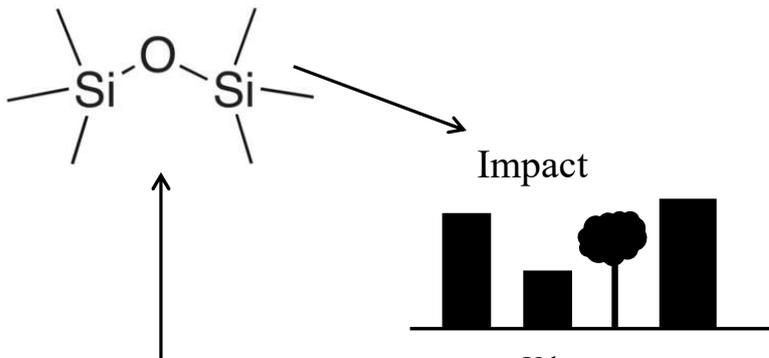


Highlights:

- VMS were evaluated in ten Catalan urban areas with different industrial impacts
- VMS were dynamically sampled using multi-sorbent tubes and analysed through TD-GC/MS
- Σ VMS (including TMS) varied between $0.3 \pm 0.2 \mu\text{g m}^{-3}$ and $18 \pm 12 \mu\text{g m}^{-3}$ (hotspot area)
- cVMS concentrations were up to 3 orders of magnitude higher than IVMS
- Population density (inh. Km^{-2}) correlated significantly ($p \leq 0.05$) with D5 and D6

Graphical Abstract (for review)



Emission to the atmosphere:

- Industry
- Waste water plants
- Use of personal care products

Evaluation of TMS, L2-L5 and D3-D6 in three Catalan urban areas outdoor air



$$0.3 \pm 0.2 \mu\text{g m}^{-3} < [\Sigma\text{VMS}] < 18 \pm 12 \mu\text{g m}^{-3}$$

1 **Volatile methyl siloxanes (VMS) concentrations in outdoor air**
2 **of several Catalan urban areas**

3

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15

16 **Abstract**

17 Volatile methyl siloxanes (VMS) were evaluated in ten Catalan urban areas with
18 different industrial impacts, such as petrochemical industry, electrical and mechanical
19 equipment, metallurgical and chemical industries, municipal solid waste treatment plant
20 and cement and food industries, during 2013-2015. 24 hour samples were taken with
21 LCMA-UPC pump samplers specially designed in our laboratory, with a flow range of
22 70 ml min⁻¹. A sorbent-based sampling method, successfully developed to collect a
23 wide-range of VOC, was used. The analysis was performed by automatic thermal
24 desorption coupled with capillary gas chromatography/mass spectrometry detector. The

25 presented methodology allows the evaluation of VMS together with a wide range of
26 other VOC, increasing the number of compounds that can be determined in outdoor air
27 quality assessment of urban areas. This aspect is especially relevant as a restriction of
28 several VMS (D4 and D5) in consumer products has been made by the European
29 Chemicals Agency and US EPA is evaluating to include D4 in the Toxic Substances
30 Control Act, regarding the concern of the possible effects of these compounds in human
31 health and the environment. Σ VMS concentrations (L2-L5, D3-D6 and trimethylsilanol)
32 varied between $0.3 \pm 0.2 \mu\text{g m}^{-3}$ and $18 \pm 12 \mu\text{g m}^{-3}$, determined in a hotspot area.
33 Observed VMS concentrations were generally of the same order of magnitude than the
34 previously determined in Barcelona, Chicago and Zurich urban areas, but higher than
35 the published from suburban sites and Arctic locations. Cyclic siloxanes concentrations
36 were up to two-three orders of magnitude higher than those of linear siloxanes,
37 accounting for average contributions to the total concentrations of $97 \pm 6\%$ for all
38 samples except for the hotspot area, where cyclic VMS accounted for $99.9 \pm 0.1\%$. D5
39 was the most abundant siloxane in 5 sampling points; however, differing from the
40 generally observed in previous studies, D3 was the most abundant compound in the
41 other 5 sampling points.

42

43 **Keywords:** volatile methyl siloxanes (VMS), thermal desorption, gas
44 chromatography/mass spectrometry, volatile organic compounds (VOC), air quality

45

46 **1. Introduction**

47 Volatile methyl siloxanes (VMS), both linear (lVMS) and cyclic (cVMS), have been
48 produced commercially since 1940 (Wang et al., 2013). Yearly, tens of thousands of

49 tonnes of VMS are used as intermediates in silicon polymers production and in several
50 industrial applications (Environment Canada 2008a-c; Brooke et al., 2009a-b; Dudzina
51 et al., 2014). Due to their outstanding chemical characteristics (i.e. high vapour
52 pressure, low surface tension and high degree of compatibility with numerous
53 ingredients used in consumer products formulations) (Dudzina et al., 2014), they are
54 widely employed in personal care products, such as cosmetics, and skin and hair care
55 products, as well as in household cleaning and coating agents (Dodson et al., 2012;
56 Nørgaard et al., 2009; Pieri et al., 2013; Yucuis et al., 2013). This leads to high and
57 continuous emissions of these compounds to air, and up to a 90% of the
58 environmentally released cyclic siloxanes diffuse directly into the atmosphere (Balducci
59 et al., 2012), where they can be subject to long-range atmospheric transport (Genualdi et
60 al., 2011; McLachlan et al., 2010; Wang et al., 2013). Even though they have been
61 recognized as safe as cosmetic ingredients (SCCS, 2010), the concern is growing in
62 respect to their environmental distribution, due to their capacity of being long range
63 transported, persistence, possible toxic and estrogenic effects and propensity to
64 bioaccumulate (Dodson et al., 2012; Hassen et al., 2013, Harvey and Everett, 2006; He
65 et al., 2003; Krogseth et al., 2103a; McLachlan et al., 2010; Quinn et al., 2007, Xu and
66 Wania, 2013; Wang et al., 2013; Warner et al., 2010). They are considered “Emerging
67 Contaminants” (EC), and further investigations to evaluate their potential human and
68 environmental exposure risks have been claimed by several researchers (Balducci et al.,
69 2012; Genualdi et al., 2011; Xu et al., 2012) and US EPA, which included D4 as a
70 chemical for its evaluation during 2013-2014 to determine whether or not this
71 compound had to be regulated under the Toxic Substances Control Act. The 26th of
72 September 2016, US EPA announced the receipt of the environmental testing

73 information on D4, submitted following the Enforceable Consent Agreement (ECA)
74 (US EPA 2106), and will be receiving monitoring information under this action.
75 According to this agreement (US EPA, 2014a, 2014b), a final report on D4 is expected,
76 to be submitted to EPA in Fall 2017 (U.S. EPA Office of Pollution Prevention and
77 Toxics, personal communication). Additionally, the 11th June 2016 the Committee for
78 Socio-economic Analysis (SEAC) of the European Chemicals Agency (ECHA) agreed
79 a restriction on the use of D4 and D5 in “wash off” personal care products, such as
80 shower gels, shaving foams and shampoos, due to the persistence, bioaccumulative
81 potential and toxicity of these compounds (ECHA, 2016).

82 Generally, VMS have been evaluated in biogas matrix due to the serious corrosion-
83 related problems that these compounds can cause in gas combustion engines (Dewil et
84 al., 2006; Rasi et al., 2010), however, their presence and concentrations in indoor and
85 outdoor air have been less studied (Balducci et al., 2012; Pieri et al., 2013), and
86 sampling methodologies for ambient air VMS analysis are relatively new and limited. In
87 2010, Kierkegaard and McLachlan published the first accurate and reliable
88 methodology to determine VMS, based on solid phase extraction cartridges sampling
89 and analysis through GC/MS. Since then, several studies have been developed based on
90 adapted or new methodologies using both active (Buser et al., 2013; Pieri et al., 2013;
91 Yucis et al., 2013; Companioni-Damas et al., 2014) and passive sampling (Genualdi et
92 al., 2011; Krogseth et al., 2013b) techniques. Ahrens et al. 2014 compared active and
93 passive sampling strategies using sorbent-impregnated polyurethane foam (SIP) passive
94 samplers and high volume (HV) air samplers, not observing significant differences
95 between VMS concentrations. However, special attention has to be paid to sampling
96 and analysis procedures, as samples can be easily contaminated by indoor air, laboratory

97 equipment and personal care products used by the employees (Wang et al., 2013).
98 Dermal exposure and inhalation have been established to be important pathways of
99 siloxanes for human exposure (Dudzina et al., 2014; Hassen et al., 2013; Wang et al.,
100 2009; Xu et al., 2012). The daily exposure rates to total methyl siloxanes have been
101 estimated to be quite variable, depending on great part of the VMS concentrations that
102 people is exposed to (indoors, outdoors and occupationally) and their personal habits
103 (Pieri et al., 2013).

104 In this manuscript we present the evaluation of VMS concentrations, including
105 trimethylsilanol, in outdoor air in several Catalan locations close to industrial areas
106 using active multi-sorbent bed tube samplers and further analysis with a TD-GC/MS
107 system. The study describes the possibility to determine, in an only sample and an only
108 analysis, VMS together with a wide range of VOC present in outdoor air; as the
109 presented technique has been widely used to determine air quality in urban areas,
110 allowing the evaluation of relevant VOC that can have adverse effects on human health
111 (i.e. irritants of mucous membranes, long-term toxics, carcinogens) (Gallego et al.,
112 2011a). As has been said before, VMS are a family of chemical compounds extensively
113 used in personal care products, and their fate in the environment and their possible
114 negative consequences onto human well-being are still being evaluated. Hence, the
115 incorporation of VMS to the assessment of air quality will become essential in the long
116 term. Additionally, the study has evaluated VMS concentrations in relation to
117 meteorological conditions (temperature and pressure) and population density (inh. Km⁻²),
118 and gives extensive information regarding the concentration of these compounds in
119 highly industrialized urban areas.

120 **2. Materials and methods**

121 2.1 Chemicals and materials

122 Standards of VMS (trimethylsilanol (>98.5%), hexamethyldisiloxane (L2, >98.5%),
123 octamethyltrisiloxane (L3, 98%), decamethyltetrasiloxane (L4, 97%),
124 dodecamethylpentasiloxane (L5, 97%), hexamethylcyclotrisiloxane (D3, 98%),
125 octamethylcyclotetrasiloxane (D4, 98%), decamethylcyclopentasiloxane (D5, 97%) and
126 dodecamethylcyclohexasiloxane (D6, 97%)) were obtained from Sigma-Aldrich (St.
127 Louis, MO, USA). Methanol for gas chromatography (SupraSolv[®]) with a purity \geq
128 99.8% was obtained from Merck (Darmstadt, Germany). Inert glass thermal desorption
129 tubes (Pyrex, 6 mm external diameter, 90 mm long), unsilanised glass wool, and
130 Carbotrap (20/40 mesh), Carbopack X (40/60 mesh) and Carboxen 569 (20/45 mesh)
131 adsorbents were purchased from Supelco (Bellefonte, PA, USA).

