ratio indicates that the Pb isotope composition has moved toward the range of natural Pb found in pristine pre-industrial sediments (^{206}Pb/^{207}Pb ratio around 1.200; Sun et al., 1980), which ultimately comes from rock weathering processes. This shift in isotope composition suggests that anthropogenic sources of Pb have become less influential over time. Using natural and anthropogenic Pb isotope values of natural and anthropogenic end-members allowed us to estimate anthropogenic Pb fraction bioaccumulated in bivalve mollusks, as expressed in Eq. 1:

$$\%_{\text{anthropogenic Pb}} = \frac{\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}_{\text{measured}} - \frac{^{206}\text{Pb}}{^{207}\text{Pb}}_{\text{natural}}\right)}{\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}_{\text{anthropogenic}} - \frac{^{206}\text{Pb}}{^{207}\text{Pb}}_{\text{natural}}\right)} \times 100 \qquad \text{(Eq. 1)}$$

The application of Eq. 1 assumes that the average anthropogenic ^{206}Pb/^{207}Pb ratio is 1.120, which falls within the range of approximately 1.100 (associated with leaded automotive gasoline; Monna et al., 1995) to 1.140 (related to industrial Pb emissions; Cloquet et al., 2006), and considers the natural ^{206}Pb/^{207}Pb ratio to be around 1.200 (characteristic of pre-industrial sediments; Sun et al., 1980). It is important to note that while we used this average value for normalization convenience, it may have resulted in underestimations or overestimations of industrial Pb and leaded gasoline contributions. More specifically, we expected a general shift over time toward a greater share of Pb emissions stemming from industrial sources, coinciding with a reduction in the relative impact of leaded gasoline due to regulatory measures. Nevertheless, quantitatively assessing this shift within anthropogenic sources is challenging, as it aligns with the direction of pre-industrial Pb emissions. In other words, both industrial and natural Pb typically have a higher ^{206}Pb/^{207}Pb ratio compared with leaded gasoline.

It is worth noting that the decision to concentrate on two primary end-members, natural and anthropogenic ones, assuming their inherent uncertainties, are aligned with the capabilities of low-resolution Q-ICP-MS. This approach is beneficial for evaluating and ranking French coastal ecosystems concerning Pb pollution (Elbaz-Poulichet et al., 1986). It facilitates the prioritization of areas for future studies and provides essential support for well-informed and relatively low-cost decision-making in environmental management. However, the chosen analytical method limits precise source apportionment, particularly when considering multiple anthropogenic sources with only marginal isotopic variations. While high-resolution spectrometers (TIMS or MC-ICP-

MS) could address this limitation, their associated costs restrict their application in large-scale monitoring programs, such as the one implemented in France.

The isotope mass balance calculations showed a decline in the percentage of anthropogenic Pb bioaccumulated in bivalves along the French coast (Fig. 8), with values ranging from approximately 30% to 90% in the 1980s, to values ranging from approximately 15% to 40% in the 2010s.

Among all the sampling stations, the Chemoulin station at the Loire Estuary exhibited Pb isotope values closest to the ranges characteristic of anthropogenic sources, particularly during the 1980s. In this period, nearly 90% of bioavailable Pb was of anthropogenic origin (Fig. 8). Remarkably, the stations near the mouth of the Loire Estuary stood out for their large range of historical Pb concentrations (Fig. 5), illustrating the greatest attenuation along the French coast. Recently, the percentage of bioaccumulated anthropogenic Pb dropped below 40% in bivalves from the Chemoulin station at the Loire Estuary (Fig. 8). This shift can mainly be attributed to the closure of a nearby alkyllead plant in 1996, which significantly contributed to local Pb contamination in the Loire Estuary (Couture et al., 2010; Shiel et al., 2013). This industrial point source seems to have had a considerable influence over the Pb concentrations (Fig. 3) and isotope ratios at neighboring points. To the north (Villaine/Er Fosse), anthropogenic Pb has declined from approximately 40% in the 1980s to 20% in the 2010s (Fig. 8).

Likewise, along the Atlantic coast, the sampling stations in the Arcachon Bay (Cap Ferret and Comprian), situated within an urban tourist area, have registered substantial reductions in anthropogenic Pb in the bioavailable pool. Both stations have witnessed a decrease of over 50% of anthropogenic Pb, from their peaks around 1990 to their lows in the 2010s (Fig. 8).

Conversely, the Gironde/La Fosse station (Atlantic), the Seine/Villerville station (English Channel), and the Cap Couronne station (Mediterranean) have exhibited relatively homogeneous Pb isotope levels (Fig. 8). These values are intermediate between those of pre-industrial sediments (average $^{206}Pb/^{207}Pb$ ratio of 1.207) and relevant anthropogenic sources (average $^{206}Pb/^{207}Pb$ ratio of 1.154 for solid waste incinerators Carignan et al., 2005; 1.158 for smelter, Cloquet et al., 2006; 1.109 for French gasoline, Monna et al., 1995; 1.169 for highway runoff, Monna et al., 1995). The absence of major fluctuations in the percentage of anthropogenic Pb (Fig. 8) indicates that there has been relatively stable Pb source apportionments in the Gironde, Seine, and Rhône Estuaries over time.

