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CYCLIC SILOXANES IN AIR INCLUDING IDENTIFICATION OF HIGH LEVELS

IN CHICAGO AND DISTINCT DIURNAL VARIATION

by

Rachel Ann Yucuis

A thesis submitted in partial fulfillment
of the requirements for the Master of
Science degree in Civil and Environmental Engineering
in the Graduate College of
The University of Iowa

May 2013

Thesis Supervisor: Professor Keri C. Hornbuckle

Graduate College
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CERTIFICATE OF APPROVAL

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MASTER'S THESIS

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This is to certify that the Master's thesis of

Rachel Ann Yucuis

has been approved by the Examining Committee
for the thesis requirement for the Master of Science
degree in Civil and Environmental Engineering at the May 2013 graduation.

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ACKNOWLEDGMENTS

ABSTRACT

The organosilicon compounds octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) are high production volume chemicals that are widely used in household goods and personal care products. Due to their prevalence and chemical characteristics, cyclic siloxanes are being assessed as possible persistent organic pollutants. D4, D5, and D6 were measured in indoor and outdoor air to quantify and compare siloxane concentrations and compound ratios depending on location type. Indoor air samples had a median concentration of 2200 ng m^{-3} for the sum of D4, D5, and D6. Outdoor sampling locations were over Lake Michigan near Chicago, downtown Chicago, Cedar Rapids, IA, and West Branch, IA, and had median sum siloxane levels of 300, 280, 73, and 29 ng m^{-3} respectively. A diurnal trend is apparent in the samples taken in downtown Chicago. Nighttime samples had a median 2.7 times higher on average than daytime samples, which is due, in part, to the fluctuations in the height of the planetary boundary layer. D5 was the dominant siloxane in both indoor and outdoor air. Ratios of D5 to D4 averaged 91 and 3.2 for indoor and outdoor air respectively.

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CHAPTER 1

INTRODUCTION

Background

Siloxanes are anthropogenic chemicals used in personal care and household products, and in the production of the silicon polymer polydimethylsiloxane (Horii and Kannan, 2008). Siloxanes in cyclic, linear, and/or polymer forms are used in an extremely wide range of applications, including antifoaming agents, automotive care products, and as coatings and sealants in construction. The primary use of the cyclic siloxanes, octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) (Figure 1) are as main ingredients in personal care products (Kaj et al., 2005). The cyclic siloxane compounds (commercial name cyclomethicone) are valued as solvents or carriers in personal care products because of their inert, odorless, and colorless qualities in addition to their volatility and smooth feel. In a recent survey of siloxanes in personal care and household products D4, D5, and D6 were found in more than 50% of the items analyzed (Horii and Kannan, 2008). In a similar study that measured siloxane levels in personal care products only, cyclic siloxanes made up as much as 68% of the total product mass (Wang et al., 2009). D4, D5, and D6 are categorized as high production volume chemicals (greater than 1 million pounds produced or imported annually in the U.S.) (Canada, 2008a, b, c).

Rationale and Study Objectives

Cyclic siloxanes are of concern because of their high rate of use and their physical properties (Howard and Muir, 2010). They are extremely volatile, have a relatively long half-life in air, and a high K_{ow} (Table 1) (Kaj et al., 2005). Accordingly, D4, D5, and D6 were recently identified as substances requiring further study because of their potential for long range transport and bioaccumulation (Howard and Muir, 2010). Since then,

several studies have demonstrated that D4 and D5 do accumulate in aquatic organisms in the environment (Kierkegaard et al., 2011; Borga et al., 2012).

Environmental risk assessments have been conducted for cyclic siloxanes in Canada (Canada, 2008a, b, c), the UK (Brooke et al., 2009a, b), Sweden (Kaj et al., 2004), and for a consortium of Nordic countries (Kaj et al., 2005). The assessment of siloxanes in the Nordic environment focused on measurements of siloxane concentrations in a number of different media. Siloxanes were found to be ubiquitous in the environment, with measurable amounts in nearly all media analyzed, including air, water, sediment, sludge, and biota, with D5 found predominantly (Kaj et al., 2005). The screening assessment conducted by Environment Canada did not include environmental concentrations, but based on fugacity modeling and a review of studies relating to environmental toxicology, they concluded that D4 and D5 are "…entering or may be entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity" (Canada, 2008a, c).

Furthermore, D4 was recently included in a list of 18 chemicals to be reviewed by the U.S. EPA in 2013 and 2014 (C&EN, 2012). The evaluation will determine whether or not the compound should be regulated under the Toxic Substances Control Act (C&EN, 2012). If regulation is to be considered, then it is important to learn more about the sources and distribution of siloxanes in the environment. Publications of indoor air measurements which could aid in source identification are especially lacking. Currently, three indoor (Shields et al., 1996; Yucuis et al. 2013; Xu et al., 2012) and eight outdoor air studies have been published (Wang et al., 2001; Kierkegaard and McLachlan, 2010; McLachlan et al., 2010; Cheng et al., 2011; Genualdi et al., 2011; Krogseth et al., 2012; Buser et al., 2013; Krogseth et al., 2013; Yucuis et al., 2013). Several studies have been conducted that have modeled concentration distributions of one or more of the cyclic siloxanes (Mueller et al., 1995; McLachlan et al., 2010; Navea et al., 2011). However,

increased monitoring is necessary in order to more accurately assess the influence siloxanes may have on humans and the environment. This is especially key in areas of high population density (i.e. Chicago) where emissions of anthropogenic compounds are much higher, and therefore the probable impact on the local population and environment will be correspondingly high (i.e. Lake Michigan).

The purpose of this work is to measure and compare concentrations of D4, D5, and D6 in outdoor air in areas with varying population densities, as well as determine indoor concentrations and provide an estimate for per-person emissions of cyclic siloxanes. Concentrations, emissions, and compound ratios will be contextualized through a discussion of current modeling and measurement data for siloxanes in air.
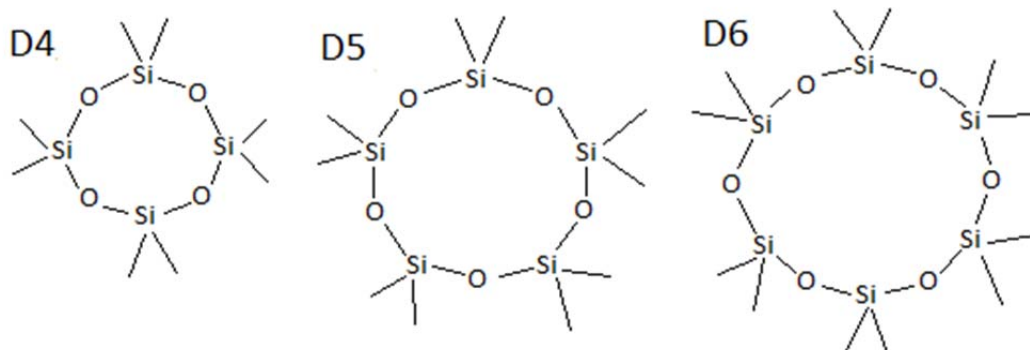
Figure 1. Chemical structures of octamethylcyclotetrasiloxane (D4), decamethyl-
cyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6).

Table 1. Selected Chemical properties of D4, D5, and D6 (Kaj et al., 2005).

