Environment International 59 (2013) 363–371

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Occurrence of linear and cyclic volatile methyl siloxanes in indoor air samples (UK and Italy) and their isotopic characterization

F. Pieri [a], A. Katsoyiannis [b,*], T. Martellini [a], D. Hughes [c], K.C. Jones [c], A. Cincinelli [a,c,**]

[a] Department of Chemistry, University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino, Florence, Italy
[b] Norwegian Institute for Air Research (NILU) at FRAM, High North Research Centre on Climate and the Environment, NO-9296 Tromsø, Norway
[c] Lancaster Environment Centre, Lancaster University, Bailrigg, LA14YQ, Lancaster, United Kingdom

ARTICLE INFO

Article history:
Received 21 January 2013
Accepted 12 June 2013
Available online 25 July 2013

Keywords:
Indoor air
Siloxanes
D4
D5
Exposure assessment
CSIA

ABSTRACT

The occurrence of linear- and cyclic-volatile methyl siloxanes (lVMSs and cVMSs, respectively) in various indoor environments, occupational and domestic, in Italy and in the United Kingdom was studied. The results show that the cVMSs are the most abundant, detected in average concentrations that in some cases were as high as 170 μg m^{-3}. Our study highlights the differences that can be observed between various indoor environments (e.g. domestic like bathrooms, bedrooms, or occupational) and between two countries. In most cases, the concentrations found in the UK are higher than in the respective indoor environments in Italy. The assessment of exposure to these two countries for adults and children revealed significant differences both not only in the levels of exposure, but also in the patterns. In Italy, the biggest part of the exposure to VMSs takes place domestically, whereas in the UK, it is observed for occupational environments.
Additionally, the compound specific isotopic analysis was employed as a source identification technique. The results are promising mainly for D5 that occurs in higher concentrations, but not for the less abundant lVMSs and cVMSs.

1. Introduction

Linear and cyclic volatile methyl siloxanes (lVMSs and cVMSs, respectively) are widely used chemicals in many personal care products, cosmetics and industrial applications (such as electronics, silicon polymers, and medical devices). These compounds are of environmental concern and are currently under consideration for regulation because of their volatility, persistence, toxicity and tendency to bioaccumulate (Hanssen et al., 2013).

The daily exposure rate to total organosiloxanes (cyclic and linear ones) from the use of different personal care products depends on a large number of parameters (i.e. environmental conditions, personal habits, etc.) and it was estimated to be 307 mg day^{-1} for women in the United States (Lu et al., 2011). Siloxanes were generally regarded as "safe" in consumer products however studies on reproductive toxicity and possible endocrine disrupting effects have suggested that exposure to cyclic siloxanes could cause direct or indirect toxic effects, such as estrogen mimicry, connective tissue disorders, adverse immunologic responses, and fatal liver and lung damage (Granchi et al., 1995; Hayden and Barlow, 1972; He et al., 2003; Lieberman et al., 1999; Quinn et al., 2007). Risk assessment studies in Canada concluded that octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) have the potential to cause ecological harm and other damaging effects on the environment and its biological diversity (Genualdi et al., 2011; Krogseth et al., 2013a, 2013b). In addition, inhalation and oral exposure studies reported histopathological changes in rat lungs for D4 and D5 (Burns-Naas et al., 1998), fertility reduction on rats for D4 (McKim et al., 2001), and potential carcinogenicity and immunosuppressant effects for D5 (McKone et al., 2009). A risk assessment of D4, D5 and D6 of the UK Environment Agency has been conducted and the current recommendations are that D4 should be classified as very persistent and very bioaccumulative (VPvB) and as persistent, bioaccumulative and toxic (PBT), and D5 should be classified as VPvB under REACH (Brooke et al., 2009a, 2009b, 2009c).

To date, studies on siloxanes have focused on the distribution and fate in various environmental compartments and levels of siloxanes have been reported in suspended solids and activated sludge from wastewater treatment plants (Cheng et al., 2011; Fendinger et al., 1997; Kaj et al., 2005a), in sludge-amended soils and sediments (Wang et al., 2012), in dust (Lu et al., 2010), in passive air samples (Genualdi et al., 2011; Kierkegaard and McLachlan, 2010; Wania and Dugani, 2003) in landfill biogases (Schweigkofler and Niessner, 1999), and in human blood, fat, and breast milk (Flassbeck et al., 2001).

Little however is known about the levels and distribution of cVMS and lVMS in indoor environments; Lu et al. (2010) reported concentrations of total siloxanes in 100 indoor dust samples from China ranging from 21.5 to 21,000 ng g^{-1} and a daily exposure to total

* Corresponding author. Tel.: +47 77750386; fax: +390554573324.
** Correspondence to: A. Cincinelli, Department of Chemistry, University of Florence, Via della Lastruccia, 3, 50019 Sesto Fiorentino, Florence, Italy.
E-mail addresses: aak@nilu.no (A. Katsoyiannis), acincinelli@unifi.it (A. Cincinelli).

0160-4120/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.envint.2013.06.006

siloxanes for adults of 15.9 ng day^{-1}. Zhou et al. (2012) reported siloxane concentrations in non-occupational environments in Canada, where D5 and D4 were the two most frequently detected VMSs.

In view of their potential toxicity, determination of siloxanes in indoor air and evaluation of human exposure are imperative to enable risk assessment, and the development of strategies for reducing exposure. Indoor air quality is a very important factor affecting the humans' wellbeing. Individuals spend >90% of their time in indoor environments (de Bruin et al., 2008; Sarigiannis et al., 2011) and it is known that the indoor air can be contaminated by numerous inorganic and organic contaminants (Katsoyiannis and Bogdal, 2012; Katsoyiannis et al., 2012a; Kurt-Karakus, 2012).

In order to better understand the occurrence and distribution of siloxanes in indoor environments, four cVMSs (D3, D4, D5, D6) and four lVMSs (L2, L3, L4, L5) were determined in air samples collected between May and August 2011, in Italy and the UK. In addition, the possibility to use compound specific isotope analysis (CSIA) for tracing siloxane sources was for the first time explored, by measuring the various C isotopic compositions ($\delta^{13}C$) of siloxanes from products from various manufacturers and by comparing these results to the $\delta^{13}C$ of siloxanes found in some indoor air samples. (Cincinelli et al., 2012)

2. Materials and methods

2.1. Sample collection

Indoor air samples (n = 91) were collected using sorbent tubes containing Tenax GR (35/60 mesh) and a Graphitized Carbon Black (Markes International). Following the EPA method TO-17 (USEPA, 1997) before sampling, the sampling tubes were conditioned at 320 °C for 120 min, then at 335 °C for 30 min with a 100 mL min^{-1} reverse flow of high purity (99.999%) helium, and plugged on both ends with brass caps with PTFE ferrules before they were used for sample collection.

Indoor air sampling campaigns were conducted from May to August 2011 in Italy and the UK.

Air samples were collected from eight types of indoor environments. In private residences, air was collected in bathrooms (n = 18), living rooms (n = 13), adult- (n = 10), boy- (n = 11) and girl- (n = 12) rooms. In settings with expected different diurnal occupancy patterns such as school (n = 5), supermarket (n = 10) and office (n = 12) buildings, samples were collected during hours that represent typical exposure. The sampling protocol followed the German guideline VDI-Richtlinie 4300-6, according to which, windows and doors should be closed at least 8 h prior to the air sampling event (Hippelein, 2004).

