



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

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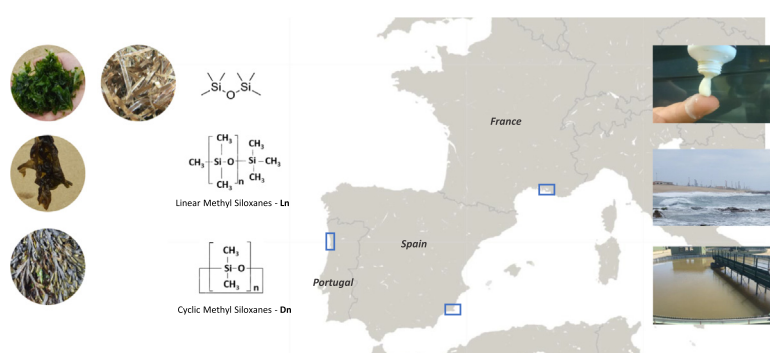
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HIGHLIGHTS

- Marine and coastal environments are potential hotspots for the presence of VMSS.
- VMSSs assessed in marine vegetation from the Atlantic and the Mediterranean coasts.
- Occurrence of VMSSs 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 VMSSs in summer months.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 May 2018

Received in revised form 8 September 2018

Accepted 1 October 2018

Available online 02 October 2018

Keywords:

Volatile methylsiloxanes

Coastal areas

Marine vegetation

QuEChERS

GC/MS

ABSTRACT

Volatile methylsiloxanes (VMSSs) are massively produced chemicals that comprise a wide range of industrial and household applications. The presence of cyclic and linear VMSSs 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 VMSSs. The massive afflux of tourists and consequent increase of the use of personal care products (PCPs) with VMSSs in their formulations highlight the importance of VMSSs 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) VMSSs employing a QuEChERS extraction methodology, followed by gas chromatography/mass spectrometry (GC/MS) quantification. VMSSs 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 VMSSs 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 VMSSs being identified mostly in summer months, clear seasonal trends were not perceived. It was also noted that generally the higher incidence of VMSSs 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 (Arespachoga 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 (IVMSs), polydimethylsiloxanes (PDMSS) and cyclic VMSs (cVMSs) 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 VMSs used (Wang et al., 2013; Dudzina et al., 2014; Capela et al., 2016a). Consequently, PCPs are considered a major source of human exposure to VMSs, 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 VMSs 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 VMSs. Considered innocuous for a long time, VMSs 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 cVMS 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 (Arespachoga et al., 2015), but the knowledge on this subject is still scarce.

The presence of VMSs 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 VMSs are able to undergo long-range atmospheric transport, reaching areas far away from their emission sources: cVMSs 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 VMSs, 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 VMSs in the air of one beach from the south of Portugal in summer than in winter. Monitoring the distribution levels of VMSs 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 VMSs 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 bio-monitoring 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) VMSs 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

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