Abbreviation	CAS #	Molecular Weight (g/mol)	W_{Sol} (mg/L, 25ºC)	Vapor Pressure (Pa)	Log K_{ow}	Half Life in Air (days)
D4	556-67-2	296.6	0.90	140	6.48	11
D5	541-02-6	370.8	.017	33	8.03	7
D6	540-97-6	444.9	0.0051	4.6	9.06	6

CHAPTER 2

EXPERIMENTAL

Materials

Octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, and dodecamethylcyclohexasiloxane (>98%) were purchased from TCI America Portland, OR. Tetrakis(trimethylsiloxy)silane was purchased from Gelest Inc. in Morrisville, PA. Solvents dichloromethane, methanol, acetone, and n-hexane (all pesticide grade) were purchased from Fischer Scientific Pittsburgh, PA. 10 mg Isolute ENV+ cartridges (Biotage AB) were employed for all samples except for the three collected over Lake Michigan, where Hydrophobic-lipophilic (HPLP) Balance Extraction Cartridges (500 mg) from Waters Chromatography in Milford, MA were used.

Sampling Locations

Indoor samples were collected in the Seamans Center for the Engineering Arts and Sciences at the University of Iowa: ten samples in one laboratory, one in a student office (Office A), and three in a second office (Office B). Both offices are used during regular daytime work hours (between 9 am and 5 pm) by up to ten people. The laboratory has between one and seven occupants during daytime hours. Eight of the samples ran overnight and five samples ran during the day. The laboratory ventilation flow rate varies between 775 and 2270 cubic feet per minute depending on laboratory hood use and heating or cooling requirements. Additional details can be found in the appendix.

Two outdoor locations in Iowa were chosen as representative of medium and low population. The rural site is approximately three miles north of West Branch, IA (41.6714° N, 91.3464° W, population 2400) at the base of a NOAA tall tower for carbon cycle gas sampling (Andrews et al., 2013). The mid-sized city selected for the transition site was Cedar Rapids, IA (42.0083° N, 91.6439° W, population 122,000) at the Linn County Public Health Department's air quality monitoring station. The urban samples

were taken at the EPA's Integrated Atmospheric Deposition Network (IADN) site at the Illinois Institute of Technology (IIT) campus in Chicago (41.8347° N, 87.6263° W). All samples used for the population-concentration comparison were taken in summer 2011. Photos of the IIT sampling location are shown in Figure 2. During the fourth week of September 2010, three samples were collected over Lake Michigan from onboard the U.S. Environmental Protection Agency's *R/V The Lake Guardian* using a preliminary method (Figure 3).

Sampling and Extraction Method

Air sampling was conducted by drawing air through an extraction cartridge using a diaphragm pump (GAST MAA-V109-HD) connected with polyethylene tubing (Watts 1/4" OD, .170" ID) (Kierkegaard and McLachlan, 2010). Tubing was connected to the pump and flow meter by Swagelok brass fittings. The SPE cartridges were attached to the tubing using Swagelok fitting and hose clamps as shown in Figure 4. Two lines were used in order to have duplicates for each sampling period, and the flow rates for each line were measured separately (Figure 5). Flow rates varied from 3 to 6 liters per minute and were measured with Toptrak mass flow meters (822-2-OV1-V1 and 822-2-OV1-PV1-V1). One flow meter did not include a volume totalizer, so flow rate and time were recorded with a USB data logger from Lascar Electronics (EL-USB-3). The SPE cartridges were installed with the open side down and were shielded from the elements with funnel attachments. Sampling times varied depending on the concentration ranges expected at each site. Indoor samples and samples taken at IIT were run for 12 to 16 hours. Cedar Rapids samples were collected over 24 hours and West Branch about 36 hours in order to ensure that detectable masses accumulated (Table 2, 3). After sampling, the cartridges were wrapped in aluminum foil and stored in glass amber jars in a cooler or freezer until extracted. The extraction process involved running approximately 1.5 mL of n-hexane through the SPE cartridge directly into a GC vial. For the cartridges used on

Lake Michigan, the samples were eluted with three aliquots and analyzed separately, although the target compounds appeared in only the first two eluents. Internal standard tetrakis trimethyl-siloxysilane (M4Q, 100 ng) was then added to each vial.

Instrumental Analysis

The samples were analyzed on a Hewlett Packard gas chromatograph mass spectrometer (HP 5973) in select ion monitoring mode. The column used was a Restek RTX-5MS. The injector temperature was 200 ^{0}C. Injection volume was 2 µL. The flow rate of helium gas was held at 1.0 mL/min. The temperature gradient was: 60 ^{0}C (2 minutes), to 150 ^{0}C at 10 ^{0}C/min, to 300 ^{0}C at 30 ^{0}C/min (2 minutes), with a detector temperature of 250 ^{0}C. The ions monitored were m/z 281 (D4 and M4Q), 355 (D5), and 341 (D6). The samples were quantified by the internal standard method. A 500 ng/mL standard containing D4, D5, D6, and M4Q was used to calculate the relative response factors for each run (Figure 6).

Quality Assurance/Quality Control

All glassware was combusted overnight at 450^{0}F before use. Temperature-sensitive sampling components were triple-rinsed with pesticide grade methanol, hexane, and acetone. SPE cartridge cleaning practices entailed soaking the cartridges overnight in n-hexane followed by a run-through three times with dichloromethane and three times with n-hexane before drying with a nitrogen stream. Cartridges were then wrapped in aluminum foil and frozen. Use of siloxane-containing products was avoided on days when lab or field work was conducted. Normal use of personal care products was maintained on days prior to sampling because it was expected that the cyclic siloxanes would quickly volatilize after evaporation (Tokarczyk, et al.).

The possibility of cartridge breakthrough, or siloxanes passing through the cartridge without being captured, was examined in three trials by sampling two cartridges in series (Table 4). The mass found in the backup cartridge was extremely low compared

to the primary cartridge and was only slightly higher on average than the masses in method blank (Table 5). The method blank is n-hexane with internal standard added. The results of the breakthrough experiment indicate that only one cartridge is necessary to use when sampling.

Extraction efficiency was evaluated by spiking the top frit of three cartridges with 100 ng of D4, D4, and D6 and running approximately 1.5 mL of n-hexane through the cartridge directly in to GC vial. Average recoveries were 99, 114, and 110 percent for D4, D5, and D6, respectively (Table 6). Percent recovery was calculated by subtracting the method blank mass from the mass recovered and dividing by the spike + internal standard (spike+IS) mass. The spike+IS was simply a GC vial that was with 100 ng of D4, D5, D6, and M4Q added. The high percent recoveries indicate that the extraction method is sufficient for removing the siloxane sample from the Isolute ENV+ media.

Field blanks and duplicates were included with all the samples except for the five indoor air samples taken in 2011 (Lab1 – Lab4 and OfficeA) and the Lake Michigan samples (RV1-RV3). All remaining outdoor and indoor air samples had a field blank attached to a capped length of tubing installed alongside the sample cartridges for the duration of each sampling period. The overall average field blank mass for indoor and outdoor air was 3.2, 10, and 12 ng per cartridge for D4, D5, and D6 respectively. A field blank concentration was determined by dividing the mass of the field blanks for each site by the average volume sampled at each site. The average sampling volumes were 9.4, 7.1, 3.2, and 2.7 m^3 for West Branch, Cedar Rapids, Chicago, and indoors respectively. A specific limit of detection (LOD) and limit of quantification (LOQ) was then calculated for each combination of site and compound (Table 7). The LOD was determined by the average of the field blank concentration plus three times the standard deviation, and the LOQ is the average plus ten times the standard deviation. The IIT LOD and LOQ were applied to the Lake Michigan samples because those samples did not include field blanks.