Sampling was performed by drawing 5 L of air through the sampling tubes at a flow rate of about 120 mL min^{-1}, using a GilAir3 operated air-pump (Gilian — Sensydine), placed in the center of the room, at a height of about 1.5 m, at the breathing zone of building occupants. Air was sucked through two sorbent tubes in series. Additional non-sampled sorbent tubes were used as field blanks. After collection, the sample tubes were stored at +4 °C.

In order to determine the $\delta^{13}C$ of each siloxane by means of GC-IRMS, air samples (n = 10) were collected on coconut charcoal cartridges, contemporary to the air sampling performed on Tenax GR (35/60 mesh) plus a Graphitized Carbon Black (Markes International) sorbent tube.

2.2. Reagents and chemical analysis

Individual cVMS and lVMS standards, with purity >98%, were purchased from Sigma-Aldrich (St. Louis, MO, USA). In particular, it contained the hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) cVMS; and the hexamethyldisiloxane (L2), octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4) and dodecamethylpentasiloxane (L5) lVMS. A 30 mg L^{-1} stock solution of each component was prepared in methanol, and further diluted to obtain standards ranging from 0.3 to 30 ng μL^{-1}. A six-point linear calibration curve was drawn by analyzing sorbent tubes pre-loaded with known amounts of the target analytes.

Sorbent tubes were analyzed on an Automatic Thermal Desorption UNITY2 (Markes International) coupled to a GC/MS-system (Agilent, GC 6890N — MS 5973i). Tubes were desorbed at 320 °C for 60 min, and separated on Agilent DB 624 capillary column (60 m × 250 μm × 1.40 μm). The column temperature was 40 °C for 4 min, programmed to 90 °C at 6 °C min^{-1}, to 120 °C at 8 °C min^{-1} and to 210 °C at 10 °C min^{-1}. The carrier gas was helium and the mass spectrometric detector was used in electron impact single ion recording mode (SIM). The run time for sample analysis, including desorption (60 min), and GC analysis (46 min) was 106 min. The ions were monitored at m/z 75 for TMS, m/z 147 for L2, m/z 207 for D3, m/z 221 for L3, m/z 281 for D4, m/z 207 and 356 for L4, m/z 355 and 267 for D5, m/z 281 and 147 for L5, and m/z 341 and 444 for D6. The quantification was performed with external standards on pre-cleaned tubes. A six level daily calibration curve was used for quantification.

2.3. Method evaluation

Blank emissions and artifact formation, which can affect the method sensitivity and overall performance, were determined using a total of 10 freshly conditioned Tenax GR (35/60 mesh) plus a Graphitized Carbon Black (Markes International) sorbent tube. Field blanks were also collected each sampling day and treated like the sampled tubes. A number of preventive measures were also taken to reduce possible contamination, such as team members avoided to use personal care products during sampling and sample analysis and cleaned sorbent tubes were stored in a clean laboratory. Moreover, to assure inertness performance, Merlin Microseal System (Supelco) replacement septa were used in the gas-chromatograph injector, and an Agilent ultra inert GC capillary column was used in chromatography separations. In addition, to reduce the background levels of siloxanes, siloxane free septa were used in the injection system and vials.

The limit of detection (LOD) was determined by applying a signal to noise ratio of 3, and defined as the average of all blank concentrations plus three times the standard deviation of the blanks and was found to range from 0.007 to 0.04 μg m^{-3}.

The retention of VMSs on the sorbent tubes was tested by using a back-up tube in series with the primary tube, using inert metal connectors. A siloxane standard mixture was loaded on the primary tube and then air was drawn through the sampling train at various flow rates. By the amounts of VMSs on the second tube, the breakthrough was evaluated.

The reproducibility was determined by spiking sorbent tubes in quadruplicate with a siloxane standard mixture containing about 5 ng μL^{-1} of each compound, in order to simulate the concentration range found in the air samples and the reproducibility was expressed as the relative standard deviation (RSD) for each concentration level. Recoveries for investigated VMSs were evaluated as the fraction of the mass recovered from the sorbent compared to that injected into the sorbent tube. Analyses were performed within 24 h after spiking the tube.

2.4. Compound specific isotope analysis (CSIA)

Indoor air samples for compound specific isotope analysis (CSIA) were collected according to a standard method developed by NIOSH using activated coconut charcoal tubes (ORBO™-32, Supelco, Inc., Bellefonte, PA). These cartridges are glass tubes with both ends flame sealed (110 cm long × 8 mm o.d.) and contain two sections of 20/40 mesh coconut activated charcoal separated by a 2-mm portion of polyurethane foam. The adsorbing section, which is the longest, contained 400 mg of activated coconut charcoal and the back-up section 200 mg. Air was drawn through

the charcoal tubes, using an air-pump (Gilian — Sensydine) calibrated to draw 0.2 L min^{-1}, and the sampling duration was about 60 min. The caps of the sampling tubes were removed immediately before sampling. The sampler was attached to the sampling pump by PTFE tubing. After sampling, the charcoal tube was removed from the sampler and the two open sides were tightly closed using special PTFE caps to prevent any contamination and desorption. To detect possible contamination, field blanks were performed by putting a charcoal tube with broken ends in the channel of the sampler at the sampling site but without passing any air sample through it. The samples and blank tubes were put into air-tight plastic bags and kept at −10 °C in a freezer until they were processed, not later than two days after collection. Before analysis, each charcoal tube was scored with a quartz blade (ORBO™ tube cutter, Supelco) in the front of the first section (i.e. the adsorbing section) of charcoal and broken open. The glass wool was removed and discarded. The charcoal in the adsorbing section was transferred to a 2-mL capped vial. The separating foam was removed and discarded; the second section (back-up section) was transferred to another capped vial. These two sections were analyzed separately. To desorb the samples, 1 mL of desorbing solution was pipetted into each sample vial. The desorption solution consisted of 5 μg m^{-3} of internal standard solution in carbon disulfide. The sample vials were capped with PTFE as soon as the solution was added. Desorption was done for 30 min in an ice bath in a sonicator with occasional shaking. The extracts, exchanged in hexane, were analyzed with a 6890 gas chromatograph coupled with a 5973 mass spectrometry using electron ionization (EI) and with an isotope ratio mass spectrometer (Isoprime Ltd., Manchester, UK) via a combustion interface maintained at 850 °C. The GC was equipped with a split/splitless injector with a Merlin Microseal septum. 2 μL of the extract was injected at an injector temperature of 200 °C. Separation of VMSs was accomplished with an Inert 30-m DB5-MS (0.25 mm i.d., 0.25 μm film thickness, J&W Scientific) and a 1 m retention gap of deactivated fused silica was used (0.32 mm i.d., Agilent Technologies). The operating conditions were as follows: injector temperature 200 °C; transfer line temperature 250 °C; and oven temperature program 70 °C (2 min), 10 °C min^{-1} to 90 °C, hold 5 min, 15 °C min^{-1} to 150 °C, and 30 °C min^{-1} to 280 °C, hold 10 min. The detector was operated in selected ion mode (SIM) to maximize sensitivity.

