

# Dimethylsilanediol (DMSD) Source Assessment and Mitigation on ISS: Estimated Contributions from Personal Hygiene Products Containing Volatile Methyl Siloxanes (VMS)

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Dimethylsilanediol (DMSD) is a small organosilicon compound present in humidity condensate on the International Space Station. Aqueous DMSD originates from volatile methyl siloxane (VMS) compounds in the ISS cabin atmosphere. DMSD is not effectively removed by the WPA (Water Processor Assembly), requiring removal and replacement of both WPA Multifiltration (MF) Beds for an estimated resupply penalty of approximately 70 kg/year. Analyses indicate that WPA can handle DMSD if the concentration in the condensate can be reduced by fifty percent. Personal Hygiene Products (PHPs) used by crew are suspected to be a significant source of VMS. Source removal of VMS will be required to achieve a measurable impact to the DMSD concentration in the condensate. The inventory of total crew provisions for ISS was analyzed to identify silicon containing materials and products used for personal hygiene that emit VMS. Accounting for the wide range in mass of hygiene product applied to skin or hair, the frequency of application, the product selection, the number of crew using a given product, the range in silicon mass fraction of different products, and the potential vaporization of the product, the potential total VMS emissions from personal hygiene products for a crew of six on ISS were estimated. The total daily VMS emissions from PHPs estimate ranges from 261 to 1145 mg-Si per day, compared to total estimated VMS generation rates on ISS of 800 to 1500 mg-Si per day. The main sources of VMS were determined to be antiperspirants (173 to 696 mg-Si per day), skin lotions (63 to 248 mg-Si per day), wipes (25 to 124 mg-Si per day) and hair conditioner (0 to 69 mg-Si per day). Several siloxanes-free options are available for deodorants, wet wipes, lotions, and leave-in conditioners. These products are now being assessed for crew member use in future increments.

## Nomenclature

<i>AQM</i>	= Air Quality Monitor	<i>L4</i>	= decamethyltetrasiloxane
<i>cVMS</i>	= cyclic volatile methyl siloxane	<i>L5</i>	= dodecamethylpentasiloxane
<i>D3</i>	= hexamethylcyclotrisiloxane	<i>MF</i>	= multifiltration
<i>D4</i>	= octamethylcyclotetrasiloxane	$\cdot\text{OH}$	= hydroxyl radical
<i>D5</i>	= decamethylcyclopentasiloxane	<i>PDMS</i>	= polydimethylsiloxane
<i>D6</i>	= dodecamethylcyclohexasiloxane	<i>PHP</i>	= personal hygiene product
<i>DMSD</i>	= dimethylsilanediol	<i>TCCS</i>	= Trace Contaminant Control System
<i>ISS</i>	= International Space Station	<i>TOC</i>	= Total Organic Carbon
<i>IVMS</i>	= linear volatile methyl siloxane	<i>TMS</i>	= trimethylsilanol
<i>L2</i>	= hexamethyldisiloxane	<i>VMS</i>	= volatile methyl siloxane
<i>L3</i>	= octamethyltrisiloxane	<i>WPA</i>	= Water Processor Assembly

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## I. Introduction

ELEVATED levels of Total Organic Carbon (TOC) in the effluent of the International Space Station (ISS) Water Processor Assembly (WPA) were observed beginning in June of 2010 by the inline Total Organic Carbon Analyzer (TOCA).<sup>1</sup> Analysis of water samples returned to the ground led to the identification of dimethylsilanediol (DMSD) as the source of TOC in the WPA effluent<sup>2,3</sup>. Subsequent investigation determined that DMSD is present in the humidity condensate, which comprises approximately half of the waste water processed by the WPA. DMSD is a water-soluble silanediol compound that originates from volatile methyl siloxane (VMS) compounds in the ISS cabin atmosphere. These VMSs decompose by multiple mechanisms to DMSD, resulting in DMSD condensing in the humidity condensate at a concentration of approximately 40 mg/L. This makes DMSD one of the major constituents in humidity condensate, though it was not known to be present in the condensate during the design of the WPA. As a result, DMSD is not effectively removed by the WPA. It is initially removed by the anion exchange resin in the WPA Multifiltration (MF) Beds due to a slight polar charge, but is preferentially pushed off the resin by ionic constituents with higher affinity for ion exchange. Once it saturates the MF Beds, it is partially removed by the WPA Catalytic Reactor, but is still present at sufficiently high concentrations in the WPA product water to ultimately require removal and replacement of both WPA MF Beds to maintain acceptable potable water quality. As a result, the estimated re-supply penalty for replacing the MF Beds is approximately 70 kg/year as of 2017. This is a significant penalty given the cost required to launch hardware to the ISS, and is unacceptable for future manned missions. NASA engineering has therefore been pursuing various means to mitigate the impact of DMSD on the WPA performance, while also evaluating preferred approaches for dealing with this contaminant for exploration missions. This approach includes reducing the concentration of DMSD in the condensate by filtering the VMS precursors from the ISS atmosphere and reducing credible sources of these VMSs.

One primary source of VMS are the products used by crew for personal care and hygiene practices. In general, siloxane-containing hygiene products are applied to the hair and skin and volatilize into the cabin atmosphere where they are either removed by the air revitalization system's Trace Contaminant Control System (TCCS) or transformed into water soluble compounds, such as DMSD. Two pathways have been proposed for the reactions that convert VMS compounds to DMSD. Both surface acid-base hydrolysis reactions and air-phase hydroxyl initiated reactions are thought to play a role in DMSD production on ISS. This paper focuses on the contribution of personal hygiene products (PHPs) to the air-phase VMS concentrations and DMSD load to humidity condensate on ISS.

