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Marine vegetation analysis for the determination of volatile methylsiloxanes in coastal areas



Filipe Rocha^a, Vera Homem^a, Javier Castro-Jiménez^b, Nuno Ratola^{a,*}

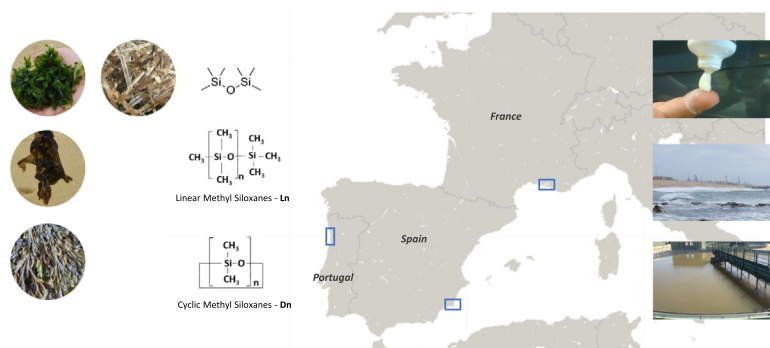
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HIGHLIGHTS

- Marine and coastal environments are potential hotspots for the presence of VMSs.
- VMSs assessed in marine vegetation from the Atlantic and the Mediterranean coasts.
- Occurrence of VMSs was confirmed in almost all samples, predominantly D5 and D6.
- Higher concentrations were reported in urban and industrialized sites, or near WWTPs.
- Seasonal trends were not clear, despite general higher levels of VMSs in summer months.

GRAPHICAL ABSTRACT



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ABSTRACT

Volatile methylsiloxanes (VMSs) are massively produced chemicals that comprise a wide range of industrial and household applications. The presence of cyclic and linear VMSs in several environmental matrices and ecosystems indicates persistence associated with a potential of (bio)accumulation and food web transfer with possible toxicological effects. Due to the high anthropogenic pressure in its vicinities particularly in summer, coastal areas in Southern European countries are potential hotspots for the presence of VMSs. The massive afflux of tourists and consequent increase of the use of personal care products (PCPs) with VMSs in their formulations highlight the importance of VMSs assessment in such areas. In this study, different species of marine vegetation (algae and seaweed) were collected in three different geographical areas, covering the Atlantic Ocean (North coast of Portugal), as well as the Mediterranean Sea (coasts of the Region of Murcia, Spain and of the city of Marseille, France). Samples were analysed for the determination of 4 cyclic (D3, D4, D5, D6) and 3 linear (L3, L4, L5) VMSs employing a QuEChERS extraction methodology, followed by gas chromatography/mass spectrometry (GC/MS) quantification. VMSs were detected in 92% of the 74 samples analysed, with the sum of the concentrations per sample ranging from below the limit of detection (LOD) to $458 \pm 26 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$ (dry weight). A strong predominance of cyclic VMSs over linear ones was verified in almost all samples studied, with D5 and D6 found at higher concentrations. Seasonal variation was also assessed and despite higher levels of VMSs being identified mostly in summer months, clear seasonal trends were not perceived. It was also noted that generally the higher incidence of VMSs occurred in samples from urban and industrialized areas or in the vicinities of WWTPs, suggesting a direct input from these sources in the levels of siloxanes observed.

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1. Introduction

Siloxanes are a vast group of chemicals consisting of a backbone of alternating silicon (Si) and oxygen (O) atoms with organic side chains. Polymeric forms of siloxanes are usually designated as silicones and depending on the functional groups selected to the side chains and the size of the polymers, their physicochemical properties may vary considerably, allowing an extensive range of uses and applications (Rücker and Kümmerer, 2015). Due to their hydrophobicity, these compounds are part of formulations of adhesives, sealants and coatings in water repellent paints (Arespachochaga et al., 2015), and in paper, leather and textile industries (Graiver et al., 2003) for the enhancement of material properties. Siloxanes are also used in the production of rubbers, resins and other matrices with low thermal and electric conductivity (Rücker and Kümmerer, 2015), and in antifoaming and wetting agents, reducing the surface tension of liquids. They also take part in agrochemical and pharmaceutical formulations, in household and industrial cleaning products (Genualdi et al., 2011), and even as additives in the food processing industry (Andriot et al., 2007). One other major application of siloxanes-derived products is in cosmetics and personal care products (PCPs), such as skin and hair care products, soaps, perfumes and fragrances, antiperspirants, sunscreens, balms or make-up (Wang et al., 2009; Capela et al., 2016a, 2016b). Under the generic designation of dimethicone and cyclomethicone, linear VMSS (IVMSSs), polydimethylsiloxanes (PDMSSs) and cyclic VMSS (cVMSSs) are commonly used as softeners and moisturizers, facilitating the application of creams and lotions (Capela et al., 2016a), with the cyclic congeners D5 and D6 being the predominant VMSSs used (Wang et al., 2013; Dudzina et al., 2014; Capela et al., 2016a). Consequently, PCPs are considered a major source of human exposure to VMSSs, as well as one of the most important source of their presence in the environment (Capela et al., 2016a). It is estimated that 90% of the VMSSs present in PCPs formulations volatilize during use (spreading via atmospheric transport), while most of the remainder are washed-off and discharged to wastewater treatment plants (WWTPs) (Allen et al., 1997; van Egmond et al., 2013; Mackay et al., 2015; Capela et al., 2016a).