132 2.2 Air sampling

133 VMS (Table S1) were evaluated in outdoor air in ten Catalan urban areas with different
134 industrial impacts (A. Tarragona: 1. Constantí, 2. El Morell, 3. Vilallonga del Camp, 4.
135 Perafort and 5. Puigdelfí (petrochemical industry); B. Vallès: 6. La Llagosta, 7.
136 Montcada i Reixac, 8. Ripollet and 9. Cerdanyola del Vallès (electrical and mechanical
137 equipment, metallurgical and chemical industries, municipal solid waste treatment
138 plant); C. Penedès: 10. Santa Margarida i Els Monjos (cement and pet food industries))
139 during 2013 and 2015. To obtain representative results, different sampling points were
140 selected for each urban area (Figure 1).

141 Eight sampling points were selected in the Tarragona industrial area (urban areas 1 to
142 5), covering the territorial area most affected by the contaminants released to air by the
143 industrial sites (Figure 1A). Two sampling campaigns (10-15 consecutive days each)
144 were conducted in each sampling point during 2013 and 2014. Additionally, during

145 April-June 2015, three more sampling campaigns (6-9 consecutive days) were
146 conducted in El Morell, Perafort and Puigdelfi, urban areas 2, 4 and 5, respectively. The
147 total number of samples in the Tarragona area was 204.

148 On the other hand, five sampling points were selected for the Vallès industrial area
149 (urban areas 6 to 9) (Figure 1B). A total number of 41 samples were taken during
150 January-February 2014.

151 Finally, three sampling points were chosen for Santa Margarida i els Monjos (urban
152 area 10), with a total of 26 samples taken during June 2015 (Figure 1C).

153 Table S2 presents the number of samples taken in each urban area during each sampling
154 date and the meteorological conditions during the sampling period. The differences in
155 the number of samples obtained for each campaign in each urban area depended
156 basically on the number of sampling points in each location and the number of
157 consecutive sampled days. This last aspect depended on the developed project, as VOC
158 were quantified together with VMS in the samples.

159 VMS in air were actively sampled during 24 hours connecting self-packed glass multi-
160 sorbent cartridge tubes (Carbotrap (20/40 mesh, 70 mg, weak sorption strength,
161 hydrophobic), Carbopack X (40/60 mesh, 100 mg, medium sorption strength) and
162 Carboxen 569 (20/45 mesh, 90 mg, high sorption strength)) (Ribes et al., 2007) to an air
163 collector pump sampler specially designed in the LCMA-UPC laboratory (Roca et al.,
164 2006). The flow sampling rate was set at 70 ml min⁻¹. Due to the characteristics of the
165 sorbents used, 90-100 l samples (24h samples at 70 ml min⁻¹) are safe volumes, as
166 breakthrough values are acceptable (<5%, US EPA, 1999) for nearly all VOCs
167 evaluated, except for very volatile organic compounds such as ethanol, acetone,
168 isopropanol and dichloromethane (Gallego et al., 2011b). Additionally, the sorbents are

169 hydrophobic enough to avoid interferences derived from the humidity in the air sampled
170 (Ribes et al., 2007). Furthermore, as an additional measure, tubes are purged at ambient
171 temperature during 2 min with a Helium flow of 50 ml min^{-1} prior to TD-GC/MS.

172 Collected air samples were analysed by thermal desorption and gas chromatography-
173 mass spectrometry (TD-GC/MSD) (Ribes et al., 2007). This methodology has been used
174 in previous studies to identify and determine a wide range of VOC in ambient air
175 (Gallego et al., 2009, 2011a) and VMS in biogas (Gallego et al., 2015). The
176 methodology allows a simultaneous quantification of VOC and VMS in only one
177 sample, even though VMS concentrations in outdoor air are generally one to three
178 orders of magnitude lower than VOC concentrations (Fig S1).

179 *2.3 Analytical procedure*

180 The analysis of VOC was performed by Automatic Thermal Desorption (ATD) coupled
181 with capillary Gas Chromatography (GC)/Mass Spectrometry Detector (MSD), using a
182 Markes Unity Series 2 (Markes International Ltd., Lantrisant, UK) and a Thermo
183 Scientific Focus GC fitted with a Thermo Scientific DSQII MSD (Thermo Fisher
184 Scientific, Austin, Texas, USA).

185 The methodology is described in the literature (Gallego et al., 2009, 2015, Ribes et al.,
186 2007). Thermal primary desorption of the sampling tubes was carried out at 300°C , with
187 a Helium flow rate of 50 ml min^{-1} for 10 minutes. The double-split applied to the TD
188 system (cold trap inlet and outlet splits of 11 ml min^{-1}) allowed 12% of the tube analytes
189 to reach the MS detector. The cold trap (U-T15ATA: TO-15/TO-17 Air Toxics trap,
190 Markes) was maintained at -30°C . After primary desorption, the cold trap was rapidly
191 heated from -30°C to 300°C (secondary desorption), and maintained at this temperature
192 for 10 minutes. Analytes were then injected onto the capillary column (DB-624, 60 m x

193 0.32 mm x 1.8 μm , inert for active compounds) via a transfer line heated at 200°C. The
194 column oven temperature started at 40°C for 1 min, increased to 230°C at a rate of 6°C
195 min^{-1} and then was maintained at 230°C for 5 min. Helium (99.999%) carrier gas flow
196 in the analytical column was approximately 1.8 ml min^{-1} .

197 Electron impact source was obtained with electron energy of 70 eV. Mass spectral data
198 were acquired over a mass range of 30-450 amu. Qualitative identification of VMSs
199 was based on the match of the ion ratios of the target qualifier ions using the MS
200 ChemStation Data System validated software package with the NIST05 mass spectral
201 library (NIST/EPA/NIH, Nist MS Search version 2.0 d, April 2005). VMSs were
202 verified using retention times of authentic standards of the target compounds.

203 Quantification of samples was conducted by the external standard method with the m/z
204 1/ m/z 2 ions presented in Table S1. The probable variability of VMS in air samples
205 requires working with two different quantification ions for each studied chemical, m/z 1
206 (generally the major characteristic ion in the spectrum) for medium-low concentrated
207 samples and m/z 2 (minor characteristic ion) for highly concentrated samples (Gallego
208 et al., 2015). In the present case, however, only m/z 1 was used, as even though
209 Puigdelfi VMS concentrations were quite high, up to one to two orders of magnitude
210 higher than in the rest of samples, m/z 1 was appropriate. Quantification ions were
211 selected taking into account possible co-elutions with other VOCs present in the sample.
212 Ten different levels of calibration standard solutions were prepared in methanol for each
213 evaluated compound (0.1-5000 $\text{ng } \mu\text{l}^{-1}$). Stock standard solutions were prepared
214 gravimetrically by adding 50 μl (via pre-weighed 100-250 μl Hamilton syringe) of each
215 liquid neat standard or 0.05 g of each solid standard into a 10 ml clean volumetric flask
216 in methanol. This solution was further diluted in methanol to obtain the different

standards. 1 μl aliquots of each standard solution were spiked onto clean multi-sorbent bed tubes using a conventional gas chromatograph packed column injector, as recommended in U.S. EPA Compendium Method TO-17 (US EPA, 1999). Tubes were connected to the injector through a stainless steel tube and Swagelock adapters. The solvent and analytes were vaporised onto the GC injector and passed through the multi-sorbent bed tube in the vapour phase, a way closely analogous to the normal air sample collection process. The injector was slightly heated at 30 $^{\circ}\text{C}$ and a flow stream of 100 ml min^{-1} of Helium was passed through the tubes during a loading time not less than 5 min, a time applied allowed a good elimination of solvent (Ribes et al., 2007). Furthermore, as an additional measure to reduce the matrix effect standard tubes were purged at ambient temperature during 2 minutes with a Helium flow of 50 ml min^{-1} prior to their TD-GC/MS analysis (Kim et al., 2013). Calibration curves of all evaluated VMSs were freshly prepared to avoid the degradation and possible formation of new siloxane species (Varaprath et al., 2006). Clean tubes were spiked with the standards and injected onto the TD-GC/MS each day.

2.4 *Quality control/Quality assurance*

Due to the fact that methylsiloxanes are present in a great number of consumer and personal care products, extreme precautions are needed to prevent sample contamination, and meticulous protocols should be applied in order to minimize siloxane contamination during sampling and analysis (Varaprath et al., 2006; Warner et al., 2013; Wang et al., 2013). Powder-free nitrile medical examination gloves were used to handle samples, and the use of fragrances and hand care products were avoided during sampling and analysis. Deodorants and hair style products used by the personnel were siloxane-free. The materials used for sampling (inert glass thermal desorption

241 tubes and unsilanized glass wool) prevented possible adsorption of the target VMSs in
242 silicon surfaces. Laboratory glassware used in standards preparation was thoroughly
243 washed with Extran[®] AP12 Detergent Alkaline and rinsed twice with deionized water.
244 Additionally, the analytical procedure used in the present paper (TD-GC/MS) averts
245 sample manipulation, as sorbent tubes are placed directly in the thermal desorber for
246 analysis, avoiding the treatment that undergo samples that have to be desorbed using
247 solvents, which can contribute to background levels of VMS, as well as the
248 contamination of samples with these compounds that can come from the injection ports
249 (i.e. septa and glass-liners) (Varaprath et al., 2006).

250 Before its first use, sorbent tubes were conditioned by thermal cleaning at 250°C,
251 300°C, 330°C, 350°C and 400°C during 20 min for each temperature. Afterwards, they
252 were prepared for sampling conditioning them at 400°C during 20 minutes, sealed using
253 Swagelok end caps fitted with PTFE ferrules and stored in a clean refrigerator at 4°C,
254 not delaying their use more than one week. Once sampled, the tubes were sealed and
255 stored in the same way and analysed within 1 week. Procedural blanks ($n=3$) were taken
256 with each batch of samples, and were analysed each day before every set of
257 samples/standards in order to evaluate instrumental and tubes background levels, and
258 the possible generation of artefacts during analysis. IVMS were not detected in any
259 blank samples, whereas TMS and cVMS (except for D6) were frequently found in the
260 blanks at trace levels, with average values < 7% of sample amounts (see Table S3). As
261 blank levels varied in a certain way depending on the sampling/injection date (Figure
262 S2), results were blank-corrected with the average values of the three procedural blanks
263 injected before the set of samples each day. Blank levels were assumed to be
264 representative for the whole batch of samples injected consecutively.

