Perfluoroalkyl substances (PFAS) occurrence, concentrations and spatial distribution along the French Mediterranean coast and lagoons, based on active biomonitoring

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ABSTRACT

The 2021 monitoring campaign for chemical contamination established a baseline for PFAS concentrations in mussels along the French Mediterranean coast. Ninety percent of the targeted PFAS measurements were below quantification limits, and no data exceeded the few guiding values available for bivalves. Long-chain PFCA's were confirmed as predominant in mussels. Spatial distribution patterns revealed continuous inputs and complex dynamics of PFAS distribution in the marine environment. Lapeyrade lagoon appeared to be the most contaminated site. Similar PFAS profiles in connected sites suggested shared sources but raised questions about accumulation processes in mussels. Some watersheds and rivers (Rhône, Aude, Huveaune) influenced PFAS distribution. Certain sites had obvious sources (e.g. military airbase for Palo lagoon), but others posed uncertainties (e.g., Toulon bay). Coastal stations (Banyuls, Cap Agde, Brégançon, Pampelonne) exhibited PFAS contamination without clear onshore sources, possibly due to insufficient information on transportation processes.

Keywords: biomonitoring, caging, *Mytilus galloprovincialis*, chemical contamination, PFAS

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Perfluoroalkyl substances (PFAS) have been the subject of increasing research and media attention over the last 15 years due to the environmental and human concerns they raise (De Silva et al., 2021; Fenton et al., 2021). Due to their amphiphilic properties, PFAS have found widespread use in various commercial and industrial products, such as surfactants, lubricants, coatings, stain repellents, dispersants, and polishes (Prevedouros et al., 2006).

However, their strong covalent carbon-florine makes PFAS chemically and physically stable, rendering them resistant to environmental degradation (Buck et al., 2011). As a result, the majority of PFAS exhibit exceptional persistence in the environment, leading to their designation as "forever chemicals". The release of PFAS into the environment occurs through direct and indirect pathways, including industrial emissions, wastewater effluents (Bossi et al., 2008; Clara et al., 2008; Sánchez-Avila et al., 2010), and consumer products (Buck et al., 2011; Paul et al., 2009), resulting in global contamination of ecosystems and humans (Houde et al., 2006; Muir et al., 2019; Wang et al., 2017). The connection between continental and marine ecosystems, associated to oceanic currents and atmospheric circulation, which are the main drivers behind the global transportation of PFAS (Armitage et al., 2006), have led to consider marine environment as the main PFAS reservoir (Yamashita et al., 2008). PFAS also tend to bioaccumulate in organisms, posing a toxic risk to both the environment and human health (Ankley et al., 2021; Grandjean and Clapp, 2015; Lau et al., 2007). Several studies have reported potential adverse effects of PFAS on the reproduction, development, immunity, and endocrine systems of both aquatic and terrestrial organisms (Giesy and Kannan, 2001; Hoff et al., 2003; Liu et al., 2007; Mortensen et al., 2011; Wei et al., 2007).

Given this context, tracking PFAS in the marine environment remains a critical issue that monitoring programs could help resolve (Aminot et al., 2023; Augustsson et al., 2021). Bioindication based on natural shellfish resources has proven to be a relevant and efficient approach to monitor PFAS (Maruya et al., 2014; Meng et al., 2022; Munschy et al., 2019, 2013; Teunen et al., 2021). However, for certain regions like the French Mediterranean Sea, the available information may not be sufficient to provide a spatial representation of PFAS (Ericson et al., 2008; Gómez et al., 2011; Munschy et al., 2019; Renzi et al., 2013; Vassiliadou et al., 2015). Indeed, in the case of French coasts, the scarcity of bivalve natural resources limits the representativeness of a passive biomonitoring approach. As a result, a dedicated monitoring network called RINBIO, based on a mussel-transplantation technique, was established in 1996 and has been conducted every three years since 2000 (Andral et al., 2011, 2004; Briand et al., 2023). Thanks to this monitoring network, a large dataset of contaminant concentrations is now available along the French Mediterranean coast (Herlory et al., 2021, https://doi.org/10.17882/96102).

The most recent session of the RINBIO program was conducted during the oceanographic campaign, SUCHIMED 2021 (Bouchoucha, 2021; Briand et al., 2023). The data obtained from this fieldwork are utilized in this article to establish a baseline of some PFAS occurrence, levels, and signatures along the Mediterranean coasts of metropolitan France and Corsica, in addition to previous investigations by Munschy et al. (Munschy et al., 2019, 2015, 2013).

The RINBIO operates on the principle of monitoring chemical contaminants along the French Mediterranean coast through active biomonitoring (de Kock, 1983; Fabris et al., 1994), specifically using mussel (*Mytilus galloprovincialis*) caging (Briand et al., 2023). This transplantation method allows for control over the source, age, and stage of sexual maturity of the mussels. Each batch consisted of 3 kilograms of adult mussels, 18–24 months old, with an average size of about 50 mm (between 35 and 65 mm), obtained from a coastal farming site (submerged mussel longlines offshore the Thau

lagoon, Figure 1). The mussels were sorted twice based on the height of the shell using a 19-mm mesh (Andral et al., 2004). The cages used for the experiment were man-made conchylicultural pouches mounted on PVC tubing (Andral et al., 2004).

In 2021, chemical contaminants were investigated at 83 sites, strategically and homogeneously distributed along the 1800 km of the French Mediterranean shoreline, from the Spanish to the Italian borders and encompassing Corsica island as well (Briand et al., 2023).

Out of these sites, PFAS analysis was planned for 55 stations (Figure 1) to obtain information under different exposure conditions, including coastal lagoons (*e.g.* Salses, Berre, Diana), areas near river mouths (Aude, Hérault, Rhône, Huveaune, Gapeau, Var, Golu), near coastal wastewater treatment plant discharges (Montpellier, Cortiou, Sicié, Bastia, Ajaccio), regions surrounding highly urbanized and/or industrialized harbors (Marseille, Toulon, Villefranche), and areas further away from potential anthropogenic stress (*e.g.* Banyuls, Fréjus, Rogliano).

The mussel cages were submerged at each station at a depth of 6 to 8 meters for 3 months, from March to July 2021. After the recovery of the pouches by scuba divers, the mussels were separated, rinsed in seawater, and pre-processed immediately on board following standardized procedures (Andral et al., 2004) in line with the proposals of the OSPAR Commission (2013).

Between 11 to 22 specimens per station were randomly selected for PFAS analysis. On board, the flesh of the mussels was carefully scraped out of the opened raw shell using a stainless steel scalpel before being stored in acid-washed glass vials. These samples were kept frozen at -20°C until their analysis by the laboratory.

Seventeen PFAS compounds were analyzed at each of the 55 stations. The analysis included six C4 to C10 perfluoroalkane sulfonic acids (PFSA) and eleven C4 to C14 perfluoroalkyl carboxylic acids (PFCA): perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluoroheptane sulfonate (PFHpS), perfluorooctane sulfonate differentiating branched (br-PFOS) and linear (n-PFOS) stereoisomers, perfluorodecane sulfonate (PFDS) and perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA).