The two main categories of air-phase VMS sources are defined as "occupant" and "non-occupant." Occupant sources are the focus of this paper and include human activities associated with hygiene and personal care practices. Non-occupant sources include all the other possible sources of VMS within a habitat structure, such as electronics, adhesives, coatings, paints, and other silicone products.

Our initial focus on occupant sources of VMS on ISS is based on their ability to be both quantified and eventually replaced by siloxane-free products. In addition, the inventory of hygiene products for a given crew of six is tractable and finite. Whereas, the presence of diverse and numerous silicone materials in the racks, electronics, subsystems and structure of ISS are difficult to quantify and challenging to replace within the habitat. This paper attempts to quantify the broad range of siloxane emissions from the hygiene practices and general activities of the crew members on ISS.

### A. Properties of VMS

VMS serve as solvents and binding agents in personal care products. VMS provide hygiene products with desirable properties for hair and skin applications, such as spreadability and softness. Their volatility is beneficial as it prevents buildup of the products on the skin over time.

Even though silicon and carbon are abundant on Earth, the Si-C bond within siloxanes is not found in nature. Despite many publications attempting to demonstrate the biotic breakdown of Si-C bonds, no enzyme has yet been found and verified that is capable of cleavage of the xenobiotic Si-C bonds in volatile methyl siloxanes.<sup>4</sup>

Polydimethylsiloxanes (PDMSs), are the most common type of silicone and are found in a wide variety of industrial applications and consumer products. Low molecular weight volatile methylsiloxanes (VMSs) are a sub group of PDMS. Figures 1 and 2 show the basic structure of VMS compounds. Siloxanes consist of  $-(CH_3)_2SiO-$  structural units. Two major groups of VMS are cyclic VSM (cVMS) and linear VMS (lVMS). The cVMS have a cyclic ring and tend to have slightly lower vapor pressures than the lVMS (Table 1).<sup>4</sup> The value of Henry's constant increases with molar volume for lVMS and the value of Henry's constant decreases with molar volume for cVMS.<sup>5</sup>

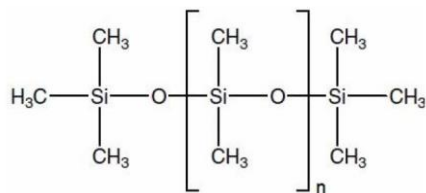


Figure 1. Structure of Linear Volatile Methyl Siloxanes, LVMS:  $n = 0$  for L<sub>2</sub>,  $n = 1$  for L<sub>3</sub>,...,  $n = m - 2$  for L<sub>m</sub>.

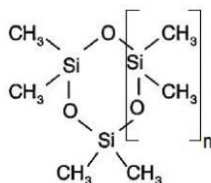


Figure 2. Structure of Cyclic Volatile Methyl Siloxanes, cVMS:  $n = 0$  for D<sub>3</sub>,  $n = 1$  for D<sub>4</sub>,...,  $n = m - 2$  for D<sub>m</sub>.

Table 1. Vapor Pressure and Dimensionless Henry's Constants for VMS Compounds,  $T = 297$  K.

Compound	MW g/mole	P <sub>vp</sub> Pascal	H <sub>c</sub> C <sub>gas</sub> /C <sub>aq</sub>
L2	162.4	4120	3.5
L3	236.5	520	59
L4	310.7	73	993
L5	384.8	9	16,800
D3	222.5	1150	77
D4	296.6	130	32
D5	370.8	23	13
D6	494.9	4	5.6

Volatilization and environmental persistence of siloxanes are demonstrated by their global presence in virtually all environmental compartments. These include the troposphere,<sup>6</sup> rainforests,<sup>6</sup> the arctic atmosphere,<sup>6</sup> indoor dust,<sup>7</sup> mountains,<sup>8</sup> fish,<sup>9</sup> and mammals.<sup>10</sup>

## B. VMS in Indoor Environments

Concentrations of VMS in indoor environments exhibit variations in time and in room and building types. Occupancy and ventilation rates with outdoor air are important parameters in VMS concentrations. Levels of linear and cyclic VMS were measured in a wide range of indoor settings in Italy and the United Kingdom.<sup>11</sup> Indoor sampling locations included bathrooms, bedrooms, living rooms, super markets, and offices. D5 was the most abundant VMS. A wide range of concentrations were observed between room types and regionally with indoor air concentrations ranging from 7.5 to 170  $\mu\text{g}/\text{m}^3$  in Italy and 45 to 270  $\mu\text{g}/\text{m}^3$  in the United Kingdom. Differences were attributed to diversity in personal care product compositions, product use by occupants, room contents including computers and printers. Cultural differences in cosmetic uses were cited as one source of regional variation.