265 Method detection limits (MDL), shown in Table S1, were calculated through the
266 analysis of 7 replicates of the lowest concentrated standards, which presented signal to
267 noise factors between 2.5 and 10. The obtained standard deviation (SD) for the
268 replicates concentrations was multiplied for 3.14 (Two sided Student's t value at the
269 99% confidence interval with 6 degrees of freedom), according to the U.S. EPA (Part
270 136-Guidelines establishing test procedures for the analysis of pollutants, Appendix B).
271 The studied compounds show standard repeatabilities (% relative standard deviation
272 values, $n=7$) $\leq 11\%$, accomplishing the EPA performance criteria (US EPA, 1999).
273 Breakthrough values were evaluated connecting two tubes in series (front tube and back
274 tube). 90 litre samples were taken from indoor air in our laboratory. Breakthrough was
275 calculated as the percentage of the analyte in the back tube in respect to the total amount
276 of analyte in the two tubes, and was negligible in all cases, with values $< 2\%$ in the
277 back tube in respect to the front tube (Table S1), accomplishing the U.S. EPA criteria
278 (US EPA, 1999). The linearity range of the multi-point calibration for each VMS is
279 presented in Table S1, and ranged from 0.1-500 to 0.1-4000 ng depending on the
280 compound. In all cases, the linear regression square coefficient was ≥ 0.999 .
281 Every day the mass spectrometer was manually tuned at $m/z=69$, 131, 264 and 502, and
282 air leaks ($m/z= 4$, 18 and 28) were controlled.

283 2.5 Meteorological data

284 Tarragona meteorological data (on a semi-hourly basis) were obtained from "Servei
285 Meteorològic de Catalunya" (Generalitat de Catalunya, 2016). The meteorological
286 station is located in Constantí (Latitude: 41.17130; Longitude: 1.16774; Altitude: 112 m
287 a.s.l.). Regarding Vallès samples, Cerdanyola samples were evaluated using Cerdanyola
288 del Vallès meteorological station (Latitude: 41.49833; Longitude: 2.1205565; Altitude:

289 110 m a.s.l.), which gives data in a quarter-hourly basis (Meteo Cerdanyola, 2016). The
290 rest of Vallès samples were evaluated using Ripollet meteorological station (Latitude:
291 41.5069444; Longitude: 2.1483333; Altitude: 118 m a.s.l.) (Casa Natura Ripollet,
292 2016), which gives data in a semi-hourly basis. Els Monjos meteorological station is
293 located in Els Monjos town hall (Latitude: 41.3208333; Longitude: 1.6624999;
294 Altitude: 180 m a.s.l.) (Els Monjos-Ajuntament, 2016), which gives data in a semi-
295 hourly basis (Figure 1).

296 *2.6 Data analysis*

297 Data treatment, statistical and graphical analysis was undertaken using Microsoft
298 Excel™ 2010, IBM Spss Statistics Version 20 (2011) and Matlab v.7 (The MathWorks,
299 Inc.). Two-tailed *t*-test and F-Snedecor test were used to evaluate significant differences
300 and significant correlations between obtained data, respectively.

301 **3. Results and discussion**

302 *3.1 Siloxane concentrations in air*

303 Average VMS concentrations, normalized for temperature (273 K) and pressure (101.32
304 kPa), following the Directive 2008/50/EC of the European Parliament and of the
305 Council of 21 May 2008 on ambient air quality and cleaner air for Europe, are shown in
306 Table 1. Even though VMS concentrations were obtained from different sampling
307 periods and during different seasons, as no significant differences were observed in each
308 sampling point between the obtained concentrations and the sampling intervals, VMS
309 concentrations were presented as average values.

310 cVMS, TMS and L2 were identified in outdoor air samples with a detection frequency
311 of 100%. L3-L5 were detected in all Vallès samples. However, in Tarragona and
312 Penedès samples, L3, L4 and L5 detection in samples ranged from 62-100%, 0-77% and

313 0-12%, respectively, depending on the sampling location. IVMS have been less studied
314 than cVMS in outdoor air, and much less data regarding these compounds is available
315 (Table 2). However, IVMS detection frequencies in background and urban worldwide
316 locations (Table 2) are generally higher than the observed in the present study, 30-100%
317 and 60-100% for L3, 60-100% and 80-100% for L4, and 40-100% and 80-100% for L5,
318 respectively (Genualdi et al., 2011; Krogseth et al., 2103b; Ahrens et al., 2014;
319 Companioni-Damas et al., 2014). Additionally, the lower IVMS concentrations found in
320 Polar locations in comparison with the concentrations found in urban areas suggest that
321 these compounds do not experience long range transport in an important way (Genualdi
322 et al., 2011), an aspect that could be favoured by their low half-lives in air (Atkinson,
323 1991; Markgraf and Wells, 1997; Whelan et al., 2004). Hence, outdoor air IVMS
324 concentrations could be much more influenced by local emissions. Moreover, as IVMS
325 and cVMS do not correlate with themselves, a different temporal and/or spatial
326 distribution of emissions can be assumed in each sampling location (Kierkegaard and
327 McLachlan, 2013).

328 Σ VMS concentrations fluctuated by a factor of 2-4 on a time scale of 1-5 days in each
329 sampling point (Figure S3), as had been observed during a VMS daily evaluation in a
330 study conducted in Sweden (Kierkegaard and McLachlan, 2013). Important differences
331 were observed between the studied locations. Σ VMS concentrations generally ranged
332 from $0.3 \pm 0.2 \mu\text{g m}^{-3}$ (Cerdanyola del Vallès) and $3.9 \pm 2.0 \mu\text{g m}^{-3}$ (La Llagosta),
333 however, Puigdelfi showed the highest concentrations, up to an order of magnitude
334 higher than the found in the rest of sampling points, with Σ VMS values between 8-40
335 $\mu\text{g m}^{-3}$, mainly due to the high concentrations of D5 and D6. In this case, very important
336 local sources coming from the nearby industrial areas, such as a petrochemical waste

337 water treatment plant, may be responsible for the obtained results. cVMS are widely
338 used in the petrochemical industry to improve productivity to control the excessive
339 foaming during production and separation processes (Oxford Economics, 2008).

340 TMS concentrations are also presented in the present paper, ranging from 22 to 214 ng
341 m⁻³. As can be seen in Tables 2 and 3, this compound has not been evaluated in a great
342 number of studies that determined VMS concentrations in outdoor and/or indoor air.
343 TMS is a highly volatile and unstable compound (Arnold and Kajolinna, 2010), and the
344 use of organic solvents, activated charcoal, Tenax TA, XAD resins and polyurethane
345 foam (PUF) for its determination have not proved to be efficient (Grümping et al., 1998;
346 Hayeck et al., 2015). However, its evaluation using methods based on adsorption in
347 special cartridges followed by cryofocusing in cold traps and GC/MS (Grümping et al.,
348 1998, Lee et al., 2012, Gallego et al., 2015) or PTR-ToF-MS (Hayeck et al., 2015) have
349 proven to be effective. Outdoor air studies presented in Table 2 use sampling and
350 analysis methodologies that are not suitable for the analysis of TMS, hence, these
351 limitations can be an explanation of the little presence of this compound in outdoor air
352 quality evaluations regarding VMS concentrations.

353 VMS concentrations in the urban areas evaluated in the present study, except Puigdelfi
354 hotspot, were generally of the same order of magnitude than the observed in Barcelona,
355 Chicago and Zurich urban areas, but higher than the published from suburban sites and
356 Arctic locations (Table 2). On the other hand, they were much lower, up to one order of
357 magnitude, than the determined in Chinese urban areas (i.e. Guangzhou, Macau and
358 Nahnai). However, IVMS concentrations in the evaluated locations were up to 2-3
359 orders of magnitude higher than the observed in background locations worldwide (Table
360 2). Additionally, in respect to background sites, cVMS were one order of magnitude

361 higher in the present study, except for D5, which was as far as 2 orders of magnitude
362 higher. Furthermore, in Puigdelfi hotspot site, D5 and D6 accounted for 3 and 2 orders
363 of magnitude higher than the found in background worldwide locations, respectively
364 (Table 2).

365 On the contrary, VMS concentrations obtained in the present study are much lower than
366 the found in indoor environments. Outdoor VMS concentrations are in the range of
367 0.01-2% for Puigdelfi hotspot and between 0.01-0.8% for the rest of sampling points in
368 respect to typical indoor concentrations (e.g. public places, work places, homes and
369 schools) (Table 3). It has to be taken into account that indoor air VMS concentrations
370 are highly affected by emissions from siloxane's containing products, mainly through
371 the transfer of these compounds, coming from hair styling products, deodorants, skin
372 lotions and make-up, to ambient air. On the other hand, other consumer products such
373 as toothpastes, shampoos, body washes and toilet soaps, will contribute in a more
374 important way to VMS concentrations in bathrooms (Horii and Kannan, 2008; Lu et al.,
375 2011; Wang et al., 2013; Companioni-Damas et al., 2014). The indoor exposure to
376 VMS is the dominant exposure pathway in residential areas and public and work places
377 (Xu et al., 2012).

378 The influence of two meteorological conditions, i.e. temperature and pressure, were
379 evaluated for the obtained VMS concentrations. Corresponding average temperature and
380 pressure values were calculated for each sample on a sampling time basis. No
381 correlations were found between individual or aggregated VMS and these variables
382 during a sampling period in a specific sampling location, aggregated samples coming
383 from different samplings in a same sampling point or all aggregated samples from all
384 sampling locations and sampling periods. Neither environmental temperature nor

385 pressure were identified as important parameters regarding the behaviour of VMS
386 concentrations outdoors. Their emission rate to the atmosphere and their behaviour in it,
387 depending on their reaction with OH radicals, seem to be more important parameters
388 than the studied environmental variables.

