

# The Incidence and Fate of Volatile Methyl Siloxanes in a Crewed Spacecraft Cabin

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**Volatile methyl siloxanes (VMS) arise from diverse, pervasive sources aboard crewed spacecraft ranging from materials offgassing to volatilization from personal care products. These sources lead to a persistent VMS compound presence in the cabin environment that must be considered for robust life support system design. Volatile methyl siloxane compound stability in the cabin environment presents an additional technical issue because degradation products such as dimethylsilanediol (DMSD) are highly soluble in water leading to a unique load challenge for water purification processes. The incidence and fate of VMS compounds as observed in the terrestrial atmosphere, water, and surface (soil) environmental compartments have been evaluated as an analogy for a crewed cabin environment. Volatile methyl siloxane removal pathways aboard crewed spacecraft are discussed and a material balance accounting for a DMSD production mechanism consistent with in-flight observations is presented.**

## Nomenclature

<i>BMP</i>	=	Russian microimpurity adsorption assembly
<i>CCAA</i>	=	Common Cabin Air Assembly
<i>CH<sub>x</sub></i>	=	condensing heat exchanger
<i>cVMS</i>	=	cyclic volatile methyl siloxane
<i>D3</i>	=	hexamethylcyclotrisiloxane
<i>D4</i>	=	octamethylcyclotetrasiloxane
<i>D5</i>	=	decamethylcyclopentasiloxane
<i>DMSD</i>	=	dimethylsilanediol
<i>HTCO</i>	=	high-temperature catalytic oxidizer
<i>ISS</i>	=	International Space Station
<i>L3</i>	=	octamethyltrisiloxane
<i>L4</i>	=	decamethyltetrasiloxane
<i>L5</i>	=	dodecamethylpentasiloxane
<i>M</i>	=	molecular weight
<i>MF</i>	=	multifiltration
<i>MSFC</i>	=	Marshall Space Flight Center
<i>MST</i>	=	methylsilanetriol
<i>PDMS</i>	=	polydimethylsiloxane
<i>REMS</i>	=	regenerative environmental control and life support module simulator
<i>TCC</i>	=	trace contaminant control
<i>TCCS</i>	=	Trace Contaminant Control System
<i>TMS</i>	=	trimethylsilanol
<i>SKV</i>	=	Russian humidity control assembly
<i>VMS</i>	=	volatile methyl siloxane
<i>WPA</i>	=	water processor assembly
<i>C</i>	=	Celsius
<i>g</i>	=	gram
<i>h</i>	=	hour

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<i>km</i>	= kilometer
<i>L</i>	= liter
<i>m</i>	= meter
<i>mg</i>	= milligram
<i>mol</i>	= mole
<i>nm</i>	= nanometer
<i>Pa</i>	= Pascal
<i>P<sub>L</sub></i>	= liquid vapor pressure
<i>ppb</i>	= parts per billion
<i>ppt</i>	= parts per trillion
$\dot{n}_i$	= molar rate of species <i>i</i>
$y_i$	= gas phase mole fraction of species <i>i</i>
$X_i$	= extent of reaction of species <i>i</i>
$\alpha$	= fractional yield
$\eta$	= efficiency

## I. Introduction

**V**OLATILE methyl siloxane (VMS) compounds, which include cyclic compounds such as hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6), are used in an extensive variety of industrial and manufacturing processes. Applications for VMS compounds include their use in elastomers for silicone components, tubing, and for manufacturing polydimethylsiloxane (PDMS) silicone polymers and co-polymers; in medical applications to coat hypodermic needles, bottle stops, implants, and other coating uses; in various gels that serve as barrier creams; in adhesives; as carrier oils; as waterproofing agents; in substrate coatings on textiles; in pharmaceuticals, lubricants, polishes, fabric softeners, paints, penetrating oils, paper products, anti-foaming agents, surfactants, and cleaning products; and in personal care and toiletry products such as deodorants, cosmetics, shampoo, conditioners, hair sprays, and shaving creams. They may also appear in food additives such as anti-foaming agents.<sup>1-4</sup>

Materials made from or incorporating PDMS-based components are implicated as a VMS compound offgassing source because the reaction processes used in polymeric silicone manufacturing are incomplete resulting in linear and cyclic VMS compound residues in the finished product.<sup>4</sup> While PDMS is not volatile and does not degrade in water,<sup>4,5</sup> the VMS residues consist of compounds such as D4, D5, and trimethylsilanol (TMS) which will volatilize or offgas over time.<sup>6-8</sup> Low molecular weight (*M*) PDMS may contain <0.1% to 0.5% VMS while higher *M* PDMS may contain 1% to 3% VMS.

