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Using air, soil and vegetation to assess the environmental behaviour ofsiloxanes

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Abstract

This study aimed to contribute to the enhancement of the knowledge of levels, trends and behaviour of eight siloxanes (four linear and four cyclic) in the environment. Adding to the prioritised scrutiny of the incidence in the atmosphere through passive samplers (sorbent-impregnated polyurethane foam disks—SIPs), the sampling of pine needles and soil was also performed, thus closing the circle of atmospheric exposure in the areas of study. Two sampling campaigns (one in summer and one in winter) were done in a total of eight sampling points in the Portuguese territory, which covered a wide range of human presence and land uses (urban, industrial, remote and beach areas). By adopting a "green" approach in terms of analytical methods, namely reducing the clean-up steps for the passive air samples and using the quick, easy, cheap, effective, rugged and safe (QuEChERS) technology for soils and pine needles, the results showed total concentration of siloxanes between 5 and 70 ng g^{-1} (dry weight) for soils and from 2 to 118 ng g^{-1} (dry weight (dw)) for pine needles, with no clear seasonal trend. For SIPs, the levels varied from 0.6 to 7.8 ng m^{-3} and were higher in summer than in winter in all sites. Overall, the cyclic siloxanes were found in much higher concentrations, with D5 and D6 being the most predominant in a great majority of cases. Also, the urban and industrial areas had the highest incidence, suggesting a strong anthropogenic fingerprint, in line with their main uses.

Keywords **Siloxanes** · Air · Soil · Vegetation · Emerging pollutants

Introduction

Siloxanes have been recently identified as emerging organic contaminants (Lu et al. 2011) and are now raising concern amongst environmental scientists. They are classified into linear and cyclic compounds and consist of a structural unit of alternating Si-O bond with organic side chains (Pedrouzo et al. 2011). They have been widely used in personal care products and cosmetics and also in industrial applications such as lubricants, paints, biomedical products and as antifoaming agents (Dudzina et al. 2014). Having high vapour pressure, they are also persistent and very lipophilic, hence prone to long-range transport and bioaccumulation (European Chemical Agency 2012; Krogseth et al. 2013a; Xu and Wania 2013; Sanchís et al. 2015). Recent reports suggest that siloxanes can undergo trophic magnification (McGoldrick et al. 2014) and indicate potential toxic effects, namely oestrogen mimicking, connective tissue disorder, adverse immunologic effects and eventually fatal liver or lung damage on exposed animals (Wang et al. 2013). D4 is classified by the European Union (EU) as an endocrine disruptor. Their presence was proven in different environmental media such as biota (Warner et al. 2010; Hong et al. 2014; Sanchís et al. 2015), wastewater, surface water and seawater (Sparham et al. 2008; Bletsou et al. 2013; Hong et al. 2014), air (Genualdi et al. 2011; Krogseth et al. 2013b), sediments (Warner et al. 2010; Hong et al. 2014), sludge (Bletsou et al. 2013) and soil (Sánchez-Brunete et al. 2010; Sanchís et al. 2015). However, there is a general lack of information about siloxanes from the production to the levels in the environment and monitoring studies are scarce. In a recent review, Rücker and Kümmerer (2015) mention that the available siloxane production data are also difficult to compare due to the wide variety of classes containing related chemicals, and some are even conflicting. Atmospheric emission patterns are also very difficult to obtain, in part due to the confidential nature of the information that could help their establishment, as reported by the Environment Agency of England and Wales in recent appraisals of D4, D5 and D6 emissions (Brooke et al. 2009a, b, c). Moreover, these and the other few studies available on this matter (Lassen et al. 2005; Environment Canada and Health Canada 2008a, b) only refer to northern latitudes (UK, Canada and Scandinavia), where the patterns can be different from, for instance, Southern Europe.

Vegetation has been chosen as a matrix for the passive sampling of a wide range of (mostly airborne) pollutants. Pine needles are favoured due to their ubiquity, which can provide short- to large-scale trans-boundary studies (Ockenden et al. 1998) and to the retention properties of their waxy layer (Simonich and Hites 1995). But to the best or our knowledge, no references are made in literature to the pres- ence of siloxanes in pine needles, and only Sanchís et al. (2015) reported very recently levels in lichens, grass and moss from Antarctica.

However, being the atmosphere the main route of transport of siloxanes emissions, it is crucial to measure the levels of the target contaminants in the air. Field-based air quality assessment represents a fundamental and strategic tool (according to European Directives 1996/62/EC, 1999/30/EC, 2002/3/EC and 2008/50/EC) regarding the characterisation of air pollution. For that, several types of passive air samplers have been recently used given their low price and easy setup. Sorbent- impregnated polyurethane foam (SIP) disks were chosen in this case, due to their proven efficiency towards siloxanes (Krogseth et al. 2013b; Ahrens et al. 2014). Also, soils were collected since together with vegetation they complete the atmospheric deposition cycle. A sampling scheme was established at eight sites of different exposure patterns, namely urban, industrial, remote and beach areas following a seasonal strategy, as some differences have been reported in the atmospheric presence of siloxanes between the warmer and colder seasons (McLachlan et al.

2010; Krogseth et al. 2013a; Ahrens et al. 2014).

The extraction of siloxanes from this kind of matrices usually relies in techniques such as Soxhlet or sonication followed in some cases by further clean-up steps (Sánchez- Brunete et al. 2010; Genualdi et al. 2011). In this study, it was decided to use a more environment-friendly approach employing the quick, easy, cheap, effective, rugged and safe (QuEChERS) method for the soils and pine needles, following previous work done in our group to extract musks from personal care products (Homem et al. 2013).

This work allowed the establishment of levels and spatial and seasonal trends of the incidence of siloxanes in the environment. Inter-matrix correlations were established to assess potential partition behaviour and anthropogenic fingerprints of these compounds, which enhanced the still poor databases existing to understand their impact on the environment.