Quantification, based on isotopic dilution used 10 internal standards. PFAS and their corresponding 13C-labeled internal standards were obtained from the company BCP Instruments (Lyon, France). All solvents used were of a high quality grade. Before analysis, the mussels were freeze-dried and liquid solid extraction was carried out with a KOH/Methanol mixture (0.01 M). After overnight at room temperature, the supernatant was evaporated and transferred to a Chromabond SPE column (300 mg, 6 mL ; MachereyNagel) then eluted with a solution of methanol/NH4OH (99.5/0.5, v/v). After gentle evaporation, an aliquot was then loaded onto an ENVI Carb SPE column (500 mg, 6 mL ; Supelco). The injection of the final extract was carried out on an LC-MS/MS system (Agilent Technology 6410) in negative electrospray mode using a Hypersil Gold column (100x2.1 mm,1.9µm).

Laberca operates an ISO/IEC 17025 :2017-certified Quality Assurance system requiring very strict controls. A continuous monitoring of the analytical procedure was implemented during the study for blanks as well as for a naturally contaminated fish used as a quality control sample for many years in the laboratory. The accuracy of the analytical method is ensured by participation twice a year to proficiency tests organized by the European Reference Laboratory (EURL) for POPs.

The occurrence of PFAS was determined based on the number of results above the limit of quantification (LOQ) at each station for each analyzed compound.

Results below the quantification limits were considered null, in accordance with the approach used to compare concentrations with the maximum regulatory levels in food (European Commission, 2023). To our knowledge, these are the only threshold values available for bivalves, as Environmental Quality Standards (EQS) for this type of biota are currently lacking. It is worth mentioning that an EQS is available for PFOS in fish (9.1 $\mu g.kg^{-1}$ ww) in European regulations (EU, 2013).

PFAS signatures at each station were determined by calculating the relative contribution of each detected compound (>LOQ) based on its concentration referred to the sum of the 17 PFAS analyzed. Correlation between PFAS compounds (Spearman test) was performed using R Statistical Software (R Core Team, 2022).

Potential sources of PFAS contamination on the shore were investigated by cross-referencing the locations of study sites with those of PFAS production facilities, contaminated sites, or sites likely to be contaminated defined by journalists of the "Forever Pollution Project" (Luimes and Horel, 2023), following a peer-reviewed methodology developed by the PFAS Project Lab (Salvatore et al., 2022).

In 2021, analysis of 17 PFAS in mussels transplanted to 55 sites distributed along the French Mediterranean coast (including lagoons and Corsica shoreline) revealed that 90% of the measurements were lower than the quantification limits (Table 1). n-PFOS, identified in 19 sites (37%>LOQs), was the most detected PFSA. Among the PFCA, PFUnDa and PFDoDA turned out to be the most prevalent, with almost 47% and 64% of values above LOQs, respectively.

These results are consistent, but only to some extent, with previous investigations of PFAS in aquatic biota. On one hand, it appears that PFOS is not necessarily the most frequently found PFAS, contrary to what has been reported in other studies (Houde et al., 2011; Martin et al., 2004; Munschy et al., 2019). On the other hand, it is confirmed that long-chain PFCA, especially PFUnDA, are predominant in Mediterranean mussels (Munschy et al., 2019, 2015, 2013). PFOA was almost not detected in our samples, confirming an absence of significant direct inputs (Nakata et al., 2006; Pan et al., 2010) along the Mediterranean shore (Munschy et al., 2019).

The sum of the 6 PFSA ranged from 0.013 to 0.474 $ng.g^{-1}$ ww, with n-PFOS being prevalent in each detection (Figure 2). Except for the Diana site in Corsica, PFSA were mainly found in lagoon samples, with the highest n-PFOS concentrations measured in Lapeyrade (0.357 $ng.g^{-1}$ ww), Bages (0.291 $ng.g^{-1}$ ww), and Vic (0.215 $ng.g^{-1}$ ww). These lagoons were also characterized by the presence of br-PFOS, and PFDS was only detected in Lapeyrade. In coastal waters, PFSA were only detected in 3 sites (Montpellier, Pampelone, and Toulon LB) with n-PFOS concentrations (0.017, 0.015, and 0.014 $ng.g^{-1}$ ww, respectively) approximately 20 times lower than in lagoons. Mediterranean Lagoons are semi-enclosed brackish environments located at the outlet of highly urbanized/anthropized watersheds. French lagoons are in the range oligo-haline (not sampled here) to poly-euhaline (Thau, Leucate…) ecosystems. With little and sometimes no exchange with the sea, these shallow, highly turbid and organic matter concentrated environments, often act as buffers areas. They can accumulate chemicals in their waters, biota and/or sediments thus preventing the coastal area from contamination. This was described by Munaron et al. (2012) for dissolved herbicides and pharmaceuticals, or by Andral et al. (2004) for transformation products of the insecticide DDT and copper in mussels in the same area. Conversely, these authors showed that coastal waters were as much or more concentrated than

lagoons with respect to cadmium, chromium or nickel in mussels or alkylphenols in waters, probably due to greater inputs to coastal waters from large coastal streams.

The concentration range of PFOS (sum of n and br-PFOS) acquired in 2021 (0.013-0.390 ng.g-1 ww) was slightly higher than the data measured in some sites of the French Mediterranean in previous years (2013-2015: 0.0017-0.173 ng.g-1 ww and 2016-2017: 0.007-0.162 ng.g-1 ww, Munschy et al., 2019). However, there are substantial methodological differences between this study and the previous one, making it challenging to establish a clear temporal trend. Indeed, while both studies collected and handled shellfish in accordance with international guidelines for contaminant monitoring in biota (OSPAR, 2018), Munschy et al. (2019) adopted a passive biomonitoring approach (using native shellfish), whereas the RINBIO network employed active biomonitoring. This active approach entails more controlled exposure conditions during the caging period, involving mussels from the same population, of the same age, and with identical immersion durations at each site (Andral et al., 2011, 2004; Briand et al., 2023). Another key difference lies in the spatial representation of each study. The scarcity of native mussels along the French Mediterranean coast limits the spatial representativeness of a passive monitoring approach, whereas the transplantation method used in the RINBIO network allows for coverage of the entire coastline. Additionally, discrepancies in site locations between the two approaches prevent a direct comparison between results obtained from natural mussels and those from caged organisms. Sampling period is another source of discrepancy. The bioaccumulation of contaminants in bivalves is known to vary seasonally (e.g. Casas and Bacher, 2006; Cossa, 1989). In Munschy et al. (2019), samples were collected during winter, whereas the RINBIO program involves immersing organisms in spring and collecting them in early summer. Moreover Munschy et al. (2019) analyzed 14 different PFAS (5 PFAS and 9 PFCA), whereas our study focused on 17 PFAS. This difference in the number of compounds analyzed could introduce a potential bias when comparing the summed concentrations between the two studies.

It is important to note that all PFOS concentrations measured in 2021 remain below the maximum level accepted in food (3 ng.g^{-1} ww), for bivalves, defined by European food regulations (European Commission, 2023). Compared to other Mediterranean data, the PFOS concentration range along the French coast is consistent with other measurements acquired in mussels (<2-3 ng.g^{-1} ww, Nania et al., 2009), in Spain (<0.06 to 0.148 ng.g^{-1} ww, Ericson et al., 2008; Gómez et al., 2011), in Greece (<0.493 ng.g^{-1} ww, Vassiliadou et al., 2015), and in Italy (0.54-1 ng/.g^{-1} ww, Renzi et al., 2013) or else in oysters (<0.22 ng.g^{-1} ww in Spain, Fernández-Sanjuan et al., 2010) or in Tunisia lagoon (0.007 ng.g^{-1} ww in mussels and 0.021 in clams, Barhoumi et al., 2022).