Personal care products contain a variety of VMS compounds which are typically referred to as cyclomethicone or by a similar “methicone” nomenclature in their ingredient lists. The VMS compounds comprising cyclomethicone typically are mixtures of D4, D5, and D6 in varying proportions.<sup>2</sup> Literature reports that cyclic VMS (cVMS) compounds are the predominant siloxane species used in personal care products with D5 being the most prevalent.<sup>4,9</sup> Estimates are that at least 90% and potentially close to 100% of cVMS in personal care products volatilize into the atmosphere.<sup>2,5,9,10</sup> The highest estimate is that cVMS released into the atmosphere partitions at 97.6% in the gas phase, 0.1% into water, 0.2% into soil, and 2.1% into sediment.<sup>5</sup>

Given the breadth of VMS compound use in materials and personal care products, a variety of sources are likely aboard the International Space Station (ISS) creating a pervasive trace contaminant control challenge. The result is a persistent total VMS concentration—inclusive of D3, D4, D5, and TMS—ranging between 1 mg/m<sup>3</sup> and 5 mg/m<sup>3</sup> in the ISS cabin atmosphere that accounts for approximately 18% of the average 10.7 mg/m<sup>3</sup> total non-methane volatile organic compound (VOC) load as shown by Figs. 1 and 2.

Figure 1 presents several interesting observations. First, the presence of VMS compounds in the general ISS cabin atmosphere has been persistent. Periodic high concentrations are evident early in the station’s assembly and during a period starting in September 2005 and extending through calendar year 2006 depicted in Fig. 1 between years 6.5 and 8. Otherwise the total VMS compound concentration has been constant and relatively uniform. It should be noted that only the TMS concentration was reported during the period between January 2007 and June 2011. This accounts for the lower concentration between years 8 and 12.4 in Fig. 1. The concentration decrease at approximately 16.3 years is attributed to deploying supplemental contamination control capability aboard the ISS in May 2015. Second, the ISS early assembly period and during later assembly stages show that VMS compounds accumulate in sealed modules. As each new module was added to the ISS, a VMS compound load was also added. Finally, cargo delivery to the ISS provides new VMS compound sources that contribute to a persistent offgassing load.