In the Gironde watershed (Atlantic coast), there is legacy contamination from a former metallurgical plant located upstream in the Riou Mort: Although it ceased activities in 1987, it has continued to contribute to metal exportation, mainly Cd, Zn, Cu, and Pb, and fluvial-origin contamination of the estuary (e.g., Audry et al., 2004; Larrosse et al., 2010). Nonetheless, the influence of anthropogenic Pb sources in the Gironde/La Fosse station has been less pronounced than in the Seine/Villerville (English Channel) and Cap Couronne (Mediterranean) stations (Fig. 8). Shiel et al. (2013) suggested that industrial activities from the Seine watershed have caused the $^{206}Pb/^{207}Pb$ ratio of bivalves along the English Channel coast to decrease. Meanwhile, on the Mediterranean coast, the Rhône River and other sources have conveyed the anthropogenic signal. The Toulon/Lazaret station, which is separated from the Rhône delta fluxes (Fig. 1), has exhibited Pb isotope values gradually converging toward the range characteristic of natural sources (Fig. 8).

The extensive near half-century Pb monitoring conducted by the French MWP has revealed a substantial decline in Pb concentrations within French bivalve mollusks over the past four decades. In 1988, 95% of monitoring stations exceeded the background reference value (1.3 mg/kg, dry weight; OSPAR, 2009), in contrast to the 39% observed in 2021. Since 2020, no station along the French coastline has presented Pb concentrations above the sanitary reference values (8.3, 9.1, and 7.9 mg/kg, dry weight, for *C. gigas*, *M. edulis*, and *M. galloprovincialis*, respectively; European Commission, 2006).

Isotope source apportionment quantifications have demonstrated a notable reduction in anthropogenic Pb bioaccumulation from the 1980s to the 2010s. This reduction has been particularly noticeable at sites with historical pollution linked to point sources, such as the Loire Estuary. While there has been an overall trend of decreasing Pb contamination levels and isotope shifts toward natural ranges, the return to natural baseline levels has not been attained in most areas. The Atlantic, English Channel, and, especially, Mediterranean coasts continue to grapple with elevated Pb concentrations that exceed the background reference values (1.3 mg/kg, dry weight; OSPAR, 2009).

The decrease in Pb contamination along the French coast is happening gradually. The slow anthropogenic Pb phaseout can be attributed to its prolonged residence time in sediments, which is particularly pronounced in areas with limited oceanic water exchange, as observed for Mediterranean lagoons and estuaries. On the other hand, chronic emissions from diffuse urban sources may hinder a return to original natural Pb baseline levels in the natural compartments.

The combination of the isotope and elemental data has substantiated the efficacy of regulatory measures initiated in the late 1970s (e.g., Council Directive 78/611/EEC), which gained momentum throughout the 1980s (e.g., Council Directive 85/210/EEC and French leaded gasoline phaseout; Von Storch et al., 2003) and 1990s (e.g., COWI and DTI, 1998).

While our study primarily emphasizes elemental and isotopic analysis in bivalve mollusks to elucidate sources of and trends in coastal Pb contamination, understanding the chemical speciation of Pb, mainly in abiotic compartments (water and sediments), holds significance for evaluating its potential impacts on both environmental and human health, resulting from the mobility, reactivity, and bioavailability of this metal. In future investigations, a comprehensive spatiotemporal exploration of the various chemical forms of Pb within bivalve mollusks along the French coastline would align with the overarching objective of advancing our understanding of the evolving dynamics of trace metal coastal contamination.

To conclude, this study emphasizes the significance of conducting continuous MWP monitoring, while also making ongoing improvements in analytical techniques and methodologies. The isotope-based approach we performed with accessible Q-ICP-MS instruments enabled us to quantify the evolution of anthropogenic Pb at target sites. This methodology can be integrated into future routine analyses of the MWP, expanding coverage to more sampling stations. Such endeavors are critical to evaluate the effectiveness of regulations in the long run, to identify new hotspots of contamination, and to develop robust policies to mitigate sources of metal pollutants.

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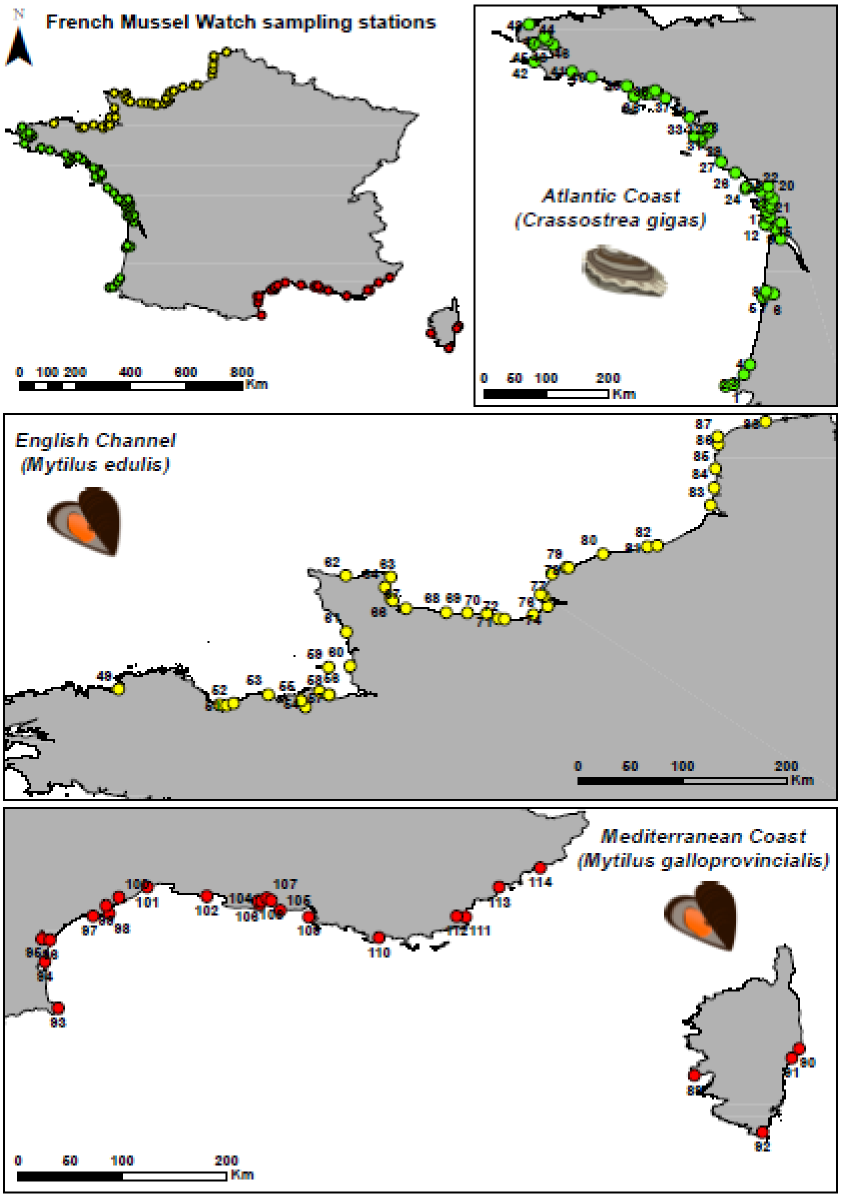