Experimental section

Chemicals and materials

Individual standards of siloxanes (L2: hexamethyldisiloxane, L3: octamethyltrisiloxane, L4: decamethyltetrasiloxane, L5: polydimethylsiloxane, D3: hexamethylcyclotrisiloxane, D4: octamethylcyclotetrasiloxane, D5: decamethylcyclopentasiloxane, D6: dodecamethylcyclohexasiloxane) and of the internal standard (M4Q: tetrakis(trimethylsiloxy)silane) were purchased from Sigma-Aldrich (St. Louis, MI, USA). All standards, stock solutions and mixes prepared subsequently were stored in the dark in amber glass vials at −20 °C until use. Analytical grade Prolabo solvents dichloromethane (DCM) and *n*-hexane (Hex) were supplied by VWR (Fontenay-sous-Bois, France). Sodium sulphate (Na2SO4) was acquired from Merck (Darmstadt, Germany), anhydrous magnesium sulphate (MgSO4) and sodium acetate (NaCH3COO) from Sigma- Aldrich and primary secondary amine (PSA)-bonded silica and C18 from Supelco (Bellefonte, PA, USA). Na2SO4 and MgSO4 were baked at 450 °C overnight before use. Commercial QuEChERS (Q1, 6 g MgSO4 +1.5 g NaCH3COO; Q2, 900 mg MgSO4+300 mg PSA+150 mg C18) were obtained from United Chemical Technologies (Bristol, PA, USA). Helium (99.9999 %) used as carrier gas in the GC-MS system and nitrogen (99.995 %) for solvent evaporation were supplied by Air Liquide (Maia, Portugal).

Sampling strategy

A total of eight sampling sites were chosen (see map shown in Fig. 1), covering different anthropogenic pressures and seasonal patterns. Two sites, Porto and Braga, are located in urban settings and are therefore prone to exposure to strong human activity. Porto is the second most populated conurbation in Portugal, reaching almost two million inhabitants as a whole. It is a densely populated area by the coast with a strong commercial and industrial presence, including a petroleum refinery, thermoelectrical plants and a considerable number of important factories of different products (foods, paints, cork, pharmaceuticals, etc.). Braga is a smaller urban centre but is still the third largest city in Portugal with a district surpassing 500,000 inhabitants. It also has a strong industrial component, namely with textile and wood processing units. Two other, ZI Mota and Estarreja, are located in industrial parks to assess the possible industrial impact of siloxanes. The first is located near the city of Aveiro (in an area with about 120,000 inhabitants) and also close to a beach and commercial port area. The industrial park is comprised of several medium-sized companies, including ceramics, metal processing or kitchenware. In its perimeter, there is a wastewater treatment plant (WWTP) which processes both industrial and urban effluents. Estarreja is one of the most important industrial complexes in the country, located in a predominantly rural area between Porto and Aveiro. It is mainly composed of companies dedicated to the production of chemical components (solvents, gases, polymers, etc.). Two sites were chosen at beach resorts, one in the northern west coast, Esmoriz, and another in the south coast of Portugal, Praia da Luz, to evaluate the seasonal variability related to different urban pressures. Esmoriz, being located in the north of Portugal (harsher climate) and close to a residential area (circa 20,000 inhabitants), is mainly affected by a tourist afflux in the summer months, whereas Praia da Luz is a small seaside village in the Algarve which is visited year-round by tourists but particularly in the summer, where its population is significantly increased. The biggest town nearby is Lagos (10 km away), with a censed population of under 20,000. And finally, Outeiro and Midões are set in remote areas, an indication of the background levels found. The first of these sites is located in the National Park of Gerês, in the far north of the country in a very sparsely populated and rural region with some electricity-generating dams nearby, profiting from the existence of many natural water courses. The second is set on a farm in a natural countryside, with low population in the surroundings and mainly focused in rural activities. Some sampling sites were located on private grounds or at public places, preferably fenced, where a previous authorisation had to be obtained. All sampling sites were in conformity with this issue and were set-up in order to cause no harm to people, animals or equipment, and it was possible to collect the three considered matrices in the proximity of each other in all cases.

After the establishment of the sites, SIP disks (14 cm diameter; 1.35 cm thick; surface area, 365 cm^2; mass, 4.40 g; volume, 207 cm^3; density, 0.0213 g cm^{-3}) were deployed at each site preferably at the height of collection of the needles (between 1 and 2 m above the ground, depending on the cases) to provide the closest comparability possible. The sorbent used was XAD-4, a polymeric material suitable for siloxanes entrapment. The disks will be protected by the common "flying saucer" stainless steel chamber, formed by two domes with external diameters of 30 and 20 cm, which protects the sampler from precipitation, UV sunlight and most particle depositions. Based on the work team's expertise and in related literature (Genualdi et al. 2011; Krogseth et al. 2013b), a deployment time of 3 months was chosen. Therefore, in order to evaluate seasonal extremes, SIPs were set-up at the beginning and collected at the end of summer and winter of 2014, completing two sampling campaigns. Solvent-rinsed tongs were used for the collection, placing them in sealed stainless steel tins and immediately frozen and kept in the dark in a cooler and transported to the lab. For the eight sampling sites, a total of 32 SIPs were collected, plus 16 field blanks. At the time of the collection of the SIPs, also pine needles and soil were sampled. The needles will be removed whole from the outer branches of the trees, wrapped in aluminium foil, placed in sealed plastic bags and immediately frozen the same way as for SIPs. Whenever possible, *Pinus pinaster* needles were collected, but in Praia da Luz, only *Pinus pinea* trees were available. Soils were collected from the top layer (0−10 cm) with an appropriate stainless steel tool into amber glass containers. After transport to the lab, the samples were sieved (2 mm) and frozen until analysis.

Sample analysis and quantification

The analytical methodology employed for the extraction and quantification of the target siloxanes from the air, soil and pine needles samples was recently validated by our workgroup and relies on "green" solvent-saving approaches of Soxhlet extraction (SIPs) and QuEChERS (soils and pine needles) (work submitted for publication).