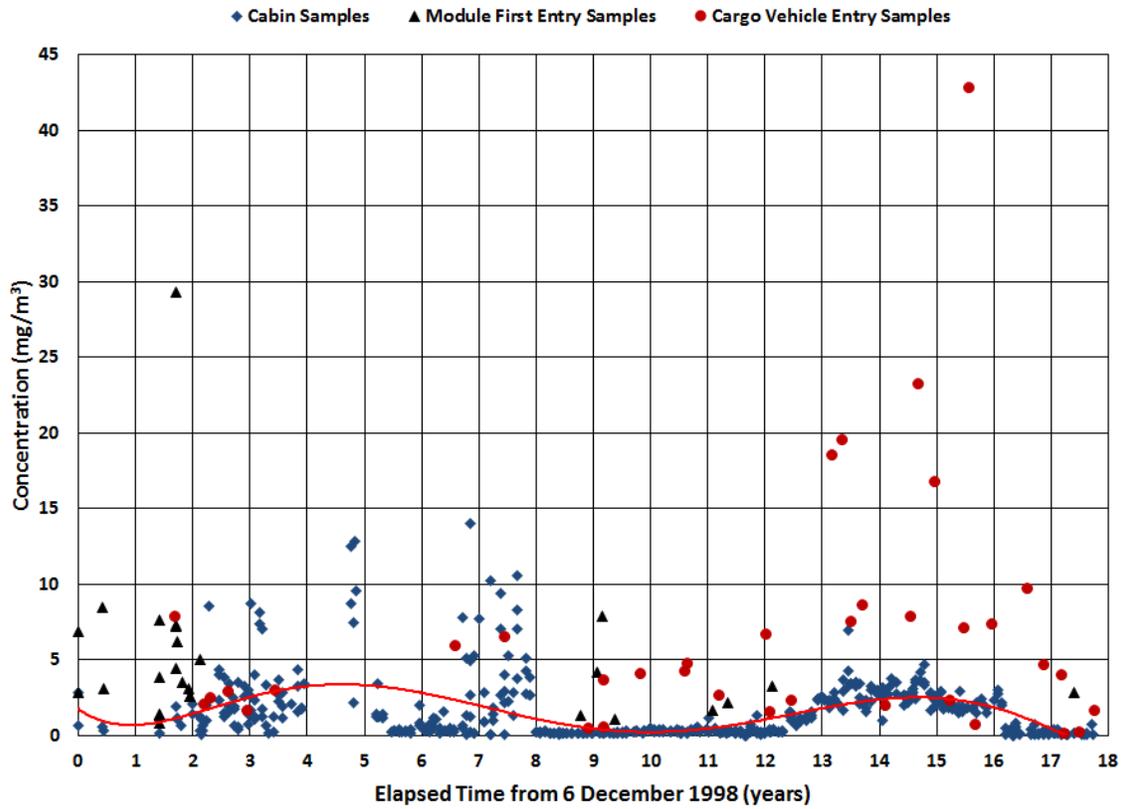


Figure 1. Total VMS concentration in the ISS cabin atmosphere. The trend line is a 6<sup>th</sup> order polynomial fit of the cabin sample data points.

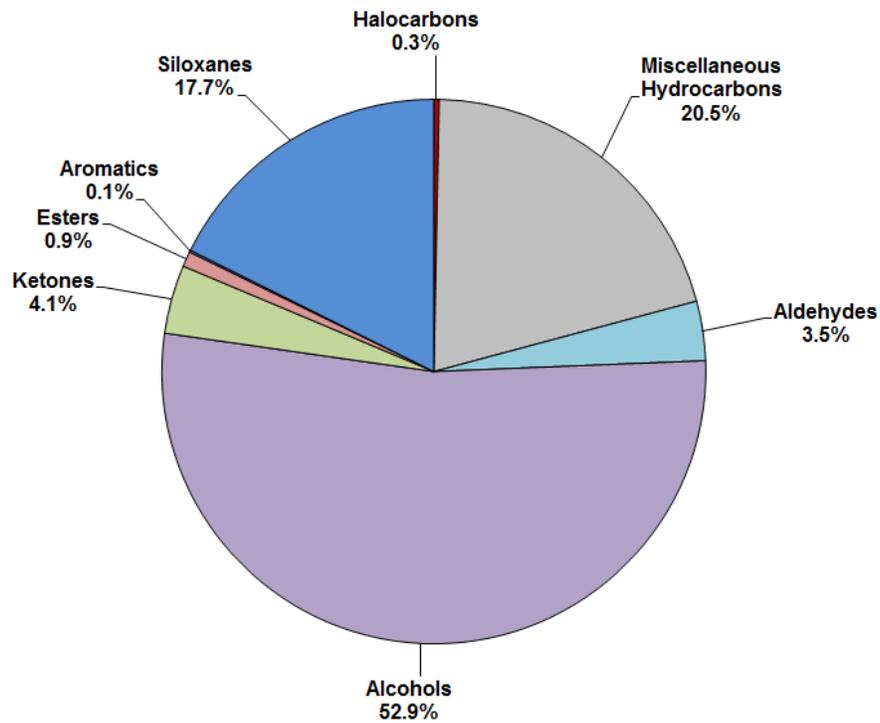


Figure 2. Functional group contributions to the non-methane VOC load in the ISS cabin atmosphere. VMS compounds contribute nearly 18% of the total load.

## II. Volatile Methyl Siloxane Removal Pathways Aboard the ISS

The cVMS compounds—D3, D4, and D5—as well as TMS and the VMS decomposition product dimethylsilanediol (DMSD) are well removed by activated carbon contained in the U.S. and Russian trace contaminant control (TCC) equipment which employ high aspect ratio adsorbent beds. Activated carbons with pore sizes between 1.7 nm and 3.0 nm have been reported to perform best for cVMS removal.<sup>4</sup> The most effective adsorbents provide a good match between surface area, pore size distribution, and VMS compound molecular size.<sup>4</sup> The activated carbon adsorption potential is such that single pass removal by the active TCC equipment aboard the ISS is 100% over the entire bed service lifetime. Besides activated carbon, VMS compounds can be removed by other porous sorbents such as silica gel and zeolites which may lead to incidental removal by the carbon dioxide removal equipment. Silica gel's VMS adsorption capacity can be four to five times greater than activated carbon's adsorption capacity under dry conditions; however, in the presence of moisture silica gel's capacity is markedly reduced to ineffective levels.<sup>4</sup> Ground testing has indicated a small removal contribution by carbon dioxide removal processes; therefore, incidental removal pathways are assumed to be <5% efficient. Once adsorbed to porous sorbents cVMS compounds partially polymerize making thermal regeneration difficult and leading to performance degradation over time.<sup>4</sup>