Fig. 1. Locations of the sampling stations: 1 Hendaye – Chingoudy; 2 Ciboure – la ivelle; 3 Adour marégraphe; 4 Hossegor limite nord parcs; 5 Cap Ferret; 6 Les Hosses; 7 Comprian; 8 Les Jacquets; 9 La Fosse; 10 Pontaillac; 11 Bonne Anse – Palmyre; 12 Bonne Anse; 13 L'Eguille; 14 Perquis; 15 Mus de loup; 16 Dagnas; 17 L'Estrée – Brouage; 18 Boyardville; 19 Les Palles; 20 Châtelaillon; 21 Escalier Gaillard; 22 Rivedoux; 23 Le Martray; 24 Fier d'Ars; 25 Baie de l'Aiguillon; 26 Talmont; 27 Dunes de Brétignolles; 28 Fromentine bas; 29 Noirmoutier – Gresse – loup; 30 Paillard; 31 Bourgneuf – Coupelasse; 32 La Sennetière; 33 Loire/Chemoulin; 34 Er Fosse; 35 Men er Roue; 36 Le Guilvin; 37 Larmor – Baden; 38 Roguedas; 39 Beg er Vil; 40 Riec sur Belon; 41 Fouesnant; 42 Suguensou; 43 Aulne rive droite; 44 Persuel; 45 Baie de Roscanvel; 46 Rossermeur; 47 Le Passage (b); 48 Aber Benoît; 49 St Michel en grève; 50 Pointe du Roselier; 51 Baie de Morieux; 52 Port Morvan; 53 Baie de la Fresnaye; 54 Port St Jean; 55 La Gauthier; 56 Cancale; 57 Vieux plan Est; 58 Le Vivier sur mer; 59 Chausey; 60 Bréville; 61 Pirou nord; 62 Grande rade de Cherbourg; 63 Le Moulard; 64 St Vaast la Hougue; 65 Ravenoville (b); 66 St Germain de Varreville; 67 Bdv Grandcamp ouest; 68 Port en Bessin; 69 Meuvaines ouest; 70 Bernières; 71 Hermanville; 72 Ouistreham; 73 Villers sur mer; 74 Villerville; 75 Digue nord du Havre; 76 Cap de la Hève; 77 Antifer – Digue; 78 Vaucottes; 79 Yport; 80 Veulettes; 81 Varengeville; 82 Bas Fort Blanc; 83 Pointe de St Quentin; 84 Berck Bellevue; 85 Dannes; 86 Ambleteuse; 87 Cap Gris nez; 88 Oye plage; 89 Ajaccio; 90 Etang de Diana; 91 Etang d'Urbino; 92 Sant'Amanza; 93 Banyuls – Labo Arago; 94 Etang de Leucate; 95 Etang de Bages; 96 Etang de l'Ayrolle; 97 Embouchure de l'Hérault; 98 Filières de Sète–Marseillan; 99 Marseillan (a); 100 Bouzigues (a); 101 Etang du Prévost; 102 Les Stes Maries de la mer; 103 Anse de Carteau; 104 Centre darse 2; 105 Cap Couronne; 106 Port pétrolier; 107 Pointe St Gervais; 108 Port de Bouc; 109 Pomègues Est; 110 Toulon/Lazaret; 111 St Tropez; 112 Port Grimaud; 113 Golfe de la Napoule; 114 Nice – La Réserve.