The sum concentration of 11 PFCAs varied between 0.012 and 1.111 ng.g^{-1} ww (Figure 3). This range of C4 to C14 PFCAs was slightly lower than the C6 to C14 levels measured in 2016-2017 (0.150-2.374 ng.g^{-1} ww) and 2013-2015 (0.078-1.979 ng.g^{-1} ww) reviewed in Munschy et al. (2019). However, differences in sampling strategies and spatial scales with this work should prevent us from observing a temporal trend. PFCA data in bivalves in the Mediterranean Sea still seem scarce. Our 2021 results along the French coast remain lower than values from Greece, measured in market products (C4 to C16: <0.18-<2.65 ng.g^{-1} ww, Vassiliadou et al., 2015). However, our data could also appear higher than concentrations of PFOA and PFNA measured in Spain (Gómez et al., 2011), where PFOA was 0.01 ng.g^{-1} ww compared to 0.044 ng.g^{-1} ww in our study, and PFNA was below the detection limit, whereas our data ranged between 0.013 and 0.177 ng.g^{-1} ww.

Similar to PFOS, PFCAs (C4-C14) levels were higher in lagoons (0.023-1.111 ng.g^{-1} ww) than in coastal sites (0.012-0.118 ng.g^{-1} ww) and a Tunisian lagoon (C8 to C14: 0.013 ng.g^{-1} ww in mussels and 0.04 in clams, Barhoumi et al., 2022). The maximum concentration of summed PFCAs was still found in Lapeyrade lagoon (1.111 ng.g^{-1} ww), followed by Monro (0.813 ng.g^{-1} ww) and Gruissan (0.321 ng.g^{-}

^{1} ww). Among the coastal sites, 13 out of 38 stations showed levels above the quantification limit, with maximum values measured at Bastia south (0.118 ng.g^{-1} ww), Cortiou (0.08 ng.g^{-1} ww), and Aude (0.076 ng.g^{-1} ww). According to European health regulation (European Commission, 2023), the PFCA of interest, with maximum concentrations of 0.044 (for PFOA) and 0.177 ng.g^{-1} ww (for PFNA), remain well below the threshold values (0.7 and 1 ng.g^{-1} ww, respectively).

PFAS signatures generally allow assessing their spatial distribution, their temporal variations, and their fate in the marine environment and trophic web (Cara et al., 2022; Meng et al., 2022; Munschy et al., 2019; Schmidt et al., 2019). In this study, the relative contributions of PFAS were utilized to identify spatial similarities/discrepancies across sites and to make assumptions about their sources based on available information regarding potential inputs.

The prevalence of PFCA over PFOS (as a proxy for PFSA) along the French Mediterranean coast, as suggested by Munschy et al. (2019, 2015) is not as straightforward as initially thought. On a larger spatial scale, with data collected from caged mussels in 2021, it appeared that 25% of sites (8 out of 31 with at least one PFAS detection) were characterized by a dominance of PFOS (Figure 4). This discrepancy might be attributed to a more extensive sampling strategy, including more coastal sites and encompassing the entire French Mediterranean shoreline. This approach offers a more refined diagnosis of PFAS contamination in the marine environment.

In three specific sites (Montpellier, Pampelone, and Palo), only n-PFOS was detected. The contamination at Montpellier could be linked to the influence of the nearby wastewater treatment plant outlet (Fenet et al., 2014) and/or the characteristics of the watershed, which includes known terrestrial contaminations and the presence of an airport (Luimes and Horel, 2023). For Pampelone, the absence of potential sources on shore (Luimes and Horel, 2023) does not explain the PFOS identification. In Palo lagoon, contamination might be attributed to the proximity of the Solenzara military airbase (Luimes and Horel, 2023).

In three lagoons (Bages, La Palme, and Leucate), PFOS predominated (>50%) the PFAS signature, which was additionally marked by the presence of C8-C13 PFCA (mainly PFTrDa) at Bages (both stations), shorter PFCA at La Palme (C9-C11, mainly PFNA), C11-C12 PFCA (mainly PFDoDa and PFUnDa in both sites of Leucate). Both PFOS were correlated to C9-C13 PFCA ($r_{Spearman}$=0.34-0.63, p<0.01, Figure 5), suggesting similar sources and behavior accumulation in bivalves. However, no common clear sources emerged for these 5 sites. The proximity of Narbonne city might explain PFOS contamination in Bages lagoon, as PFOS contamination is known to be related to population levels (Pistocchi and Loos, 2009). Industrial activities in the watershed, such as cement plant, uranium purification plant or former pesticide production sites might also be investigated as potential PFAS sources (Galgani et al., 2009; Vouvé et al., 2014). The PFAS identification in La Palme lagoon might be linked to naval activities as consumer products (Paul et al., 2009). For Leucate lagoon, the proximity of Perpignan city, its airport, and the identification of a potential contamination source in the watershed (Luimes and Horel, 2023) could explain the detection of PFAS in this lagoon.

Among the sites where PFOS contribution is lower than 50%, Monro lagoon stood out due to its PFAS profile dominated by a short-chain PFCA (58% of PFBA). In this case, at least two different sources of PFAS inputs are hypothesized. One potential source is a paper manufacturing facility identified upstream of the lagoon (Luimes and Horel, 2023). Such industries are now recognized as potential sources of PFOS (Clara et al., 2008). Additionally, the Monro lagoon is influenced by the river Rhône, which has been identified as another PFAS source (Bertin et al., 2014; Miège et al., 2012). According to the correlation matrix (Figure 5), it seems that the PFBA source could be related to PFNA and PFOA ($r_{Spearman}$=0.46 and 1 respectively, p<0.001), which might be degradation products of fluorotelomer

alcohols (FTOHs) and consequently indicators of atmospheric inputs (Ellis et al., 2004; Martin et al., 2004).

Certain PFAS profiles exhibited a prevalence of PFDoDA (>50%) in the lagoons of Ponant, Berre, Prévost, and the coastal site of Toulon LB, where the PFCA signature is complemented by PFTeDA (30%). In the lagoons of Vic, Thau (Marseillan, Bouzigues sites), and Lapeyrade, PFDoDa remained the most prominent PFCA, albeit not dominant, with diversified PFAS profiles and contributions of PFCAs from C9 to C13.