Taking into account the large (and increasing) amount of siloxanes being produced worldwide, the concern about these compounds is growing, especially regarding VMSSs. Considered innocuous for a long time, VMSSs were recently classified as emerging pollutants. A report from the Norwegian Pollution Control Authority in 2007 placed D5 on a priority list of substances of which the emissions should be considerably reduced or halted (Schlabach et al., 2007). Environment Canada and Health Canada published in 2008 reports assessing the risk of cVMSS to the environment, stating that D4 and D5 were identified as persistent, bioaccumulative, toxic and prone to ecological harm, while D6 was not considered likewise (EC/HC, 2008a, 2008b, 2008c). The European Commission classified D4 as an endocrine disruptor, possibly interfering with the human endocrine function and impairing human fertility (EC no. 1272/2008, 2008), and in 2009 a risk assessment report by the UK Environment Agency considered D4 and D6 as a threat to the environment, while D5 was considered not hazardous (Brooke et al., 2009a, 2009b, 2009c). Also the United States Environmental Protection Agency (USEPA) included D4 in a list of chemicals to be reviewed for further assessment under the Toxic Substance Control Act (Sanchís et al., 2015). These risk assessment reports are mostly based on model predictions, and the lack of experimental data results in great uncertainties and controversies. However, studies developed in mice suggest that a continuous inhalation exposure to D4 is related to the occurrence of uterine endometrial adenocarcinomas in female rats, as well as increased liver weight (hepatic hyperplasia) and inducing of drug metabolizing liver enzymes (Zhang et al., 2000). D4 was also correlated with hormonal changes on oestrogen levels, resulting in impairment of fertility and reproductive complications (McKim Jr. et al., 2001; He et al., 2003; Quinn et al., 2007; Meeks et al., 2007). On the other hand, D5 although not affecting fertility in mice, showed possible carcinogenic

effects related to high chronic exposure to liver and lungs in animal studies (EC/HC, 2008b). In the specific case of marine environments, siloxanes were reported as generally non-toxic to organisms at their low levels of solubility in the aqueous media (Arespachochaga et al., 2015), but the knowledge on this subject is still scarce.

The presence of VMSSs has been reported in numerous environmental compartments like sea water, sediment and biota samples in European Nordic Countries (Kaj et al., 2005), river sediment in the United Kingdom (Sparham et al., 2011), the pelagic food webs of two Norwegian lakes (Borgå et al., 2013), in wastewater, surface water and sediments in Catalonia (Sanchís et al., 2013), in seawater, marine sediment and fish samples in Northeast China (Hong et al., 2014), in the marine food web of Dalian Bay, Northern China (Jia et al., 2015), and in pine needles, soil and air in Portugal (Ratola et al., 2016). Some studies suggest that VMSSs are able to undergo long-range atmospheric transport, reaching areas far away from their emission sources: cVMSSs were detected in Arctic air (Genualdi et al., 2011 and Krogseth et al., 2013), sediment and biota (Warner et al., 2010), as well as in Antarctic soils, vegetation, phytoplankton and krill (Sanchís et al., 2015). Considering that some of the emission routes of these compounds are through WWTPs discharges and the common use of siloxanes in PCPs formulations, marine and coastal environments are potential hotspots for the presence of VMSSs, especially considering the high anthropogenic pressure and the increased use of protective PCPs in the summer months with the rise of the temperature and the exponential growth of tourism. Ratola et al. (2016) found much higher levels of VMSSs in the air of one beach from the south of Portugal in summer than in winter. Monitoring the distribution levels of VMSSs in such areas is therefore very important, and to date there is not much information available on the distribution, fate and trends of siloxanes in marine environments in Southern European latitudes. Considering marine vegetation, to the authors' best knowledge, only one study on VMSSs in seaweed is available (Jia et al., 2015). Due to the tendency to accumulate pollutants in their tissues and surface area, marine vegetation has been used in the biomonitoring of pollutants in aquatic environments (Roberts et al., 2008). Moreover, these matrices occupy low trophic levels in food chains, making them a potential vehicle for the accumulation of pollutants into higher trophic levels (Gutow et al., 2016).

This work aimed to determine the presence, levels and possible trends of three linear (L3–L5) and four cyclic (D3–D6) VMSSs in marine vegetation, using a QuEChERS extraction followed by gas chromatography–mass spectrometry (GC/MS) analysis. Different species (algae and seaweed) were collected from several sites in the Atlantic (North and centre regions of Portugal), and the Mediterranean (coast of the Region of Murcia in southeast Spain and surroundings of Marseille city in the south of France).

2. Materials and methods

2.1. Sampling strategy

In this study, different marine vegetation was sampled in three different geographical areas (Fig. 1): three species of macroalgae (*Fucus vesiculosus*, *Porphyra* sp. and *Ulva lactuca*), collected in the Atlantic coast of the north and centre of Portugal, and a species of sea grass (*Posidonia oceanica*) endemic from the Mediterranean Sea, collected in the Region of Murcia, southeast of Spain, and in the surroundings of Marseille, south of France. Samples were collected using disposable nitrile gloves, stored in sealed polyethylene bags and kept refrigerated and protected from light until proper storage in the lab at -20°C until analysis.

Macroalgae samples from 7 different locations in the seashore of the North Region of Portugal, in Porto Metropolitan Area, and 2 other further South, close to the city of Aveiro, were detached from the rocks during low tide conditions in the months of May, June, July, August, September and December 2016, to assess possible seasonal



Fig. 1. Geographical locations of the different sampling sites.

variations. Locations were selected based on their different surroundings and anthropogenic pressure in its vicinities and most of all consist of beach areas, with different affluence levels during the bathing season in Portugal. The most common macroalgae species were collected according to their availability, hence it was not possible to guarantee the collection of the samples from the same species in the same spots in every sampling campaign. Nevertheless, three different species of seaweed were found frequently enough to ensure the coverage of 9 different spots throughout the 6 sampling months. *Fucus vesiculosus* was collected in the beaches of Barra and Biarritz (the latter in a salt water lagoon close to the shore) near Aveiro (an urban area with about 120,000 inhabitants), as well as in 3 other beaches in the North coast of Portugal in the Porto Metropolitan Area (the second biggest urban area in the country, with almost two million inhabitants): Paraíso, Conchinha and Afurada (the latter in the estuary of the Douro river, very close to the mouth). Another two species were collected in the North coast of Portugal: *Porphyra* sp. in the beaches of Paraíso, Aterro, Matosinhos, Canide Norte and Miramar, and *Ulva lactuca* in the beach of Conchinha.