The IRMS was routinely tested for resolution, system and signal stabilities, relative and absolute sensitivity, peak flatness and ratio linearity as per the operational manual. Standard reference material (hydrocarbon mixtures from Indiana) of known isotope ratio was included in each analytical sequence to check the bias of isotope ratio measurement. For all measured individual compounds, the standard deviation for multiple analyses ranged between 0.07 and 0.32‰. An internal standard, n-dodecane with $\delta^{13}C$ −31.99 (measured value), was used to monitor the performance of the instrument during each sample run. All sample isotope values were calculated based on a standard gas injected at the beginning of each sample run. The $\delta^{13}C$ values for VMS standards showed a precision of ±0.15‰.

Blank emissions were also evaluated for 10 coconut charcoal tubes. CSIA analysis showed values below the instrumental detection limit.

3. Results and discussion

3.1. Method validation

The breakthrough of the standard VMS mixture was <0.4% (n = 10) at the flow rate applied. Therefore, the sampling protocol was considered as efficient. Nevertheless, in a number of samples, for control purposes, a second tube was placed to control the breakthrough also during proper sampling (air flow was separately controlled when 2 tubes were used).

The standard VMSs showed very good reproducibility with high to low relative standard deviation, ranging between 6.1% (L5) and 13.7% (D3). The mean recoveries of standards spiked into the sorbent tubes ranged from 82 ± 5.6% to 92 ± 8%.

3.2. Occurrence of siloxanes

Detailed concentrations of all studied compounds are presented in Tables 1–2, for Italy and the UK, respectively. Most abundant chemical was D5, in almost all samples, with average concentrations ranging from 7.5 to 170 μg m^{-3} in samples from Italy and 45 to 270 μg m^{-3}, in indoor environments in the UK. D5 accounted routinely for more than 50% of the total VMSs, although there have been cases where D5 accounted for as low as 26%. Other compounds that occurred in high concentrations were D3 that was the most abundant in living rooms in Italy (180 μg m^{-3}) and D6, which dominated the respective samples in the UK (160 μg m^{-3}). The predominance of D5 is in accordance with the results from previous studies which determined the content of cVMSs in a variety of cosmetic products. Fig. S1 presents the profiles of cVMSs as reported by Wang et al. (2009) for 36 cVMSs-containing products, where, it can be seen that D5 is the chemical that dominates almost all analyzed products. Only two products belonging to the category of body lotions have been found to contain almost exclusively D4. Higher emission rates for D3 and D6 than for D5 have been observed in emissions from computers and printers, respectively (McKone et al., 2009). Emissions from these types of products may be the reason for the dominance of D3 and D6 in living room samples in both countries.

Linear VMSs were in substantially lower levels and only in few cases, average concentrations exceeded 10 μg m^{-3}. The highest concentrations of lVMSs were observed in the supermarket samples, followed by the kindergarten and the living room ones, all of them in the UK. There are only few studies reporting indoor air concentrations of VMSs. A study in indoor environments in Sweden reported average values below 10 μg m^{-3} for all individual VMSs and, interestingly, average concentrations almost at the same levels for D5, D4 and D6 (9.7, 9.0 and 7.9 μg m^{-3}, respectively, Kaj et al., 2005b). Wu et al. (2011) measured D5 in a number of commercial buildings in the US and found that D5 ranged between 1.30 and 120 μg m^{-3}, Hodgson et al. (2003) reported a range of 16.7–112 μg m^{-3} for a call center office building and Katsoyiannis et al. (2012b) reported levels of few to 30 μg m^{-3} in various university indoor environments.

Important differences were observed both between the studied countries and between the different indoor environments. The occurrence

Table 1
Concentrations of linear and cyclic methylsiloxanes in Italian indoor environments (μg m^{-3}).

Italy		L2	L3	L4	L5	D3	D4	D5	D6	Total
Bathroom	Average	2.8	0.36	1.4	1.1	69	42	98	16	230
n = 15	Max	13	5.4	8.5	9.8	350	27	300	79	820
	Min	ND	ND	ND	ND	1.3	1.9	3.8	ND	17
Boy bedroom	Average	0.7	ND	ND	0.24	26	8.0	110	1.0	150
n = 6	Max	4.4	ND	ND	1.4	140	35	350	6.2	360
	Min	ND	ND	ND	ND	0.23	0.74	2.5	ND	13
Girl bedroom	Average	2.4	ND	0.77	0.46	27	19	137	5.4	190
n = 6	Max	9.6	ND	3.7	1.2	140	73	510	18	690
	Min	ND	ND	ND	ND	0.39	0.72	ND	ND	2.1
Living room	Average	3.3	ND	0.15	0.32	3.5	8.2	38	45	100
n = 5	Max	11	ND	0.76	1.6	8.2	22	79	180	300
	Min	ND	ND	ND	ND	0.51	2.1	8.4	ND	26
Adult room	Average	0.86	ND	0.64	ND	36	11	170	19	240
n = 9	Max	3.9	ND	4.8	ND	250	60	730	120	940
	Min	ND	ND	ND	ND	ND	ND	1.7	ND	7.6
Supermarket	Average	ND	ND	ND	ND	3.9	5.2	54	2.2	66
n = 2	Max	ND	ND	ND	ND	4.5	5.2	62	3.1	75
	Min	ND	ND	ND	ND	3.3	5.2	45	1.3	58
Office	Average	3.3	0.08	0.12	0.17	3.3	2.2	7.5	ND	18
n = 5	Max	4.3	0.42	0.58	0.83	5.5	5.2	11	ND	21
	Min	ND	ND	ND	ND	0.85	0.94	4.4	ND	14

Table 2
Concentrations of linear and cyclic methylsiloxanes in UK indoor environments (μg m^{-3}).

UK		L2	L3	L4	L5	D3	D4	D5	D6	Total
Bathroom	Average	3.3	ND	2.1	0.75	110	68	120	26	340
n = 9	Max	13	ND	8.5	3.4	350	270	300	79	820
	Min	ND	ND	ND	ND	1.3	2.3	3.8	1.4	17
Boy bedroom	Average	ND	9.3	ND	ND	13	8.4	150	24	210
n = 5	Max	ND	46	ND	ND	28	15	290	65	310
	Min	ND	ND	ND	ND	2.9	3.8	90	5.3	120
Girl bedroom	Average	4.2	9.0	ND	0.46	58	15	97	8.1	190
n = 5	Max	15	40	ND	2.3	267	62	170	31	430
	Min	ND	ND	ND	ND	0.22	ND	3.2	0.47	6.2
Living room	Average	18	1.2	0.63	1.3	160	43	84	12	320
n = 5	Max	93	7.1	2.5	2.2	270	80	160	32	520
	Min	ND	ND	ND	ND	3.1	2.3	31	5.1	78
Adult room	Average	ND	ND	ND	ND	1.2	1.9	45	5.4	56
n = 1	Max									
	Min									
Kindergarten	Average	18	16	7.5	ND	14	17	270	4.3	350
n = 1	Max									
	Min									
Office	Average	1.0	0.35	1.5	0.36	6.6	9.8	54	4.6	78
n = 4	Max	4.2	0.71	5.9	1.4	16	20	170	15	220
	Min	ND	ND	ND	ND	2.7	3.5	2.4	0.04	16
Supermarket	Average	21	31	7.8	0.77	15	6.9	230	8.4	330
n = 3	Max	63	52	23	2.3	34	12	440	13	630
	Min	ND	ND	ND	ND	4.7	3.5	110	4.2	130