Duplicate samples exhibit an average relative percent difference of 13% for 34 sample pairs. The results were not blank corrected.

We found little evidence of decay or loss during storage. Krogseth et al. (2012) reported that D5 may convert to D4 within the cartridge during storage. We found that D4 concentrations were positively correlated with storage time (p = .023), but that D5 concentrations were not. There was no correlation between storage time and the ratio of D5/D4. Therefore, no corrections were made for storage, although we recognize that some D4 may be present due to transformation after sampling.

Boundary Layer Height

The atmospheric boundary height during each of the Chicago sampling periods were retrieved from the National Oceanic and Atmospheric Administration (NOAA) archived meteorological simulations for the latitude and longitude of the Illinois Institute of Technology (41°50'4.10" N; 87°37'25.59" W). The North American Mesoscale (NAM) model 12 km Forecast Data Archive product (boundary layer depth variable) was used and was accessed at http://ready.arl.noaa.gov/READYamet.php. This product has 3 hour time resolution. To produce an average height during a sampling period, the heights were linearly interpolated to a 15 minute time basis, and then averaged. Since the conceptual model we are working with is that emissions are diluted throughout and well-mixed within the boundary layer, we utilize an inverse weighted mean boundary layer height $\bar{h}^I = \Delta t [\int h(t)^{-1} dt]^{-1}$ which has the useful property that $\bar{h}^I \bar{c} = \overline{h(t) \cdot c(t)}$ under the assumption of a constant loading of pollutant under the boundary layer. In these formulas $h(t)$ is the time varying boundary layer height, Δt is the sampling interval, $c(t)$ is the time varying concentration, and $\bar{c}$ is the time averaged sample concentration measured in this work. $\bar{h}^I$ is lower than the arithmetic mean boundary layer height.

As an example, if the boundary layer height was 100 m for one hour and 1000 m for one hour, the simple arithmetic mean boundary layer height would be 550 m while $\bar{h}^I$

would be 182 m. A well-mixed pollutant with loading within the boundary layer of 1000 mg m^{-2} would have concentration 10 mg m^{-3} during the first hour and 1 mg m^{-3} during the second hour, and $\bar{c}$ of 5.5 mg m^{-3}. The column loading of 1000 mg m^{-2} can be recovered by 5.5 mg m^{-3} times $\bar{h^l}$ but would be overestimated by multiplying $\bar{c}$ by the arithmetic mean boundary layer height. This is of course an extremely simplified model of the boundary layer processes, but it is suitable for the purposes of this paper, which are to contrast daytime and nighttime concentration measurements with an adjustment for the effect of the changes in boundary layer height.[1]

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[1] Explanation of the boundary layer height determination and calculations courtesy of Charlie Stanier and Nate Janecheck.
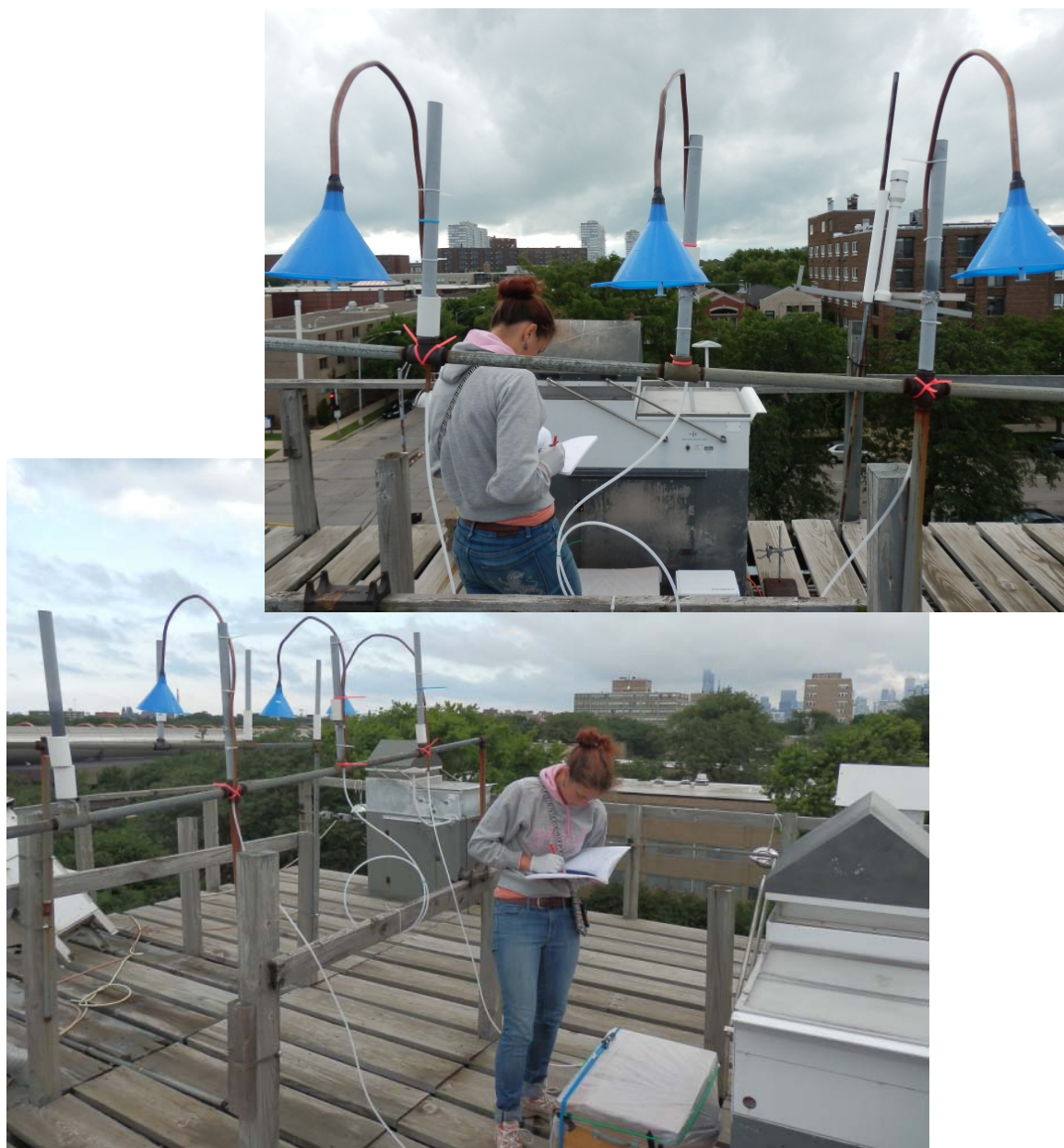
Figure 2. Photos of the roof-top sampling location on the Illinois Institute of Technology Campus in Chicago, IL.

Figure 3. Photos from the Lake Michigan Sampling trip. The top photo shows myself and the sampling set-up. The bottom photo shows, from left to right, myself, Zach Rodenburg (a PhD student), and my advisor, Keri Hornbuckle.