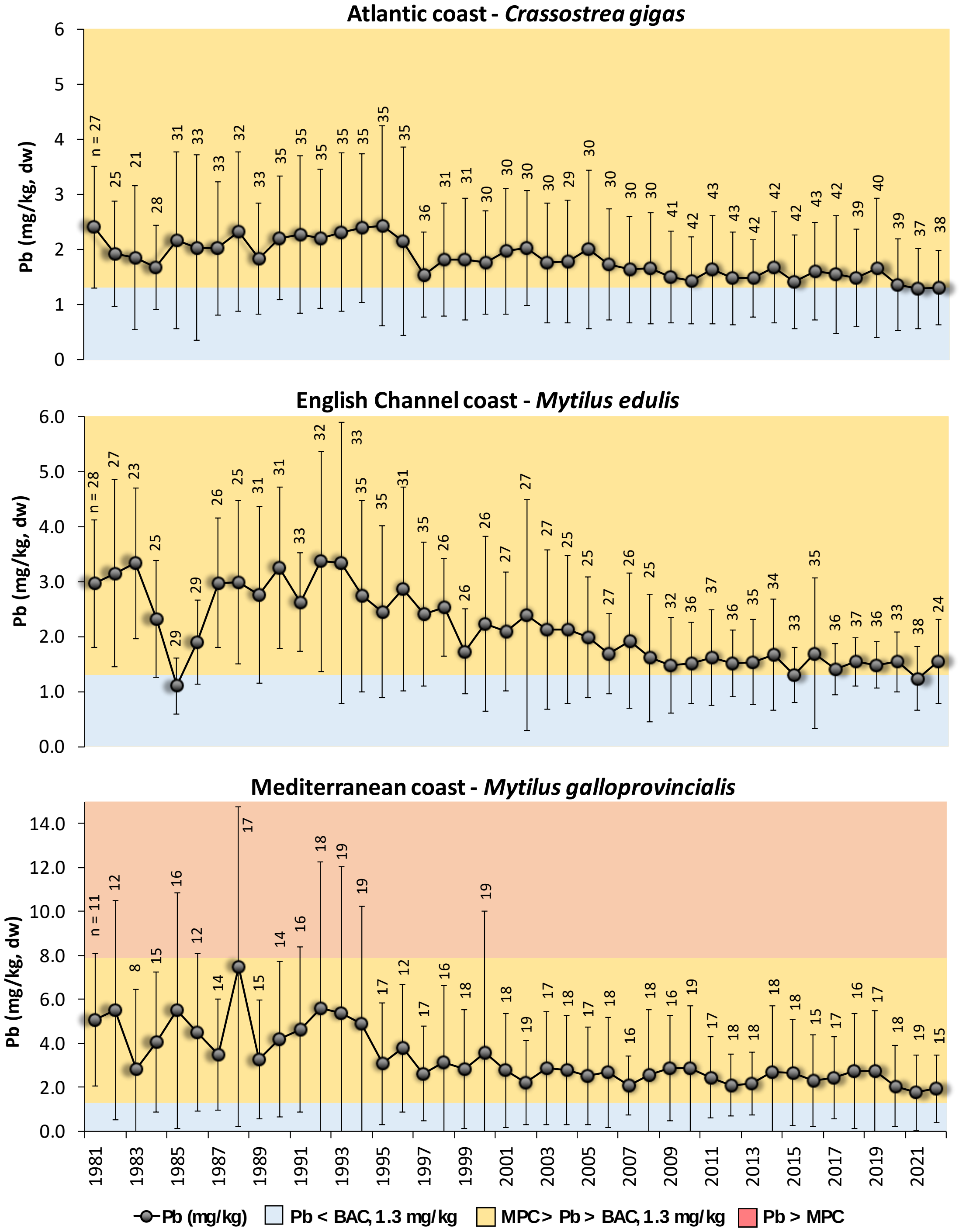

Fig. 2. Temporal changes in the average lead (Pb) concentration (mg/kg) and standard deviation from 1981 to 2022 in bivalves from the French Atlantic (*Crassostrea gigas*), English Channel (*Mytilus edulis*), and Mediterranean (*Mytilus galloprovincialis*) coasts. The gray circles represent the annual mean Pb concentrations (mg/kg) in dry weight (dw). The error bars refer to standard deviations of Pb concentrations for all sampling stations in a given year. The background assessment concentration (BAC, 1.3 mg/kg, dw) was used to assess the environmental status of metal concentrations. Mean concentrations significantly below the BAC are said to be near background (OSPAR, 2009). The maximum permissible concentration (MPC) in food is the reference value for the protection of the human health. The wet weight reference value of 1.5 mg/kg (European Commission, 2006) was corrected based on the percentage (%) of dw for each species (DOME, 2022), resulting in an MPC of 8.3, 9.1, and 7.9 mg/kg, dw, for *C. gigas*, *M. edulis*, and *M. galloprovincialis*, respectively.