Posidonia oceanica, a seagrass species with ribbon-like leaves, endemic to the Mediterranean Sea, was also part of this study, covering regions with different socio-geographic and climatic patterns. Samples were collected in 7 sites in the Region of Murcia (Spain) in two sampling campaigns: summer (July 2015) and winter (February 2016), collecting the samples in the shore. The Region of Murcia coastline is a very popular summer destination, which increases considerably the urban pressure in those months. Four sites (La Manga North Mediterranean, La Manga North Mar Menor, La Manga South Mediterranean and La Manga South Mar Menor) were located in La Manga, a 21 km long and 100 m wide land strip that separates the Mediterranean Sea from the Mar Menor lagoon and has an intense urban pressure in the summer. Cala Cortina is an urban beach with high occupancy levels in the city of Cartagena, very close to a very important industrial complex that includes the Port and a petroleum refinery and a power plant. La Azohía is a smaller town with strong afflux of tourists in the summer,

while Cala Blanca, a remote beach in an area with no urban development, can be considered a background site. Samples from the surroundings of Marseille were taken from 5 different spots a few meters from the coastline with the help of trained divers, in a single winter campaign in 2016. Marseille is a highly populated area (about 2 million people in the whole conurbation) with a strong social, economic and industrial activity, and with several beaches in the city and in the surrounding areas. Sites were in this case also selected to cover different backgrounds. Frioul (a small archipelago just in front of Marseille) and La Vesse (about 20 km away from Marseille, in the Côte Bleue) are considered low-density populated spots but with high tourist affluence and, in the case of Frioul, intense maritime traffic. Plateau de Chèvres and Cassis are located in the Calanques National Park, but in the vicinity of the WWTP outlet from Marseille and Cassis conurbations, respectively. Marseille Rade Sud is located in the south harbour of the city, close to the Huveaune river outlet.

2.2. Chemicals and materials

Individual standards of octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), dodecamethylpentasiloxane (L5), hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) with purity levels higher than 97%, were purchased from Sigma-Aldrich (St. Louis, MO, USA), as well as tetrakis(trimethylsilyloxy)silane (M4Q), used as the internal standard. The standards and all solutions were prepared in analytical grade *n*-hexane, obtained from VWR (Fontenay-sous-Bois, France), and protected from light in amber glass vials. All preparations were kept in the dark at -20°C until use. Sodium acetate (CH_3COONa), acquired from Merck (Darmstadt, Germany), anhydrous magnesium sulphate (MgSO_4) from Panreac AppliChem (Barcelona, Spain), primary and secondary amine (PSA)-bonded silica and octadecyl-silica (C18), from Supelco (Bellefonte, PA, USA), were used for the QuEChERS preparation. MgSO_4 was baked overnight at 450°C before use. Nitrogen (99.995%) for sample

evaporation and helium (99.9999%) used as carrier gas in the GC/MS system were supplied by Air Liquide (Maia, Portugal).

2.3. Sample extraction and quantification

The development of the extraction procedure was initially based on the protocol validated by Ramos et al. (2016) for the extraction and quantification of VMs in pine needles and soils, and recently optimized and validated for the analysis of 7 VMs in marine vegetation samples (work submitted for publication).

In brief, 2.5 g of finely cut sample was weighted directly into a 50 ml polypropylene conical bottom centrifuge tube, spiked with internal standard (M4Q) at $15 \text{ ng} \cdot \text{g}^{-1}$, and extracted with 10 ml of *n*-hexane in a 720 W JP Selecta ultrasonic bath (Barcelona, Spain) for 15 min after 3 min of vortex. Then, a first QuEChERS, containing 6 g of anhydrous MgSO_4 and 1.5 g of CH_3COONa , was added and the mixture was vortexed for 3 min and centrifuged for 10 min at 2670g. The supernatant was transferred to the second QuEChERS, consisting of 900 mg of MgSO_4 , 300 mg of PSA-bonded silica and 150 mg of C18, used to remove undesired compounds in a dispersive solid-phase clean-up step. The mixture was vortexed and centrifuged as before, with the resulting supernatant being collected and its volume reduced under a nitrogen stream until a final extract of 150 μl . Samples were extracted in duplicate and stored at -20°C prior to analysis. Instrumental analysis was performed using a Varian Ion Trap GC–MS system (Walnut Creek, CA, USA), equipped with a 4000-GC gas chromatograph, a 240-MS ion trap mass spectrometer, a CP-1177 split/splitless injector adapted with a Merlin microseal system (a microvalve alternative to the conventional silicone rubber septa) and an CP-8410 auto-sampler. To prevent bleeding from common chromatographic columns and minimize background contaminations of siloxanes, compound separation was obtained in a low-bleed Agilent DB-5 ms ultra-inert column (30 m \times 0.25 mm I.D., 0.25 μm film thickness) at a constant flow of helium ($1.0 \text{ ml} \cdot \text{min}^{-1}$). The temperature programme was the following: 35°C hold for 5 min, raised at $10^\circ\text{C} \cdot \text{min}^{-1}$ to 95°C , then $5^\circ\text{C} \cdot \text{min}^{-1}$ to 140°C and finally $35^\circ\text{C} \cdot \text{min}^{-1}$ to 300°C (hold for 5.43 min), in a total runtime of 30 min. Injection volume was 1 μl and the temperatures of manifold, ion trap, transfer line and injector were 50, 200, 250 and 200°C , respectively. The mass spectrometer was operated in the electron ionization (EI) mode (70 eV) and for quantitative analysis of target compounds, time-scheduled selected ion storage (SIS) mode was applied. The filament emission current was 50 μA .

2.4. Quality assurance and quality control

The linearity responses were good, ranging from 1 to $750 \mu\text{g} \cdot \text{l}^{-1}$ for each VMs studied, with R^2 values higher than 0.996 and low LODs (between $11.7 \text{ pg} \cdot \text{g}^{-1}_{\text{dw}}$ (D5) and $62.9 \text{ pg} \cdot \text{g}^{-1}_{\text{dw}}$ (L3)), suitable for the detection of these contaminants at trace levels. Global mean of recoveries of $93 \pm 7\%$ were obtained, and good intraday and interday precision values were achieved (RSD values lower than 10 and 15%, respectively, for most target compounds). LODs, limits of quantification (LOQs) and recovery values for each of the target compounds are presented in Supplementary material (Table S1).

Due to the ubiquitous presence of siloxanes and their reported use in PCPs and in some laboratory equipment, special precautions were taken to minimize possible external contaminations throughout the different steps of the experiment. Analysts avoided the use of lotions, perfumes, hand creams and other PCPs, and nitrile gloves were used and constantly changed during sample manipulation. All glass material was rinsed with acetone and the non-calibrated pieces baked at 400°C for at least 4 h before use. Instrumental analysis was also enhanced to eradicate possible contamination sources of siloxanes: together with the use of the Merlin microseal system in the injection port, the inlet liner was free from silanized glass wool and frequently changed. A low bleed ultra-inert column was used and at the end of each

chromatographic run, a temperature of 300°C was kept for about 5.5 min as a clean-up step to remove impurities possibly remaining in the column. To avoid possible memory effects and guarantee the column rinsing, chromatographic blanks of *n*-hexane were frequently run. Procedural blanks (extractions performed with no sample) were also performed and analysed with every extraction batch (Table S2 in Supplementary material) and, whenever needed, the results were blank corrected. Injections of pure solvent were also performed from time to time to assess possible contamination of the solvent itself, but this never happened.