389 *3.2 Siloxane distributions and possible sources*

390 cVMS were the most abundant compounds, with concentrations up to 2-3 orders of
391 magnitude higher than those of the IVMS, as it had been observed in other studies
392 (Genualdi et al., 2011; Krogseth et al., 2013b; Pieri et al., 2013; Ahrens et al., 2014),
393 accounting for average contributions to the total VMS concentrations between $94\pm 12\%$
394 for Tarragona samples and $99\pm 1\%$ for Penedès samples. On Puigdelfí hotspot location,
395 cVMS accounted for $99.9\pm 0.1\%$. Poor information regarding IVMS emission sources is
396 available, but IVMS emissions have been estimated to be much lower than cVMS
397 (Kierkegaard and McLachlan, 2013). Wastewater treatment plants and landfills are
398 important sources of VMS to ambient air. In these types of facilities, cVMS are emitted
399 in much higher concentrations than IVMS, between 20 and 600 fold (Cheng et al., 2011,
400 Tansel and Surita, 2014); an aspect related to the VMS composition of personal care
401 products. cVMS occurrence frequency in personal care products is higher than that of
402 IVMS; being cVMS concentrations in these products generally two fold the
403 concentrations of IVMS (Horii and Kannan, 2008). Apart from the different emission
404 patterns of these kinds of compounds, IVMS vapour pressures are lower than that of
405 cVMS, being less volatile (Xu et al., 2012). Finally, another aspect that could influence
406 the lower IVMS concentrations observed is their lower half-lives in the atmosphere
407 (Atkinson, 1991; Markgraf and Wells, 1997; Whelan et al., 2004).

408 D5 was the most abundant siloxane in Vallès samples, accounting from 52-80% of all
409 cVMS, depending on the sampling location. Additionally, Puigdelfí presented the
410 highest D5 percentage, up to $82\pm 11\%$ in respect to the other cVMS (Figure 2). D5 has
411 been found to be the highest concentrated cVMS in cosmetic products (Wang et al.,
412 2009), as well as it is the most abundant compound generally found in developed
413 countries' urban areas (Table 2). The importance of D5 in respect to other cVMS in air
414 has been related to personal care products usage (Balducci et al., 2012; Buser et al.,
415 2013; Pieri et al., 2013; Yucuis et al., 2013) and to the influence of industrial activities
416 (Genualdi et al., 2011; Xu et al., 2012). Hence, as has been said before, possible local
417 sources related to the industrial use of these kinds of products may be the responsible of
418 the high concentrations of D5 found in Puigdelfí. Significant correlations of D5 and D6
419 concentrations with S to WSW wind directions were observed in Puigdelfí, with r^2
420 values between 0.81-0.98 ($0.001 \leq p \leq 0.05$) and 0.80-0.96 ($0.001 \leq p \leq 0.05$), respectively.
421 These wind directions correspond to Polígon Nord, a 470 Ha industrial park, with 8
422 enterprises specialized in the manufacture of petrochemical products and auxiliary
423 industries. cVMS are widely used for defoaming in the petrochemical industry in order
424 to improve productivity during several processes, such as drilling, extracting, producing
425 and purifying/separating (Oxford Economics, 2008). A petrochemical wastewater
426 treatment plant is located approximately at 500 meters from Puigdelfí. Hence, the higher
427 concentration of these cVMS found in Puigdelfí outdoor air, the highest of all the study,
428 could be derived from this WWTP. Additionally, several auxiliary activities, i.e.
429 industrial cleaning and plastic treatment plants are located near Puigdelfí. These kinds
430 of business activities also use siloxanes or products that contain siloxanes (e.g. cleaners

431 and polishers, water/heat resistance coatings, sealants, etc.) for their
432 production/performance (Oxford Economics, 2008).

433 D4 estimated emissions using emission inventories are approximately 9% of the D5
434 estimated emissions in European air (Brooke et al, 2009a-b; Kierkegaard and
435 McLachlan, 2013). In Puigdelfí hotspot, this ratio percentage is $7\pm 4\%$, very similar to
436 the estimated emissions, whereas in the rest of the sampling points this ratio is variable
437 ($26\pm 25\%$, $278\pm 357\%$ and $21\pm 30\%$ in Vallès, Tarragona and Penedès samples,
438 respectively). This indicates that in Puigdelfí concentrations are very similar to the
439 estimated emissions of these cVMS to outdoor air, supporting the hypothesis that the
440 petrochemical wastewater treatment plant located near the sampling location would be
441 the main source of these compounds in Puigdelfí outdoor air. Additionally, Vallès and
442 Penedès samples present ratios very similar to the found in regional background sites in
443 Sweden (27%) (Kierkegaard and McLachlan, 2013). The use of ratios estimated using
444 emission inventories present several limitations, as several emissions from some source
445 classes are not provided by the industries as are treated as confidential (Brooke et al.
446 2009a-b). Hence, emission inventories estimated ratios use lower boundary VMS
447 concentrations, and not considerable differences between calculated and real ratios (i.e.
448 9% vs. 26 or 21%) would be explained by this discrepancy (Kierkegaard and
449 McLachlan, 2013). On the other hand, Tarragona samples present really different ratios,
450 up to an order of magnitude higher. This important differences should be evaluated
451 more deeply in future studies. Differences in temporal emissions and/or spatial
452 distribution of emissions to the air should be studied more thoroughly in this concrete
453 area.

454 On the other hand, D3 was the most abundant cVMS in Tarragona and Penedès
455 samples, accounting from 45-64% (Figure 2), a finding that is not in accordance with
456 the data found in developed countries' outdoor air. Nevertheless, D3 was observed to be
457 the highest concentrated cVMS in several Chinese cities (Wang et al., 2001), however,
458 in American and European urban areas D5 is generally the most abundant compound
459 (Table 2). On arctic air, though, D3 has been found to be the most concentrated cVMS
460 in the atmosphere (Genualdi et al., 2011), an aspect that could be related to its highest
461 half-life in the environment (Atkinson et al., 1991; Krogseth et al., 2013a). Balducci et
462 al., 2012 stated that a great variability in percent profiles of VMS in outdoor air has
463 been observed worldwide, and that the behaviour of these kinds of compounds in the
464 atmosphere has to be much more studied in order to clarify it.

465 Several studies indicated that higher population density could be a significant
466 explaining variable for higher VMS concentrations in outdoor air (Wang et al., 2001;
467 Krogseth et al., 2013b; Yucuis et al., 2013). Additionally, Genualdi et al., 2011 found
468 that D5 and D6 dominate in urban areas influenced by industrial activities, being the
469 main sources of D4, D5 and D6 to these urban environments their release from
470 production of silicone processes and the use and disposal of personal care products.
471 Besides, Ahrens et al., 2014 observed a great influence from local/regional sources in
472 VMS outdoor air concentrations. In the present study, excluding the high values
473 determined in Puigdelfi, population density (inh. Km⁻²) correlates significantly with
474 average D5 ($r^2=0.622$, $p\leq 0.05$) and D6 ($r^2=0.697$, $p\leq 0.05$) concentrations (Figure 3),
475 implying higher emissions of these cVMS in more populated areas.

476 Furthermore, the determination of possible source changes of VMS emission over time
477 can be done comparing the ratios of individual VMS congeners. The only location with

478 all over the year data is the Tarragona region. In this specific case, L2/L3 ratios were
479 constant throughout the year (i.e. from 9.3 to 9.7); however, cVMS ratios (D4/D3,
480 D5/D3 and D6/D3) varied depending on the season, suggesting seasonal specific
481 emissions (Ahrens et al., 2014) (Figure S4). Spring and winter cVMS ratios were quite
482 similar, 0.6 and 0.5 (D4/D3), 1.0 and 2.0 (D5/D3), 0.5 and 0.2 (D6/D3) for spring and
483 winter, respectively, not showing significant differences between them. However,
484 summer ratios were inferior, up to two orders of magnitude lower. D5/D3 showed a
485 summer ratio of 0.1, being significantly different ($p \leq 0.001$) from spring and winter
486 values. D6/D3 showed a summer ratio of 0.02, being also significantly different from
487 spring ($p \leq 0.001$) and summer ($p \leq 0.005$) ratios. In these cases, D5 and D6
488 concentrations were much lower in summer. Apart from different emission patterns
489 depending on the season, a higher degradation of siloxanes, due to the reaction of these
490 compounds with hydroxyl radicals (Wang et al., 2013), can also be an important aspect
491 in summer periods (McLachlan et al., 2010; Kierlegaard and McLachlan, 2013;
492 Krogseth et al., 2013a; Ahrens et al., 2014). Rate constants for the reaction of VMS
493 with OH radicals (considering $7.7 \cdot 10^5$ molecule cm^{-3} over a 24-h period) range from
494 0.52 to $2.66 \cdot 10^{-12}$ cm^3 molecule $^{-1}$ s $^{-1}$, with $L4 > L3 > D6 > D5 > L2 > D4 > D3$ (Atkinson,
495 1991; Markgraf and Wells, 1997; Krogseth et al., 2013a). These constants seem to be
496 divided in two categories, the cVMS and the IVMS. The rate constants increase with the
497 number of methyl substituent groups in each category (Atkinson, 1991). Additionally,
498 D5 and D6 have the lowest half-life in the atmosphere, i.e. 6.7 and 5.8 days,
499 respectively, in respect to D3 and D4, i.e. 30 and 10 days, respectively (Atkinson et al.,
500 1991; Krogseth et al., 2013a). It has to be noted that, taking into account all samples, D3
501 and D4 were the only VMS that correlated significantly with each other ($r^2=0.822$,

502 $p < 0.001$, Figure 4) indicating common sources and transport mechanisms (Genualdi et
503 al., 2011; Ahrens et al., 2014), an aspect that could also be linked to the higher half-
504 lives that they present. On the other hand, the absence of correlations between IVMS
505 and cVMS could be related to different temporal and/or spatial distribution of emissions
506 (Kierlegaard and McLachlan, 2013) and different volatilization patterns (Xu et al.,
507 2012).

508

509 **Conclusions**

510 Outdoor air VMS concentrations in several Catalan urban areas have been evaluated
511 using active sampling followed by TD-GC/MS analysis. Σ VMS (including TMS)
512 concentrations varied between 0.3 ± 0.2 and $3.9 \pm 2.0 \mu\text{g m}^{-3}$ (fluctuating by a factor of 2-4
513 on a time scale of 1-5 days) depending on the sampling point, except for Puigdelfí
514 hotspot, where average concentrations were $18 \pm 12 \mu\text{g m}^{-3}$. cVMS concentrations were
515 up to 3 orders of magnitude higher than IVMS. D5 was the most abundant siloxane in
516 Vallès and Puigdelfí samples; however, D3 was the most abundant in Penedès and
517 Tarragona samples, except for Puigdelfí. These findings are not in accordance with the
518 data found in developed countries' outdoor air, and the behaviour of these kinds of
519 compounds in the atmosphere has to be much more studied in order to clarify it.
520 Population density (inh. Km^{-2}) correlates significantly ($p \leq 0.05$) with average D5 and D6
521 concentrations, implying higher emissions of these cVMS in more populated areas.

522

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530 **References**

531 Ahrens L., Harner T., Shoeib M., 2014. Temporal variations of cyclic and linear volatile
532 methylsiloxanes in the atmosphere using passive samplers and high-volume air
533 samplers. *Environmental Science & Technology* 48, 9374-9381.