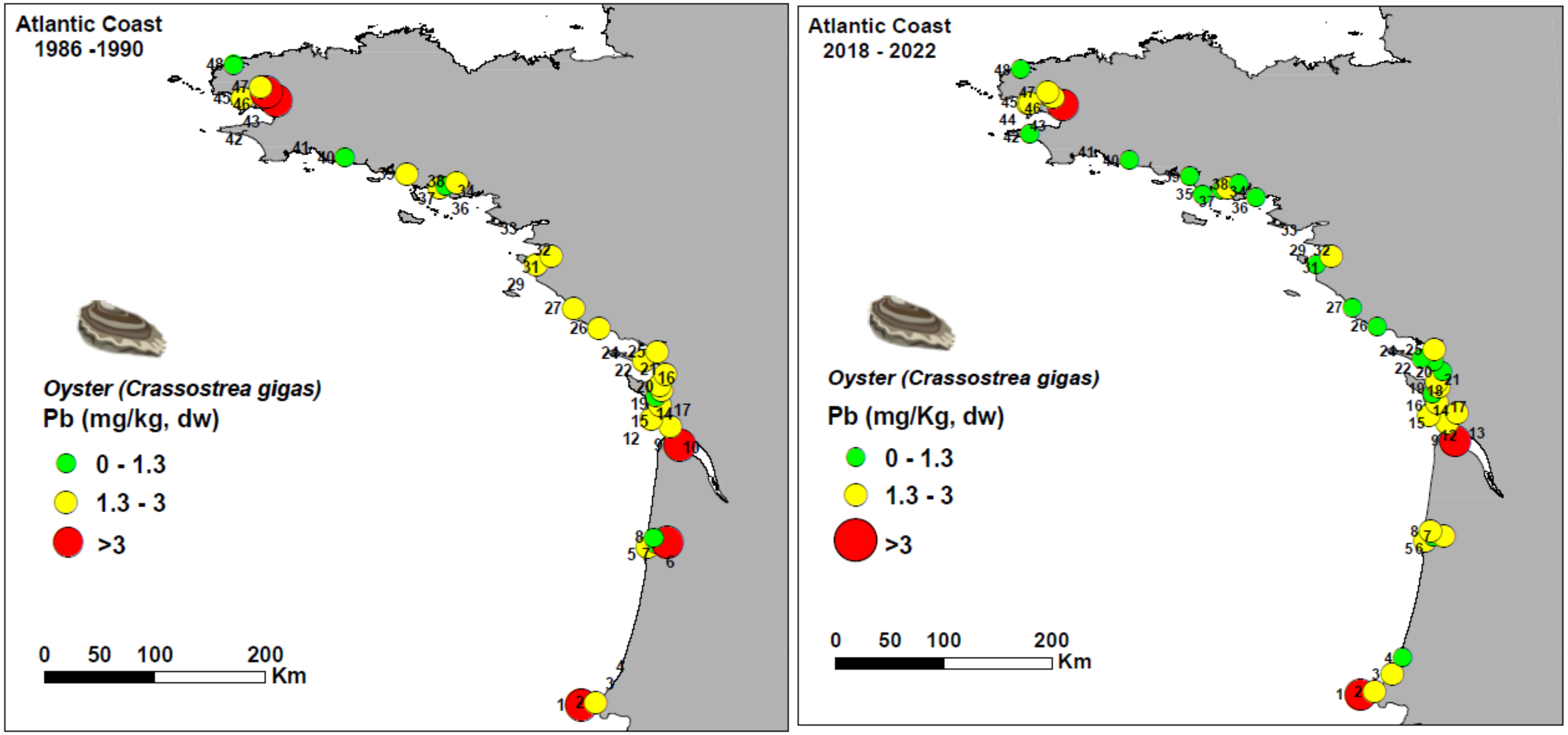

Fig. 3. Snapshots of the spatial distribution of the average dry weight (dw) lead (Pb) concentrations (mg/kg) in bivalves from the French Atlantic coast (*Crassostrea gigas*) for 1986–1990 and 2018–2022. The background assessment concentration (BAC) of 1.3 mg/kg (OSPAR, 2009) determines the threshold value for background concentrations. The station names are in the Fig. 1 caption. Empty values refer to data gaps in the time series