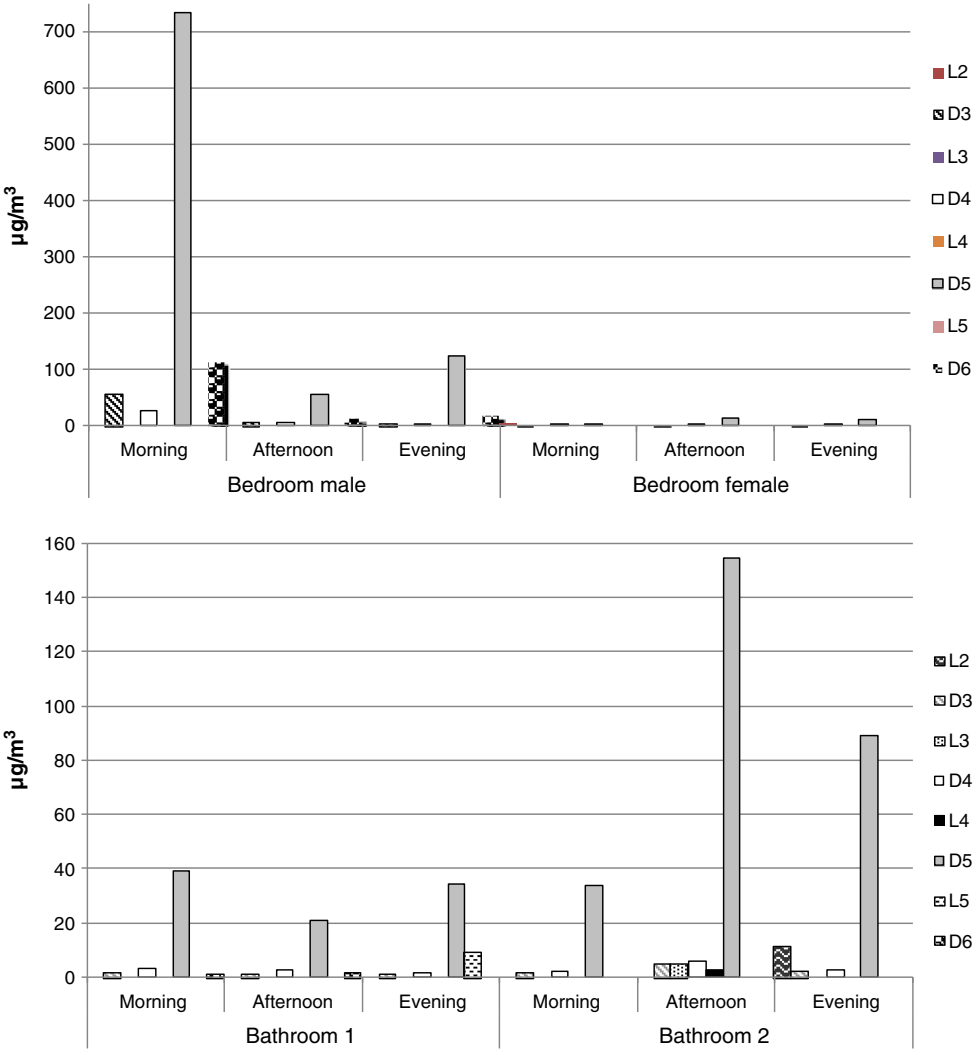

Fig. 1. Intra-day variation of siloxanes in two bedrooms and two bathrooms.

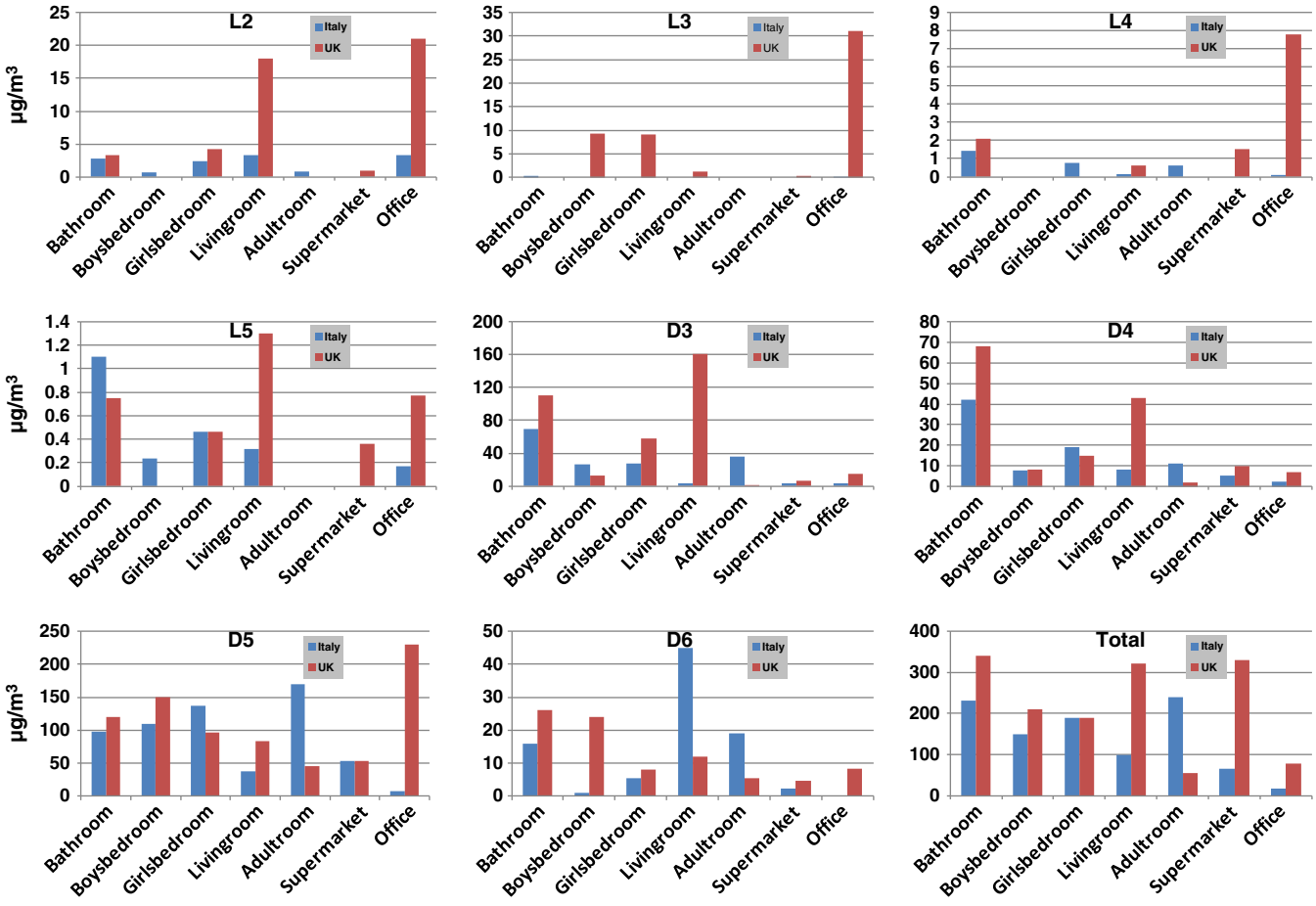

Fig. 2. Comparison between average concentrations (µg m^{-3}) in UK and Italian indoor environments.