534 Arnold M., Kajolinna T., 2010. Development of on-line measurement techniques for
535 siloxanes and other trace compounds in biogas. *Waste Management* 30, 1011-1017.

536 Atkinson R., 1991. Kinetics of the gas-phase reactions of a series of organosilicon
537 compounds with OH and NO₃ radicals and O₃ at 297 ± 2 K. *Environmental Science &*
538 *Technology* 25, 863-866.

539 Balducci C., Perilli M., Romagnoli P., Cecinato A., 2012. New developments on
540 emerging organic pollutants in the atmosphere. *Environmental Science and Pollution*
541 *Research* 19, 1875-1884.

542 Brooke D.N., Crookes M.J., Gray D., Robertson S., 2009a. *Environmental Risk*
543 *Assessment Report: Decamethylcyclopentasiloxane*. Environmental Agency of England
544 and Wales, Bristol, pp. 221.

545 Brooke D.N., Crookes M.J., Gray D., Robertson S., 2009b. *Environmental Risk*
546 *Assessment Report: Octamethylcyclotetrasiloxane*. Environmental Agency of England
547 and Wales, Bristol, pp. 187.

548 Buser A.M., Kirkegaard A., Bogdal C., MacLeod M., Scheringer M., Hungerbühler K.,
549 2013. Concentrations in ambient air and emissions of cyclic volatile methylsiloxanes in
550 Zurich, Switzerland. *Environmental Science & Technology* 47, 7045-7051.

551 Casa Natura Ripollet, 2016. <https://app.weathercloud.net/d0987187421#profile> [last
552 accessed on 2.02.2017].

553 Cheng Y., Shoeib M., Ahrens L., Harner T., Ma J., 2011. Wastewater treatment plants
554 and landfills emit volatile methyl siloxanes (VMSs) to the atmosphere: Investigations
555 using a new passive air sampler. *Environmental Pollution* 159, 2380-2386.

556 Companioni-Damas E.Y., Santos F.J., Galceran M.T., 2014. Linear and cyclic
557 methylsiloxanes in air by concurrent solvent recondensation-large volume injection-gas
558 chromatography-mass spectrometry. *Talanta* 118, 245-252.

559 Dewil R., Appels L., Baeyerns J., 2006. Energy use of biogas hampered by the presence
560 of siloxanes. *Energy Conversion and Management* 47, 1711-1722.

561 Dodson R.E., Nishioka M., Standley L.J., Perovich L.J., Green Brody J., Rudel R.A.,
562 2012. Endocrine disruptors and asthma-associated chemicals in consumer products.
563 *Environmental Health Perspectives* 120, 935-943.

564 Dudzina T., von Goetz N., Bogdal C., Biesterbos J.W.H., Hungerbühler K., 2014.
565 Concentrations of cyclic volatile methylsiloxanes in European cosmetics and personal
566 care products : Prerequisite for human and environmental exposure assessment.
567 *Environment International* 62, 84-94.

568 Environment Canada, Health Canada, 2008a. Screening Assessment for the Challenge
569 Octamethylcyclotetrasiloxane (D4). Chemical Abstracts Service Registry Number 556-
570 67-2.

- 571 Environment Canada, Health Canada, 2008b. Screening Assessment for the Challenge
572 Decamethylcyclopentasiloxane (D5). Chemical Abstracts Service Registry Number
573 541-02-6.
- 574 Environment Canada, Health Canada, 2008c. Screening Assessment for the Challenge
575 Dodecamethylcyclohexasiloxane (D6). Chemical Abstracts Service Registry Number
576 540-97-6.
- 577 Gallego E., Roca F.J., Perales J.F., Guardino X., 2009. Simultaneous evaluation of odor
578 episodes and air quality. Methodology to identify air pollutants and their origin
579 combining chemical analysis (TD-GC/MS), social participation, and mathematical
580 simulation techniques. In: Romano G.C. and Conti A.G. (Eds.), Air Quality in the XXI
581 Century, Nova Science Publishers, New York, pp. 139-209.
- 582 Gallego E., Roca F.J., Perales J.F., Guardino X., 2011a. Odor control in urban areas
583 originated from multiple focuses. Identification of potentially toxic compounds. In:
584 Daniels J.A. (Ed.), Advances in Environmental Research. Volume 14, Nova Editors,
585 New York, pp. 261-288.
- 586 ECHA, 2016. [https://www.echa.europa.eu/-/committee-for-socio-economic-analysis-](https://www.echa.europa.eu/-/committee-for-socio-economic-analysis-concludes-on-restricting-d4-and-d5)
587 [concludes-on-restricting-d4-and-d5](https://www.echa.europa.eu/-/committee-for-socio-economic-analysis-concludes-on-restricting-d4-and-d5), last accessed 2.02.2017.
- 588 Els Monjos-Ajuntament, 2016. <https://app.weathercloud.net/d1533741809#profile> [last
589 accessed on 2.02.2017].
- 590 Gallego E., Roca F.J., Perales J.F., Guardino, X, 2011b. Comparative study of the
591 adsorption performance of a multi-sorbent bed (Carbotrap, Carbopack X, Carboxen
592 569) and a Tenax TA adsorbent tube for the analysis of volatile organic compounds
593 (VOCs). Talanta 81, 916-924.

594 Gallego E., Roca F.J., Perales J.F., Guardino X., Gadea, E., 2015. Development of a
595 method for determination of VOCs (including methylsiloxanes) in biogas by TD-
596 GC/MS analysis using SupelTM Inert Film bags and multisorbent bed tubes.
597 International Journal of Environmental Analytical Chemistry 95, 291-311.

598 Generalitat de Catalunya, 2016.

599 <http://www.meteo.cat/observacions/xema/dades?codi=VQ&dia=2016-04-05T14:00Z>

600 [[last accessed on 2.02.2017](#)].

601 Genualdi S., Harner T., Cheng Y., MacLeod M., Hansen K.M., van Egmond R., Shoeib
602 M., Lee S.C., 2011. Global distribution of linear and cyclic volatile methyl siloxanes in
603 air. Environmental Science & Technology 45, 3349-3354.

604 Grümping T., Mikolajczak D., Hirner A., 1998. Determination of trimethylsilanol in the
605 environment by LT-GC/ICP-OES and GC/MS. Fresenius Journal of Analytical
606 Chemistry 361, 133-139.

607 Harvey P.W., Everett D.J., 2006. Regulation of endocrine-disrupting chemicals: Critical
608 overview and deficiencies in toxicology and risk assessment for human health. Best
609 Practice & Research: Clinical Endocrinology and Metabolism 20, 145-165.

610 Hassen L., Warner N.A., Braathen T., Odland J.Ø., Lund E., Nieboer E., Sandanger
611 T.M., 2103. Plasma concentrations of cyclic volatile methylsiloxanes (VMS) in
612 pregnant and postmenopausal Norwegian women and self-reported use of personal care
613 products (PCPs). Environment International 51: 82-87.

614 Hayeck N., Temime-Roussel B., Gligorovski S., Mizzi A., Gemayel R., Tlili S., Maillot
615 P., Pic N., Vitrani T., Poulet I., Wortham H., 2015. Monitoring of organic
616 contamination in the ambient air of microelectronic clean room by proton-transfer

617 reaction/time-of-flight/mass spectrometry (PTR-ToF-MS). *International Journal of*
618 *Mass Spectrometry* 392, 102-110.

619 He B., Rhodes-Brower S., Miller M.R., Munson A.E., Germolec D.R., Walker V.R.,
620 Korach K.S., Meade B.J., 2003. Octamethylcyclotetrasiloxane exhibits estrogenic
621 activity in mice via ER α . *Toxicology and Applied Pharmacology* 192, 254-261.

622 Horii Y., Kannan K., 2008. Survey of organosilicone compounds, including cyclic and
623 linear siloxanes, in personal-care and household products. *Archives of Environmental*
624 *Contamination and Toxicology* 55, 701-710.

625 Kaj L., Schlabach M., Andersson J., Cousins A.P., Shemidbauer N., Brorström-Lundén
626 E., 2005. Siloxanes in the Nordic environment. *ThemaNord*. Nordic Council of
627 Ministers, Copenhagen, pp. 93.

628 Katsoyiannis A., Anda E.E., Cincinelli A., Martinelli T., Leva P., Goetsch A.,
629 Sandanger T.M., Huber S., 2014. Indoor air characterization of various
630 microenvironments in the Arctic. The case of TromsØ, Norway. *Environmental*
631 *Research* 134, 1-7.

632 Kierkegaard A., McLachlan M.S., 2010. Determination of
633 decamethylcyclopentasiloxane in air using commercial solid phase extraction cartridges.
634 *Journal of Chromatography A* 1217, 3557-3560.

635 Kierkegaard A., McLachlan M.S., 2013. Determination of linear and cyclic volatile
636 methylsiloxanes in air at a regional background site in Sweden. *Atmospheric*
637 *Environment* 80, 322-329.

638 Kim, K.-H., Kim, Y.-H., Brown, R.J.C., 2103. Conditions for the optimal analysis of
639 volatile organic compounds in air with sorbent tube sampling and liquid standard

640 calibration: demonstration of solvent effect. *Analytical and Bioanalytical Chemistry*
641 405, 8397-8408.

642 Krogseth I.S., Kierkegaard A., McLachlan M.S., Breivik K., Hansen K.M., Schlabach
643 M., 2103a. Occurrence and seasonality of cyclic volatile methyl siloxanes in Arctic air.
644 *Environmental Science & Technology* 47, 502-509.

645 Krogseth I.S., Zhang X., Lei, Y.D., Wania F., Breivik K., 2103b. Calibration and
646 application of a passive air sampler (XAD-PAS) for volatile methyl siloxanes.
647 *Environmental Science & Technology* 47, 4463-4470.

648 Lee J.H., Jia C., Kim Y.D., Kim H.H., Pham T.T., Choi Y.S., Seo Y.U., Lee I.W., 2102.
649 An optimized adsorbent sampling combined to thermal desorption GC-MS method for
650 trimethylsilanol in industrial environments. *International Journal of Analytical*
651 *Chemistry* 2010, 1-10.

652 Lu Y., Yuan T., Wang W., Kannan K., 2011. Concentrations and assessment of
653 exposure to siloxanes and synthetic musks in personal care products from China.
654 *Environmental Pollution* 159, 3522-3528.

655 Markgraf S.J., Wells J.R., 1997. The hydroxyl radical reaction rate constants and
656 atmospheric reaction products of three siloxanes. *International Journal of Chemical*
657 *Kinetics* 29, 445-451.

658 Meteo Cerdanyola, 2016. <http://www.meteocerdanyola.com> [last accessed on
659 [2.02.2017](http://www.meteocerdanyola.com)].