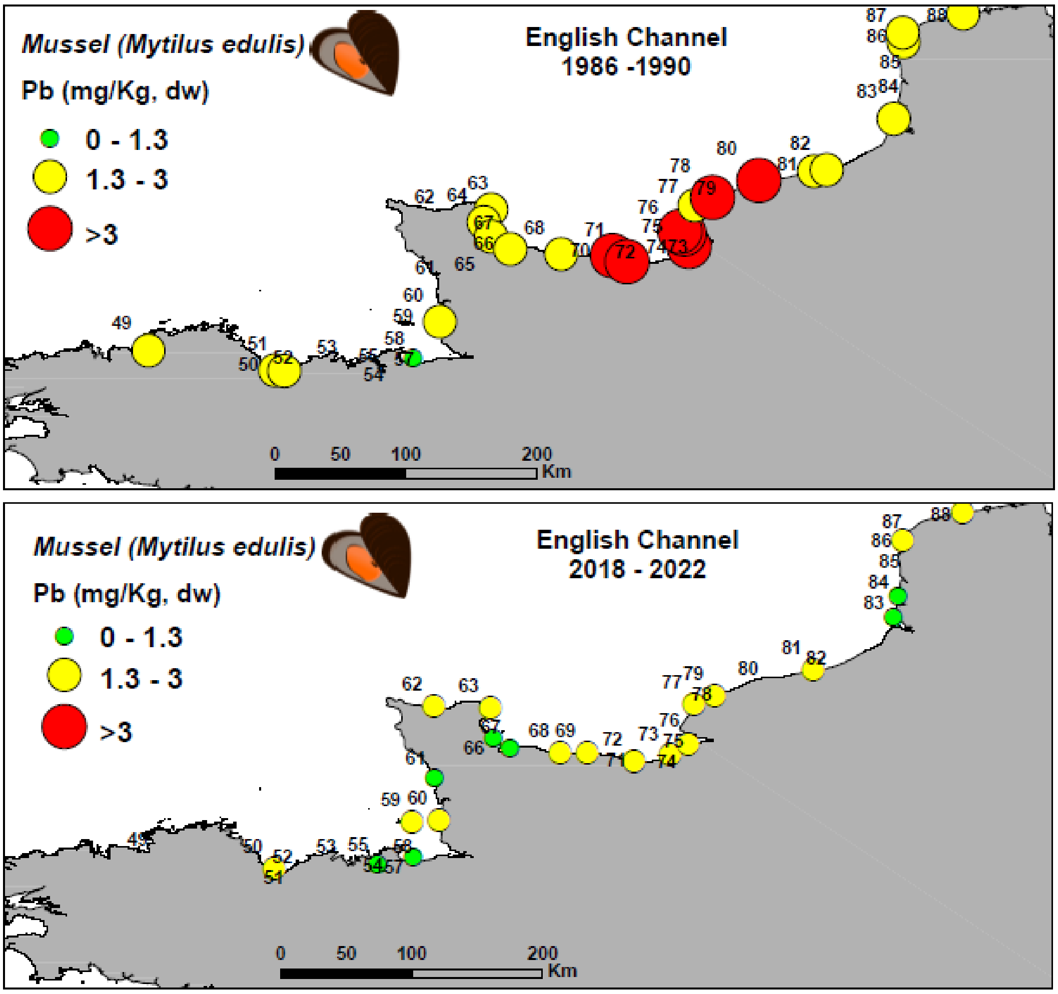

Fig. 4. Snapshots of the spatial distribution of the average dry weight (dw) lead (Pb) concentrations (mg/kg) in bivalves from the English Channel coast (*Mytilus edulis*) in 1986–1990 and 2018–2022. The background assessment concentration (BAC) of 1.3 mg/kg (OSPAR, 2009) determines the threshold value for background concentrations. The station names are in the Fig. 1 caption. Empty values refer to data gaps in the time series.

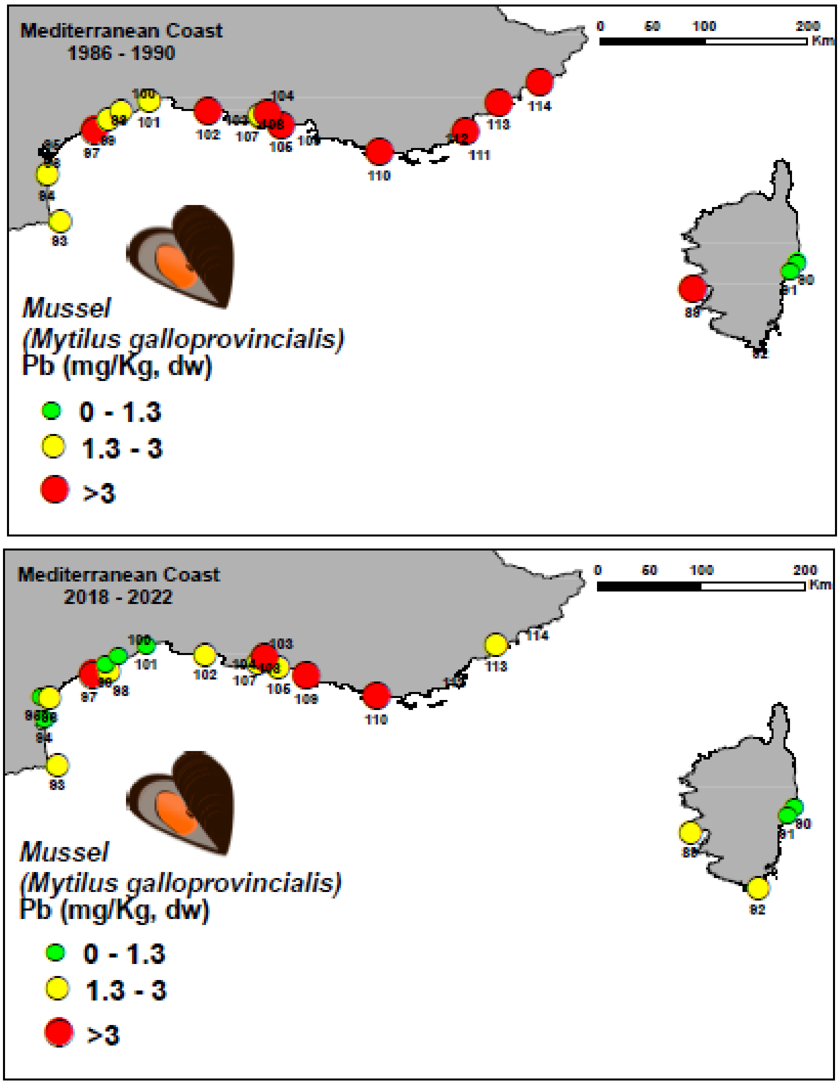

Fig. 5. Snapshots of the spatial distribution of the average dry weight (dw) lead (Pb) concentrations (mg/kg) in bivalves from the Mediterranean coast (*Mytilus galloprovincialis*) in 1986–1990 and 2018–2022. The background assessment concentration (BAC) of 1.3 mg/kg (OSPAR, 2009) determines the threshold value for background concentrations. The station names are in the Fig. 1 caption. Empty values refer to data gaps in the time series.