PFAS presence in Ponant could be linked to detected contaminations in the lagoon's watershed (Luimes and Horel, 2023). Intense chemical and oil refinery activities around Berre and the presence of an airport are presumed sources of PFAS contamination in the lagoon (Luimes and Horel, 2023). For Prévost and Vic lagoons, the potential sources of PFAS might be the same as the coastal site Montpellier. Indeed, until 2005, these lagoons were exposed to direct discharge from the Montpellier wastewater treatment plant, before the outlet was moved to the sea (Derolez et al., 2019). Although the PFAS profiles were somewhat less marked in PFOS, the hypothesis of similar sources remains consistent due to the correlation of PFOS with C10-C13 PFCA ($r_{Spearman}$=0.34-0.63, p<0.01), including PFDoDA (Figure 5). In Toulon bay, the detection of PFTrDA, not correlated with PFOS and PFDoDA (Figure 5), suggests at least two different inputs of PFAS, potentially from the Eygoutier river (showing signs of PFAS contamination) or the naval base (Luimes and Horel, 2023). The connectivity between the lagoons of Thau (Marseillan and Bouzigues sites) and Lapeyrade and the correlation of C9 to C13 PFCA ($r_{Spearman}$=0.28-0.63, p<0.05, Figure 5) suggest that these sites are under the influence of the same PFAS inputs. Indeed, the Lapeyrade lagoon is located close to an oil refinery, which refined oil for almost 80 years before becoming an oil storage site over the last 40 years until now. This historical activity could explain the high levels of PFAS found in mussels at this site. The Ayrolle and Gruissan lagoons were characterized by C10-C14 PFCAs and a prevalence (30%) of PFTrDA. The detection of PFOS and PFTrDA are common characteristics with Bages lagoon, to which they are connected. The difference in proportions could suggest the same potential sources of PFAS but a different fate in the environment and in mussels depending on the site (Munschy et al., 2019).

All sites without PFSA detection were coastal stations. The PFAS signatures of most of them were marked by the dominance of PFUnDA and PFDoDA.

Grau du Roi and Saintes Maries were exclusively contaminated by PFUnDa (100%). PFUnDA is generally attributed to fluoropolymer and polyvinylidene fluoride manufacturing plants (Dauchy et al., 2012), but such industries do not seem to be present near the study sites. Therefore, the presence of PFUnDA might be related to the influence of the Rhône river (associated with its PFAS signature) and/or atmospheric inputs (Cousins et al., 2022) via the degradation of precursors like FTOHs (Martin et al., 2004).

Hérault and Cap Agde displayed an almost balanced contribution of PFUnDA and PFDoDA (almost 50/50), while Banyuls, Rhône, Huveaune, Cortiou, and Plane profiles were more dominated by PFDoDA (approximately 70/30). For Hérault, Cap Agde, and Banyuls, no signs of PFAS contamination were detected nearby on the shore or in their watersheds (Luimes and Horel, 2023). Considering their locations, the fact that Hérault and Cap Agde share the same PFAS signature may eliminate the potential source from the river Hérault.

The PFAS signature of Rhône (PFDoDA 77% and PFUnDA 23%) was consistent with previous studies showing that fish and sediments from the river were characterized by long-chain PFAS (Bertin et al., 2014; Miège et al., 2012). The contamination signs of Huveaune, Cortiou, and Plane could be more

related to the watershed, as these 3 sites are under the influence of the Huveaune river or its by-pass, rather than the wastewater treatment plant of Marseille city, the outlet of which is located at Cortiou.

The PFAS signature at the Aude station was characterized by contributions of PFNA (17%), in addition to PFUnDA and PFDoDA. Considering the correlated groups of long-chain PFCA (Figure 5), C9 to C11 ($r_{Spearman}$=0.4-0.55, p<0.01) and C10 to C13 ($r_{Spearman}$=0.28-0.63, p<0.05), this suggests several sources of contamination for this site or different bioaccumulation processes, even though only one sign of contamination was identified in surface water of the nearby watershed (Luimes and Horel, 2023) (Luimes and Horel, 2023).

Brégançon and Bastia south stand out from other sites without PFSA due to the presence and dominance of the longest-chain PFCAs (PFTrDA and PFTeDA), which are significantly correlated ($r_{Spearman}$=0.55, p<0.001, Figure 5). The detection of PFTrDA, like PFUnDA, is attributed to fluoropolymer and polyvinylidene fluoride industry (Dauchy et al., 2012), but it seems that no such industry was identified near the study sites (Luimes and Horel, 2023). For Bastia, the influence of the city, wastewater treatment plant, naval activities, oil terminal, and the presence of the airport could be potential sources of PFAS (Luimes and Horel, 2023).

The data from the RINBIO network in 2021 provided a first large scale baseline of PFAS concentrations in mussels along the French Mediterranean coast, including lagoons and Corsica.

It was found that 90% of the measurements of the 17 targeted PFAS remained below the quantification limits. Contrary to expectations, PFOS was not necessarily the most detected PFAS in the mussels from the French Mediterranean coast, but it was confirmed that long-chain PFCA's were predominant.

Among the lagoons, Lapeyrade seemed to be the most contaminated, along with Bages and Vic lagoons for PFOS, and Monro and Gruissan lagoons for PFCA. The PFOS concentrations were consistent with other available Mediterranean data, although drawing conclusions on PFCA was challenging due to the scarcity and diversity of data in shellfish for the region. In any case, PFHxS, PFOS, PFNA, and PFOA detections remained below the threshold values for bivalves according to European food regulations.

By crossing PFAS signatures and information on potential sources, the data enabled the description of spatial distribution patterns of PFAS along the French Mediterranean coast. This not only confirmed the hypothesis that the PFAS contamination detected in shellfish is a result of continuous inputs of PFAS, rather than isolated point sources (Munschy et al., 2019), but also shed further light on the complex dynamics of PFAS distribution in the marine environment.

Some signs of a lagoon-sea continuum based on similarities in PFAS profiles were observed, such as between Prévost and Vic lagoons and Montpellier station, which could reflect the influence of the watershed, especially characterized by contaminated surface waters and potential sources, such as a large city and an airport.

Similarities in PFAS profiles in connected sites like Thau/Lapeyrade lagoons, Bages/Ayrolle/Gruissan lagoons, or close sites Bages/La Palme/Salses-Leucate lagoons were interpreted as clues of related contaminant sources. However, they also raised some questions about potential different accumulation processes in mussels.

PFAS signatures provided insights into the influence of watersheds and rivers. The south area of Marseille investigated seemed to be more impacted by the Huveaune river than other sources. Inputs of long-chain PFAS were confirmed for the Rhône river and were also detected for the Aude river.

However, it is important to note that some rivers did not show signs of PFAS inputs, such as Var, Golu, or, to a lesser extent, Hérault.

For a few sites, PFAS sources seemed obvious, such as the influence of the military airbase for Palo lagoon. However, for other stations, the PFAS inputs were more questionable. In the bay of Toulon, the differences in PFAS signatures between both sites raises questions about sources and behavior of these compounds.

For the coastal stations of Banyuls, Cap Agde, Brégançon, and Pampelonne, PFAS contamination did not find potential sources onshore, possibly due to a lack of information on input transportation processes (marine currents, atmospheric pathways).