The concentrations of the target compounds in each sample were presented in a dry weight (dw) basis. The water content of each sample was determined according to a procedure proposed by Littler and Littler (1985) for macroalgae: approximately 2.5 g of sample was left to dry at 105°C until constant weight was achieved. A portion of each collected species was reserved for the dry weight determination and tests were performed in duplicate. The results are presented in Supplementary Material (Table S3).

2.5. Statistics

Quantification of the target compounds was performed using the VARIAN, INC. Mass Spectrometry Workstation software, version 6.9.3. Univariate statistic tests for a 95% confidence interval were applied to the results in order to clarify their interpretation and discussion, according to Miller and Miller (1989).

3. Results and discussion

The concentrations found in samples of marine vegetation collected in the Atlantic coast of Portugal and in the Mediterranean coasts of the Region of Murcia (Spain) and Marseille (South of France) will be presented and discussed separately, to cover different points of view in the whole study.

3.1. VMs in macroalgae from the Atlantic Ocean

As mentioned previously, 6 sampling campaigns in 6 different months (May, June, July, August, September and December) were conducted in several locations in the surroundings of the city of Aveiro and of Porto Metropolitan Area (Portugal). Several species of macroalgae were collected in the selected sampling sites, upon availability. *Fucus vesiculosus* and *Porphyra* sp. were collected in the majority of the sampling campaigns in 5 locations, while *Ulva lactuca* was only frequent in one of the selected sites. The presence of VMs was confirmed in 51 out of the 55 samples analysed, and at least one of the target compounds was found at concentrations higher than the LOQ in 48 of them. The levels and mean values of VMs are presented separately for each species and per month, in Figs. 2, 3 and 4. Complete concentrations for each VM, beach and macroalgae species are presented in Supplementary Material (Tables S4 to S6).

Overall, 99% of the VMs quantified in all the samples were cVMs, with a predominance of D5 (44%) and D6 (38%), followed by D4 (12%) and D3 (5%). Considering IVMS, L3 was only detected below the LOQ in *Ulva lactuca* from Conchinha in July, while L4 and L5 were found in concentrations ranging from below LOD to $1.9 \pm 0.9 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$ and $0.6 \pm 0.2 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$, respectively, both in samples of *Porphyra* sp. from the beach of Miramar in June and August. On the other hand, cVMs were detected in a higher frequency and amount, with concentrations ranging between below the LOQ for all cVMS and a maximum of $2.7 \pm 0.8 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$ for D3 (*Fucus vesiculosus*, Conchinha in August), $5.0 \pm 2.7 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$ for D4 (*Porphyra* sp., Canide Norte in August), $27.0 \pm 20.4 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$ for D5 (*Fucus vesiculosus*, Conchinha in August) and $33.3 \pm 19.6 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$ for D6 (*Porphyra* sp., Canide Norte in August). It is important to note that in some cases the levels have high standard deviations, which reflects the complexity of the selected matrixes

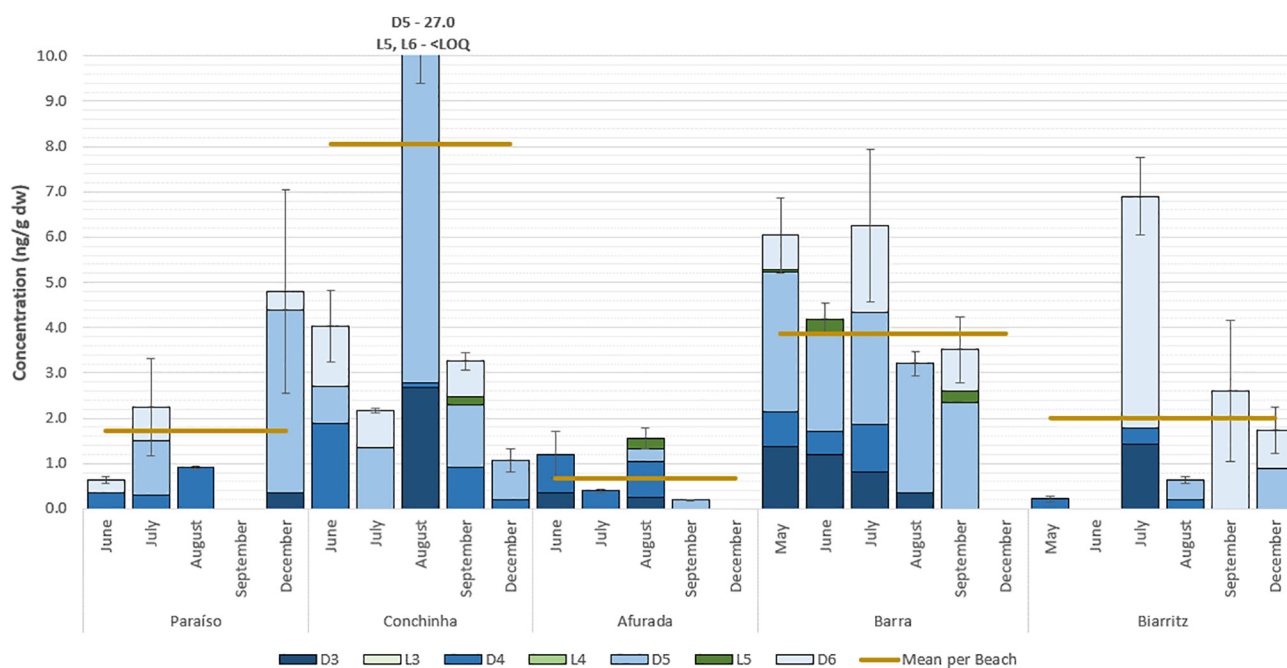


Fig. 2. Concentrations of VMs in samples of *Fucus vesiculosus* (n = 2) from 5 sites. Error bars represent the standard deviation of total concentrations per month.