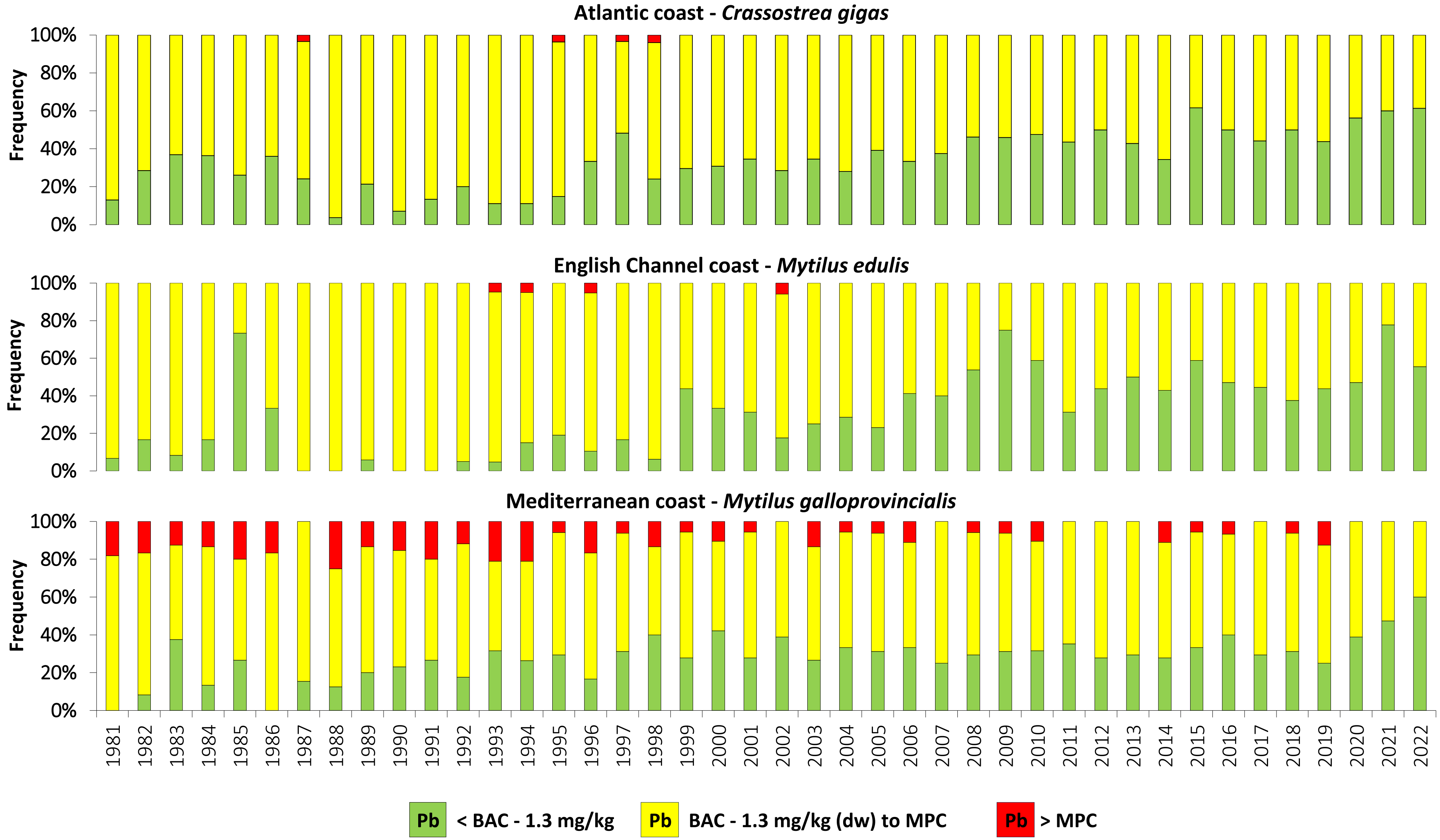

Fig. 6. Annual frequency distribution (%) of dry weight (dw) lead (Pb) concentrations (mg/kg) between 1981 and 2022. The background assessment concentration (BAC, 1.3 mg/kg, dw) determines the threshold value for background concentrations (OSPAR, 2009). The maximum permissible concentration (MPC) in food recommends the maximum acceptable concentration to assure human health safety. The wet weight reference value of 1.5 mg/kg (European Commission, 2006) was corrected based on the percentage (%) of dry weight for each species (DOME, 2022), resulting in MPCs of 8.3, 9.1, and 7.9 mg/kg (dw) for *Crassostrea gigas*, *Mytilus edulis*, and *Mytilus galloprovincialis*, respectively.