Table 2. Summary of sample information for indoor air. The room sizes were approximately 34 m^3 for Office A, 28 m^3 for the lab, and 42 m^3 for Office B.

Name	Day Or Night	Max Occ-upants	Start Date	Start Time	End Time	Flow Primary (slpm)	Flow Duplicate (slpm)	Volume P (Liters)	Volume D (Liters)	Date Extracted	Days in Storage
Lab1	Night	0	3/17/11	14:59	11:09	5.3	*	3416	*	3/18/11	0
OfficeA	Night	0	3/21/11	16:51	10:53	4.7	*	5140	*	3/22/11	0
Lab2	Night	0	3/28/11	16:54	9:49	3.4	*	3410	*	3/29/11	0
Lab3	Night	0	3/29/11	16:21	10:07	3.2	*	3405	*	3/30/11	0
Lab4	Night	0	3/30/11	16:20	10:27	3.1	*	3402	*	3/31/11	0
Lab5	Day	6	1/14/13	12:18	16:42	4.7	4.6	1259	1384	1/14/13	0
Lab6	Night	0	1/14/13	17:09	9:25	4.6	4.8	4494	4518	1/15/13	0
Lab7	Day	7	1/15/13	10:42	16:28	4.4	4.3	1510	1484	1/15/13	0
Lab8	Night	0	1/15/13	16:52	9:39	4.7	3.7	4813	3676	1/16/13	0
Lab9	Day	6	1/16/13	10:04	16:35	4.5	4.5	1750	1744	1/16/13	0
Lab10	Night	0	1/16/13	16:59	9:31	4.6	4.4	4504	4322	1/17/13	0
OfficeB1	Day	10	1/17/13	11:48	16:26	4.2	4.7	1198	1311	1/18/13	1
OfficeB2	Night	0	1/17/13	17:08	9:30	4.3	4.4	4231	4352	1/18/13	0
OfficeB3	Day	10	1/18/13	9:49	15:12	3.7	3.9	1156	1266	1/18/13	0

* Samples Lab1 to Lab5 and OfficeA did not have duplicates.

Table 3. Summary of sample information for West Branch, IA (WB), Cedar Rapids, IA (CR), Chicago, Ill (IIT), and Lake Michigan (RV).

Name	Start Date	Start time	End Time	Flow Primary (slpm)	Flow Duplicate (slpm)	Volume Primary (Liters)	Volume Duplicate (Liters)	Date Extracted	Days in Storage
CR1	6/29/11	0:01	0:01	*	*	7944	7944	6/28/11	2
CR2	7/2/11	1:30	1:27	*	*	7473	9523	7/8/11	2
WB1	7/6/11	16:14	10:20	3.98	4.31	9547	10053	7/8/11	0
CR3	7/14/11	0:46	0:37	*	*	5790	6647	7/18/11	3
WB2	7/15/11	16:40	8:54	3.94	3.75	8505	9553	7/18/11	1
WB3	7/17/11	9:14	16:02	4.12	4.08	6756	7347	7/22/11	4
WB4	7/18/11	16:21	10:25	4.00	3.98	9450	9827	7/22/11	2
WB5	7/20/11	10:41	10:12	4.46	3.77	10146	12727	7/22/11	0
CR4	7/26/11	1:10	1:07	*	*	5817	5893	8/11/11	15
IIT1	8/13/11	10:08	19:03	4.08	5.18	2038	2909	8/23/11	10
IIT2	8/13/11	19:36	7:52	5.11	4.43	3798	3153	8/23/11	9
IIT3	8/14/11	8:08	19:00	4.86	4.66	3065	2793	8/23/11	9
IIT4	8/14/11	19:11	7:05	5.29	4.41	3732	3096	8/23/11	8
IIT5	8/15/11	7:18	19:08	5.15	4.79	3342	2959	8/23/11	8
IIT6	8/15/11	19:22	7:08	4.88	4.32	3439	3011	8/23/11	7
IIT7	8/16/11	7:31	18:59	5.85	4.52	3525	2675	8/23/11	7
IIT8	8/16/11	19:17	7:01	4.6	3.77	3273	2652	8/23/11	6
IIT9	8/17/11	7:16	18:55	5.47	4.91	3512	3017	8/23/11	6
IIT10	8/17/11	19:07	6:56	5.16	4.77	3556	3226	8/23/11	5

Table 3 - Continued

IIT11	8/18/11	7:11	18:56	5.28	4.84	3477	3060	8/23/2011	5
IIT12	8/18/11	19:13	7:03	4.17	4.64	2996	3218	8/23/2011	4
IIT13	8/19/11	7:12	19:07	5.29	4.33	3419	2696	8/23/2011	4
IIT14	8/19/11	19:17	7:04	5.15	4.04	3598	2696	8/23/2011	3
IIT15	8/20/11	7:12	18:59	5.4	4.39	3631	5505	8/23/2011	3
IIT16	8/20/11	19:11	7:08	4.67	4.42	3344	3115	8/23/2011	2
RV1	9/20/10	19:52	19:46	**	**	8676	**		
RV2	9/21/10	19:52	19:53	**	**	8718	**		
RV3	9/22/10	19:58	6:29	**	**	3818	**		

* Not present at start time – sample was set up and then started with a timer in order to sample from midnight to midnight.