660 McLachlan M.S., Kierkegaard A., Hansen K.J., van Egmond R., Christensen J.H.,
661 Skjøth C.A., 2010. Concentrations and fate of demethylcyclopentasiloxane (D₅) in the
662 atmosphere. *Environmental Science & Technology* 44, 5365-5370.

663 Nørgaard A.W., Jensen K.A., Janfelt C., Lauritsen F.R., Clausen P.A., Wolkoff P.,
664 2009. Release of VOC and particles during use of nanofilm spray products.
665 Environmental Science & Technology 43, 7824-7830.

666 Oxford Economics, 2008.. Economic Evaluation of Siloxanes in Canada. Oxford, UK,
667 p. 1-15.

668 Pieri F., Katsoyiannis A., Martellini T., Hughes D., Jones K.C., Cincinelli A., 2013.
669 Occurrence of linear and cyclic volatile methyl siloxanes in indoor air samples (UK and
670 Italy) and their isotopic characterization. Environment International 59, 363-371.

671 Quinn A.L., Regan J.M., Tobin J.M., Marinik B.J., McMahon J.M., McNett D.A.,
672 Sushynski C.M., Crofoot S.D., Jean P.A., Plotzke K.P., 2007. *In vitro* and *in vivo*
673 evaluation of the estrogenic, androgenic and progestagenic potential of two cyclic
674 siloxanes. Toxicological Sciences 96, 145-153.

675 Rasi S., Lehtinen J., Rintala J., 2010. Determination of organic silicon compounds in
676 biogas from wastewater treatment plants, landfills, and co-digestion plants. Renewable
677 Energy 35, 2666-2673.

678 Ribes A., Carrera G., Gallego E., Roca X., Berenguer M.J., Guardino X., 2007.
679 Development and validation of a method for air-quality and nuisance odors monitoring
680 of volatile organic compounds using multi-sorbent adsorption and gas
681 chromatography/mass spectrometry thermal desorption system. Journal of
682 Chromatography A 1140, 44-55.

683 Roca F.J., 2006. Disseny d'un sistema de control d'olors i de qualitat de l'aire.
684 Caracterització, quantificació i assignació de l'origen dels compostos orgànics volàtils.
685 Thesis, Departament d'Enginyeria Minera i Recursos Naturals, Manresa, Spain.

- 686 SCCS (Scientific Committee on Consumer Safety), 2010. Opinion on cyclomethicone,
687 octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5). Available
688 online at [http://ec.europa.eu/health/scientific_committees/consumer_safety/
689 docs/sccs_o_029.pdf](http://ec.europa.eu/health/scientific_committees/consumer_safety/docs/sccs_o_029.pdf). [last accessed on 2.02.2017].
- 690 Tansel B., Surita S.C., 2014. Differences in volatile methyl siloxane (VMS) profiles in
691 biogas from landfills and anaerobic digesters and energetics of VMS transformations.
692 Waste Management 34,: 2271-2277.
- 693 Tran T.M., Kannan K., 2015. Occurrence of cyclic and linear siloxanes in indoor air
694 from Albany, New York, USA, and its implications for inhalation exposure. Science of
695 the Total Environment 511, 138-144.
- 696 U.S. EPA, 1999. Compendium of Methods for the Determination of Toxic Organic
697 Compounds in Ambient Air, Method TO-17, Center for Environmental Research
698 Information, Office of Research and Development.
- 699 US EPA, 2014a. Enforceable Consent Agreement for Environmental Testing for
700 Octamethylcyclotetrasiloxane (D4) (CASRN 556-67-2). Docket No. EPA-HQ-OPPT-
701 2012-0209.
- 702 US EPA, 2014b. [https://www.regulations.gov/document?D=EPA-HQ-OPPT-2012-
703 0209-0067](https://www.regulations.gov/document?D=EPA-HQ-OPPT-2012-0209-0067) [last accessed on 2.02.2017].
- 704 US EPA, 2016. [https://www.regulations.gov/document?D=EPA-HQ-OPPT-2012-0209-
705 0106](https://www.regulations.gov/document?D=EPA-HQ-OPPT-2012-0209-0106) [last accessed on 2.02.2017].
- 706 Varapath S., Stutts D.H., Kozerski G.E., 2006. A primer on the analytical aspects of
707 silicones at trace levels-challenges and artifacts-A review. Silicon Chemistry 3, 79-102.
- 708 Volland G., 2014. Exposure analysis for indoor contaminants. In: Reichl F.-X.,
709 Schwenk M. (Eds.), Regulatory Toxicology, Springer, Berlin Heidelberg, p. 277-288.

- 710 Wang X.M., Lee S.C., Sheng G.Y., Chan L.Y., Fu J.M., Li X.D., Min Y.S., Chan C.Y.,
711 2001. Cyclic organosilicon compounds in ambient air in Guangzhou, Macau and
712 Nanhai, Pearl River Delta. *Applied Geochemistry* 16, 1447-1454.
- 713 Wang R., Moody R.P., Koniecki D., Zhu J., 2009. Low molecular weight cyclic volatile
714 methylsiloxanes in cosmetic products sold in Canada: Implication for dermal exposure.
715 *Environment International* 35, 900-904.
- 716 Wang D.-G., Norwood W., Alaei M., Byer J.D., Brimble S., 2013. Review of recent
717 advances in research on the toxicity, detection, occurrence and fate of cyclic volatile
718 methyl siloxanes in the environment. *Chemosphere* 93, 711-725.
- 719 Warner N.A., Evenset A., Christensen G., Gabrielsen G.W., Borgå K., Leknes H., 2010.
720 Volatile siloxanes in the European Arctic: assessment of sources and spatial
721 distribution. *Environmental Science & Technology* 44, 7705-7710.
- 722 Warner N.A., Kozerski G., Durham J., Koerner M., Gerhards R., Campbell R., McNett
723 D.A., 2013. Positive vs. false detection: A comparison of analytical methods and
724 performance for analysis of cyclic volatile methylsiloxanes (cVMS) in environmental
725 samples from remote regions. *Chemosphere* 93, 749-756.
- 726 Whelan M.J., Estrada E., van Egmond R., 2004. A modelling assessment of the
727 atmospheric fate of volatile methyl siloxanes and their reaction products. *Chemosphere*
728 57, 1427-1437.
- 729 Wu X., Apte M.G., Maddalena R., Bennet D.H., 2011. Volatile Organic Compounds in
730 small-and medium-sized commercial buildings in California. *Environmental Science &*
731 *Technology* 45, 9075-9083.
- 732 Xu L., Shi Y., Wang T., Dong Z., Su W., Cai Y., 2012. Methyl siloxanes in
733 environmental matrices around a siloxane production facility, and their distribution and

734 elimination in plasma of exposed population. *Environmental Science & Technology* 46,
735 11718-11726.

736 Xu S., Wania F., 2013. Chemical fate, latitudinal distribution and long-range transport
737 of cyclic volatile methylsiloxanes in the global environment: A modeling assessment.
738 *Chemosphere* 93, 835-843.

739 Yucuis R.A., Stanier C.O., Hornbucke K.C., 2013. Cyclic siloxanes in air, including
740 identification of high levels in Chicago and distinct diurnal variation. *Chemosphere* 92,
741 905-910.

Table 1
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Table 1. Average VMS concentrations (ng m⁻³), total population (inh.) and population density (inh. Km⁻²) in the studied locations.

Urban area (Fig. 1)	Constantí	El Morell	Vilallonga	Perafort	Puigdelfí	La Llagosta	Montcada	Ripollet	Cerdanyola	Els Monjos
	1	2	3	4	5	6	7	8	9	10
	<i>n</i> = 46	<i>n</i> = 66	<i>n</i> = 40	<i>n</i> = 28	<i>n</i> = 24	<i>n</i> = 7	<i>n</i> = 8	<i>n</i> = 18	<i>n</i> = 8	<i>n</i> = 26
TMS	53 ± 37	157 ± 156	39 ± 18	45 ± 24	214 ± 118	173 ± 90	119 ± 81	94 ± 50	22 ± 17	178 ± 128
L2	11 ± 23	4 ± 4	11 ± 12	3 ± 3	6 ± 5	215 ± 244	79 ± 93	31 ± 39	4 ± 3	4 ± 2
L3	1 ± 1	1 ± 1	1 ± 1	0.4 ± 0.3	7 ± 12	35 ± 56	9 ± 6	7 ± 3	2 ± 1	0.3 ± 0.1
L4	0.5 ± 0.4	0.2 ± 0.1	n.d.	0.4 ± 0.3	4 ± 10	12 ± 16	5 ± 3	5 ± 3	2 ± 2	1.6
L5	1.0 ± 0.4	n.d.	n.d.	n.d.	18 ± 17	3 ± 1	2 ± 1	2 ± 1	2 ± 1	n.d.
D3	792 ± 971	1166 ± 1320	409 ± 449	729 ± 489	1358 ± 920	803 ± 547	343 ± 252	670 ± 389	39 ± 29	250 ± 199
D4	378 ± 491	483 ± 602	130 ± 136	221 ± 104	642 ± 394	676 ± 552	209 ± 179	256 ± 195	9 ± 8	40 ± 64
D5	159 ± 128	87 ± 68	68 ± 56	218 ± 203	14,914 ± 11,631	1942 ± 854	591 ± 303	1287 ± 1232	230 ± 114	173 ± 147
D6	32 ± 37	16 ± 16	17 ± 17	22 ± 15	449 ± 240	68 ± 46	34 ± 30	66 ± 57	16 ± 24	32 ± 18
Total siloxanes (µg m⁻³)	1.4 ± 1.6	1.9 ± 2.0	0.7 ± 0.6	1.2 ± 0.6	18 ± 12	3.9 ± 2.0	1.4 ± 0.8	2.4 ± 1.4	0.3 ± 0.2	0.7 ± 0.5
Total population 2014 (inh.)*	6539	3530	2229	1107	180	13,430	34,394	37,233	57,402	7337
Population density (inh. Km⁻²)*	211	598	248	136	136	4477	1646	8659	1878	427

*Source: IDESCAT: Official Statistics Website of Catalonia (www.idescat.cat)

Table 2
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Table 2. VMS outdoor air concentrations (ng m⁻³) in several worldwide locations.