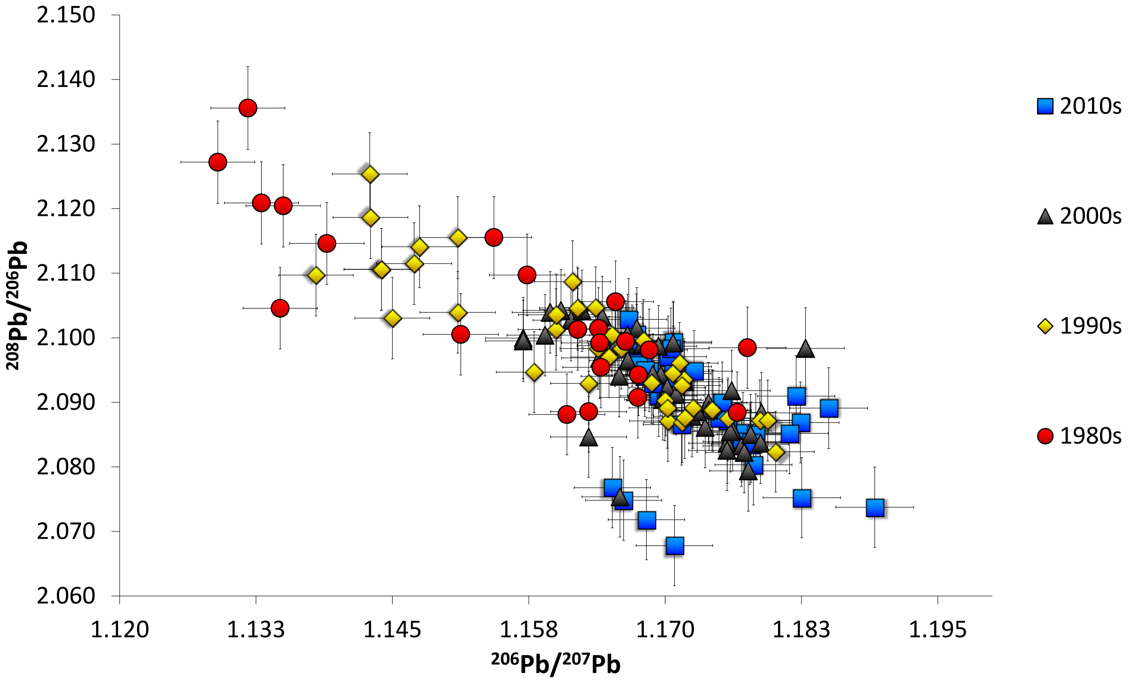

Fig. 7. Decadal changes (1980s to 2010s) of lead (Pb) isotopes in bivalve mollusks from emblematic French coastal watersheds: the Seine (Villervile station), Loire (Chemoulin station, nº 33), and Gironde (La Fosse station, nº 9) Estuaries; the Arcachon (Cap Ferret and Comprian stations, nº 5 and 7, respectively), Toulon (Lazaret station, n° 110), and Vilaine (Er Fosse station, n° 34) bays and the Cap Couronne (Cap Couronne station, nº 105) peninsula.

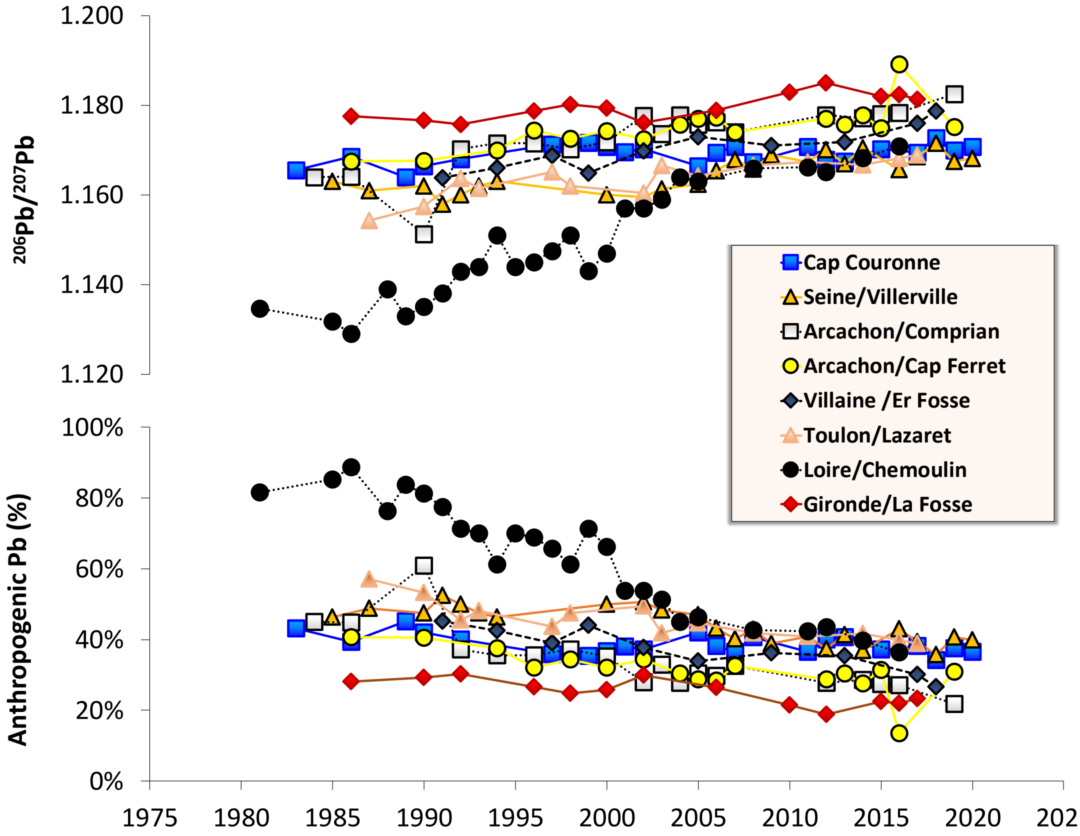

Fig. 8. Temporal lead (Pb) isotope profiles and anthropogenic Pb (%) quantifications in oyster and mussel samples from target sites covered by the French "Mussel Watch" Program. The error bars refer to analytical uncertainties of isotope ratio measurements for unknown samples and certified reference material (CRM), typically around ± 0.3% We assume that the anthropogenic $^{206}Pb/^{207}Pb$ ratio is 1.120 for all sampling stations, falling within the range of approximately 1.100 (associated with automotive leaded gasoline; Monna et al., 1995) to 1.140 (related to industrial Pb emissions; Cloquet et al., 2006), and the natural $^{206}Pb/^{207}Pb$ ratio is around 1.200 (characteristic of pre-industrial sediments; Sun et al., 1980).