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Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) used CHAT GPT from Open AI in order to proofread English. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

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Table 1. PFAS concentrations (ng.g^{-1} ww) measured in the 55 stations of SUCHIMED 2021 campaign. Coastal lagoon stations are labelled (L). Shaded cells indicate values below the quantification limit. Maximum levels in bivalves came from European regulation for food (European Commission, 2023)

		PFSA (ng.g^{-1} ww)					PFCA (ng.g^{-1} ww)											
Region	Station	Perfluoro-butane sulfonate	Perfluoro-hexane sulfonate	Perfluoro-heptane sulfonate	branched Perfluoro-octane sulfonate	linear Perfluoro-octane sulfonate	Perfluoro-decane sulfonate	Perfluoro-butanoic acid	Perfluoro-pentanoic acid	Perfluoro-hexanoic acid	Perfluoro-heptanoic acid	Perfluoro-octanoic acid	Perfluoro-nonanoic acid	Perfluoro-decanoic acid	Perfluoro-undecanoic acid	Perfluoro-dodecanoic acid	Perfluoro-tridecanoic acid	Perfluoro-tetradecanoic acid
		PFBS	PFHxS	PFHpS	br-PFOS	n-PFOS	PFDS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
Max level in food (bivalves)		*1.5*			*3 (PFOS)*							*0.7*	*1*					
Occitania	Banyuls	<0.015	<0.014	<0.015	<0.013	<0.014	<0.015	<0.142	<0.245	<0.24	<0.035	<0.022	<0.013	<0.023	0.021	0.037	<0.097	<0.106
	Leucate-Salses (L)	<0.018	<0.017	<0.018	<0.015	0.059	<0.018	<0.24	<0.266	<0.452	<0.043	<0.027	<0.016	<0.017	0.022	0.033	<0.033	<0.032
	Leucate-parks (L)	<0.016	<0.015	<0.016	<0.013	0.058	<0.015	<0.209	<0.401	<0.393	<0.037	<0.024	<0.014	<0.015	0.023	<0.023	<0.029	<0.028
	La Palme (L)	<0.014	<0.013	<0.014	<0.012	0.054	<0.014	<0.183	<0.202	<0.345	<0.023	<0.021	0.02	0.017	0.014	<0.02	<0.025	<0.024
	Port La Nouvelle	<0.015	<0.015	<0.015	<0.014	<0.014	<0.015	<0.146	<0.252	<0.246	<0.025	<0.023	<0.014	<0.023	<0.011	<0.029	<0.1	<0.109
	Bages-south (L)	<0.014	<0.013	<0.014	0.015	0.174	<0.014	<0.189	<0.208	<0.355	<0.023	<0.021	<0.013	0.022	0.025	0.037	0.044	<0.025
	Bages-north (L)	<0.015	<0.014	<0.015	0.019	0.291	<0.014	<0.196	<0.216	<0.369	<0.035	<0.022	0.015	0.021	0.015	0.024	0.042	<0.026
	Ayrolle (L)	<0.015	<0.014	<0.015	<0.013	0.111	<0.015	<0.203	<0.224	<0.382	<0.036	<0.023	<0.014	0.017	0.03	0.067	0.118	0.052
	Gruissan (L)	<0.016	<0.015	<0.016	<0.013	0.102	<0.015	<0.209	<0.231	<0.28	<0.037	<0.024	<0.014	0.022	0.024	0.108	0.123	0.044
	Aude	<0.013	<0.013	<0.013	<0.012	<0.012	<0.014	<0.129	<0.223	<0.218	<0.032	<0.02	0.013	<0.021	0.027	0.036	<0.088	<0.096
	Hérault	<0.017	<0.017	<0.017	<0.016	<0.016	<0.017	<0.165	<0.284	<0.278	<0.041	<0.026	<0.015	<0.026	0.031	0.042	<0.113	<0.123
	Cap Agde	<0.016	<0.016	<0.016	<0.014	<0.015	<0.016	<0.153	<0.264	<0.258	<0.038	<0.024	<0.014	<0.024	0.027	0.036	<0.105	<0.115
	Thau-Marseillan (L)	<0.013	<0.012	<0.013	<0.011	0.081	<0.012	<0.17	<0.207	<0.308	<0.029	<0.017	<0.017	0.024	0.042	0.094	<0.115	<0.084
	Thau-Bouzigues (L)	<0.019	<0.018	<0.019	<0.016	0.088	<0.018	<0.254	<0.309	<0.46	<0.044	<0.026	<0.025	0.029	0.068	0.11	<0.172	<0.126
	Lapeyrade (L)	<0.017	<0.017	<0.017	0.033	0.357	0.084	<0.234	<0.285	<0.423	<0.04	<0.024	<0.023	<0.026	0.095	0.675	0.341	<0.116
	Vic (L)	<0.016	<0.015	<0.016	0.017	0.215	<0.016	<0.219	<0.266	<0.396	<0.038	<0.022	0.052	0.055	0.056	0.13	<0.148	<0.109
	Prévost (L)	<0.016	<0.016	<0.016	<0.014	0.097	<0.016	<0.221	<0.269	<0.277	<0.026	<0.022	<0.021	<0.025	<0.044	0.192	<0.149	<0.11
	Montpellier	<0.014	<0.014	<0.014	<0.013	0.017	<0.014	<0.135	<0.232	<0.227	<0.023	<0.021	<0.013	<0.021	<0.011	<0.026	<0.092	<0.1
	Grau du Roi	<0.015	<0.019	<0.015	<0.013	<0.014	<0.015	<0.142	<0.245	<0.24	<0.025	<0.022	<0.013	<0.023	0.012	<0.028	<0.097	<0.106
	Ponant (L)	<0.018	<0.017	<0.018	<0.015	<0.016	<0.018	<0.244	<0.297	<0.306	<0.029	<0.025	<0.024	<0.028	<0.049	0.109	<0.165	<0.121
	Saintes Maries	<0.017	<0.016	<0.017	<0.015	<0.016	<0.017	<0.163	<0.28	<0.274	<0.028	<0.025	<0.015	<0.026	0.013	<0.032	<0.111	<0.121
	Monro (L)	<0.015	<0.014	<0.015	<0.012	0.086	<0.015	0.523	<0.244	<0.362	<0.034	0.044	0.177	<0.023	0.069	<0.056	<0.135	<0.099