Personal care products are the principal source of cVMS exposure for humans and the environment.<sup>16</sup> All occupants of a room, even those who do not use hygiene products are exposed to VMS by inhalation. The daily mass of VMS exposure from the air-phase is the product of the breathing rate ( $\text{m}^3/\text{day}$ ), concentration of VMS ( $\text{mg}/\text{m}^3$ ), and the time of various activities or time spent in a given location (day). Daily inhalation rates of total VMS for adults were estimated to be 1.6 mg-VMS per day in Italy and 1.9 mg-VMS per day in the United Kingdom.<sup>11</sup>

Indoor air samples were measured at 60 different locations (20 homes, 7 offices, 13 laboratories, 6 schools, 6 salons, and 8 public places) for 14 VMS (D3 to D7 and L3 to L11) compounds in Albany, New York. The total VMS concentrations (vapor phase plus particulate phase) ranged from 0.25 to 6.21  $\mu\text{g}/\text{m}^3$ , with the highest levels in hair salons.<sup>7</sup> D5 was the most abundant compound in indoor air samples with an average concentration of 0.7  $\mu\text{g}/\text{m}^3$ . High

molecular weight linear siloxanes (L7, L8, and L9) existed predominantly in the particulate phases. The estimated average inhalation exposure to total siloxanes by indoor air was 19.1  $\mu\text{g}/\text{day}$ .

VMS concentrations were measured during 19 university class sessions in a classroom in order to estimate VOC and VMS emissions from students.<sup>12</sup> Peak emissions were observed at the start of class and were associated with elevated body temperature and removal of outer layers of clothes. VMS emissions were higher in the morning classes than afternoon classes. D5 was the dominant VMS compound accounting for greater than 90% of the total VMS mass. The maximum observed D5 concentration was 14 ppb (0.21  $\text{mg-D5}/\text{m}^3$ ) followed by D6 at 0.17 ppb (0.003  $\text{mg-D6}/\text{m}^3$ ). Mass of cVMS compounds accounted for approximately one-third of the total VOC mass concentration.

In a landmark paper, the generation rates of DSMD from four primary VMS compounds were quantified. The dominant DSMD production pathway (88 to 94%) was determined to hydroxyl radical ( $\cdot\text{OH}$ ) initiated oxidation of VMS in the gas-phase of ISS.<sup>13</sup> For cabin concentrations of 1.12  $\text{mg-D3}/\text{m}^3$ , 0.35  $\text{mg-D4}/\text{m}^3$ , 0.29  $\text{mg-D5}/\text{m}^3$ , and 0.29  $\text{mg-TMS}/\text{m}^3$ , a material balance including removal and reaction estimated total generation rates of 1.16  $\text{mg-D3}/\text{day}$ , 0.41  $\text{mg-D4}/\text{day}$ , 0.31  $\text{mg-D5}/\text{day}$ , and 0.32  $\text{mg-TMS}/\text{day}$ . The associated total DSMD production rate was 158  $\text{mg-DMSD}/\text{day}$ . Figure 3 shows a conceptual depiction of the silicon cycle on ISS and Figure 4 shows the material balance for the May 2015 timeframe on ISS.

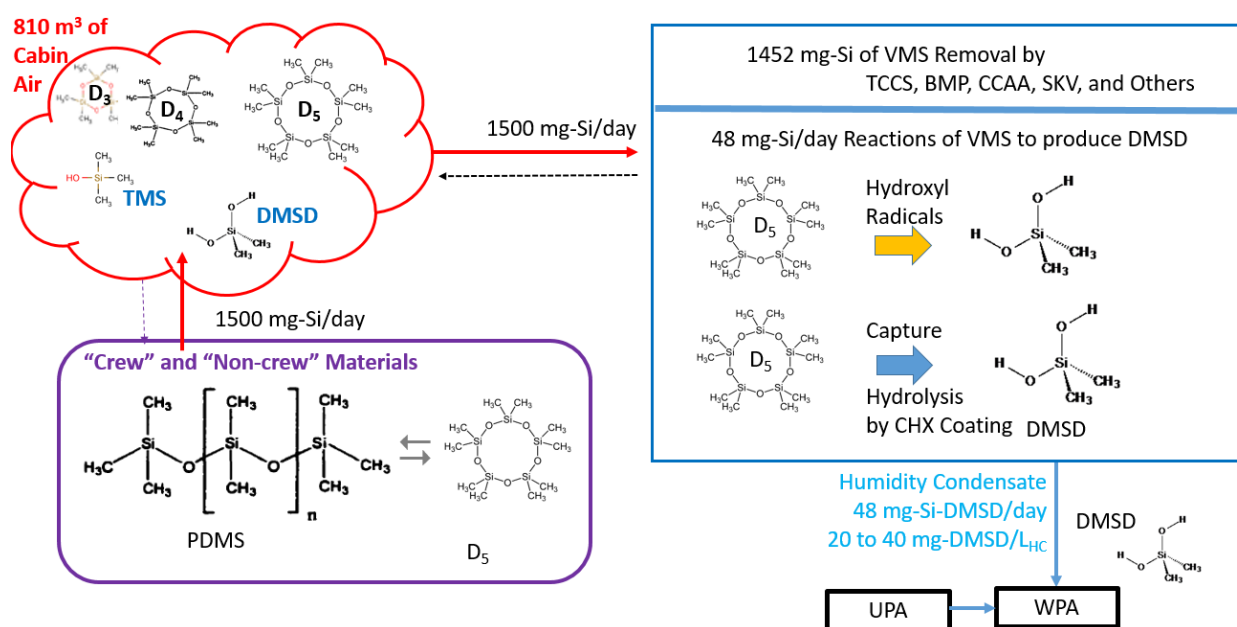


Figure 3. Simplified Mass Balance of Sources, Removal, and Reactions of VMS to DMSD on ISS.<sup>13</sup>

Figure 5 compares the range of D5 emissions from students<sup>12</sup> to total estimated D5 emissions from all sources on ISS for the May 2015 timeframe.<sup>13</sup> The total generation rates of D5 on ISS were on the same order of magnitude as the lower 95<sup>th</sup> percentile of the student emissions. Figure 6 shows the concentrations of D5 on ISS for Increments 47 to 51. The data is shown for the crew of three and then when they are joined by three new crew members.