(due to natural variability of biological materials, such as marine vegetation), and the challenges associated with the analyses of these volatile compounds at trace levels. Similar standard deviations were reported in the only work found so far in the literature regarding siloxanes in seaweed (Jia et al., 2015), in which the trophic transfer of cVMs was assessed in the Dalian Bay, Northern China. The siloxanes found in this study at higher concentrations in sea lettuce (*Ulva pertusa*) were also D4, D5 and D6, with 6.3 ± 2.3 , 5.8 ± 3.4 and $10.5 \pm 11.7 \text{ ng} \cdot \text{g}^{-1}_{\text{ww}}$ (wet weight), respectively. Those values were lower when compared to the same compounds concentration in other biota samples in the same study, with an estimated higher trophic level (for instance, mean D4, D5 and D6 concentrations detected in 5 different fish species were 14.0 ± 8.9 , 31.7 ± 29.6 and $19.1 \pm 2.2 \text{ ng} \cdot \text{g}^{-1}_{\text{ww}}$, respectively).

The site with the highest concentrations of VMs throughout this study was Canide Norte, followed by Miramar. Both are highly-visited beaches, located in the suburban areas of Vila Nova de Gaia, across the Douro River from Porto. If in Canide Norte VMs were only detected during the official bathing season (July, August and September), in concentrations up to $50.4 \pm 20.8 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$, in Miramar a background concentration is more constant throughout the 6 sampling months, ranging between 9.0 ± 4.6 and $22.9 \pm 1.4 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$, in December and August, respectively. In this beach there is a small stream (Ribeira do Espírito Santo) which flows through small urbanized areas until it enters the ocean in this location. This may be a potential contribution to the background concentrations of VMs observed. The third location with higher incidence of VMs was Conchinha, a small beach with great occupancy

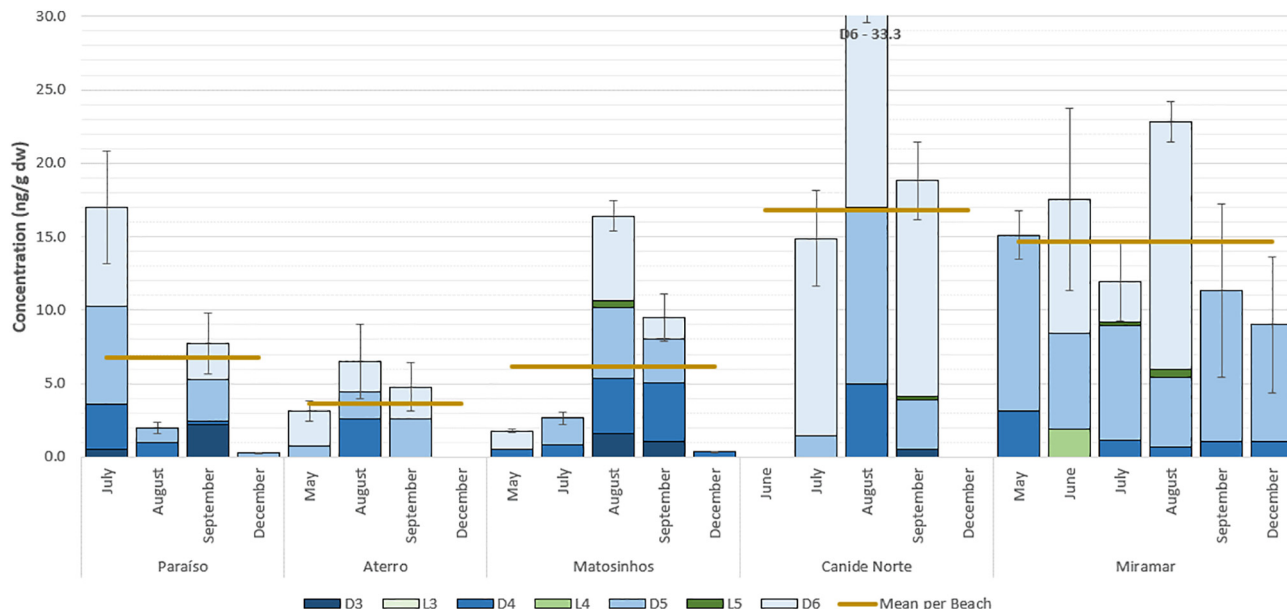


Fig. 3. Concentrations of VMs in samples of *Porphyra* sp. (n = 2) from 5 sites. Error bars represent the standard deviation of total concentrations per month.

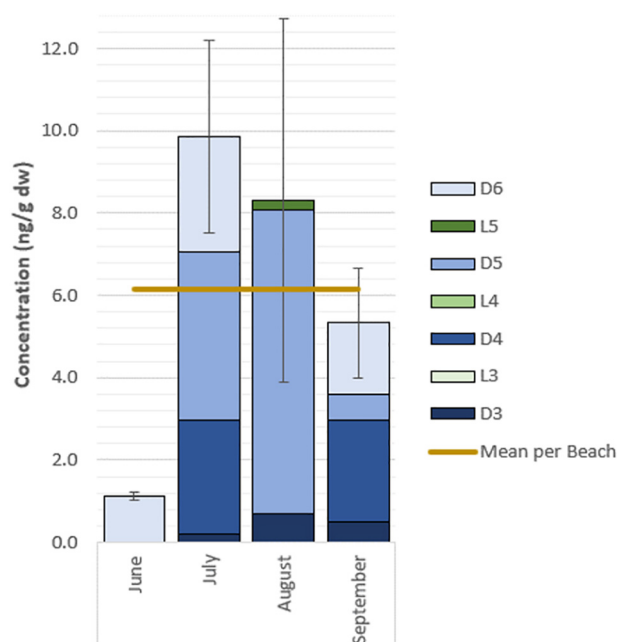


Fig. 4. Concentrations of VMSs in samples of *Ulva lactuca* (n = 2) from the beach of Conchinha. Error bars represent the standard deviation of total concentrations per month.

rate in summer, despite being located near the industrial complex of the Matosinhos refinery and in the vicinities of the Matosinhos WWTP. The highest concentration of the sum of VMSs was $29.8 \pm 20.4 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$ in a *Fucus vesiculosus* sample in August. Other target locations near the same infrastructures, such as the beaches of Paraíso, Aterro and even Matosinhos (the latter closer to Leixões, one of the major seaports in the country), registered mean total VMSs values in samples of *Porphyra* sp. of 6.8 , 3.6 and $6.1 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$, respectively. The lowest values of VMSs were found in Afurada, an estuarine area (Douro River) with no sunbathing activities where *Fucus vesiculosus* was sampled and the sum of the target compounds in each month ranged between not detected (December) and $1.2 \pm 0.5 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$. Further south, the two sites near Aveiro (with *Fucus vesiculosus*) revealed that Biarritz, also not in the open sea (salt water lagoon), presented a concentration of VMSs (global mean value of the sum of VMSs of $2.0 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$) lower than that found for Barra, $3.9 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$, a very popular beach in the warmer months.