	Rhône	<0.013	<0.013	<0.013	<0.012	<0.012	<0.013	<0.124	<0.213	<0.208	<0.021	<0.019	<0.012	<0.02	0.013	0.041	<0.085	<0.092
	Ponteau	<0.014	<0.014	<0.015	<0.013	<0.013	<0.015	<0.14	<0.241	<0.235	<0.024	<0.022	<0.013	<0.022	<0.011	<0.027	<0.096	<0.104
	Berre (L)	<0.018	<0.017	<0.018	<0.015	0.152	<0.017	<0.238	<0.29	<0.431	<0.028	<0.024	<0.023	<0.027	<0.047	0.198	<0.161	<0.118
	Carry	<0.013	<0.013	<0.013	<0.012	<0.012	<0.013	<0.124	<0.213	<0.209	<0.022	<0.019	<0.012	<0.02	<0.01	<0.024	<0.085	<0.093
	Pomègues	<0.012	<0.012	<0.013	<0.011	<0.012	<0.013	<0.122	<0.21	<0.205	<0.021	<0.019	<0.011	<0.019	<0.009	<0.024	<0.083	<0.091
	Huveaune	<0.013	<0.013	<0.014	<0.012	<0.012	<0.014	<0.131	<0.225	<0.22	<0.033	<0.021	<0.012	<0.021	0.022	0.046	<0.09	<0.098
	Cortiou	<0.016	<0.015	<0.016	<0.014	<0.015	<0.016	<0.152	<0.263	<0.257	<0.038	<0.024	<0.014	<0.024	0.024	0.056	<0.104	<0.114
	Plane	<0.013	<0.012	<0.013	<0.012	<0.012	<0.013	<0.123	<0.211	<0.206	<0.03	<0.019	<0.011	<0.02	0.02	0.044	<0.084	<0.092
	Embiez	<0.012	<0.012	<0.013	<0.009	<0.011	<0.012	<0.156	<0.188	<0.223	<0.022	<0.02	<0.012	<0.012	<0.012	<0.02	<0.021	<0.022
South	Sicié	<0.012	<0.011	<0.012	<0.009	<0.01	<0.012	<0.147	<0.177	<0.21	<0.02	<0.019	<0.011	<0.011	<0.012	<0.019	<0.019	<0.02
	Toulon SB	<0.013	<0.013	<0.014	<0.01	<0.012	<0.014	<0.171	<0.206	<0.244	<0.024	<0.022	<0.013	<0.013	<0.013	<0.022	<0.022	<0.024
	Toulon LB	<0.011	<0.01	<0.011	<0.008	0.014	<0.011	<0.136	<0.163	<0.193	<0.019	<0.017	<0.01	<0.01	<0.011	0.046	<0.018	0.026
	Hyères	<0.012	<0.012	<0.012	<0.009	<0.011	<0.012	<0.152	<0.183	<0.217	<0.021	<0.02	<0.011	<0.012	<0.012	<0.02	<0.02	<0.021
	Brégançon	<0.013	<0.012	<0.013	<0.01	<0.011	<0.013	<0.162	<0.195	<0.231	<0.022	<0.021	<0.012	<0.012	<0.013	<0.021	0.022	<0.022
	Pampelone	<0.013	<0.013	<0.014	<0.01	0.015	<0.014	<0.171	<0.206	<0.244	<0.024	<0.022	<0.013	<0.013	<0.013	<0.022	<0.022	<0.024
	Fréjus	<0.012	<0.012	<0.012	<0.009	<0.01	<0.012	<0.194	<0.182	<0.215	<0.021	<0.019	<0.011	<0.011	<0.012	<0.02	<0.02	<0.021
	Antibes south	<0.011	<0.01	<0.011	<0.008	<0.009	<0.011	<0.137	<0.165	<0.195	<0.019	<0.018	<0.01	<0.01	<0.011	<0.018	<0.018	<0.019
	Antibes north	<0.013	<0.013	<0.014	<0.01	<0.012	<0.014	<0.17	<0.205	<0.243	<0.023	<0.022	<0.013	<0.013	<0.013	<0.022	<0.022	<0.024
	Var	<0.011	<0.011	<0.011	<0.008	<0.01	<0.011	<0.142	<0.171	<0.202	<0.02	<0.018	<0.011	<0.011	<0.011	<0.019	<0.019	<0.02
	Villefranche	<0.011	<0.011	<0.011	<0.008	<0.01	<0.011	<0.14	<0.169	<0.2	<0.019	<0.018	<0.011	<0.011	<0.011	<0.018	<0.018	<0.019
	Menton	<0.01	<0.009	<0.01	<0.007	<0.008	<0.01	<0.121	<0.146	<0.173	<0.017	<0.016	<0.009	<0.009	<0.01	<0.016	<0.016	<0.017
	Rogliano	<0.009	<0.009	<0.009	<0.007	<0.008	<0.009	<0.116	<0.139	<0.165	<0.016	<0.015	<0.009	<0.009	<0.009	<0.015	<0.015	<0.016
	Bastia north	<0.01	<0.01	<0.01	<0.008	<0.009	<0.01	<0.129	<0.156	<0.184	<0.018	<0.017	<0.01	<0.01	<0.01	<0.017	<0.017	<0.018
	Bastia south	<0.01	<0.01	<0.011	<0.009	<0.01	<0.01	<0.141	<0.155	<0.112	<0.025	<0.016	<0.009	<0.01	<0.01	<0.016	0.044	0.074
	Golu	<0.012	<0.011	<0.012	<0.01	<0.011	<0.011	<0.155	<0.171	<0.123	<0.019	<0.018	<0.01	<0.01	<0.011	<0.017	<0.021	<0.02
Corsica	Poggio-Mezzana	<0.01	<0.01	<0.01	<0.009	<0.01	<0.01	<0.136	<0.151	<0.109	<0.024	<0.015	<0.009	<0.009	<0.009	<0.015	<0.019	<0.018
	Diana (L)	<0.014	<0.014	<0.014	<0.012	<0.013	<0.014	<0.192	<0.234	<0.241	<0.022	<0.019	<0.019	<0.022	<0.038	<0.053	<0.13	<0.095
	Palo (L)	<0.01	<0.009	<0.01	<0.008	0.013	<0.01	<0.134	<0.163	<0.168	<0.016	<0.013	<0.013	<0.015	<0.027	<0.037	<0.091	<0.066
	Figari	<0.012	<0.012	<0.012	<0.01	<0.012	<0.012	<0.161	<0.178	<0.128	<0.02	<0.018	<0.011	<0.011	<0.011	<0.018	<0.022	<0.021
	Gravone	<0.012	<0.012	<0.012	<0.01	<0.012	<0.012	<0.163	<0.18	<0.13	<0.02	<0.019	<0.011	<0.011	<0.011	<0.018	<0.023	<0.022
	Ajaccio	<0.011	<0.011	<0.011	<0.009	<0.011	<0.011	<0.149	<0.164	<0.118	<0.018	<0.017	<0.01	<0.01	<0.01	<0.017	<0.021	<0.02
	Cargèse	<0.011	<0.01	<0.011	<0.009	<0.01	<0.011	<0.145	<0.16	<0.115	<0.018	<0.016	<0.01	<0.01	<0.01	<0.016	<0.02	<0.019
	Revellata	<0.011	<0.01	<0.011	<0.009	<0.01	<0.011	<0.142	<0.157	<0.113	<0.025	<0.016	<0.01	<0.01	<0.01	<0.016	<0.02	<0.019