In brief, SIPs disks were put into a 200-mL Soxhlet extractor, spiked with 75 ng of internal standard (M4Q) and extracted overnight either with DCM/Hex 1:1. Then, the extract was passed through a glass column containing Na_2SO_4. The eluate was then reduced to approximately 1 mL by rotary evaporation, transferred to glass vials, evaporated to near dryness by N_2 and redissolved in 150 μL of Hex. For soils and pine needles, the QuEChERS technology employed was based in a previous setup developed for the determination of synthetic musk fragrances in personal care products (Homem et al. 2013). Soils or pine needles (2.5 g) spiked with 15 ng g^{-1} of M4Q and placed into 50-mL polypropylene conical bottom centrifuge tubes were extracted for 15 min in an ultrasonic bath (420 W) with 10 mL of DCM/Hex 1:1. The extract was left to cool to room temperature in order to avoid the loss of analytes by evaporation, and the first QuEChERS (Q1) was added to the centrifuge tubes and vortexed for 3 min to pro- mote a thorough mixing of the phases, before being separated by centrifugation at 400 rpm for 10 min. The extract was transferred to clean tubes already containing the second QuEChERS (Q2) and again vortexed and centrifuged. The supernatant was then transferred to glass vials and evaporated to near dryness by N_2 blow down and redissolved in 150 μL of *n*-hexane.

Samples were then quantified by chromatographic analysis in a Varian 4000 GC/MS system (Walnut Creek, CA, USA), with the conventional CP-1177 split/splitless injector adapted with a Merlin Microseal System and a special low-bleed Agilent DB-5ms ultra-inert column (30 m× 0.25 mm I.D., 0.25 μm film thickness) to minimise siloxane bleeding from the instrument. With helium as the carrier gas at 1 mL min^{-1}, the GC oven temperature programme was as follows: start at 35 °C (hold for 5 min), then raised to 160 °C at 10 °C min^{-1}.

The injector was at 200 °C with a liner without glass wool and the injection volume was 1 μL in splitless mode. The detection of the target compounds was performed using the ion trap mass spectrometer operating in electron ionisation mode (70 eV) and time-scheduled selected ion storage (SIS) acquisition.

A good linear behaviour was obtained for all compounds and matrices at concentrations between 1 and 500 μg L^{-1}, with coefficients of determination (R^2) ranging between 0.9946 and 0.9997 overall. Despite some problems with possible external siloxane contaminations in the lab and during the GC/MS operation, good LODs were obtained, in the order of the low nanogram per sample or even less. In terms of precision, acceptable values were also found for this kind of complex matrices being under 21 % for pine needles, under 10 % for soils except for the more volatile L2 and D3 and again under 9 % for SIPs, except for L2 and D6. The mean recovery for SIPS is 87 %, whereas pine needles and soils reach 75 and 69 %, respectively. Considering the type of matrices and the low concentrations involved, these values reflect a reliable methodology.

Statistics

Basic univariate statistics were applied in the first interpretation and discussion of the results. The significance of the correlations tested was assessed using the Pearson test (with a significance of at least $p < 0.05$). A subsequent chemometric approach using principal component analysis (PCA) allowed a wider treatment of the dataset and subsequent clarification of the results. PCA was performed using the PLS Toolbox (Eigenvector Research, Manson, WA, USA) functions of the MATLAB programme (The Mathworks, Natick, MA, USA).

Results and discussion

As mentioned above, at the end of the 3 months of exposure of the SIP disks (in summer and winter), these were collected in the eight sampling sites, together with soils and pine needles, comprising two sampling campaigns. The results after the pertinent analysis and quantification are presented below.

Pine needles

For pine needles, there was the intention to have all samples from the same species, but in the end, this was not possible. Most sites had *P. pinaster* trees, but in Praia da Luz, only *P. pinea* was available. In Midões and Porto, there was a chance to sample needles of both species but in the latter case only for the winter campaign. As such, it was decided to pres- ent the results separately for each species, as it is known that the inter-species comparability of the uptake of semi-volatile organic compounds (SVOCs) is often not verified (Piccardo et al. 2005; Ratola et al. 2011). In order to have a better characterisation of all the samples, their water and lipid content was measured, and the results are consistent with others re- ported previously for the same species (Ratola et al. 2011).

Figure 2 shows the sum of the concentrations of all siloxanes, separated by pine species and season and on a dry weight basis. Lipid weight results were also calculated but presented very similar patterns and are thus not shown. As this is (to our best knowledge) the first study that reports levels of siloxanes in pine needles, it is difficult to find external references for the results. Roughly, the total concentrations of the eight siloxanes in study present levels one order of magnitude lower than the sum of the 16 Environmental Protection Agency (EPA) polycyclic aromatic hydrocarbons (PAHs) in the same pine species (Ratola et al. 2010), reaching almost 120 ng g^{-1} (dry weight (dw)) in Esmoriz and ZI Mota, the sites that clearly show the highest values. In the only study reporting levels of siloxanes in vegetation (lichens, mosses and grass), Sanchís et al. (2015) obtained values between not detected (n.d.) and 77 ng g^{-1} (dw) for the sum of D3 to D6 in Antarctica, where indeed the levels are expected to be lower to those in Portugal. Again, the different species sampled make a more accurate comparison very difficult.

It is complicated to establish patterns, as although the higher incidence relies mainly on urban and industrial sites, the level in the background ones (Outeiro and Midões) is not much lower. In fact, Midões has a similar presence of siloxanes as Estarreja, near an industrial complex. Concentrations are generally higher in winter than in summer except for ZI Mota in *P. pinaster* samples and Praia da Luz in *P. pinea*'s. This may have an explanation with the fact that the site in ZI Mota is located near a WWTP, facilities which are considered one of the strongest emission sources of siloxanes (Wang et al. 2015). In this case, it is also located in a coastal area and receives domestic and industrial effluents. In summer, the population in the area increases due to the afflux to the beaches nearby, hence increasing the use of personal care products like sun blocks, which are also an important source of siloxanes (Lu et al. 2011). This seasonal phenomenon is even more important in Praia da Luz, a beach in the Algarve, a region famous for receiving numerous tourists in the warmer months. In the Lagos area (where Praia da Luz is located), the population is estimated to increase up to fourfold (INE 2015). For a small community, this is a considerable impact, also regarding environmental safety. Considering the only sites where both pine species coexist (Midões and Porto only in winter), the uptake of *P. pinaster* is higher than that of *P. pinea*, as observed in previous studies for PAHs, for in- stance (Ratola et al. 2011).