### C. Use and Application of Personal Hygiene Products

Estimates of the hygiene practices and product applications to the skin and hair have been conducted using Monte Carlo simulations in order to assess dermal and breathing exposure to VMS and their toxicological safety. One of the challenges of quantifying the mass of products used is the inter-individual variability in large populations. A large population study utilizing three databases was conducted in Europe to quantify the range of individual hygiene practices.<sup>14,15</sup> Five countries were selected to represent a cross-section of the European Union and its population of 248.5 million inhabitants in the 2003 to 2009 timeframe. Data was supplied from 124,100 households and 32,470 individuals. The database included participants using their own products and maintaining their hygiene practices in their homes. The twelve product types studied were estimated to represent 95% of daily exposure to personal hygiene products. One finding of the study was that for certain products (skin lotion, toothpaste, and shampoo), the mass

applied per use decreased as the frequency of use increased. No correlation was found for lipstick and antiperspirants. The results of the usage rates are shown in Table 2. The authors also provided application rates in units of gram per mass of person per day (g/kg/day).



Figure 4. Generation, Removal, and Reaction of VMS Compounds to DMSD.<sup>13</sup>

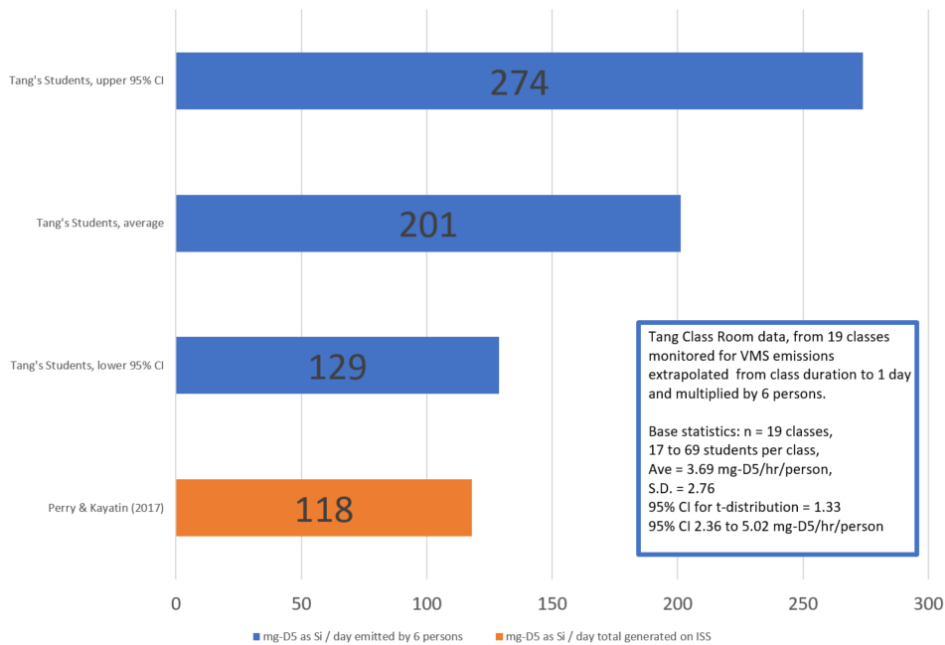
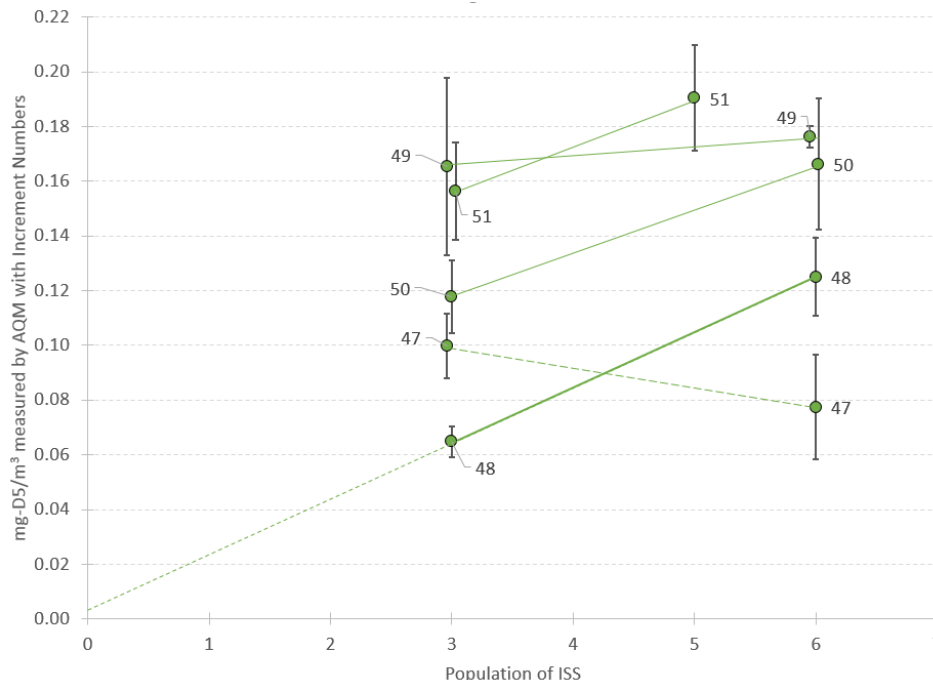


Figure 5. Comparison of Student D5 emissions in a Classroom to estimated Total Generation of D5 on ISS.<sup>12,13</sup>



**Figure 6. Concentrations (Ave. ± 1 S.D.) of D5 on ISS as function of Increment and Crew Size.**

The area of skin to which hygiene products are applied has been quantified.<sup>16</sup> Nominal areas of application were: 200 cm<sup>2</sup> (both axillary cavities) for antiperspirants/deodorants, 565 cm<sup>2</sup> (half area head, female) for face creams, 860 cm<sup>2</sup> (both hands) for hand creams, and 15,670 cm<sup>2</sup> (whole body area without head, females) for body lotions.