Looking into the results under a temporal perspective, seasonal tendencies are in most cases unclear, with the sum of the concentrations of VMSs per month suggesting a background level of contamination, with differences among months not statistically significant most of the times. Nevertheless, some exceptions must be pointed out. For instance, in Canide Norte, VMSs were obtained in *Porphyra* sp. in much higher concentrations in July, August and September (mostly D6), with the highest total VMSs value in August ($50.4 \pm 20.8 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$) statistically different ($p < 0.05$) from all other months. The same species from the beach of Matosinhos also showed a significantly higher concentration of the sum of VMSs in August ($16.4 \pm 1.0 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$), followed by September ($9.5 \pm 1.6 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$), while the other months presented much lower values. In Conchinha, *Fucus vesiculosus* in registered a total amount of VMSs of $29.8 \pm 20.4 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$ in August (91% of which D5), significantly different from the other months. However, a sample of *Ulva lactuca*, another species collected in Conchinha from June to September, revealed a different seasonal pattern, as well as different levels of total VMSs in each month. July had the highest value ($9.9 \pm 2.3 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$), followed by August ($8.1 \pm 4.4 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$, D5 representing 89%). Comparing the results between these two species collected in the same site, the total VMSs values vary considerably, possibly a consequence of their significant differences in shape, superficial area, composition,

life cycle and even position on the shore (Skene, 2011; Parmar et al., 2016). Interestingly, D5 is the compound in higher proportion in both, an indication of consistent sources of VMSs. Finally, in Paraíso, samples of *Porphyra* sp. collected between July and September showed that July was the month with the highest values of VMSs ($17.0 \pm 3.8 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$), significantly different from August and December, but not from September ($7.8 \pm 2.1 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$). However, *Fucus vesiculosus* collected from June to December in the same location, revealed much lower concentrations of VMSs during summer, peaking in December instead. Paraíso is a beach with very limited sunbathing which receives the discharge of a nearby WWTP through a local stream. This can be an indication that VMSs have background values in this site, being the seasonal variations not evident. In fact, even the total VMSs levels are some of the lowest found in the study, which concurs with the previous explanation. Overall, these different levels in different species from the same sampling site suggest that inter-species comparison of the uptake of VMSs in macroalgae must be taken with caution. Besides the structural and biological differences between species, it is impossible to determine in which conditions and for how long each organism has been exposed to the different environmental elements in their natural habitat.

3.2. VMSs in *Posidonia oceanica* from the Mediterranean Sea

Concentrations of VMSs in this marine plant collected in those two regions are presented in Figs. 5 and 6. Complete concentrations for each VMS and sampling site are presented in Supplementary Material (Tables S7 to S9). Similarly to the results obtained in the macroalgae samples in Portugal, VMSs were found in most of the samples analysed (17 out of 19), with a clear prevalence of cVMSs (96%) over IVMSs.

3.2.1. Mediterranean coastline of the Region of Murcia, Spain

In the samples from the Region of Murcia, the total concentration of VMSs ranged between not detected (Cala Blanca, in summer) and $292.0 \pm 41.5 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$ (Cala Cortina, also in summer), with D5 and D6 being the predominant VMSs, representing 57 and 38%, respectively, of the total concentrations. D3 and D4 are almost absent in the samples collected in summer, being usually more frequent in winter samples. This suggests their volatilization from the water phase, due to higher temperatures during the warmer months (consistent with their higher vapour pressure), making these compounds less available for uptake by *Posidonia oceanica* seagrass.

Comparing the results between summer and winter seasons, the total VMSs concentrations were higher in the summer in 4 sites (La Azohía, La Manga North in both Mediterranean and Mar Menor sides, and Cala Cortina), and in the winter in the remaining ones. The remotest area considered in this sampling was Cala Blanca, a pristine beach with very limited access to population. VMSs were not detected in the summer, and in the winter, only very low levels of L4, L5, D5 and D6, with a total concentration of $3.6 \pm 0.7 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$, consistent with its remote location. Having no direct sources of siloxanes identified, the VMSs found may be more subject to the common incidence of VMSs in the atmosphere, which was reported as higher in winter by several authors, due to lower transformation phenomena in this season, such as the reaction of VMSs with OH radicals in the air (McLachlan et al., 2010). In La Azohía, the total concentration of VMSs in summer ($15.1 \pm 1.5 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$) is about 4 times higher to that of the winter season ($4.3 \pm 0.7 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$), with the prevalence of D5 (63%), followed by D6 (22%). Despite being a small urbanized area, La Azohía faces in summer the aforementioned increase of its population due to the afflux of tourists to its beaches. These results suggest the increasing use of PCPs such as sunscreens, deodorants and other body lotions in these areas. Similar trends were observed in three other beaches: in both samples from La Manga North (in both beaches from Mediterranean Sea and Mar Menor) and in Cala Cortina. In La Manga North, similar values of VMSs were registered in both sides of the land strip, with a total maximum for the sample collected in the Mediterranean side in summer