of VMSs in the indoor environment is reflecting the use of specific products and the existence of other typical sources. Therefore, even within the same room types, big differences are to be expected. To investigate intra-day differences within the same room, sets of three samples (day, afternoon and evening) were collected randomly from two bedrooms and two bathrooms. As seen in Fig. 1, two of the studied rooms exhibited very high differences within the same day. In particular, in a male bedroom, D3, D4 and D5 were particularly high in the morning and then showed a 10-fold decrease during the afternoon and evening. Similarly, in one of the studied bathrooms, the concentrations of VMSs were low

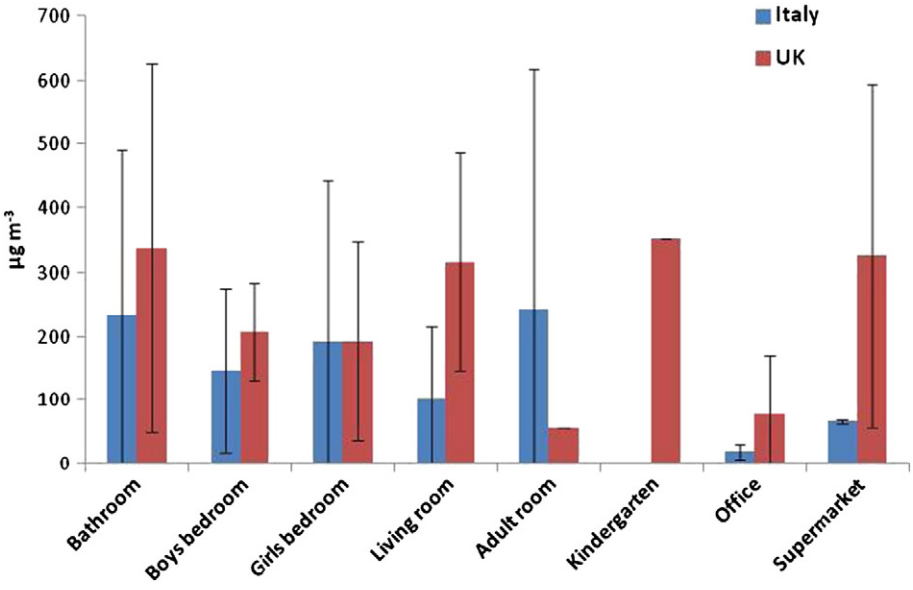

Fig. 3. Comparison of total volatile methylsiloxanes between Italy and the UK.

in the morning, increased by 5 times in the afternoon and remained high in the evening. It is interesting to note also the differences in the profiles (Fig. S2), which underline the contribution of different products/sources during the day.

Fig. 2 presents the average concentrations of all individual compounds in both countries and per room type. Big differences can be observed for TMS and L3; TMS was detected in all types of rooms in Italy and only in three types of rooms in the UK, whereas L3 was detected in considerable concentrations in four UK room types, but was always non-detectable, or very low, in Italy. If we look at the sub-figures, we note again the differences between the two countries; in particular in most cases, the UK samples are characterized by higher average concentrations. Average total VMSs (Fig. 3) ranged between 18 and 240 μg m^{-3} in Italy and between 56 and 350 μg m^{-3} in the UK. In the Italian indoor environments it can be seen that residential spaces are characterized by higher concentrations, contrarily to the working environments where the lowest concentrations were observed. In UK samples instead, such a clear trend (domestic vs occupational) is not observed. The highest concentrations were observed in the kindergarten (although it was only one sample), followed by bathrooms and supermarkets with almost similar VMS concentrations. The highest UK average concentrations and the different trends can be attributed to different consumption and usage behaviors between these two countries. A study of the European cosmetic industry, prepared for the European Commission in 2007 (Global-Insight, 2007), reported important facts about the use of cosmetics in EU countries and worldwide. In that report it could be seen that UK had a greater share than Italy in the EU market (15.7% vs 13.9%, respectively) and also a greater annual expenditure on cosmetics and personal care products per capita (165 vs 149 €). Regarding finally the differences in usage, the two population consume different products and in different rates. As an example, sun care products in the UK account for 21% of the total skin care consumption, whereas in Italy the respective rate was only 13%. Fig. S3 shows the profiles of the five major categories for cosmetics in the two countries, where also slight differences can be observed. To study further the differences observed between the samples collected in the two countries, a correlation analysis was performed (Table 3). It can be seen that, in general, poor correlations are observed between the various individual VMSs, with only few exceptions, in both cases. It can also be seen that the pairs of individual VMSs that exhibit a correlation statistically significant at the 95% confidence level (or higher) are different between the samples from the two countries. The only "common" pairs observed are those of D4 with D3, D5 and D6, and in both cases at the same levels of statistical significance, which could be indicative of an important source of D4 in products used in both countries. Due to the big number of products emitting VMSs and the differences in their ingredients, strong correlations would be rather improbable or, if observed, accidental.

3.3. Comparison with existing limits

To our knowledge, VMSs in the indoor air are not regulated by any environmental agency or other authority, nor are they considered as priority pollutants for indoor air (i.e. EU INDEX project report, Koistinen et al., 2008). They are instead subject to regulation in Canada, because of their potential POP-like behavior (Genualdi et al., 2011).

The only proposed/existing recommendations for indoor air which could be applied in VMSs, are those regulating total volatile organic compound (TVOC) concentrations. The latter are summarized in Table 4. By comparing these recommendations to the concentrations of total VMSs (Fig. 3), it can be seen that average siloxane concentrations are generally below or just above the value of 300 μg m^{-3}, however, as these recommendations concern the sum of all volatile organic compounds (benzene, toluene, xylene, terpenes etc. should also be added), it is suggested that levels of VMSs higher than 150 μg m^{-3}, should be considered as exceeding the TVOC recommendations for good indoor air quality. Seifert (1990, as cited in ECA, 1997) suggested an approach for TVOC regulation, which apart from the concentration of 300 μg m^{-3} for TVOCs, suggested also that no individual chemical should exceed the 10% of TVOCs. In the case of D5, it is observed that in the vast majority of samples, its concentrations are so high that the Seifert (1990, as cited in ECA, 1997) recommendation would never be met.

Table 3
Pearson correlation analysis of the siloxane concentrations.