#### D. VMS Compositions in Personal Hygiene Products

VMS are used as carrier solvents and emollients and are found in numerous personal care products in a wide range of concentrations and mixtures. Industrial production started in the 1940's and grew rapidly in the 1970's.<sup>16</sup> Today they are a basic ingredient in many products, especially antiperspirants and leave-in hair products. They are present in the ingredient list under a variety of names. Generally, "cyclomethicone" refers to a mixture of siloxanes.

The concentrations of D4 and D5 in 51 of the most popular personal care products sold in Europe were measured.<sup>16</sup> Among the three VMS compounds, D5 had the highest concentrations. Concentration of D5 ranged from a low of 0.01% of total wet mass in hand creams to greater than 35% in antiperspirants. Across the board, D5 was 1 to 2 orders greater than D4 concentrations, and D4 was 1 to 3 orders greater than D3 concentrations. This suggests that D3 and D4 were present as impurities. A great deal of variability in concentrations was found between VMS concentrations in products in the same category. For example, the full range of concentrations of siloxane-containing liquid foundations ranged from 21 to 213 mg-D5 per g-wet mass. In some products, VMS compounds were detected that were not listed on the ingredient list.

Levels of VMS in the personal care products categories were similar in European products were similar to concentrations of products sold in the U.S. and Canadian markets.<sup>16</sup> Compared to products from the Chinese market,<sup>17</sup> European products had much higher levels of cVMS.<sup>17</sup> This was attributed to the use of long-chain linear siloxanes in substitute of cVMS by Chinese manufacturers.

The levels of D3, D4, D5, and D6 were determined in 252 cosmetics and personal care products collected from retail stores from various regions in Canada.<sup>18</sup> D5 was the most predominant cVMS with the highest concentration of 680 mg/g-wet mass in an antiperspirant. The authors concluded that human dermal exposure to VMS compounds are about one-tenth the exposure of inhalation.

**Table 2. Daily Applications in Grams per Day per User from European Population Model. (Non-users are excluded).<sup>14,15</sup>**

	<b>n of simulation</b>	<b>mean</b>	<b>S.D.</b>	<b>P5</b>	<b>P10</b>	<b>P50 (median)</b>	<b>P90</b>	<b>P95</b>
Antiperspirant/Deodorant, g/day	30,000	0.898	0.494	0.221	0.363	0.820	1.509	1.806
Body Lotion, g/day	30,000	4.543	2.707	0.556	1.129	4.556	7.822	8.951
Facial Moisturizer, g/day	30,000	0.906	0.533	0.138	0.261	0.851	1.536	1.801
Hand Cream, g/day	150,000	1.058	0.925	0.099	0.147	0.872	2.156	2.740
Shampoo, g/day	30,000	6.034	3.296	1.482	2.178	5.503	10.456	12.181
Toothpaste, g/day	30,000	2.092	0.577	1.204	1.370	2.101	2.749	2.960
Mouthwash, g/day	150,000	12.622	9.359	1.826	2.982	11.076	21.62	27.576
Liquid Foundation (females), g/day	150,000	0.225	0.209	0.016	0.023	0.174	0.513	0.640
Lipstick (females), mg/day	30,000	24.61	24.05	1.68	2.95	17.11	56.53	72.51
Shower gel, g/day	150,000	11.34	6.400	2.414	3.738	10.910	18.671	22.765
Hair styling gel, g/day	150,000	1.914	1.640	0.147	0.270	1.552	4.000	4.987

## II. Methodology

In order to estimate the potential contributions of hygiene products to air concentrations of VMS on ISS, a simple model was used to represent the wide range of possible variation associated with product selection, product uses, and inter-individual variability between crewmembers. The quantity of the mass of siloxanes from hygiene products that enter the cabin atmosphere depend on several variable factors that vary for each of the six inhabitants of ISS (Table 3).

**Table 3. Factors affecting Potential Siloxane emissions from a Given Hygiene Product and its Usages on ISS by One Crew Member.**

	<i>Factor</i>
1	Product's Siloxane Composition
2	Mass of Product Applied to Hair or Skin per Use
3	Number and Timing of Uses of Product (Applications) per Day
4	Type of Physical Activities before and following Applications
5	Chemical and Physical Changes of the Product after applied to skin or hair
6	Fraction of Siloxanes that Volatilize to Cabin Atmosphere
7	Rinse/Washoff with Towel/Wipe including Fate of Towel or Wipe

The total mass of total siloxanes (as silicon) applied to the skin and hair and volatilized to the air phase is estimated by equation 1:

$$\dot{m} \left( \frac{g \text{ Si}}{\text{day}} \right) = \sum_i^{\text{all crew}} \sum_j^{\text{all products}} \sum_k^{\text{all applications}} \alpha_{i,j,k} \left( \frac{mg\text{-Si}}{g\text{-product}_j} \right) \left( \frac{g\text{-product}_j}{\text{application}_k} \right) \left( \frac{\text{application}_k}{\text{day}} \right) \quad (1)$$

Where  $\alpha$  is the fraction of the siloxane mass that volatilize from the skin, hair, or container to the air phase.