**RV samples did not have duplicates.
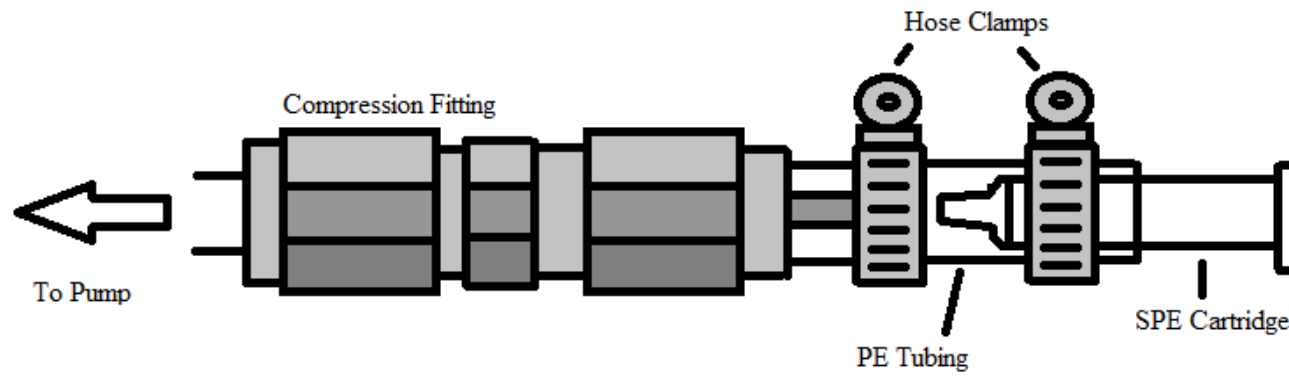
Figure 4. Diagram of the method used to attach the SPE cartridge to the PE tubing.
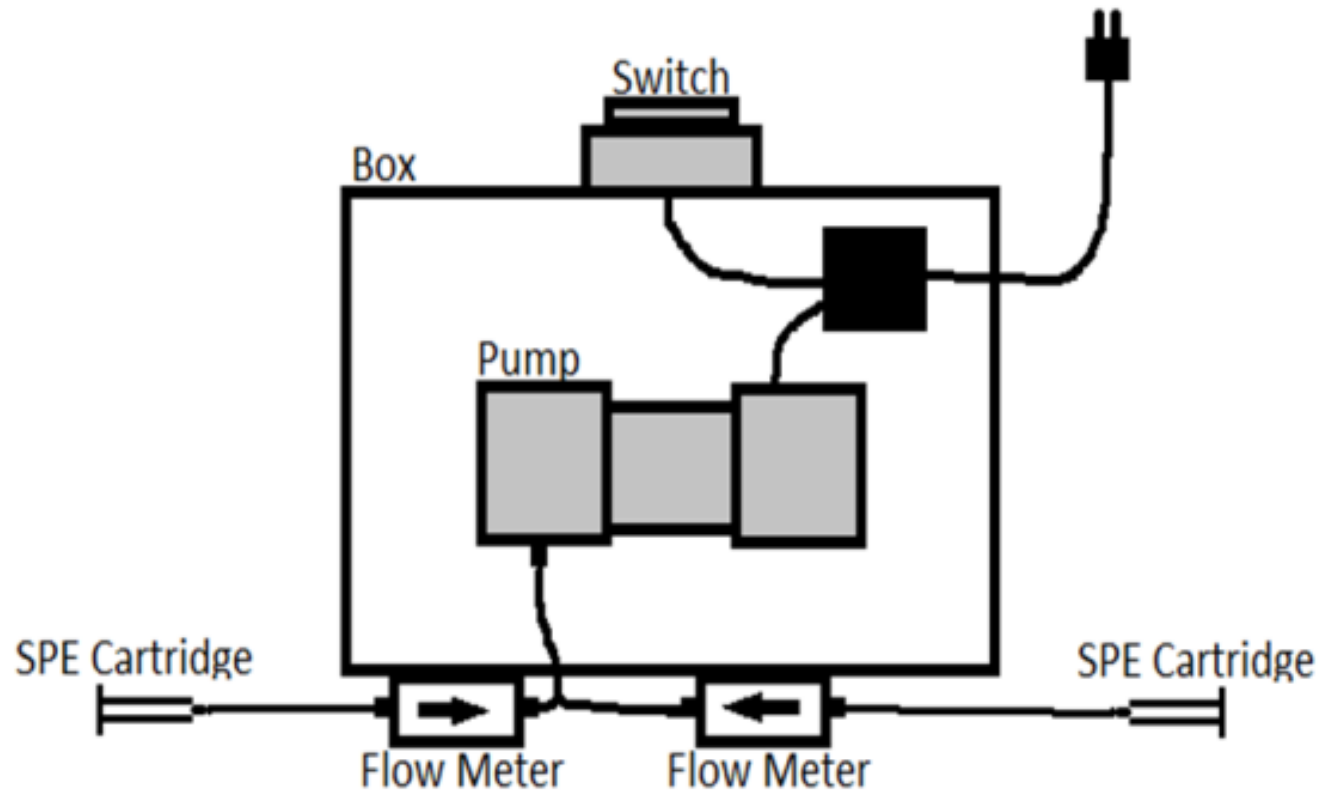
Figure 5. Above-view diagram of the siloxane sampler.
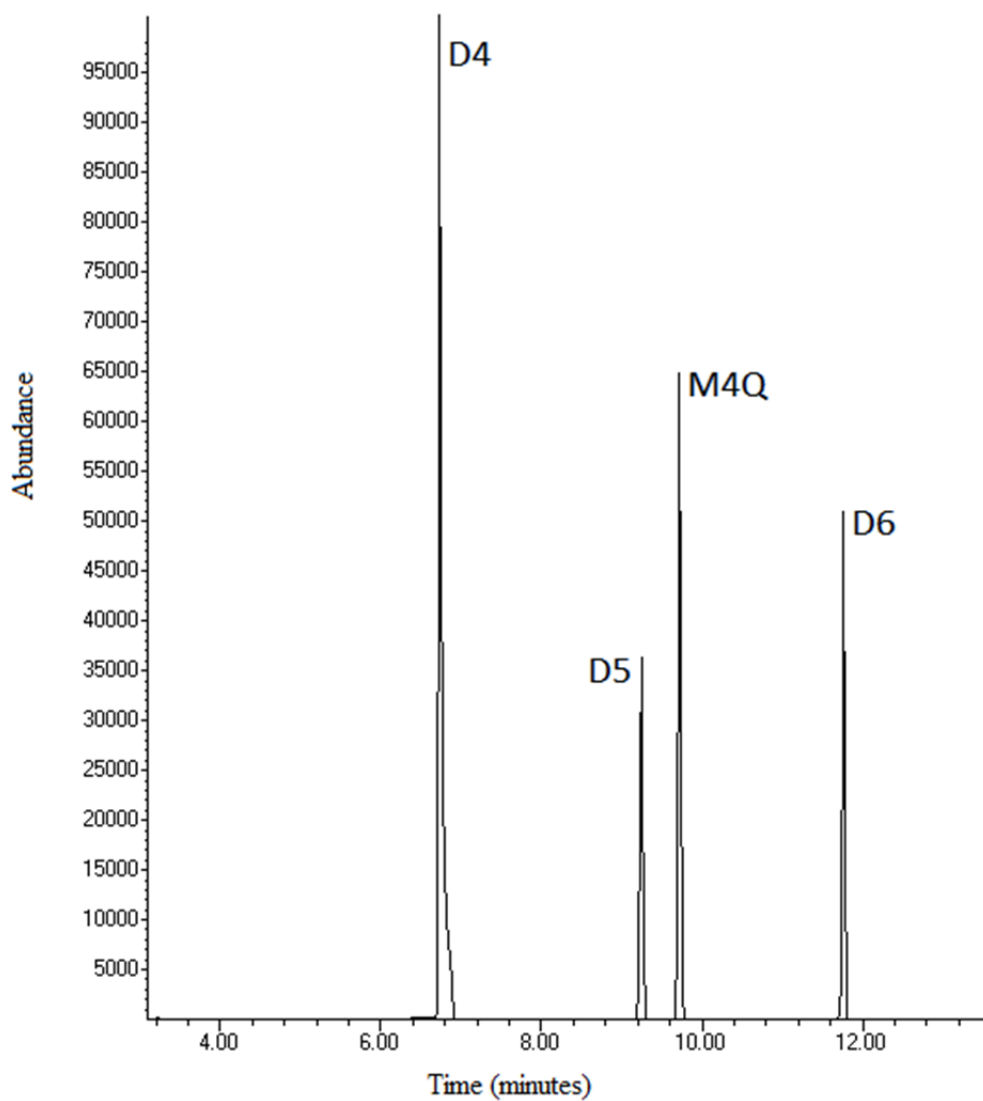
Figure 6. Chromatogram of the 500 ng/mL calibration standard used for quantification.

Table 4. Sampling times, flow rates, and total volumes sampled in the breakthrough experiment.

Trial	Time (min)	Flow Rate (slpm)	Total Volume (m^3)
1	1015	3.36	3.41
2	1066	3.20	3.41
3	1087	3.13	3.40

Table 5. Mass for each compound in the primary and backup cartridges, and in the method blank, for each trial (1-3) of the breakthrough experiment.