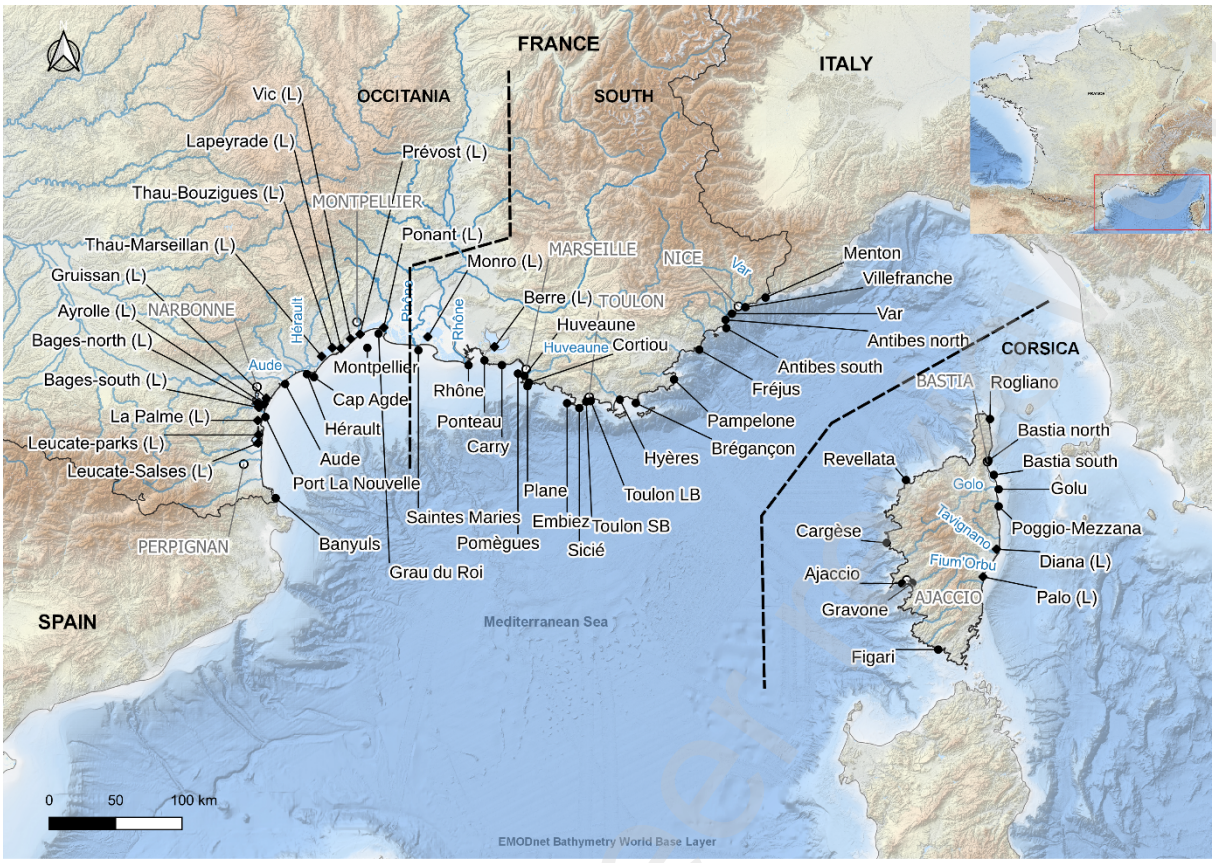

Figure 1. Location of the 55 study sites along the French Mediterranean coast from the SUCHIMED campaign 2021 where PFAS analyses were conducted (diamonds for lagoons and circles for coastal stations)

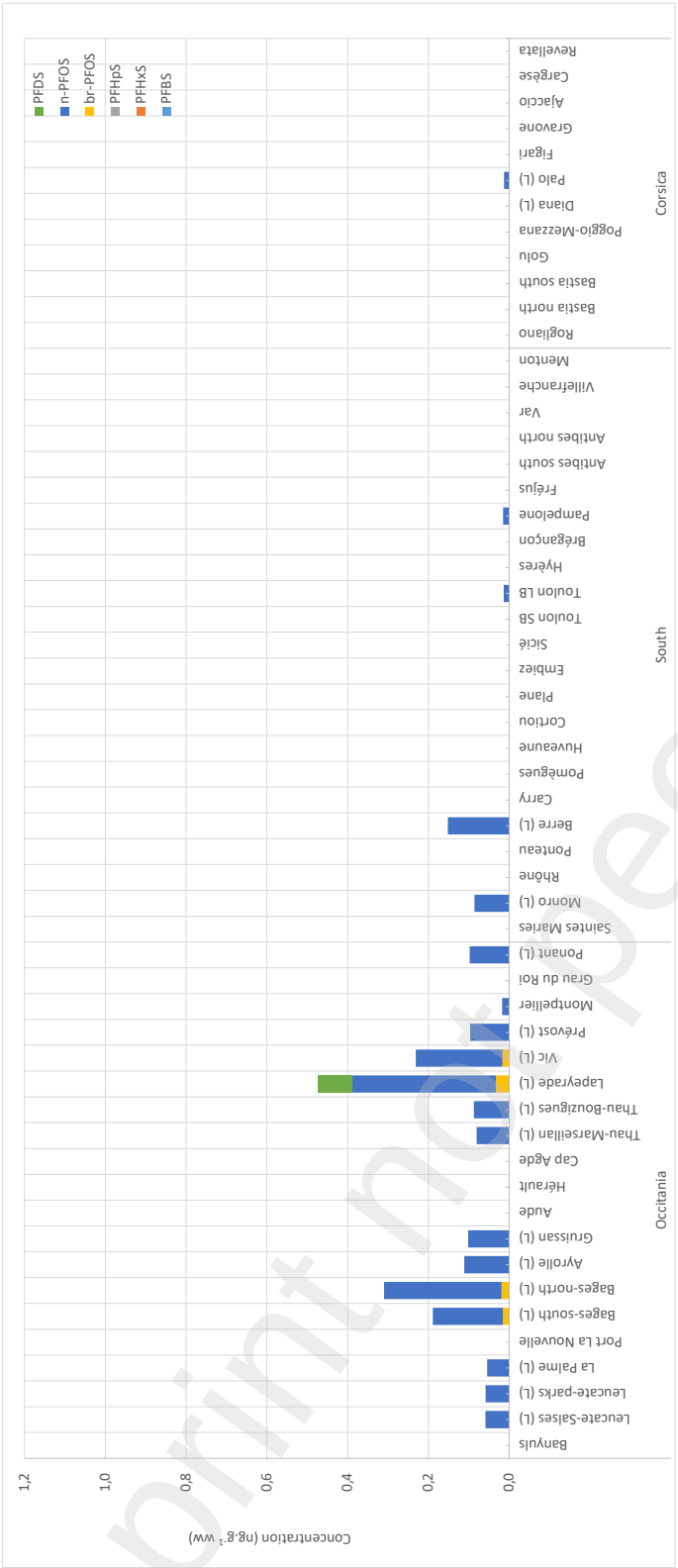

Figure 2. Concentrations (ng.g-1 ww) of 6 PFSAs measured in caged mussels in 2021 along the French Mediterranean coast. Data below limit of quantification are counted as 0. Coastal lagoon stations are labelled (L)