TMS	L2	L3	L4	L5	D3	D4	D5	D6	Location	Citation
OUTDOOR AIR (ng m⁻³)										
Polar										
-	-	<lod	<lod-0.01	<lod	0.5-21	0.7-18	0.3-4	0.1-0.5	Arctic	Genualdi et al., 2011*
-	-	-	-	-	n.d.-2.8	n.d.-2.1	0.2-3.9	0.1-0.8	Arctic	Krogseth et al., 2013a
Background										
-	-	<lod-0.02	<lod-0.7	<lod-0.04	0.5-117	0.9-45	<lod-15	<lod-4.5	Background (Europe, America and Australia)	Genualdi et al., 2011*
-	-	0.1-0.5	0.01-0.05	<0.003-0.03	0.4-2.4	1.8-8.0	5.6-28	0.5-2.7	Background, Sweden	Kierkegaard and McLachlan, 2013
-	-	-	-	-	-	-	0.7-8.3	-	Rural site, Sweden	Kierkegaard and McLachlan, 2010
-	-	-	-	-	-	-	0.3-9	-	Rural site, Sweden	McLachlan et al., 2010
-	-	-	-	-	-	5.6-14	10-29	<1.4-2.3	Rural site, USA	Yucuis et al., 2013
Urban										
22-178	3-215	0.3-35	n.d.-12	n.d.-3	39-1166	9-676	87-1942	16-68	Urban areas, Spain	Present study
214	6	7	4	18	1358	642	14,914	449	Urban area hot-spot, Spain	Present study
-	12-22	14-16	16-17	6-8	2.2-5.0	73-79	375-439	45-60	Urban area, Barcelona, Spain	Companion-Damas et al., 2014
-	-	<lod-0.1	0.06-0.7	0.1-0.5	0.7-30	3.9-50	55-280	4.0-53	Urban areas (Europe and America)	Genualdi et al., 2011*
-	-	-	-	-	-	18-190	100-1100	n.d.-7.6	Urban area, Chicago, USA	Yucuis et al., 2013
-	-	-	-	-	-	-	100-650	10-79	Urban area, Zurich, Switzerland	Buser et al., 2013
-	-	-	-	-	0-11,300	0-3300	n.d.-traces	-	Urban area, Guangzhou, China	Wang et al., 2001
-	-	-	-	-	2100-5800	800-4300	n.d.-traces	-	Urban area, Macau, China	Wang et al., 2001
-	-	-	-	-	0-2300	0-3500	n.d.-traces	-	Urban area, Nahnai, China	Wang et al., 2001
-	-	-	-	-	1900-9300	6400-20,500	n.d.-traces	-	Industrial area, Guangzhou, China	Wang et al., 2001
-	-	-	-	-	-	5.1-37	22-65	3.3-9.3	Medium sized urban, USA	Yucuis et al., 2013
-	-	-	-	-	-	-	45-160	7-16	Suburban site, Switzerland	Buser et al., 2013
-	-	1.8	1.2	0.5	<lod	24.2	93.5	65.9	Suburban site, Toronto, Canada	Krogseth et al., 2013b*
-	-	0.2-4.9	0.4-6.5	0.7-4.8	0.5-4.7	2.8-77	15-247	1.9-22	Semiurban site, Toronto, Canada	Ahrens et al., 2014
-	-	-	-	-	100-1000	0-1600	n.d.-traces	-	Suburban area, Guangzhou, China	Wang et al., 2001

*VMS concentrations obtained through passive sampling.

Table 3
[Click here to download Table: Table 3.docx](#)

Table 3. VMS indoor air concentrations ($\mu\text{g m}^{-3}$) in several worldwide locations.

TMS	L2	L3	L4	L5	D3	D4	D5	D6	Location	Citation
INDOOR AIR ($\mu\text{g m}^{-3}$)										
Public places										
-	-	-	-	-	-	-	1.3-120	-	Commercial buildings, California	Wu et al., 2011
-	-	n.d.-0.003	n.d.-0.006	n.d.-0.03	0.01-0.04	0.03-0.5	0.2-2.4	0.004-0.3	Public places, Albany, NY, USA	Tran and Kannan, 2015
-	n.d.	n.d.	n.d.	n.d.	3.3-4.5	5.2	45-62	1.3-3.1	Supermarkets, Italy	Pieri et al., 2013
-	n.d.-63	n.d.-52	n.d.-23	n.d.-2.3	4.7-34	3.5-12	110-440	4.2-13	Supermarkets, UK	Pieri et al., 2013
Work places										
-	-	-	-	-	1-2	1-1.8	3-4	0.2	Work environments, Norway	Katsoyiannis et al., 2014
-	-	n.d.-0.001	n.d.	n.d.-0.05	0.002-0.006	0.001-0.008	0.006-0.09	0.003-0.05	Offices, Albany, NY, USA	Tran and Kannan, 2015
-	n.d.-4.3	n.d.-0.4	n.d.-0.6	n.d.-0.8	0.9-5.5	0.9-5.2	4.4-11	n.d.	Offices, Italy	Pieri et al., 2013
-	n.d.-4.2	n.d.-0.7	n.d.-5.9	n.d.-1.4	2.7-16	3.5-20	2.4-170	0.04-15	Offices, UK	Pieri et al., 2013
-	-	n.d.-54	n.d.-3.7	n.d.-39	3.8-61	5.3-88	16-163	4.7-111	Laboratories, Albany, NY, USA	Tran and Kannan, 2015
-	0.03	0.01	0.01	0.004-0.005	0.05-0.1	0.2-0.4	1.7-2.4	0.2-0.4	Offices, Barcelona, Spain	Companiononi-Damas et al., 2014
-	0.09-0.3	0.01-0.02	<loq-0.01	0.04-0.07	0.5	0.6-0.8	2.3-2.9	0.4-0.6	Laboratories, Barcelona, Spain	Companiononi-Damas et al., 2014
Homes										
-	-	-	-	-	1	1	5-8	0.2	Home rooms, Norway	Katsoyiannis et al., 2014
-	-	n.d.-0.003	n.d.-0.009	0.002-0.03	0.006-0.02	0.2-0.7	0.4-3.7	0.1-0.9	Salons, Albany, NY, USA	Tran and Kannan, 2015
-	-	n.d.-0.006	n.d.-0.008	n.d.-0.1	0.004-0.7	0.004-0.2	0.02-0.8	0.008-0.2	Homes, Albany, NY, USA	Tran and Kannan, 2015
-	n.d.-4.4	n.d.	n.d.	n.d.-1.4	0.2-140	0.7-35	2.5-350	n.d.-6.2	Boy bedroom, Italy	Pieri et al., 2013
-	n.d.	n.d.-46	n.d.	n.d.	2.9-28	3.8-15	90-290	5.3-65	Boy bedroom, UK	Pieri et al., 2013
-	n.d.-9.6	n.d.	n.d.-3.7	n.d.-1.2	0.4-140	0.7-73	n.d.-510	n.d.-18	Girl bedroom, Italy	Pieri et al., 2013
-	n.d.-15	n.d.-40	n.d.	n.d.-2.3	0.2-267	n.d.-62	3.2-170	0.5-31	Girl bedroom, UK	Pieri et al., 2013
-	n.d.-3.9	n.d.	n.d.-4.8	n.d.	n.d.-250	n.d.-60	1.7-730	n.d.-120	Adult room, Italy	Pieri et al., 2013
-	n.d.	n.d.	n.d.	n.d.	1.2	1.9	45	5.4	Adult room, UK	Pieri et al., 2013
-	n.d.-11	n.d.	n.d.-0.8	n.d.-1.6	0.5-8.2	2.1-22	8.4-79	n.d.-180	Living room, Italy	Pieri et al., 2013
-	n.d.-93	n.d.-7.1	n.d.-2.5	n.d.-2.2	3.1-270	2.3-80	31-160	5.1-32	Living room, UK	Pieri et al., 2013
-	0.01-0.02	0.02	0.02	0.1-0.3	0.1-0.2	1.6-3.1	229-293	23-85	Homes, Barcelona, Spain	Companiononi-Damas et al., 2014
Bathrooms										
-	-	-	-	-	1	1	1.5	0.2	Bathrooms, Norway	Katsoyiannis et al., 2014
-	n.d.-13	n.d.-5.4	n.d.-8.5	n.d.-9.8	1.3-350	1.9-27	3.8-300	n.d.-79	Bathrooms, Italy	Pieri et al., 2013
-	n.d.-13	n.d.	n.d.-8.5	n.d.-3.4	1.3-350	2.3-270	3.8-300	1.4-79	Bathrooms, UK	Pieri et al., 2013
Schools										
-	-	n.d.	n.d.-0.003	n.d.-0.004	0.006-0.02	0.01-0.3	0.1-1.0	0.01-0.1	Schools, Albany, NY, USA	Tran and Kannan, 2015
-	18	16	7.5	n.d.	14	17	270	4.3	Kindergarten, UK	Pieri et al., 2013

Figure captions

Figure 1. Sampling points. Blue polygons indicate industrial areas. A: Tarragona; B: Vallès; C: Penedès. Numbers correspond to the urban areas indicated in Tables 1 and S2. Red dots correspond to sampling points in each urban area. Green dots correspond to the meteorological stations.

Figure 2. cVMS distribution in the sampling points. Percentage of each cVMS in respect to Σ cVMS.

Figure 3. Correlations between D5 and D6 concentrations and population density.

Figure 4. Correlations between D3 and D4 for all samples ($n=271$).