	Mass/cartridge (ng)		
	D4	D5	D6
Primary1	157	4314	100
Backup1	2.2	3.2	1.8
Primary2	174	5747	108
Backup2	2.5	5.3	1.2
Primary3	193	3291	96
Backup3	2.2	5.7	1.9
Method Blank	1.9	2.5	1.3

Table 6. Results from the test of extraction efficiency.

	Mass (ng)			Percent Recovery		
	D4	D5	D6	D4	D5	D6
Cartridge 1	110	120	120	99	120	110
Cartridge 2	110	110	110	96	110	100
Cartridge 3	110	120	120	100	120	110
Spike+IS	110	96	96			
Method Blank	4.6	7.6	7.7			

Table 7. Summary of field blank concentrations, standard deviations, and LODs/LOQs for each site and compound. All values are in ng m^{-3}.

		D4	D5	D6
WB	Average	0.08	0.23	0.54
	Standard Dev	0.12	0.20	0.09
	LOD	0.43	0.83	0.80
	LOQ	1.25	2.23	1.41
CR	Average	0.08	0.43	0.83
	Standard Dev	0.17	0.29	0.18
	LOD	0.59	1.30	1.36
	LOQ	1.76	3.32	2.60
IIT	Average	0.42	1.74	1.84
	Standard Dev	0.25	0.38	0.67
	LOD	1.19	2.88	3.84
	LOQ	2.97	5.55	8.51
Indoor	Average	3.3	9.8	11.2
	Standard Dev	1.1	2.6	4.8
	LOD	6.6	18	26
	LOQ	14	36	59

CHAPTER 3

RESULTS AND DISCUSSION

Indoor Air Concentrations

Indoor concentrations of individual cyclic siloxanes ranged from not detected (D4), to as much as 57,000 ng m^{-3} for D5 (Table 8). High indoor air concentrations were expected because of the prevalence of siloxane-containing products and their subsequent accumulation in small indoor areas. Concentrations of D4 and D5 have been shown previously to be reflective of occupant density (Shields et al., 1996). The influence of occupancy is best illustrated by the variation in D5 concentrations depending on the time of day the sample was taken (Figure 7).

D5 is the dominant cyclic siloxane in indoor air, accounting for an average of 97% of the mass found in the fourteen samples. Interestingly, the only previous study of indoor air (conducted in 1991) reported levels of D4 that were on the same order of magnitude as D5 (Shields et al., 1996). This difference from our study may be a reflection of formulation changes in personal care products over the last 20 years. Two recent studies of cyclic and linear siloxanes in common products report that D5 was the largest contributor to siloxane mass in the personal care items surveyed (Horii and Kannan, 2008; Wang et al., 2009). Based on product use profiles for women in the U.S., and the concentrations measured, Horii and Kannan estimated that the average use rate of D5 is 233 mg (person-day)$^{-1}$ (2008). Wang et al. estimated a D5 exposure of 306 mg (person-day)$^{-1}$ from body lotion alone also using data for use rates of lotion for women in U.S. (2009).

Outdoor Air Concentrations

For outdoor air, the median concentrations of the cyclic siloxanes increased with population density (Table 9). The lowest concentrations were found in West Branch, IA with a median of 29 ng m^{-3}. Siloxane levels were slightly higher in Cedar Rapids at 73 ng

m^{-3}, and the IIT concentrations were 280 ng m^{-3}. The siloxane levels determined over Lake Michigan had a median of 300 ng m^{-3}. Average sum concentrations were significantly different in Chicago compared to both Cedar Rapids and West Branch (p-value = .005 and .012), with the Chicago median 4 and 10 times greater than Cedar Rapids and West Branch respectively.

Lake Guardian samples were not included in any statistical comparison due to the difficulty of detecting a significant difference with only three data points. It was not possible to conclude whether or not the lake data could be included in the Chicago data. The concentrations measured over Lake Michigan are also not as trustworthy because a preliminary method was used that did not include field blanks or mass flow meters, and used a SPE cartridge of a different size with different media. The volume sampled was calculated by calibrating the pump once the flow meter was available. However, the levels over Lake Michigan are very similar to those found at IIT, which suggests that the method yielded accurate results.

A diurnal trend is apparent in the samples collected at the IIT site in Chicago. The samples were collected over consecutive 12-hour periods with cartridges exchanged at approximately 7 am and 7 pm daily. The trend is most clearly illustrated by the fluctuations in the compound with the highest concentrations, D5 (Figure 8). D5 concentrations were significantly different during the day versus the night (p = .0014) with a median concentration of 138 ng m^{-3} in the daytime, and 338 ng m^{-3} at night. D4 day and nighttime concentrations were also significantly different (p = .024), and the D6 concentrations were generally above the LOQ during the day, and below the LOD at night. This is contrary to what we would expect if the majority of the siloxane concentration comes from volatilization during morning or daytime personal care product use. The major degradation pathway for siloxanes is by hydroxyl radical (OH) attack, and concentrations of OH are higher in the presence of sunlight, which could explain, in part,

the diurnal variation (Navea et al., 2011). However, the predicted magnitude of the OH effect is small, ±10% of the mean concentration.

The effect of the variation in the average planetary boundary layer height on the day and nighttime concentrations was investigated with a regression analysis. D5 concentration was found to be significantly correlated with boundary layer height ($p = .003$, $R^2 = 0.49$). D4 concentrations were not significantly correlated with the height of the boundary layer, and the correlation of D6 concentrations with boundary layer height were not analyzed because of the number of samples that were below the LOQ. This analysis included all samples except for IIT6. No obvious explanation is apparent for the high concentrations found in sample 6, as the NAM boundary layer height was not particularly low for that nighttime sampling period, nor was any unusual activity observed that could have caused a spike in siloxane concentration. Nevertheless, sample 6 is an outlier, with a standardized residual of 3.52 so it was removed from the data set for the analysis.

A rough estimate of column abundance in the mixed layer was calculated by multiplying the sample concentrations by the boundary layer heights with the temporal averaging of boundary layer heights as described above. The daytime column abundances of D4 and D5 are higher than their nighttime abundances, with day/night ratios of 1.9 and 1.4, respectively. But the differences are not consistent enough to be statistically significant given the small sample size. The interpretation of this is that emissions occur throughout both the day and nighttime sampling periods; that the relative day and night emission rates remain uncertain; and that there is inconclusive evidence that daytime emission rates are larger than nighttime emissions.

<center>Emissions from Indoor Air</center>

Emissions were calculated using the data from the laboratory because sufficient information about the ventilation systems for Office B was not available. The laboratory

however, is ventilated directly from an HVAC system that receives 100 percent outside air. Per person mass emission rates are therefore given by

$$E = (C_{indoor} - C_{outdoor}) * \frac{Q}{n} \qquad (1)$$

where E is the emission rate per person-day, Q is the volumetric flow rate of the ventilation system, and n is the number of occupants of the lab. Building design data constrain Q to between 775 and 2270 cubic feet per minute depending on laboratory hood use and heating or cooling requirements, and n ranges from 1 to 7 people. Table 10 contains information about each lab member's personal care product use. The flow rate and number of people, while not known exactly during the sampling periods, are varied across these bounds to give minimum and maximum values for E. As we do not have simultaneous measurement of C_{indoor} and $C_{outdoor}$, we approximate the $C_{outdoor}$ by the indoor nighttime concentration, when the room is not occupied and the indoor and outdoor concentrations should be equal.