In terms of the individual siloxane compounds, the pre- dominance of the cyclic ones is almost total in comparison with the linear ones in all sites, as can be seen in Fig. S1 (Supplementary Material). This is in line with their reported presence in the atmosphere (Genualdi et al. 2011). In fact, most linear siloxanes are not detected, and the highest incidence is of only 6 % of the total siloxanes for L3 in the winter sample from Outeiro (Fig. S1). Within the cyclic, D6 prevails, with a mean incidence of 72 % in *P. pinaster* samples (max 92 %) and 52 % in *P. pinea*'s (max 85 %), followed by D5 (mean of 22 % in *P. pinaster* and 42 % in *P. pinea*) and, with much less impact, D4 (mean of 3 % and max of 16 % in *P. pinaster* and mean 2 % and max 3 % in *P. pinea*). Again, these are the most used siloxanes in several formulations and can even be found in background areas of high northern latitudes (Kierkegaard and McLachlan 2013). It is interesting to notice however that for both pine species, D5 has its highest concentrations in the beach sites in the summer (40 % in Esmoriz and 97 % in Praia da Luz). This may have to do with the formulations used in sun care and other personal care products. Unfortunately, it was impossible to obtain such in- formation for the Portuguese market, and other reports in literature mention that it is common to have blends of D4, D5 and D6 with a wide range of percentages in cosmetics (SCCS 2010 and references therein), making it ever more difficult to have precise estimates. The 2009 report of the Cosmetic Ingredient Review lists past and current uses of cyclomethicones in cosmetics and the myriad of ranges of applications and contents (Cosmetic Ingredient Review 2009). For our target compounds, Horii and Kannan (2008) also show widespread percentages of D4, D5 and D6 in cosmetics such as hair care products, body washes or skin lotions. D5 was the most predominant in the skin lotions, which included three sun screens, which may be in line with the findings of the beach sites. But again, these studies are made in markets such as the USA or Japan that most likely have different rules and means of fabrication, which makes it complicated to apply the figures to our domain of study.

The difficulty in handling the pine needles in analytic terms can also account for some uncertainty in the patterns. Obviously, a more extensive sampling strategy must be con- ducted, especially when even within the same species, the conditions of a tree can vary depending on numerous internal or external factors.

Soils

In order to characterise the soil samples properly, the total organic carbon (TOC) and dry matter content were quantified. Again, the results are presented in a dry weight basis, as the amount of TOC did not show an appreciable influence in the overall trends. The results for the total concentrations of siloxanes in soil samples are presented in Fig. 3. In this case, the patters are easier to draw than for pine needles, even though the concentrations are slightly lower, reaching up to 70 ng g^{-1} (dw). In fact, ZI Mota is again the site where the highest levels were registered, followed closely by Porto, the biggest urban conglomeration of the study. The remote sites have very reduced concentrations, below 10 ng g^{-1} (dw). Estarreja, although being downwind to an industrial complex, is an area of lower population density and is probably "too close" to the complex, hence not suffering the full impact of the plumes that are likely to be transported further away. Moreover, being an important chemical hub, the activity of all units is under strict regulatory control, both internal and externally, to ensure the good practice and safety of the processes involved. These may be some explanations for having about half the siloxane incidence as ZI Mota, the other industrial site and the city of Porto. Interestingly, in Praia da Luz, again the values in summer surpass those in winter, probably due to the population increase in the warm season. In Braga, the summer concentrations double those in winter, but there is no apparent explanation for this fact other than some difficulties in the collection and analysis of the samples. To maintain the consistency of sampling soils very close to the places where the pine needles and passive air samples were located, it was impossible to find out if those soils suffered some kind of treatment or physical removal that could lead to changes not attributed to the deposition of siloxanes alone.

The individual profiles of siloxanes (Fig. S2, Supplementary Material) are similar to those of pine needles, with mean incidences of 65 % for D6 (max 98 %), 24 % for D5 (max 78 %) and 8 % for D4 (max 58 % in the industrial site of Estarreja in the winter). This again reflects the predominant use of these three compounds in industrial and personal care products. However, in some cases, D6 is residual or missing (Braga winter and Estarreja winter). This was due to an unusual level of the blank in these two samples. It also influences the maximum level of D4 found in Estarreja, but there is still a common trend for D4 levels to be higher in winter than in summer. The higher temperatures of the soil in summer suggest that part of it may have been revolatilised into the atmosphere.

Soil samples are an easier matrix to handle than pine needles and can also be more "stable" if the soil is left to rest. But again, more samples and sites must be considered in future studies, as only two were found in literature reporting levels of siloxanes in soils. In the first one, Sánchez-Brunete et al. (2010) showed overall very similar mean total concentrations of five siloxanes (from 15 to 84 ng g^{-1}, dw) for agricultural, sludge-amended and industrial soils from Spain. Only in two industrial soils that higher values were registered (up to 611 ng g^{-1}, dw), and more recently, Sanchís et al. (2015) obtained levels of 0.5 to 175 ng g^{-1} (dw) in soils from the Antarctica. These levels are not only unexpected (as the authors themselves consider), given the remote location, but also reinforced the possibility of long-range transport potential for these chemicals.

Air (SIPs)

Siloxanes in air have been more studied that the previous matrices. Being semi-volatile compounds, the atmosphere is a privileged medium for hosting and transporting them. And this transport can be long, as mentioned above, as their presence was detected in remote Arctic and Antarctic areas (Genualdi et al. 2011; Krogseth et al. 2013a; Sanchís et al. 2015). Some works reported levels up to 10 ng m^{-3}. In our case (Fig. 4), the levels are generally lower that those found in literature, reaching a total of almost 8 ng m^{-3} in ZI Mota, which was again the location with the highest incidence. Porto and Braga, the two urban sites, followed closely and the remote sites were below 1.5 ng m^{-3}. The most noteworthy feature of these results is that, contrarily to the rule of the studies presented so far in literature, the levels in summer are higher than in winter. This is particularly noticed, again, in Praia da Luz, where the total concentration of siloxanes trebles. One possible explanation is that all the other studies on seasonality were performed in high northern latitudes, and the patterns of emissions, use and, most important, climate are very different from the south of Europe. McLachlan et al. (2010) simulated the concentrations of D5 in the whole northern hemisphere from January to August, and although the overall trend was for a visible decrease of its presence in the warmer months, there was still a "hot spot" covering the area of the Iberian Peninsula, where this decrease was residual. And moreover, the projected levels are similar to those obtained in the current study. This is a very interesting phenomenon and should deserve full attention in future studies that must yet again comprise a wider sampling coverage.