The total crew provisions list was assessed for products used by crew that contain siloxanes. For each product, the siloxane content was either taken from the literature or measured by assuming all of the total silicon content was in the form of siloxanes. The value of  $\alpha$  was taken to be 1 for this paper. Therefore, the estimated masses of siloxane represent the mass applied to the skin and hair.

Product practices are based on US Crew product information and practices and extrapolated to a crew of six. The goal is an order of magnitude estimate of potential siloxane emissions from hygiene product uses. Products not included in this assessment due to their low siloxane content and mass applied to skin were: shaving creams, lip balm, toothpaste, and mouthwash. The main body wash currently used on skin and hair on ISS does not contain siloxanes.

#### A. Antiperspirants

The mass of antiperspirants applied to both axillary cavities each day was estimated from the European Population model. The median mass was 0.82 grams of product per day per person (see Table 2). The mass of D5 per gram of product was estimated by calculating the average value of D5 content of antiperspirants from two references.<sup>14,16</sup> The average D5 content of antiperspirants used in this assessment was 23.3% of the total product (233 mg-D5/g-product). The full range of application masses was estimated by adding and subtracting one standard deviation from the median value (Table 2):  $0.82 \pm 0.49$  grams of product applied per day per person. A crew of six was assumed, all with the same product use patterns. For these baseline assumptions the mass of silicon in the form of siloxanes applied to the skin by antiperspirants each day for a crew of six ranges from 173 to 696 mg-Si per day. The value of  $\alpha$  in Equation 1 is assumed to be 1 in this and all calculations, as a worst case scenario. The volatility of siloxanes in antiperspirants applied to the axillary cavities has been found to be greater than 95% within 6 hours of application.<sup>16</sup>

#### B. Moisturizers

The mass of moisturizers applied to the skin was estimated from the European Population model for the body lotion category. The median mass was 4.56 grams of product per day per person (see Table 2). The average siloxane content of moisturizers used in this assessment was 15 mg-D5 total wet mass of product.<sup>16</sup> The full range of application masses was calculated by adding and subtracting one standard deviation from the median value (Table 2):  $4.56 \pm 2.71$  grams of product applied per day per person. A crew of six was assumed. For these baseline assumptions the mass of silicon in the form of siloxanes applied to the skin each day for a crew of six ranges from 63 to 248 mg-Si per day.

#### C. Wet-Wipes

14,560 wet wipes are flown to ISS per year for use in hygiene practices. Each wipe has a total mass of 7 grams. Each wipe contains 5 grams of liquid. The total Silicon content of the liquid was measured by ICP-MS to be 620 mg-Si per kilogram. From this information, and assuming all wipes are used by all six crew in a given year, the mass of silicon applied to the skin from the wipes was estimated. The full range was based on only 1 gram of liquid being retained on the skin (the low range) to all 5 grams of liquid evaporating to the air phase (high range). These assumptions resulted in the range of 25 to 124 mg-Si per day for gas emissions from wipes.

#### D. Hair Conditioners

The main leave-in hair conditioner used on ISS was analyzed for total silicon concentration. The concentration of total silicon was 4.6 mg-Si per mL of liquid. Assuming a nominal application of 15 mLs of liquid applied per application, the mass of siloxanes as Si applied is 69 mg-Si per application.

#### E. Cosmetics

Cosmetics are a crew preference item. In general, lipstick and eyeliner do not contain a significant mass of siloxanes. The mass applied to lips and eyelashes is small as well. Liquid foundations often do contain D5 and some D6.



An average value of D5 of 107 mg-D5 per gram of product was used along with 0.2 grams of product applied per day per person to estimate 21.4 mg-D5 (8.1 mg-Si) applied to skin per day for one person.<sup>16</sup> Similarly, for the same product's D6 content of 55.2 mg-D6 per gram of product, the resulting mass of D6 applied to skin was 11.0 mg-D6 (4.2 mg-Si) per day per person. The sum total of siloxanes was thus calculated to be 12.3 mg-Si per day per person using liquid foundation assuming this average product composition.

### III. Results

The results are summarized in Figures 7 and 8. The values represent the range of siloxanes applied to the skin and hair for a crew of 6 with one person applying liquid foundation and leave-in hair conditioner. The wide range of estimated values is due to inter-individual variability in the amount of product applied to the skin. For the product siloxane contents, which are also highly variable, average values were used from the literature. The mass of siloxanes applied to the skin each day are compared to the estimated mass of siloxanes generated on ISS each day for the 2015 timeframe.<sup>13</sup> For the full range of baseline assumptions used in the calculations, the relative contribution of hygiene products to total siloxane emissions could be between 17 and 76%, depending on actual crew product selection and hygiene practices.