Per-person emissions were calculated using equation 1 and the average day and nighttime concentrations found in the laboratory air. The minimum emission rate, using 7 people and a flow rate of 22 m^3/minute for D4 and D5 is 0.0090 and 29 mg (person-day)$^{-1}$ respectively. The maximum emissions rate (1 person and 64 m^3 minute^{-1}) is 0.027 and 590 mg (person-day)$^{-1}$ for D4 and D5. Because the sample involved a small n, it is not meant to be representative of population averaged emission rates. However, due to the potential for wider applicability of the method (using indoor air mass balance approaches to estimate emission rates) and the scarcity of per capita emission data, we report and compare the values here. The measured D5 emission rate (590 mg (person-day)$^{-1}$) is within a factor of 3 of the value found by Horii and Kannan (230) and larger than the value used in modeling by Navea et al. (140). This seems consistent with the higher outdoor measured concentrations (18-210 ng m^{-3}) in this study when compared with the

modeled concentrations by Navea et al. (3-45 ng m^{-3}) – which will be discussed further in the following section.

For D4, the conclusions to draw from comparison of this work with Horii and Kannan and Navea et al. are perhaps more intriguing and worthy of future research. Both the mass emission rate from this work (<0.027 mg (person-day)$^{-1}$) and the value reported by Horii and Kannan based on personal care product usage (1.1 mg (person-day)$^{-1}$) are much lower than the value used by Navea et al. in modeling (90 mg (person-day)$^{-1}$). However, as discussed in the section below, the Navea et al. D4 emission rate better explains observed atmospheric measurements.

Comparison of Measured and Modeled Concentrations and
D5/D4 ratios

The D4 concentrations found in our study and a measurement study by Genauldi et al. fall within a factor of two when compared to Navea et al.'s predictions in high and medium population density locations (Table 11). On the other hand, the measured concentrations of D5 in this work are five to ten times higher than those predicted by Navea et al.   As the ambient measurements are the strongest constraint on emissions, this suggests that the per person emission rate of D4 reported in this work and the emission rate of Horii and Kannan are not representative of the average per capita emission rate from all sources. This further suggests that the emission rates measured in this work and the per person per day usage estimates (from personal care products) of Horii and Kannan for D5 are likely more accurate than the 140 mg (person-day)$^{-1}$ value used in the Navea simulations.

It is interesting to note the variations in the measured and modeled D5/D4 ratio between the urban, suburban, and rural locations. The measured average ratio is 4.5, 3.1, and 2.1 for Chicago, Cedar Rapids, and West Branch respectively. Half-lives of D4 and D5 with respect to atmospheric oxidation are (under average conditions) 11 and 7 days,

respectively. Because of this, D5/D4 ratios will be highest at the points of common emission of the two chemicals, and will decrease as air masses move away from source regions and undergo oxidative aging. Evidence of this phenomenon is apparent in the measured data, although the difference is statistically significant only between West Branch and Chicago (p-value = .002). This is also predicted in the Navea model, although with much smaller variation than that measured in this study. The modeling assumption in Navea et al. - that the majority of airflow was coming from a remote background- is likely not correct for the Midwestern United States. Future work utilizing 3D chemical transport modeling of D4 and D5, and comparison to other similar "chemical clock" ratios such as the benzene to toluene ratio (Warneke et al., 2007), could be used to explore and exploit geographic patterns in siloxane ratios.

Conclusions

In this study we found that cyclic siloxane concentrations in outdoor air to be in the ng m^{-3} range and to vary diurnally. Concentrations in the indoor environments reached into the μg m^{-3} range, demonstrating that emissions from indoor air can be a significant contributor to outdoor air concentrations. The dominance of D5 mass (which is especially notable in indoor air) indicates that personal care product use is one of the primary sources of cyclic siloxanes to the environment. Comparisons between this study and others support the conclusion that the major aspects of degradation and transport of siloxanes in air are well understood. However, significant sources of uncertainty remain in the magnitudes, diurnal pattern, and compound ratios in emissions estimates, which is an area for further study.

Table 8. Indoor air concentrations for D4, D5, and D6, and D5/D4 ratios.

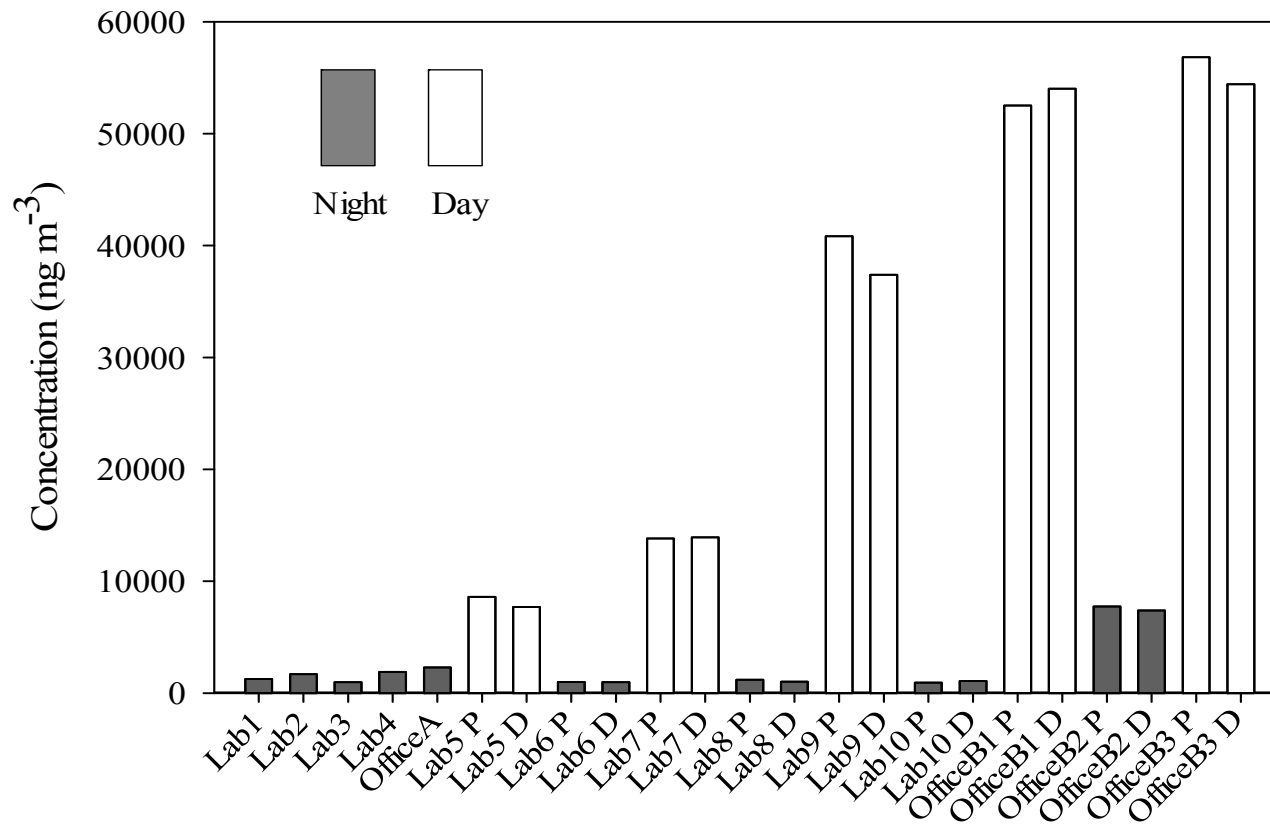|	Concentration (ng m^{-3})			
	D4	D5	D6	D5/D4
Lab1	46	1300	<59	27
Lab2	51	1700	<59	33
Lab3	57	970	<59	17
Lab4	63	1900	<59	30
OfficeA	73	2300	<59	31
Lab5	23	8100	70	350
Lab6	47	970	<59	21
Lab3	58	14000	200	240
Lab4	31	1100	<59	36
Lab5	75	39000	220	520
Lab6	27	1000	nd	38
OfficeB1	340	53000	1600	160
OfficeB2	260	7600	314	29
OfficeB3	500	56000	2800	110

Figure 7. Indoor air concentrations of D5. Primary (P) and duplicate (D) concentrations are provided where available.