The individual patterns are for the air samples show that there is a more equilibrated distribution (Fig. S3, Supplementary Material) but with the same predominance of the cyclic compounds. In this case, D5 is the predominant congener (mean 44 % and max 83 % incidence) followed by D6 (mean 24 %, max 45 %), D4 (mean 21 %, max 47 %) and even D3 reaches 25 % incidence in Estarreja in the winter. It can be seen that in this industrial site, the presence of the cyclic siloxanes is the most evenly distributed, probably reflecting the several uses in industrial processes. D6 is absent in Outeiro, again due to a high blank problem. The linear siloxanes have again a very low presence, but in the remote site of Midões, L5 reaches 17 % in the summer (mean of 4 % overall), with no apparent justification other than an extraordinary use of silicone-based product nearby. It would again be helpful to access data on formulations in order to draw more definitive conclusions.

Having a more detailed insight on the differences between site types for soils and air, which are the most consistent matrices in terms of sampling (pine needles have two species to account for), Fig. 5 confirms the highest mean concentrations for the urban and industrial sites, followed by the beach and the remote sites, which present significant differences with the other site types in both matrices. In soils (Fig. 5, top), all but the urban areas have a slight but not significant predominance in the winter samples, and for the air samples (Fig. 5, bottom), the same sequence urban > industrial > beach > remote is confirmed for the mean total levels, as well as the predominant incidence in summer. In this case, there is a significant difference in the beach sites between the two seasons, which rein- forces that there may be an important anthropogenic finger- print in these results and a strong impact of the population fluxes and variations in these touristic areas.

Statistics and correlations

In order clarify further these results and try to reach an enhanced interpretation of some of the hypotheses, some correlations were sought resorting to statistical methods, both univariate (Pearson correlation) and multivariate (PCA).

The first step was to apply the Pearson test to assess if some significant correlations could be found for individual and total siloxanes comparing the matrices of study, considering the total samples and those of summer and winter separately. The results are shown in Table 1, where the shaded cells rep- resent the significant correlations ($p < 0.05$). For the pine needles, only the *P. pinaster* samples were considered, as they were more than the *P. pinea*'s. It is noteworthy that no corre- lation is found for the winter samples, except for the total siloxane concentration between SIPs and soils. In fact, it is between these two matrices that the most significant correlations are found but for compounds that have a smaller incidence in general (D3 and D4). SIPs and pine needles have a correspondence for D5 and D6 in the total samples and the summer ones, confirming that the needles predominantly trap the contaminants according to their presence in the atmosphere, if in the gas phase. Soils and pine needles show an affinity for D6, the "heaviest" siloxane in study, hence prone to deposit from the atmosphere both in the needles and in the soil.

Between summer and winter (Table 1), some correlations could be obtained. More coincident between SIPs and soils is that D6 and the total siloxanes have a significant link between the two seasons, which is not verified for pine needles, where only L2, D3 and L5 (compounds of a residual presence) show significant inter-season correlation. In light of these results, the general rule confirms that there are differences between seasons and matrices, but again, wider datasets should be considered in the future to enhance the validity of these findings. In the meantime, multivariate statistical methods can be used to complement and improve the range of possible correlations embedded in the results. PCA is a decomposition technique commonly employed in many fields with the objective of extracting relevant and uncorrelated information from the original dataset. This information is condensed in a consecutive sequence of principal components (PCs) comprised by a score vector (related to the samples) and a loading vector (related to the variables). The first PC (usually PC1) explains the most variance, followed by PC2, PC3 and so on, and with decreasing percentage of variance explained (Massart et al. 1997). The output of this analysis is more frequently represented as two-dimensional plots of the first two PCs, which tend to reveal the most significant correlations. In this work, PC1 and PC2 explain almost 50 % of the variability in the results. When PCA is applied, the PCs obtained may be associated with the sources of the target com- pounds in study, with the help of a loading plot. In Fig. 6, it can be seen that the loadings for PC1 (left chart) are positive for all siloxanes, with lower values for L3, D4 and L4. Given that there are not so many differences, PC1 does not have a marked fingerprint on its own, but PC2 however indicates a separation between the cyclic and the linear siloxanes (with the exception of L4 and D5) which can help in the interpretation of the score crossplots. In this case, it was intended to distinguish between matrix, site type and season (subpanels a, b and c Figs. 7, respectively). The dataset divided by matrix (Fig. 7a) shows a separation between air and soils, whereas air samples, although grouped closer, share some of the plot with both needles and soils. This confirms that the loads of siloxanes that reach these two matrices are predominantly provided

by the atmosphere. Moreover, this separation is given by PC2, with pine needles with positive scores and soils with negative ones. By inspecting the loading plot (Fig. 6), soils are linked to D4, D3 and D6 and pine needles to the linear (more volatile) siloxanes and D5, one of the most present in the atmosphere, reinforcing the previous assumptions that the atmosphere may act as a "provider" for the other matrices. There seems to be no particular affinity of the air samples towards any of the siloxanes in particular, confirming the wider distribution of the individual congeners in these matrices. The site type distribution (Fig. 7b) is somewhat chaotic, with the samples reasonably scattered and with no clear distinction between them, which is in line with the results presented above. Only the remote sites seem to have a different behaviour and are more grouped, again backing the previous findings. More or less the same pattern can be seen for the seasons (Fig. 6c), which show no important difference in the crossplot, with all samples reasonably distributed along PC1 and PC2. Thus, despite of some significant differences identified previously in particular cases, the separation between seasons cannot be seen as a whole in all the sampling sites and matrices of this study.

Overall, such a reduced dataset is not the ideal basis to establish patterns of behaviour and obtain numerous significant relationships, but the results are very promising and indicate that this is the right path to pursue increasing knowledge on the environmental behaviour of siloxanes. If more data in emissions and formulations of products containing siloxanes are obtained in the near future, particularly on a regional basis, a more accurate assessment of sources and distribution of siloxanes will be much easier to achieve.