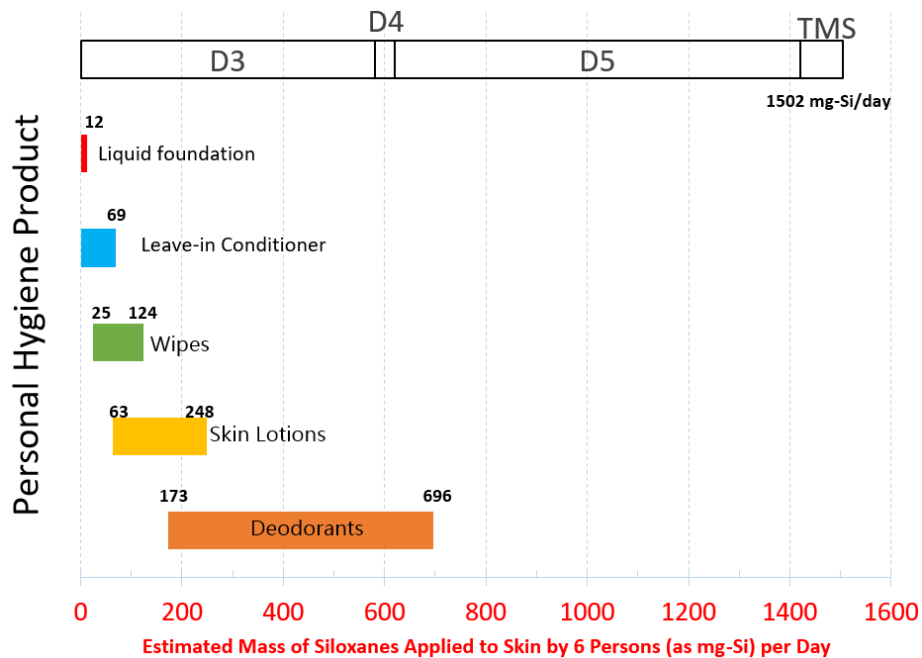
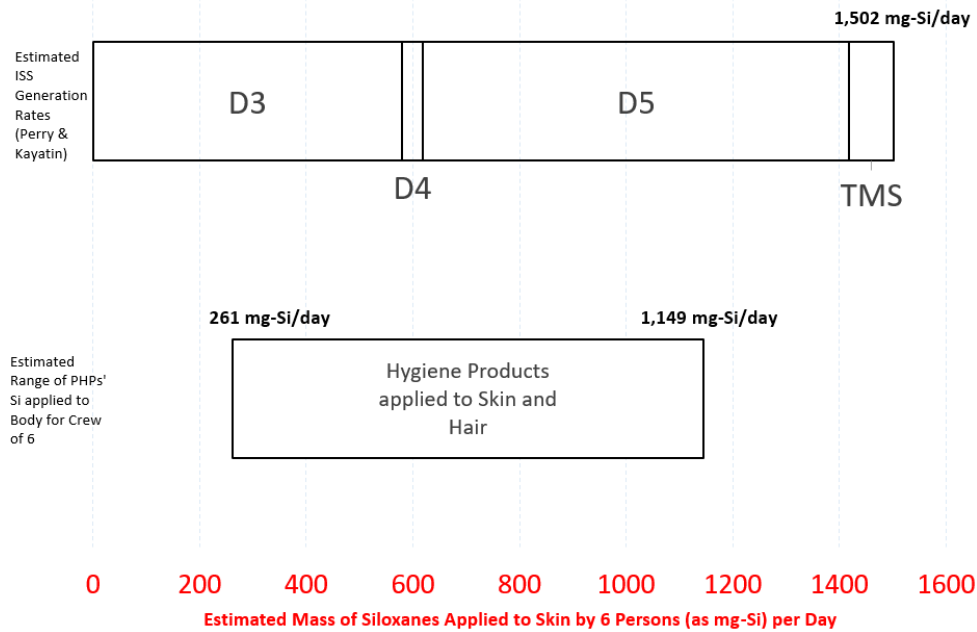


Figure 7. Estimated Mass of Siloxanes applied to Skin for the Major Personal Hygiene Products.



**Figure 8. Estimated Mass of Siloxanes applied to Skin for the Major Personal Hygiene Products.**

#### IV. Conclusions

DMSD has proven to be a problematic contaminant on ISS. Though initially removed by the WPA, it still provides a significant impact to ISS resupply mass due to the required changeout of WPA MF Beds. Reducing the precursor VMSs in the atmosphere is the most credible path toward reducing the concentration of DMSD in the humidity condensate while also prolonging life of the heat exchanger coating. Current analysis indicates that charcoal filters and source reduction will be required to achieve the desired threshold of 50% reduction of DMSD in condensate.

Due to inter-individual variability and inter-product variability in siloxane content, there is a wide range of DMSD in various crew products brought to the ISS. This work estimated the mass of siloxanes applied to the skin and hair of six crew members to be in the range of 260 to 1,150 mg-Si per day on ISS during the 2017 timeframe. This siloxane mass compares to an estimated total generation rate of VMS on ISS during 2015 of 1,500 mg-Si per day.<sup>13</sup> Antiperspirants provide the greatest emission source of VMS from hygiene activities due to their high D5 content (~25% by mass). Antiperspirants, body lotions, wet wipes and leave-in hair conditioner are all significant contributors to the siloxane load on ISS. Credible alternatives to these products have been identified that contain no VMSs. This information has been provided to the ISS Program Office and crew assessments are being performed to evaluate the acceptability of these alternatives.

#### V. Future Work

Viable alternatives to anti-perspirants, lotions, wet wipes, and leave-in hair conditioner are available that will not contribute to the VMS load on ISS. Crew selection and acceptance of siloxane-free products is underway. The current plan is to use these siloxane-free products in 2019 (in concert with atmospheric filtration of VMSs) to evaluate the effect on DMSD concentration in the ISS humidity condensate.