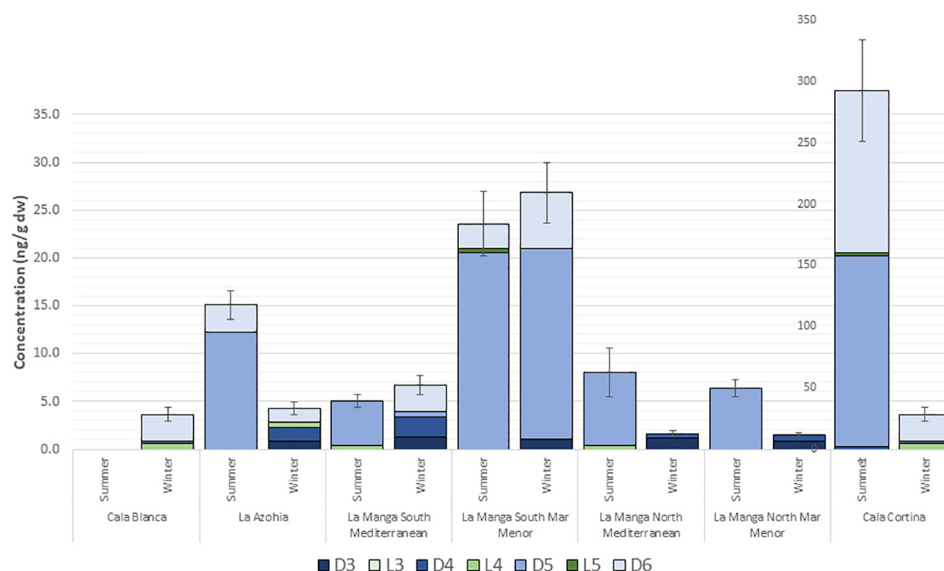


Fig. 5. Concentrations of VMSs in summer and winter samples of *Posidonia oceanica* ($n = 2$) from 7 sites in the Mediterranean coastline of the Region of Murcia, Spain. Error bars represent the standard deviation of the total VMSs concentrations.

($8.0 \pm 2.6 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$), followed by the same season in the Mar Menor side ($6.4 \pm 0.9 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$), while the values of VMSs found in winter in both locations were 5 to 4 times lower. However, in La Manga South, both beach sites in Mediterranean Sea and Mar Menor showed slight higher total concentrations of VMSs in the samples collected in Winter (6.7 ± 1.0 and $26.8 \pm 3.1 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$, respectively), with the prevalence of D5 (74%) followed by D6 (18%). This result was not consistent with the seasonal pattern verified for La Manga North, suggesting that other sources of VMSs in these locations were present. It is also interesting to note that in La Manga South, total VMSs were about 4 times higher in both seasons in the Mar Menor side when compared

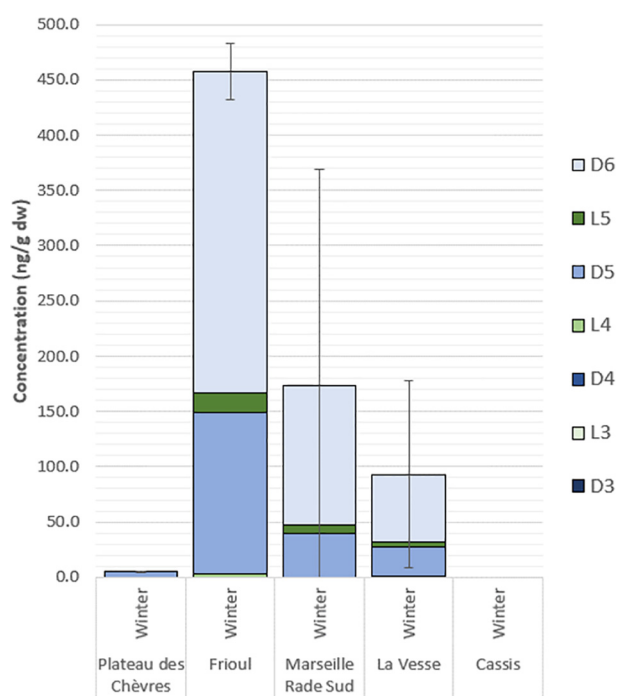


Fig. 6. Concentrations of VMSs in samples of *Posidonia oceanica* ($n = 2$) from 5 sites in the Mediterranean coastline of Marseille, South France. Error bars represent the standard deviation of the total VMSs concentrations.

to the Mediterranean side. Mar Menor is an enclosed salt water lagoon with limited water exchanges and high levels of pollution reported, mostly due to the impacts of mining and agricultural activities, as well as a major urban development in its surroundings during the last decades (Conesa and Jiménez-Cárceles, 2007; Moreno-González et al., 2015; Carratalá et al., 2017). Also, the south part of La Manga suffers more strongly with the urban pressure, and although not as intensively as in summer, even in winter the nice weather conditions attract a considerable number of tourists, adding to the local population, which is more concentrated in this area. Moreover, recent reports highlight the occurrence of plastic debris in the Mar Menor area, and their role as transport vectors of organic pollutants, including PCPs, to this enclosed environment (León et al., 2018). Although the authors did not measure VMSs specifically, plastic debris could be a currently unexplored source for this family of compounds. The sample collected in the summer in Cala Cortina showed the highest levels of total VMSs ($292.0 \pm 41.5 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$), mostly D5 (53%) and D6 (46%). Being a highly-frequented urban beach close to a heavy industrial complex, Cala Cortina is prone to suffer the effects of the use of PCPs by the population during the bathing season, but also the potential use of silicone-based polymers commonly applied as coatings in ship hulls, producing a surface which discourages the settling and accumulation of marine fouling, mostly in cruise and fast container ships (Bohlander, 2009). However, the total concentrations of VMSs in winter are significantly ($p < 0.05$) lower ($3.6 \pm 0.7 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$), suggesting the importance of the afflux of sunbathers in the summer and the enhanced use of sunscreens and other PCPs.

Overall, statistically significant differences between summer and winter ($p < 0.05$) were only found in Cala Cortina (values in summer much higher than in winter). The absence of a clear seasonal or geographical pattern considering the other locations in both seasons can also be attributed to the characteristics of the marine vegetation, which can have different responses in terms of development depending on the exposure. Also, the extremely high temperatures observed in the Region of Murcia in the summer may induce phenomena of volatilization of VMSs into the atmosphere and of enhanced reaction with OH radicals that have a stronger presence in the warmer months (Vaughan et al., 2012), counteracting the effect of more local sources of VMSs via the enhanced urban pressure and use of PCPs. *Posidonia oceanica* is considered an indicator of seawater quality (Gobert et al., 2009), being absent if the exposure to pollution is high. Consequently,

the ubiquity of VMSs and their behaviour, transport and distribution in the environment is a challenging task to take on.

3.2.2. Mediterranean coastline of Marseille, South France

The sum of VMSs varied between not detected (in Cassis) and $457.5 \pm 25.8 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$ (in Frioul) in the *Posidonia oceanica* samples collected in winter, and the prevalent individual congeners were D6 (65%), followed by D5 (30%). Once again, D5 and D6 are found at higher concentrations, consistent with the results in the other Mediterranean region and with the trends found in previous studies (Bletsou et al., 2013; Xu et al., 2014; Sanchís et al., 2015; Capela et al., 2016a).