	L2	D3	L3	D4	L4	D5	L5	D6
Italy								
L2	1.00							
D3	0.14	1.00						
L3	−0.08	−0.06	1.00					
D4	0.33	**0.67**	−0.05	1.00				
L4	0.18	*0.28*	0.16	**0.75**	1.00			
D5	−0.13	**0.42**	0.04	*0.35*	0.21	1.00		
L5	−0.13	0.11	−0.04	−0.01	−0.09	−0.11	1.00	
D6	−0.02	0.11	−0.07	*0.31*	0.16	**0.40**	−0.05	1.00
UK								
L2	1.00							
D3	−0.09	1.00						
L3	0.30	−0.20	1.00					
D4	−0.03	**0.67**	−0.20	1.00				
L4	**0.46**	0.05	**0.44**	0.28	1.00			
D5	0.24	0.09	*0.37*	*0.34*	**0.76**	1.00		
L5	−0.12	**0.59**	−0.06	0.18	−0.12	−0.13	1.00	
D6	−0.07	−0.02	−0.06	*0.38*	0.04	0.14	−0.08	1.00

$p = 0.05$ in italics, $p = 0.01$ in bold and $p = 0.005$ in italics and bold.

3.4. Exposure assessment through breathing

It is known that dermal exposure is the most important pathway for human exposure to VMSs (Wang et al., 2009). Nevertheless, it was shown from the present study that exposure to VMSs through breathing takes place to all indoor environments, in different extents. Based on average values of total VMSs, and approximate everyday life habits (Table S1), the average daily intake inhalation was estimated for the UK and Italy.

To calculate the total amount of VMSs inhaled daily (working days) through all activities, the following formula was used for every individual activity:

$$I_{act} = B \times C \times T$$

where, I_{act} is the inhalation rate during each activity (mass of VMSs inhaled), B is the breathing rate (volume of air per time), C is the concentration of total VMSs in each indoor environment and T is the duration of the activity, in hours. The sum of all individual I_{act} gives the sum of

Table 4
Recommendations about total volatile organic compound concentrations in indoor air.

Country	TVOC concentration (μg m^{-3})	Reference
Germany	300 (for long term exposure)	Charles et al. (2005) (and references therein)
Finland	200: very good IAQ 300: good IAQ 600: satisfactory IAQ	Sateri (2002)
Japan	400	Charles et al. (2005) (and references therein)
Hong Kong	600	Charles et al. (2005) (and references therein)
Mølhave approach	<200: comfort range 200–3000: multifactorial exposure range 3000–25,000: discomfort range >25,000: toxic range	Mølhave et al. (1990) (as cited in ECA, 1997).

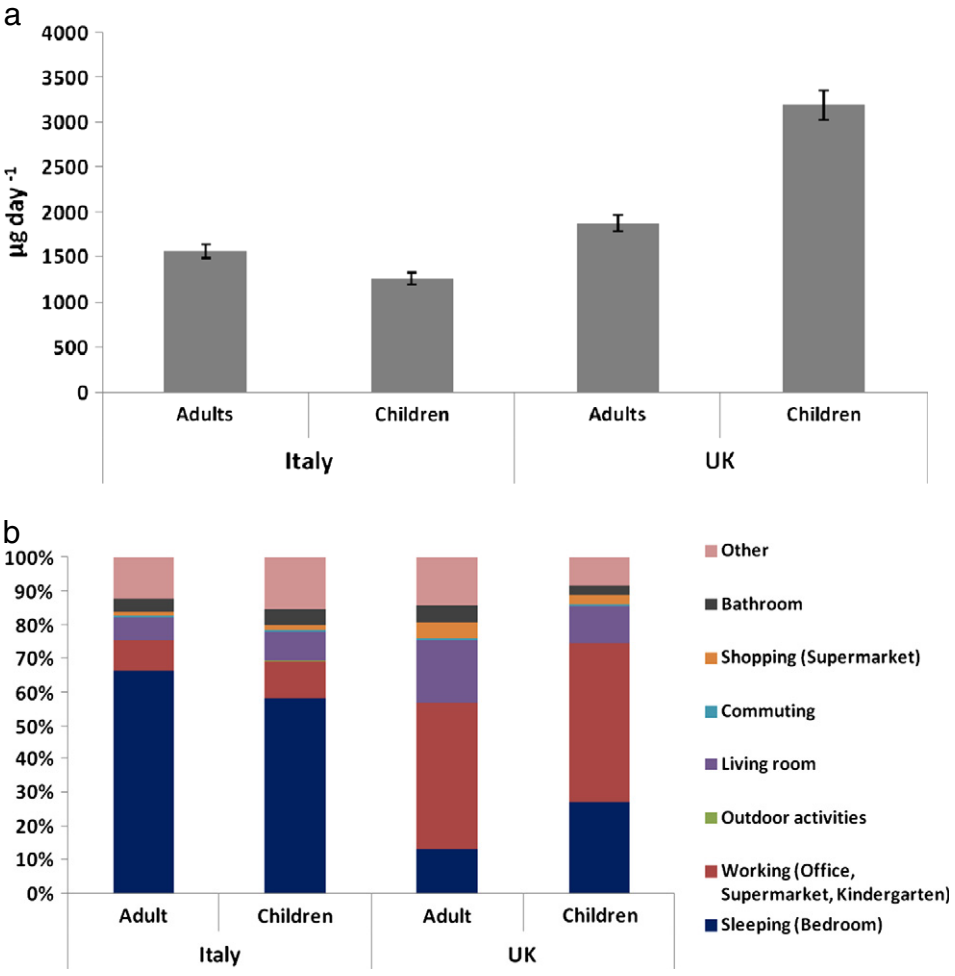

Fig. 4. Daily exposure of adults and children to siloxanes daily (a) and exposure patterns (b) in Italy and the UK.

VMSs inhaled daily. To simplify calculations, it is assumed that average inhalation rate is 13 $m^3\ d^{-1}$ (or 0.54 $m^3\ h^{-1}$) both for adults and children (details about breathing volumes taken from CEPA, 1994). By applying the aforementioned formula and the assumptions of Table S1, the daily exposure to VMSs is calculated (Fig. 4a). As seen, the highest exposure is observed for children in the UK (3188 µg d^{-1}), followed by adults in the UK (1875 µg d^{-1}), adults in Italy (1563 µg d^{-1}) and finally by children in Italy (1261 µg d^{-1}). Apart from the differences in the total exposure, a big difference between the two countries is observed at the exposure pattern (Fig. 4b). Thus, it can be seen that while

Table 5
The $\delta^{13}C$ values (‰) ± standard deviations of cVMSs supplied from different manufacturers and for some of the indoor air samples.

$\delta^{13}C$ values (‰)	D3	D4	D5	D6
Supplier/manufacturer				
A	−39.51 ± 0.08	−48.04 ± 0.10	−40.50 ± 0.08	−44.45 ± 0.015
B	−37.45 ± 0.09	−42.78 ± 0.12	−45.30 ± 0.07	−42.46 ± 0.012
C	−41.38 ± 0.10	−44.19 ± 0.09	−48.14 ± 0.09	
D	−42.82 ± 0.07	−47.9 ± 0.08	−50.09 ± 0.13	
Average $\delta^{13}C$			−44.63 ± 0.12	
Indoor air samples				
Bathroom 1	−32.41 ± 0.21	−41.82 ± 0.17	−44.85 ± 0.23	−36.02 ± 0.28
Bathroom 2	−27.69 ± 0.19	−44.62 ± 0.18	−46.86 ± 0.22	−37.28 ± 0.31
Bathroom 3		−43.13 ± 0.18	−49.51 ± 0.25	
Bathroom 4		−43.94 ± 0.16	−45.27 ± 0.21	
Adult room	−31.24 ± 0.18	−43.11 ± 0.20	−44.11 ± 0.19	
Living room 1			−50.80 ± 0.16	
Living room 2			−50.10 ± 0.15	
Office 1			−46.23 ± 0.21	
Office 2			−46.51 ± 0.32	

in the UK more than 50% of the exposure takes place in occupational environments, in Italy, around 60% of the exposure occurs in bedrooms.