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## References

- <sup>1</sup> Carter, L., Kayatin, M., Gazda, D., McCoy, T., Limero, “Investigation of DMSD Trend in the ISS Water Processor.” American Institute of Aeronautics and Astronautics, *40<sup>th</sup> International Conference on Environmental Systems*, Barcelona, Spain, 2010.
- <sup>2</sup> McCoy, C., Flint, S., Straub, J., Gazda, D., Schultz, J., “The Story Behind the Numbers: Lessons Learned from the Integration of Monitoring Resources in Addressing an ISS Water Quality Anomaly.” American Institute of Aeronautics and Astronautics, *41<sup>st</sup> International Conference on Environmental Systems*, Portland, Oregon, 2011.
- <sup>3</sup> Rutz, J. A.; Schultz, J. R.; Kuo, C. M.; Cole, H. E.; Manuel, S.; Curtis, M.; Jones, P. R.; Sparkman, O. D.; McCoy, J. T., “Discovery and Identification of Dimethylsilanediol as a Contaminant in ISS Potable Water,” AIAA-2011-5154, *41<sup>st</sup> International Conference on Environmental Systems*, Portland, Oregon, 2011.
- <sup>4</sup> Rucker, C., Kummerer, K., *Chemical Reviews: Environmental Chemistry of Organosiloxanes*. American Chemical Society, 59 pages, 2014.
- <sup>5</sup> Kochetkov, A, Smith, J., Ravikrishna, R, Valsaraj, K, Thibodeaux, L., Air-Water Partition Constants for Volatile Methyl Siloxanes. *Environmental Toxicology and Chemistry*, 2001, Vol. 20, No. 10, pp. 2184 – 2188.
- <sup>6</sup> Genualdi, S., Harner, T., Cheng, Y., MacLeod, M., Hansen, K.M., van Egmond, R., Shoeib, M., Lee, S.C., L., Global Distribution of Linear and Cyclic Volatile Methyl Siloxanes in Air. *Environmental Science and Technology*, Vol. 45, 2011, pp. 3349 – 3354.
- <sup>7</sup> Tran, T.M., Kannan, K., Global Distribution of Linear and Cyclic Volatile Methyl Siloxanes in Air. *Science of the Total Environment*, 2015, pp. 138 – 144.
- <sup>8</sup> Daly, G.L., Wania, F., Organic Contaminants in Mountains. *Environmental Science and Technology*, Vol. 39, No. 2, 2005, pp. 385 – 398.
- <sup>9</sup> Danish Ministry of the Environment, C., Kummerer, K., *Siloxanes (D3, D4, D5, D6, HMDS): Evaluation of Health Hazards and Proposal of a Health-Based Quality Criterion for Ambient Air*. The Danish Environmental Protection Agency, Copenhagen, Denmark, 82 pages, 2014.
- <sup>10</sup> Danish Ministry of the Environment, C., Kummerer, K., *Siloxanes: Consumption, Toxicity and Alternatives*. The Danish Environmental Protection Agency, Copenhagen, Denmark, 110 pages, 2005.
- <sup>11</sup> Pieri, G.L., Wania, F., Occurrence of Linear and Cyclic Volatile Methyl Siloxanes in Indoor Air Samples (UK and Italy) and their Isotopic Characterization. *Environment International*, Vol. 59, 2013, pp. 363 – 371.
- <sup>12</sup> Tang, X., Misztal, P.K., Nazaroff, W.M., Goldstein, A.H., Siloxanes Are the Most Abundant Volatile Organic Compound Emitted from Engineering Students in a Classroom. *Environmental Science and Technology Letters*, Vol. 39, 2015, pp. 303 – 307.
- <sup>13</sup> Perry, J.L., Kayatin, M.J. “The Incidence and Fate of Volatile Methyl Siloxanes in a Crewed Spacecraft Cabin,” ICES-2017-233, *47<sup>th</sup> International Conference on Environmental Systems*, Charleston, South Carolina, 2017.
- <sup>14</sup> Hall, B., Tozer, S., Safford, B., Coroama, M., Steiling, W., Lenever-Duchemin, M.C., McNamara, C., Gibney, M., European Consumer Exposure to Cosmetic Products: A Framework for Conducting Population Exposure Assessments. *Food and Chemical Toxicology*, Vol. 45, 2007, pp. 2097 – 2108.
- <sup>15</sup> Hall, B., Steiling, W., Safford, B., Coroama, M., Tozer, S., Firmani, C., McNamara, C., Gibney, M., European Consumer Exposure to Cosmetic Products: A Framework for Conducting Population Exposure Assessments Part 2. *Food and Chemical Toxicology*, Vol. 49, 2011, pp. 408 – 422.
- <sup>16</sup> Dudzina, T., von Goetz, N., Bogdal, C., Biesterbos, J.W.H., Hungerbühler, K., Concentrations of Cyclic Volatile Methylsiloxanes in European Cosmetics and Personal Care Products: Prerequisite for Human and Environmental Exposure Assessment. *Environment International*, Vol. 62, 2014, pp. 86 – 94.
- <sup>17</sup> Lu, Y., Yuan, T, Yun, S.H., Wang, W., Wu, Q., Kannan, K., Occurrence of Cyclic and Linear Siloxanes in Indoor Dust from China and Implications for Human Exposure. *Environmental Science and Technology*, Vol. 44, 2010, pp. 6081 – 6087.
- <sup>18</sup> Wang, R., Moody, R.P., Koniecki, D., Zhu, J., Low Molecular Weight Cyclic Volatile Methylsiloxanes in Cosmetic Products Sold in Canada: Implication for Dermal Exposure. *Environment International*, Vol. 35, 2009, pp. 900 – 904.