VMSs were not detected (Cassis) or exhibited the lowest concentrations (Plateau de Chèvres, only D5 at $5.0 \pm 0.6 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$) in samples collected in the Calanques National Park, in spite of their vicinity to the WWTPs. The other three locations are spots facing the city of Marseille directly, thus bearing higher and more diverse anthropogenic pressures in its surroundings, which is reflected on the total amount of VMSs found. In La Vesse, a total concentration of VMSs of $93.1 \pm 84.4 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$ was measured, mostly D6 (65%) and D5 (29%), and samples from Marseille Rade Sud (South harbour of the city of Marseille), also showed high values ($173.1 \pm 195.4 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$), with D6 (72%), D5 (23%) and L5 (5%) being the only compounds detected and showing a potential riverine/WWTP influence. Interestingly, the samples collected close to the Frioul archipelago exhibited the highest VMSs concentrations. This area is known for its intense maritime traffic of commercial and leisure vessels and important tourist pressures. D6 and D5 were again the predominant compounds (290.8 ± 2.2 and $146.3 \pm 25.7 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$, respectively), followed by the IVMSs L5 ($17.1 \pm 1.4 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$) and L4 ($3.3 \pm 1.0 \text{ ng} \cdot \text{g}^{-1}_{\text{dw}}$). In addition, this area has been recently found as a microplastic accumulation spot in the bay of Marseille (Schmidt et al., 2017), consistent with our hypothesis of plastic debris as potential sources of VMSs.

The observed VMSs relative distribution in some samples, like la Vesse or Marseille Rade Sud may also point towards a potential influence of WWTPs (Wang et al., 2015). However, more sampling sites and longer and more frequent observation periods are needed to really ascertain the potential influence of the WWTPs on the VMSs occurrence on *Posidonia* samples in the study area due to the high variability on the time and intensity of the discharges. It is interesting to note that in the three locations with the highest VMSs concentrations, D6 is predominant over D5, with L5 also being quantified in all of the three determinations. Since samples were collected in winter, these levels are unlikely to be related to the direct inputs by beach attendants, so probably a combination of the intense urban and industrial pressures, the presence of nearby WWTPs and plastic debris could have influenced the observed pattern.

The mean concentrations found in Marseille are higher than in Murcia and in addition only two sites in Murcia (Cala Blanca and Cala Cortina) showed the same predominance of D6 in winter as the samples in Marseille. This may reflect different patterns of VMSs usage and emissions. However, there is a high variability, and factors such as the different sampling strategies could have contributed to the observed differences.

The clear predominance of cVMSs over IVMSs verified in all samples considered in this study is consistent with the results on the determination of siloxanes in biota samples in marine environments (Kaj et al., 2005; Warner et al., 2010; Hong et al., 2014; Jia et al., 2015), as well as in terrestrial vegetation (pine needles) in Portugal (Ratola et al., 2016). Besides, these results are also in line with the prevalence of cyclomethicones use in wash-off PCPs, mostly D5 and D6, and the resulting higher mass loadings of these compounds to WWTPs when compared to IVMSs (van Egmond et al., 2013; Xu et al., 2013; Capela et al., 2016a), suggesting that these facilities are one of the possible route of these pollutants into coastal environments. Another source could probably be the release of siloxanes due to its presence in sun care and other PCPs used by the population attending the beaches

during the bathing season. In addition, plastic fragments, in particular those coming from PCPs containers could constitute a not-yet investigated source of VMSs in marine waters and vegetation. Nevertheless, marine vegetation is not directly impacted, in the sense that receives the input from the amount of VMSs present in seawater or air. Since VMSs are not strongly water-soluble, the variations in the levels found or the absence of significant seasonal trends in some cases highlight the difficulty in quantifying VMSs. But their detection in almost all samples is an evidence of their ubiquitous presence. Thus the need to pursue the research in coastal areas, involving more matrices, with a wider temporal coverage, and eventually including the analysis of other siloxanes. For instance, higher molecular IVMSs and the lowest one, L2, (the latter excluded from the current study due to an overlap with the solvent peak in the GC/MS analysis). The influence of other factors such as pH, temperature, seawater dissolved oxygen or nutrient availability (among others) may also be relevant in future efforts.

4. Conclusions

An analytical methodology based on QuEChERS extraction followed by GC/MS was successfully employed for the assessment of 3 linear (L3–L5) and 4 cyclic (D3–D6) VMSs in different marine vegetation. Sampling campaigns were conducted in the central and North Atlantic coastline of Portugal with three species of seaweed, *Fucus vesiculosus*, *Porphyra* sp. and *Ulva lactuca*, collected in 9 different sites, as well as in the Mediterranean coastlines of the Spanish Region of Murcia (7 sites in summer and winter) and South of France, in the surroundings of Marseille (5 locations only in winter), using *Posidonia oceanica* with samples. From a total of 74 samples analysed, a clear prevalence of cVMSs over IVMSs was seen, mostly D5 and D6. In general, higher concentrations of siloxanes were reported in locations with higher urban and industrial pressures, and WWTPs as well as the use of PCPs by the population attending beach areas during the bathing seasons appear to be two of the main sources of VMSs in the coastal environments investigated. However, our results also indicate that other sources may exist, such as the plastic debris introduced in the marine environment, in particular those coming from PCPs containers. Seasonal patterns were also investigated, with results suggesting a tendency for higher concentrations of VMSs (mostly the cyclic ones) in some of the beach areas with high attendances during summer. However, there were also some results pointing otherwise, hence more studies in coastal areas should be conducted in the future for a better disclosure on this topic. Marine vegetation was a hard matrix to work with for the analysis of such ubiquitous compounds at trace levels, with difficulties and limitations being accounted since the sampling starting point of this study to the end point of the quantification of the extracts. And despite the obtained results contributed for a better understanding of the siloxanes levels, sources and trends in the studied coastal environments, other matrices (such as sediment, or possibly other biota samples with a higher trophic level) should be considered in the future for a more consistent indicator of the presence and behaviour of VMSs in the unique and delicate ecosystems that constitute coastal areas.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.10.012>.

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