Conclusions

In order to obtain a wide scope of information on the behaviour and environmental incidence of siloxanes, a sampling scheme to collect air with SIP disks, pine needles and soils were established at eight sites of different exposure patterns, namely urban, industrial, remote and beach areas. A strategy of seasonal sampling was implemented, with one campaign in winter and another in summer. The results from the sample analysis allowed the establishment of levels, spatial and seasonal trends and partitioning features of the siloxanes, and a clear anthropogenic fingerprint was perceived, as the remote sites generally showed lower concentrations that the other more urbanised or industrialised areas. The cyclic siloxanes (particularly D5 and D6) were predominant in almost all cases. Univariate and multivariate statistics helped to shed some light on the differences between the warm and cold seasons, the four site types available and the three matrices studied.

This study was also a first portrait of current situation of siloxanes in Portugal. And it led to the finding that some trends on the levels may not be in line with the available literature, namely in the seasonal assessments in the atmosphere. This is a very interesting matter that is worth to continue looking into, with wider and lengthier sampling schemes to help, complemented with modelling strategies at a local, regional and global level. Moreover, special care should be given to WWTP, due to their strong potential as emitting sources of siloxanes into the environment and to the impacts of the population fluxes on a more local level. In consequence, the knowledge of siloxanes still has considerable gaps, and more integrated studies have to be conducted to enhance the awareness of both scientists and stakeholders on a wider scale.

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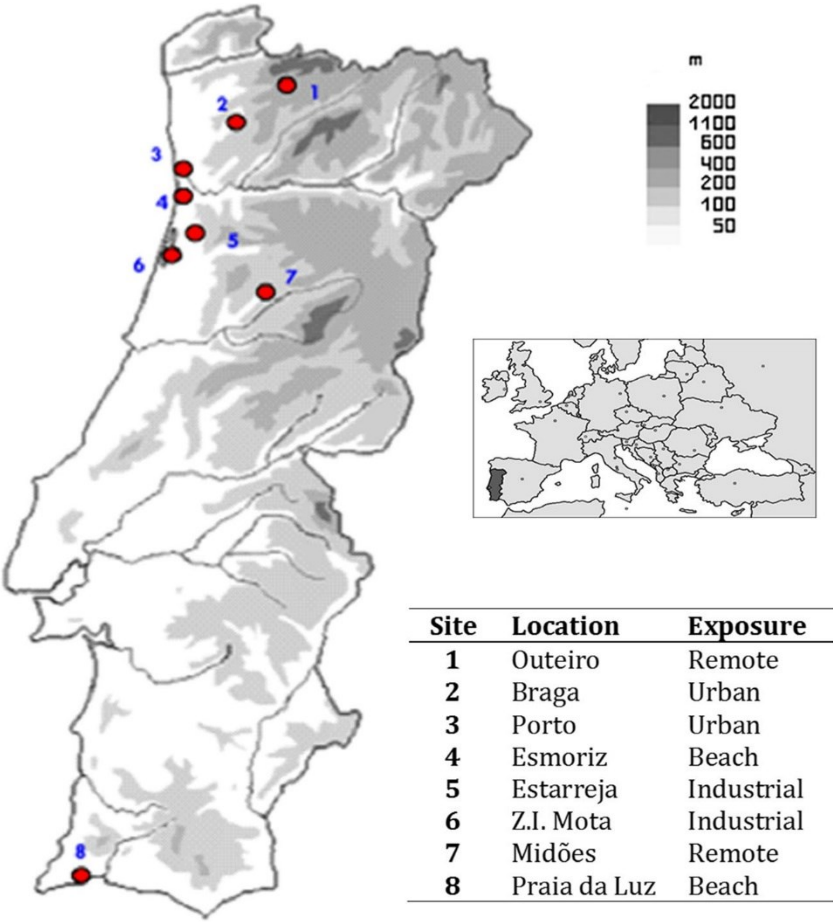

Site	Location	Exposure
1	Outeiro	Remote
2	Braga	Urban
3	Porto	Urban
4	Esmoriz	Beach
5	Estarreja	Industrial
6	Z.I. Mota	Industrial
7	Midões	Remote
8	Praia da Luz	Beach

Fig. 1 Map of the sampling sites

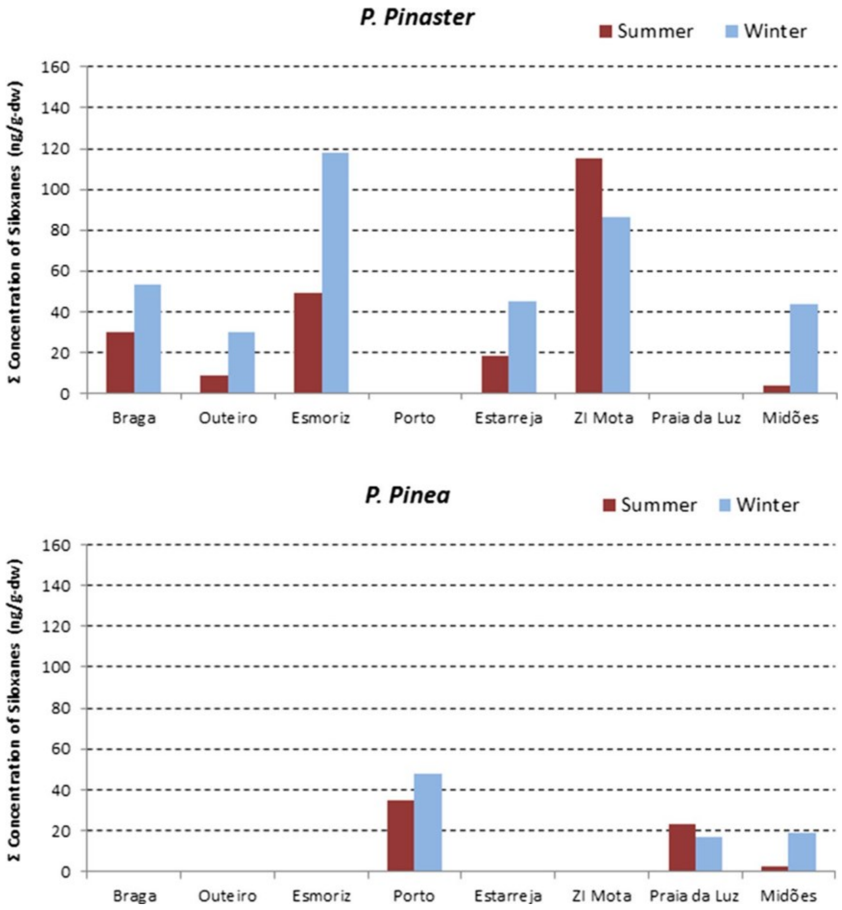

Fig. 2 Total concentrations of siloxanes in *P. pinaster* (*top*) and *P. pinea* (*bottom*) samples, separated by season