Table 9. Outdoor air concentrations for D4, D5, and D6, and D5/D4 ratios.

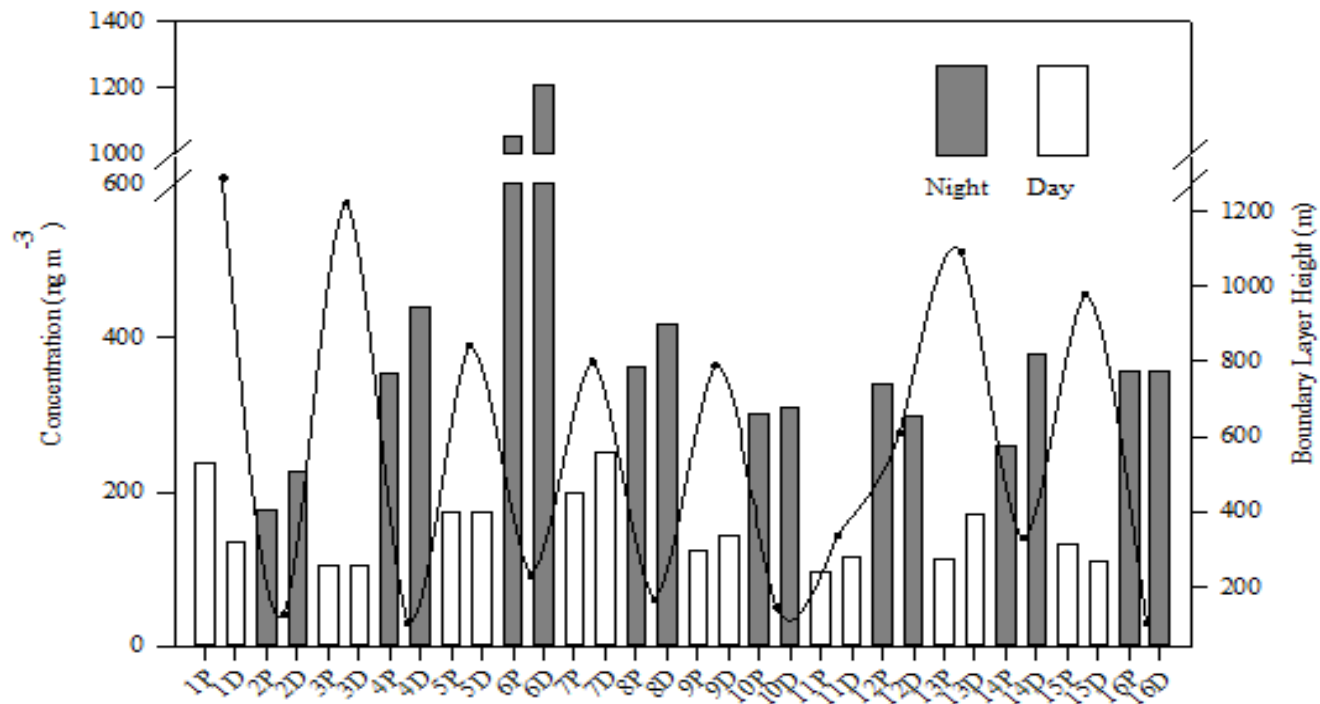|	Concentration (ng m^{-3})			
	D4	D5	D6	D5/D4
WB1	9.7	28	1.75	2.9
WB2	8.1	18	<1.4	2.2
WB3	14	17	2.2	1.2
WB4	12	29	2.3	2.4
WB5	5.6	10	<1.4	1.7
CR1	16	52	9.3	3.2
CR2	5.1	22	4.0	4.3
CR3	16	52	5.6	3.1
CR4	37	65	3.3	1.7
IIT1	45	190	8.7	4.1
IIT2	53	200	9.4	3.8
IIT3	23	100	<8.5	4.5
IIT4	72	400	21	5.5
IIT5	95	170	<8.5	1.8
IIT6	190	1100	50	5.8
IIT7	64	230	<8.5	3.5
IIT8	52	390	14	7.6
IIT9	51	130	<8.5	2.7
IIT10	57	310	13	5.4
IIT11	18	110	<8.5	6.0
IIT12	120	320	12	2.7
IIT13	44	140	nd	3.2
IIT14	55	320	15	5.9
IIT15	25	120	<8.5	4.9
IIT16	66	360	18	5.4
RV1	37	270	9.5	7.2
RV2	25	130	<8.5	5.1
RV3	37	250	11	6.9

Figure 8. Outdoor air concentrations for D5 at IIT in Chicago, IL along with average boundary layer heights for the corresponding sampling period. IIT1 was started on a Saturday morning, and all additional samples were taken at subsequent 12 hour increments. Primary (P) and duplicate (D) concentrations are provided.

Table 10. Gender and personal care product types regularly used by each laboratory member who used the Hornbuckle lab during the time air samples were taken. Names in parentheses are the ingredient name indicating the presence of a siloxane or silicon polymer mix.

	Gender	Products Used
1	F	Shampoo, conditioner (dimethicone), Facial Cleanser (dimethicone), Lotion (dimethicone), soap, night moisturizer (dimethicone, cyclopentasiloxane), sunscreen
2	M	Shampoo (dimethiconol), deodorant (cyclopentasiloxane)
3	M	Soap, conditioner, deodorant, aftershave, shaving soap
4	F	Lotion, deodorant (cyclopentasiloxane and dimethicone), shampoo (divinyldimethicone, amodimethicone), soap
5	M	Shaving cream, deodorant, shampoo, soap
6	M	Deodorant, shampoo (dimethicone), soap
7	M	Shampoo (dimethicone), soap (dimethicone)
8	F	Shampoo (dimethicone), conditioner (dimethicone), face wash, deodorant (cyclopentasiloxane and dimethicone), soap, lotion (dimethicone)

Table 11. Results from a modeling study conducted by Navea et al. that reported modeled outdoor air concentrations for D4 and D5 in urban, suburban, and rural locations for July in the U.S., compared to the measured D4 and D5 concentrations from this study and the study by Genualdi et al.

	D4 (Standard Error) ng m^{-3}			D5 (Standard Error) ng m^{-3}		
Reference	Urban	Suburban	Rural	Urban	Suburban	Rural
This Study	54 (43)	17 (14)	9.7 (3.3)	210 (250)	52 (18)	18 (8.2)
Navea	30	16	2.4	45	22	3.0
Genualdi	18 (22)	N/A	13 (15)	130 (103)	N/A	4.6 (4.1)

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