3.5. Source identification based on CSIA analysis

The $\delta^{13}C$ values of cVMSs supplied from different manufacturers are reported in Table 5. It can be seen that their $\delta^{13}C$ values vary substantially for all individual cVMSs. The differences were particularly high for D5 (up to 25% that is from −49.49‰ to −40.5‰, for brands A and D, respectively) and slightly lower for the other cVMSs. The same analysis was also performed for some of the indoor air samples collected during the present study (Table 5). A first visual inspection suggests that almost all indoor environments had totally different profiles, although this is biased by the fact that it was not possible to analyze the CSIA signature for all cVMSs in all samples. In general, it can be seen that D5, in most rooms, presents a $\delta^{13}C$ value that is very close to the average $\delta^{13}C$ value of the analyzed industrial products (−45.86‰). D5 is the most abundant cVMS and from the present results it can be concluded that its occurrence in the indoor air, is most likely a result of emissions from products of all known manufacturers. In the living rooms, the $\delta^{13}C$ value for D5 was much lower (−50.8‰ to −50.1‰), similar to the D5 $\delta^{13}C$ value of the product D formulation (−49.49‰). In the case of D3, D4 and D6, real samples exhibited in general much higher $\delta^{13}C$ values than the commercial products. The biggest differences were observed for D3, for which the $\delta^{13}C$ values in commercial products ranged between −42.82‰ and −37.45‰, whereas in indoor air samples the range was from −32.4‰ to −27.68‰. Similar results were seen for D6, while for D4, most indoor air samples were close to the product B value and substantially higher than the average value of commercial products. The results obtained for D3 and D6 suggest that after these chemicals are emitted, they are degraded/transformed, and probably this mechanism is not occurring proportionally for all stable isotopes, but rather, it takes place in such a way that the $\delta^{13}C$ values are affected. It should be mentioned that for D3, D4, and D6, it was not possible to quantify $\delta^{13}C$ values in all samples, whereas for D5, this was possible in all indoor samples and commercial products. Probably the amounts of these cVMSs in the indoor environments were under the sensitivity of the adopted method in this study.

Our dataset on compound specific isotope analysis suggests that CSIA could be a reliable method for VMS source identification, however applicable mainly to D5. The number and variety of siloxane sources in the indoor environment though, make the understanding of sources through CSIA analysis a particularly challenging task.

This investigation will provide a baseline for future laboratory and field studies on deciphering degradation processes for VMSs, and percentage contribution of different brands using VMSs in their products to the siloxane release in the environment.

4. Conclusions

The present study characterized for the first time, in a comprehensive way, the levels of linear and cyclic volatile methyl siloxanes in various indoor domestic and occupational environments and presented exposure levels and patterns in indoor environments in Italy and the UK. The cVMS D5 was the most abundant chemical, something that is in accordance with its predominance in most personal care products. The results of the present study highlight the different exposure patterns that can exist between occupational and domestic environments, between the various room types, within the same room types and finally, even within the same indoor environment, as the emissions of VMSs are episodic and not constant throughout the whole emission period. Additionally, we have presented evidence of the differences in the exposure to VMSs that can result from different consumption patterns observed between different regions.

Finally, the employment of compound specific stable isotopic analysis in a limited number of samples suggests that this source identification technique is a challenging task, likely applicable only for D5, however, further studies are considered necessary.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.envint.2013.06.006.

Acknowledgments

This work was in part supported by a Marie Curie Intra European Fellowship within the 7th European Community Framework (Dr. Alessandra Cincinelli was the supported fellow).

References

Brooke DN, Crookes MJ, Gray D, Robertson S. Environmental risk assessment report: decamethylcyclopentasiloxane. Bristol: Environmental Agency; 2009a.
Brooke DN, Crookes MJ, Gray D, Robertson S. Environmental risk assessment report: dodecamethylcyclohexasiloxane. Bristol: Environment Agency; 2009b.
Brooke DN, Crookes MJ, Gray D, Robertson S. Environmental risk assessment report: octamethylcyclotetrasiloxane. Bristol: Environmental Agency; 2009c.
Burns-Naas LA, Mast RW, Meeks RG, Mann PC, Thevenazt P. Inhalation toxicology of decamethylcyclopentasiloxane (D5) following a 3-month nose-only exposure in Fischer 344 rats. Toxicol Sci 1998;43(2):230–40.
CEPA. How much air do we breathe? In: Agency CEP, editor. Brief reports to the scientific and technical community; 1994. [http://www.arb.ca.gov/research/resnotes/notes/94-11.htm].
Charles K, Magee RJ, Won D, Lusztyk E. Indoor air quality guidelines and standards. Final report 5.1 - CMEIAQ-II: consortium for material emission and IAQ modelling II. http://archive.nrc-cnrc.gc.ca/obj/irc/doc/pubs/rr/rr204/rr204.pdf. 2005 [last dowloaded at 12/7/2013].
Cheng Y, Shoeib M, Ahrens L, Harner T, Ma J. Wastewater treatment plants and landfills emit volatile methyl siloxanes (VMSs) to the atmosphere: investigations using a new passive air sampler. Environ Pollut 2011;159(10):2380–6.
Cincinelli A, Pieri F, Zhang Y, Seed M, Jones KC. Compound specific isotope analysis (CSIA) for chlorine and bromine: a review of techniques and applications to elucidate environmental sources and processes. Environ Pollut 2012;169:112–27.
de Bruin YB, Koistinen K, Kephalopoulos S, Geiss O, Tirendi S, Kotzias D. Characterisation of urban inhalation exposures to benzene, formaldehyde and acetaldehyde in the European Union. Environ Sci Pollut Res 2008;15(5):417–30.
ECA. Total Volatile Organic Compounds (VOC) in indoor air quality investigations. http://www.buildingecology.com/publications/ECA_Report19.pdf, 1997.
Fendinger NJ, McAvoy DC, Eckhoff WS, Price BB. Environmental occurrence of polydimethylsiloxane. Environ Sci Technol 1997;31(5):1555–63.
Flassbeck D, Pfleiderer B, Grümping R, Himer AV. Determination of low molecular weight silicones in plasma and blood of women after exposure to silicone breast implants by GC/MS. Anal Chem 2001;73(3):606–11.
Genualdi S, Harner T, Cheng Y, MacLeod M, Hansen KM, Van Egmond R, et al. Global distribution of linear and cyclic volatile methyl siloxanes in air. Environ Sci Technol 2011;45(8):3349–54.
Global-Insight. A study of the European cosmetics industry. http://ec.europa.eu/enterprise/newsroom/cf/_getdocument.cfm?doc_id=4561, 2007.
Granchi D, Cavedagna D, Ciapetti G, Stea S, Schiavon P, Giuliani R, et al. Silicone breast implants: the role of immune system on capsular contracture formation. J Biomed Mater Res 1995;29(2):197–202.
Hanssen L, Warner NA, Braathen T, Odland JØ, Lund E, Nieboer E, et al. Plasma concentrations of cyclic volatile methylsiloxanes (cVMS) in pregnant and postmenopausal Norwegian women and self-reported use of personal care products (PCPs). Environ Int 2013;51:82–7.
Hayden JF, Barlow SA. Structure–activity relationships of organosiloxanes and the female reproductive system. Toxicol Appl Pharmacol 1972;21(1):68–79.
He B, Rhodes-Brower S, Miller MR, Munson AE, Germolec DR, Walker VR, et al. Octamethylcyclotetrasiloxane exhibits estrogenic activity in mice via ERα. Toxicol Appl Pharmacol 2003;192(3):254–61.
Hippelein M. Background concentrations of individual and total volatile organic compounds in residential indoor air of Schleswig-Holstein, Germany. J Environ Monit 2004;6(9):745–52.
Hodgson AT, Faulkner D, Sullivan DP, DiBartolomeo DL, Russell ML, Fisk WJ. Effect of outside air ventilation rate on volatile organic compound concentrations in a call center. Atmos Environ 2003;37(39–40):5517–27.
Kaj L, Schlabach M, Andersson J, Palm Cousins A, Schmidtbauer N, Brorstrom-Lunded E. Siloxanes in the Noric environment; 2005a.
Kaj L, Andersson J, Palm Cousins A, Remberger M, Brorstrom-Lunded E. Results from the Swedish National Screening Programme, 2004. Subreport 4: siloxanes; 2005b [Downloaded from: http://www.imm.ki.se/Datavard/PDF/B1643_siloxaner.pdf (IVL report B1643, last accessed 10/5/2013)].
Katsoyiannis A, Bogdal C. Interactions between indoor and outdoor air pollution — trends and scientific challenges. Environ Pollut 2012;169:150–1.
Katsoyiannis A, Leva P, Barrero-Moreno J, Kotzias D. Building materials. VOC emissions, diffusion behaviour and implications from their use. Environ Pollut 2012a;169:230–4.
Katsoyiannis A, Roberts H, Birgul A, Cincinelli A, Leva P, Sweetman AJ, et al. Air quality evaluation in various indoor environments in the Lancaster University. In: SETAC, editor. Berlin: SETAC; 2012b. p. TUPC 3–8.