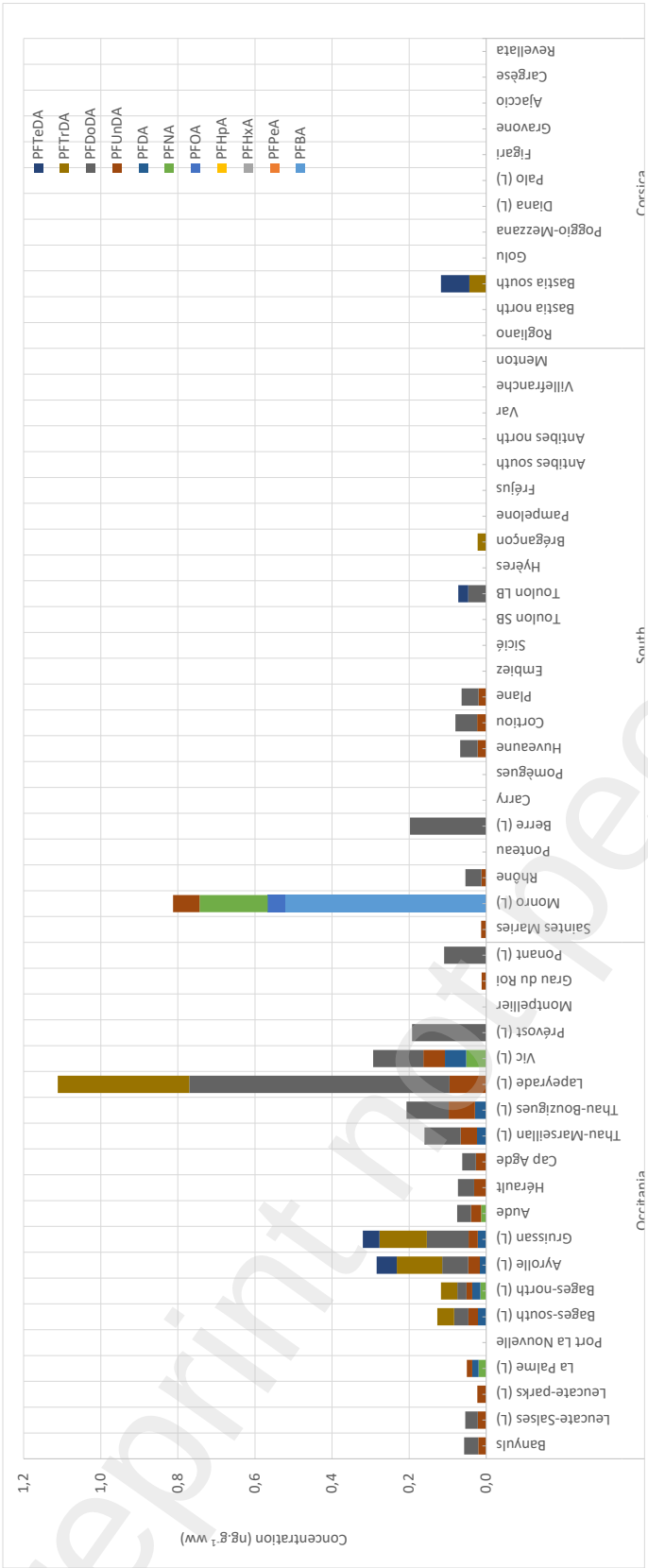

Figure 3. Concentrations (ng.g-1 ww) of 11 PFCAs measured in caged mussels in 2021 along the French Mediterranean coast. Data below limit of quantification are counted as 0. Coastal lagoon stations are labelled (L).

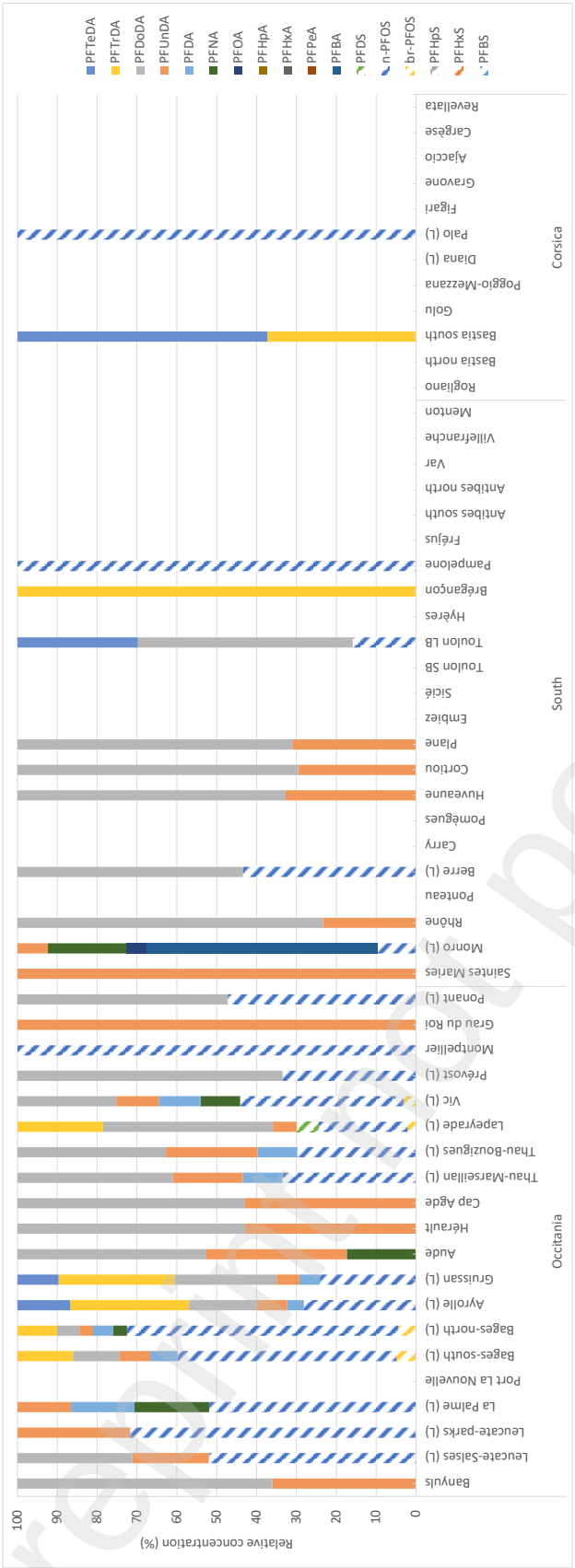

Figure 4. Relative contribution (%) of each PFAS measured in caged mussels in 2021 along the French Mediterranean Hatch filled patterns represent PFSAs and plain bars correspond to PFCA. Data below limit of quantification are not showed since considered as 0. Coastal lagoon stations are labelled (L).

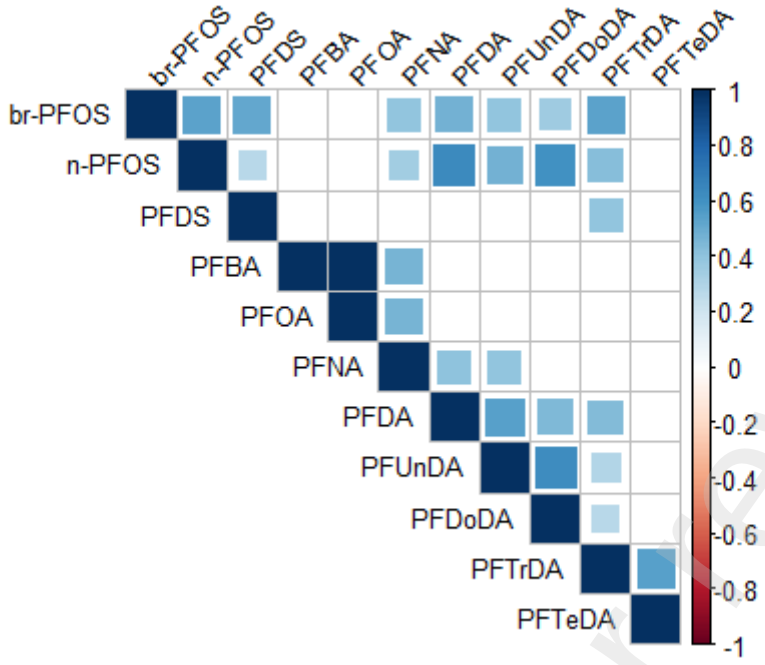

Figure 5. Correlation matrix (Spearman test) between each PFAS, which presented at least one measure above the quantification limit. Squares indicate significant correlation, size and color correspond to the Spearman coefficient.