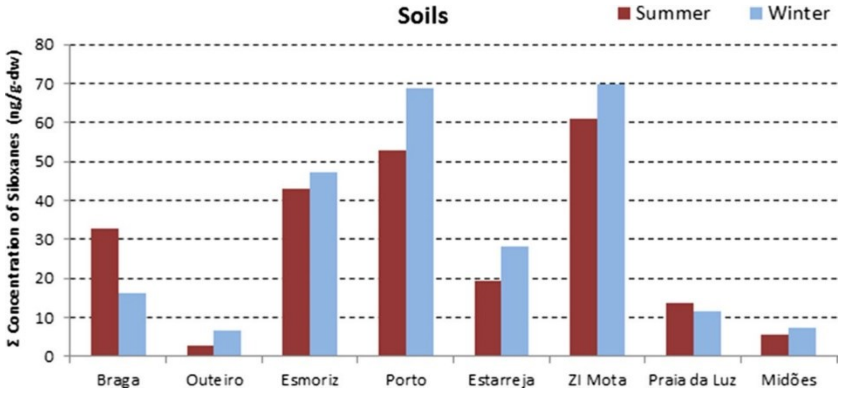

Fig. 3 Total concentrations of siloxanes in soil samples, separated by season

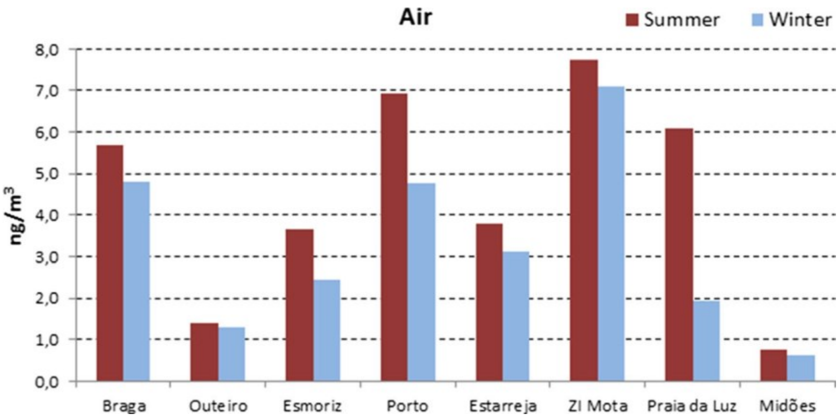

Fig. 4 Total concentrations of siloxanes in air samples, separated by season

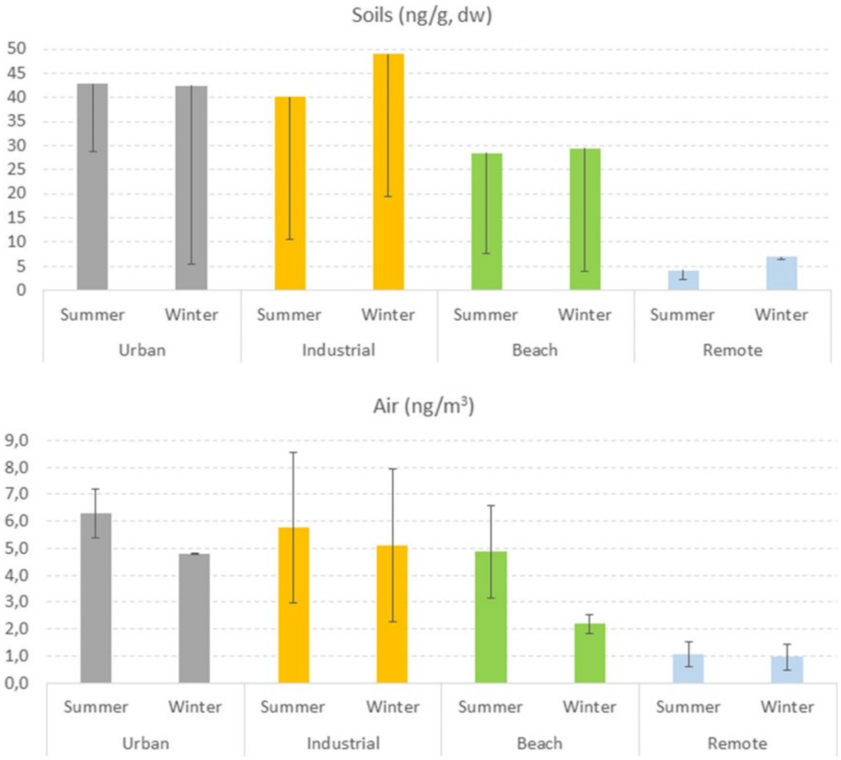

Fig. 5 Mean of the total concentrations of siloxanes in soil (*top*) and air (*bottom*) samples, considering site type and season

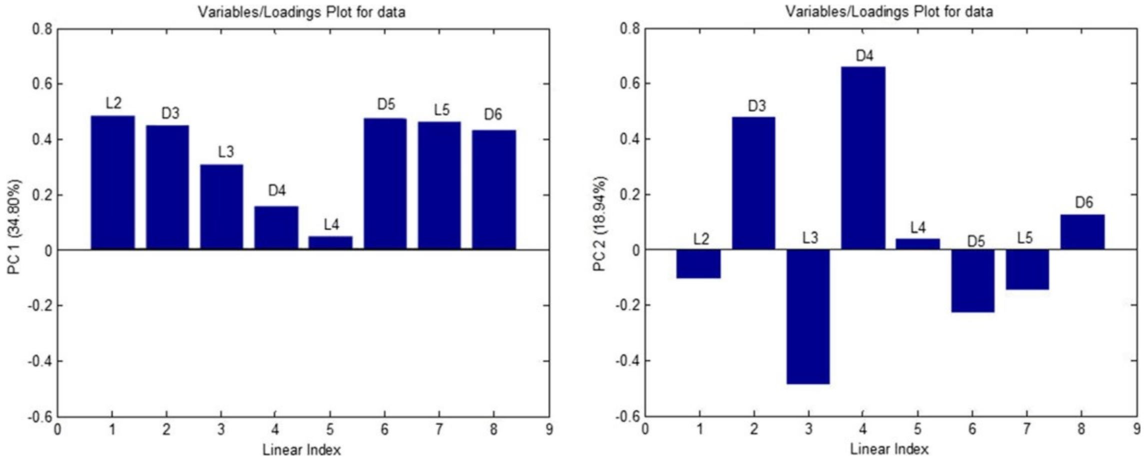

Fig. 6 Loadings plot for PC1 (*left*) and PC2 (*right*) for all individual siloxanes