Figure 1
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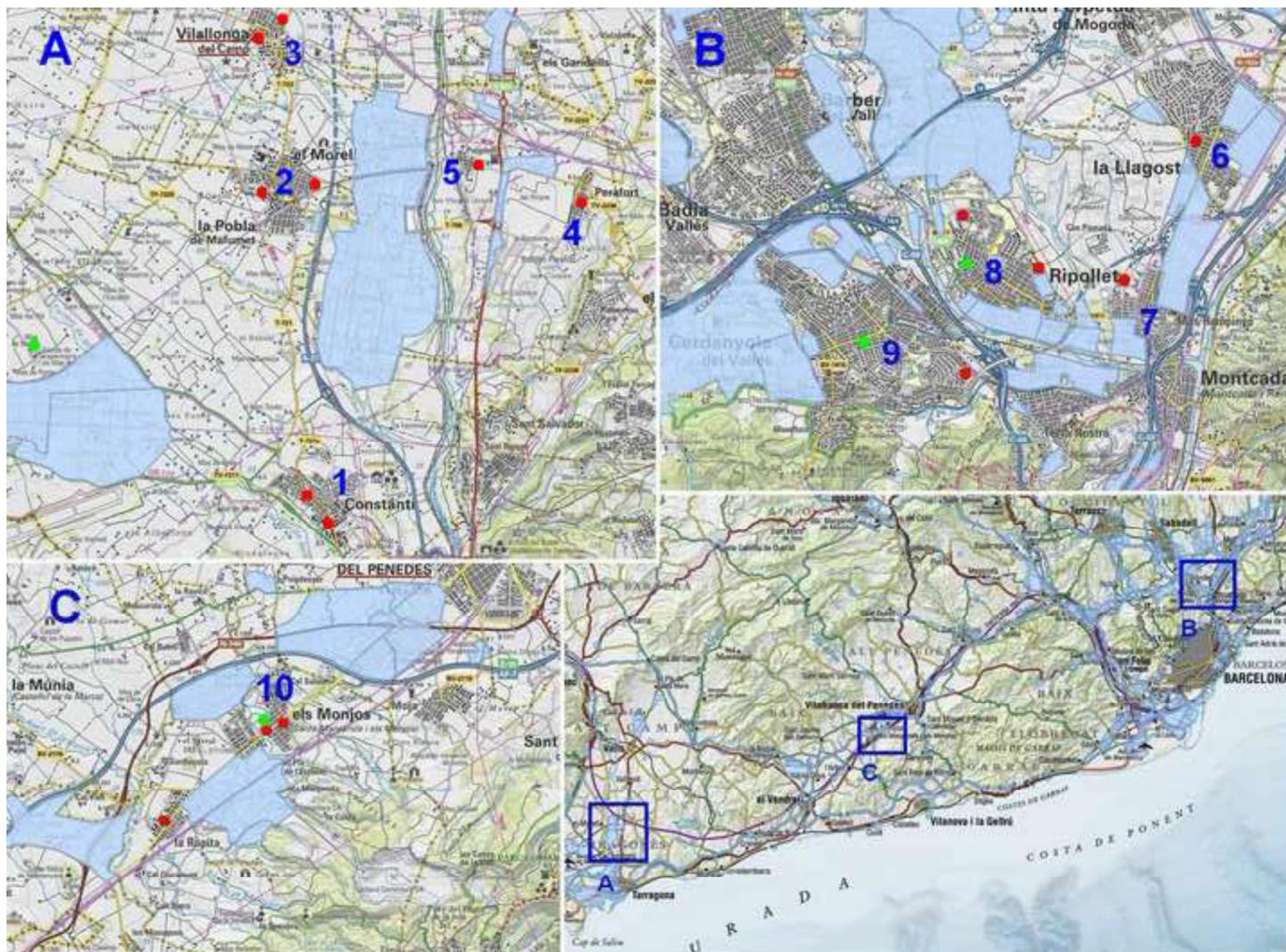


Figure 2

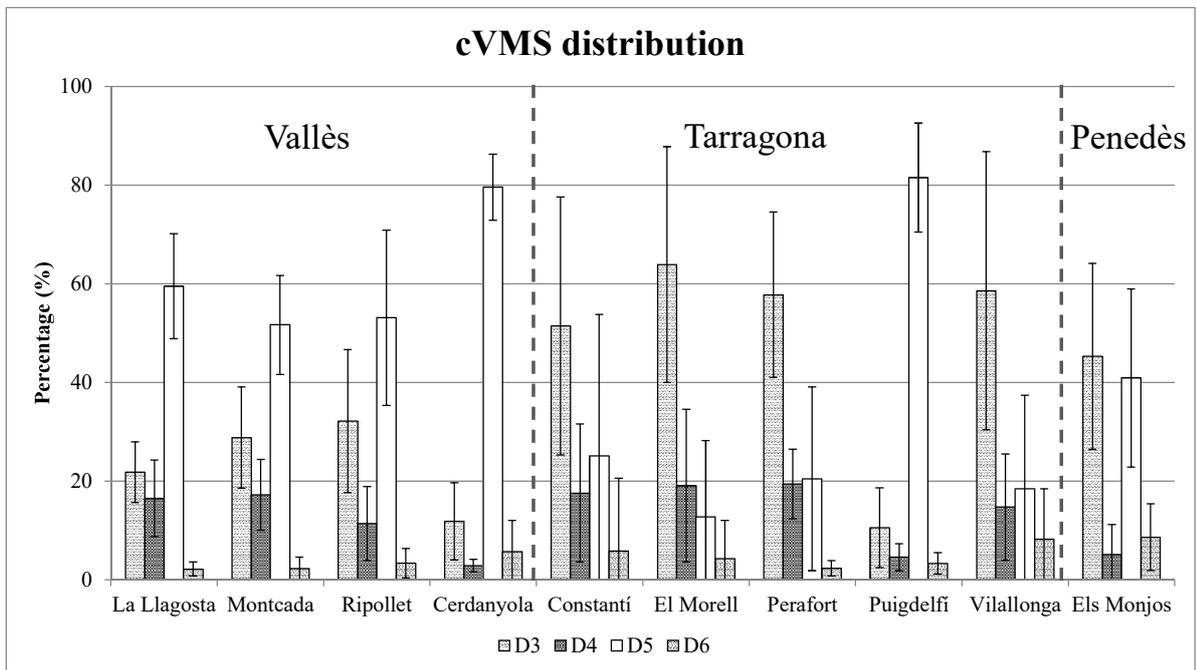


Figure 3

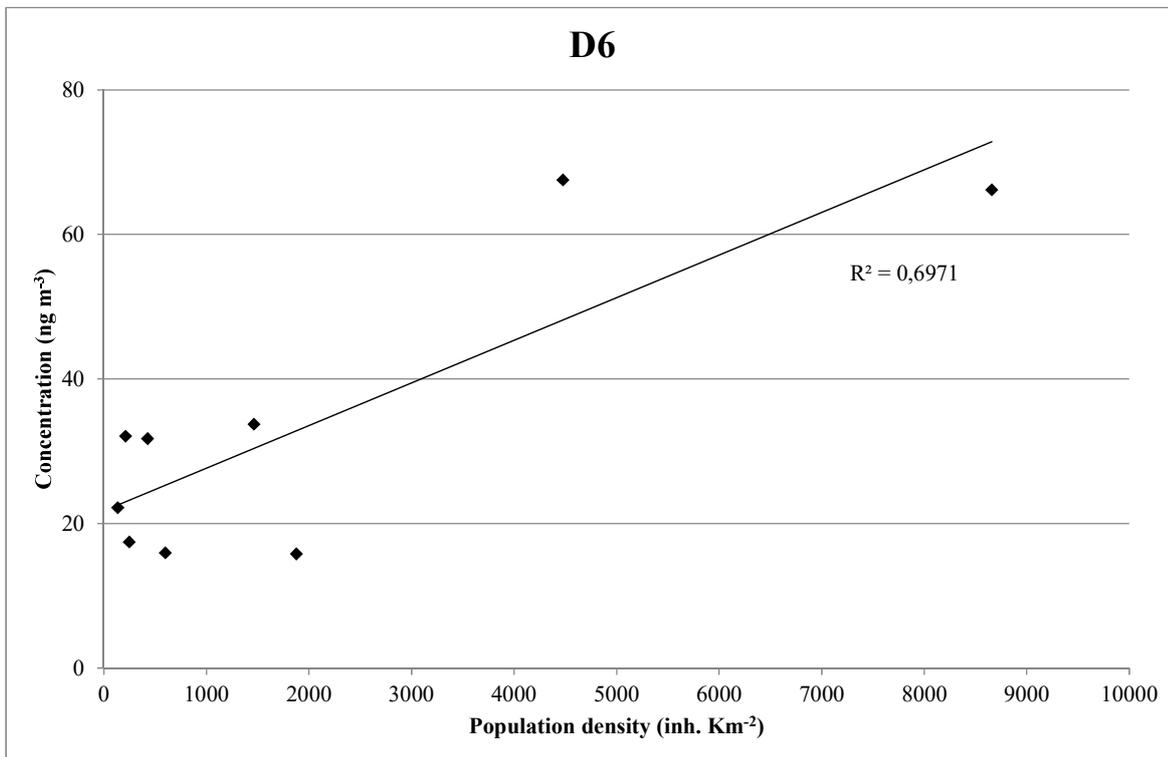
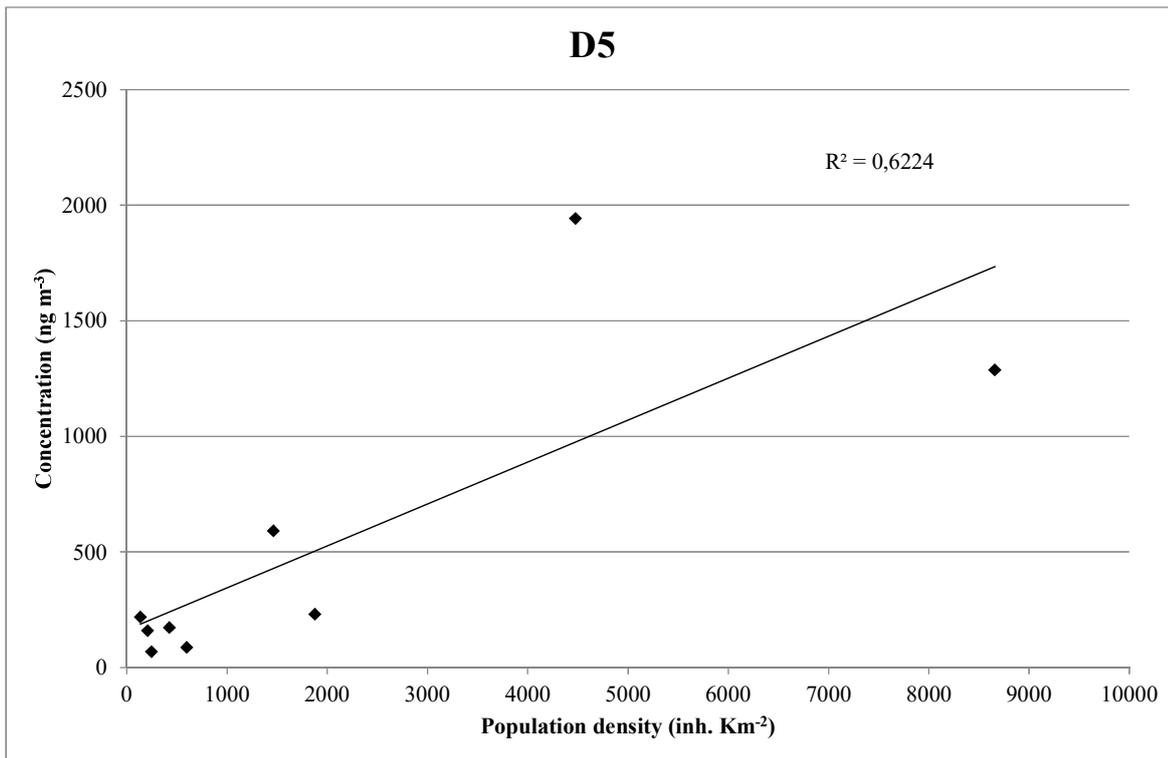


Figure 4