Kierkegaard A, McLachlan MS. Determination of decamethylcyclopentasiloxane in air using commercial solid phase extraction cartridges. J Chromatogr 2010;1217(21):3557–60.
Koistinen K, Kotzias D, Kephalopoulos S, Schlitt C, Carrer P, Jantunen M, et al. The INDEX project: executive summary of a European Union project on indoor air pollutants. Allergy Eur J Allergy Clin Immunol 2008;63(7):810–9.
Krogseth IS, Zhang X, Lei YD, Wania F, Breivik K. Calibration and application of a passive air sampler (XAD-PAS) for volatile methyl siloxanes. Environ Sci Technol 2013a;47(9):4463–70.
Krogseth IS, Kierkegaard A, McLachlan MS, Breivik K, Hansen KM, Schlabach M. Occurrence and seasonality of cyclic volatile methyl siloxanes in arctic air. Environ Sci Technol 2013b;47(1):502–9.
Kurt-Karakus PB. Determination of heavy metals in indoor dust from Istanbul, Turkey: estimation of the health risk. Environ Int 2012;50:47–55.
Lieberman MW, Lykissa ED, Barrios R, Ou CN, Kala G, Kala SV. Cyclosiloxanes produce fatal liver and lung damage in mice. Environ Health Perspect 1999;107(2):161–5.
Lu Y, Yuan T, Yun SH, Wang W, Wu Q, Kannan K. Occurrence of cyclic and linear siloxanes in indoor dust from China, and implications for human exposures. Environ Sci Technol 2010;44(16):6081–7.
Lu Y, Yuan T, Yun SH, Wang W, Kannan K. Occurrence of synthetic musks in indoor dust from China and implications for human exposure. Arch Environ Contam Toxicol 2011;60(1):182–9.
McKim Jr JM, Wilga PC, Breslin WJ, Plotzke KP, Gallavan RH, Meeks RG. Potential estrogenic and antiestrogenic activity of the cyclic siloxane octamethylcyclotetrasiloxane (D4) and the linear siloxane hexamethyldisiloxane (HMDS) in immature rats using the uterotrophic assay. Toxicol Sci 2001;63(1):37–46.
McKone T, Maddalena R, Destaillats H, Hammond SK, Hodgson A, Russell M, et al. Indoor pollutant emissions from electronic office equipment. Downloaded from:http://www.arb.ca.gov/research/seminars/mckone/mckone.pdf, 2009. [Last accessed, 10/5/2013].
Quinn AL, Regan JM, Tobin JM, Marinik BJ, McMahon JM, McNett DA, et al. In vitro and in vivo evaluation of the estrogenic, androgenic, and progestagenic potential of two cyclic siloxanes. Toxicol Sci 2007;96(1):145–53.
Sarigiannis DA, Karakitsios SP, Gotti A, Liakos IL, Katsoyiannis A. Exposure to major volatile organic compounds and carbonyls in European indoor environments and associated health risk. Environ Int 2011;37(4):743–65.
Sateri J. Finnish Classification of indoor climate 2000: revised target values. Indoor Air 2002;37:512–7.
Schweigkofler M, Niessner R. Determination of siloxanes and VOC in landfill gas and sewage gas by canister sampling and GC–MS/AES analysis. Environ Sci Technol 1999;33(20):3680–5.
USEPA. Compendium o methods for the determination of toxic organic compounds in ambient air; 1997 [Washington, DC].
Wang R, Moody RP, Koniecki D, Zhu J. Low molecular weight cyclic volatile methylsiloxanes in cosmetic products sold in Canada: implication for dermal exposure. Environ Int 2009;35(6):900–4.
Wang DG, Alaee M, Steer H, Tait T, Williams Z, Brimble S, et al. Determination of cyclic volatile methylsiloxanes in water, sediment, soil, biota, and biosolid using large-volume injection-gas chromatography–mass spectrometry. Chemosphere 2012. http://dx.doi.org/10.1016/j.chemosphere.2012.10.044.
Wania F, Dugani CB. Assessing the long-range transport potential of polybrominated diphenyl ethers: a comparison of four multimedia models. Environ Toxicol Chem 2003;22(6):1252–61.
Wu X, Apte MG, Maddalena R, Bennett DH. Volatile organic compounds in small- and medium-sized commercial buildings in California. Environ Sci Technol 2011;45(20):9075–83.
Zhou SN, Chan CC, Zhy J. Detection of volatile methylsiloxanes in indoor air using thermal desorption GC/MS method. 3rd workshop on organosilicones in the environment, Burlington, Ontario, Canada; 2012.