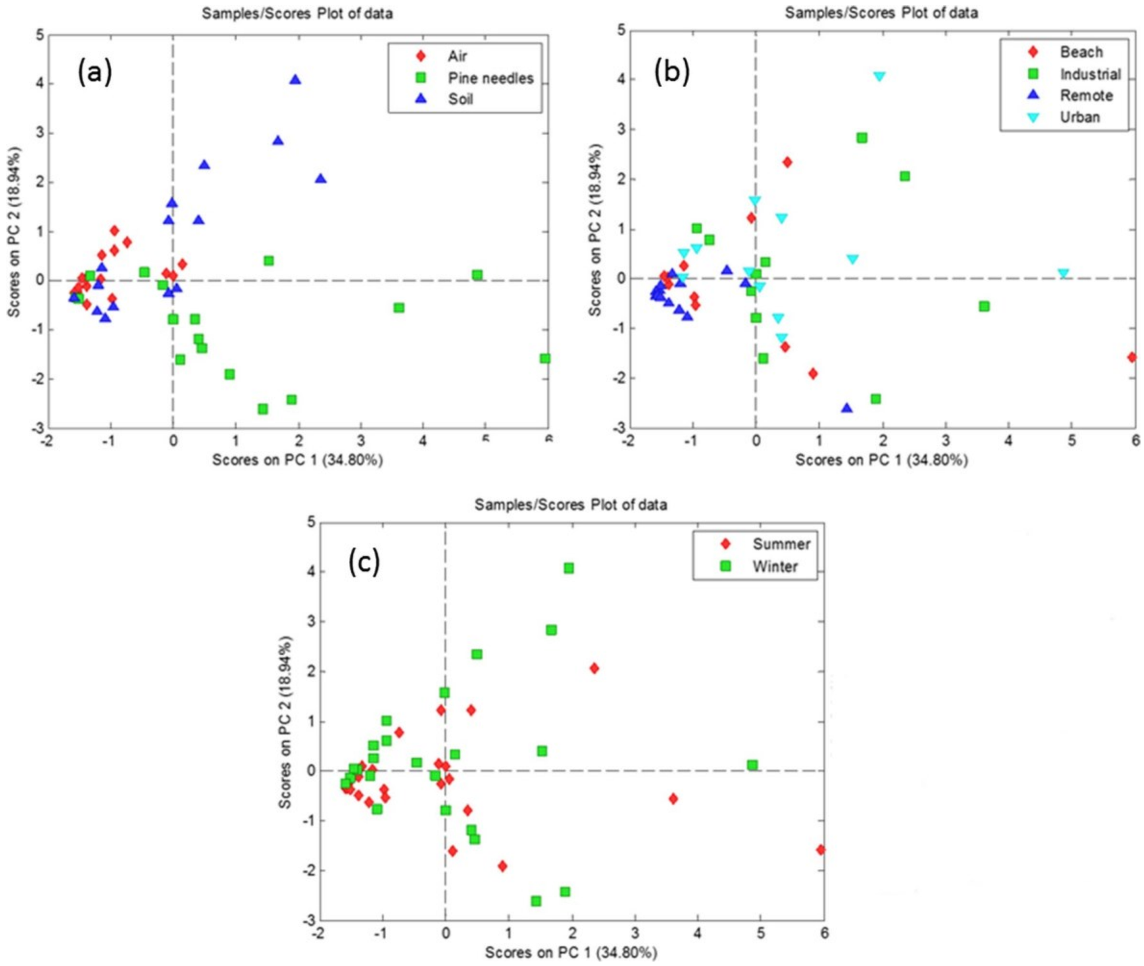

Fig. 7 Crossplots of PC1 vs PC2 scores for all samples divided by matrix (a), site type (b) and season (c) and the respective loadings for all samples including the individual siloxanes (d)

Table 1 Pearson correlation coefficients for individual and total siloxanes: (a) comparing the matrices of study and considering the total, summer and winter samples and (b) comparing between seasons for each of the matrices of study

(a)	SIPs vs soils			SIPs vs *P. pinaster*			Soils vs *P. pinaster*		
	Total	Summer	Winter	Total	Summer	Winter	Total	Summer	Winter
L2							−0.189	−0.277	−0.167
D3	0.664	0.783	0.594	−0.113	−0.052	−0.141	0.157	0.230	0.119
L3	−0.316	−0.185	−0.507	−0.073	−0.595	−0.044	−0.167	0.239	−0.406
D4	0.529	0.248	0.556	−0.016	0.463	−0.570	−0.179	0.159	−0.342
L4				−0.353	−0.301	−0.501			
D5	0.016	0.025	0.525	0.554	0.879	−0.192	−0.066	0.390	−0.663
L5	0.392	0.515	0.254	−0.238	−0.340	−0.133	0.065	0.155	−0.005
D6	0.709	0.762	0.702	0.690	0.964	0.505	0.674	0.876	0.638
Total	0.713	0.785	0.760	0.296	0.449	0.410	0.633	0.669	0.650

(b)	Summer vs winter		
	Air	Soils	Pine
L2		−0.215	0.928
D3	0.208	0.314	0.842
	−		
L3	0.289	−0.449	0.541
D4	0.758	−0.056	−0.292
L4	0.541		−0.213
D5	0.550	0.864	0.199
L5	0.606	0.359	0.894
D6	0.756	0.925	0.616
Total	0.849	0.939	0.663

Grey-shaded cells indicate a significant correlation ($p<0.05$)