Calculations based on Henry's Law<sup>11</sup> show that cVMS compound removal by absorption into humidity condensate is very low at 10<sup>-8</sup>% to 10<sup>-7</sup>% on a single pass basis. Trimethylsilanol is removed by absorption into humidity condensate at 0.023% to 0.054% on a single pass basis. The Henry's Law coefficients provided by Table 1 are adjusted for the condensing heat exchanger (CHx) temperature condition using a vapor pressure ratio technique.<sup>12</sup> Humidity condensate absorption efficiency is calculated using the adjusted Henry's Law constants in Table 1 via the method documented by Ref. 11.

Some literature sources indicate that PDMS and cVMS compounds may adsorb to organic matter<sup>13</sup> and airborne particulate matter.<sup>14, 15</sup> However, the degree that interaction with airborne particulate matter may contribute to airborne siloxane removal is uncertain.<sup>3</sup> Recently, the tendency of VMS to sorb to aerosols has been quantified in relation to the available aerosol surface area.<sup>16</sup> Notably, only VMS compounds having *M* greater than those of hexadecamethylheptasiloxane (L7) and hexadecamethylcyclooctasiloxane (D8) are expected to partition from the vapor phase in this manner and therefore aerosol sorption is excluded as a significant removal route aboard the ISS.

A simple steady state cabin material balance, summarized by Table 2, was conducted according to the methods documented by Ref 11. This material balance, which is based on the average VMS compound concentrations observed before the supplemental trace contaminant control deployment in May 2015 and the average reported 35.7 mg DMSD/L in humidity condensate for this period, provides insight on the fate of these compounds. Not accounting for reaction as a removal mechanism, the active TCC equipment accounts for ~92% of the average cVMS removal and ~85% of the TMS removal from the cabin atmosphere. Other removal routes account for ~4%.

The DMSD cabin concentration in Table 2 is the gas phase concentration calculated to be in equilibrium at steady state with the 35.7 mg DMSD/L observed in the humidity condensate according to Henry's Law. Dimethylsilanediol is miscible in water and calculations based on Henry's Law predict 95% to 98% single pass removal via absorption into humidity condensate. Under this condition, Table 2 shows that 92% of volatilized DMSD is expected to be removed in humidity condensate with the remainder removed by TCC equipment.

As noted previously, VMS reaction is not considered in the simple material balance. The base VMS generation in Table 2 must be supplemented by the quantity that reacts to form DMSD. The following sections explore VMS stability and reaction pathways and applies them to the VMS material balance to achieve better mass accountability.

**Table 2. Cabin steady state material balance with no reaction considered.**

VMS COMPOUND	CABIN CONCENTRATION		REMOVAL RATES					BASE GENERATION	
			TCCS	BMP	CAA	SKV	OTHER	(mole/day)	(g/day)
	(mg/m <sup>3</sup> )	(mole/m <sup>3</sup> )	(mole/day)	(mole/day)	(mole/day)	(mole/day)	(mole/day)	(mole/day)	(g/day)
D3	1.12	5.03E-06	1.85E-03	3.02E-03	7.26E-10	7.39E-10	2.09E-04	5.07E-03	1.13E+00
D4	0.35	1.19E-06	4.36E-04	7.13E-04	1.52E-09	1.29E-09	4.94E-05	1.20E-03	3.56E-01
D5	0.29	7.71E-07	2.83E-04	4.63E-04	1.11E-09	7.99E-10	3.21E-05	7.78E-04	2.89E-01
TMS	0.29	3.04E-06	1.12E-03	1.82E-03	5.72E-06	5.72E-06	1.26E-04	3.08E-03	2.90E-01
DMSD	0.013	1.41E-07	5.18E-05	8.46E-05	1.10E-03	4.82E-04	5.87E-06	1.72E-03	1.58E-01

**Table 1. VMS compound Henry's Law constants and temperature adjustment factors at ISS CHx process conditions.**

VMS COMPOUND	HENRY'S LAW CONSTANT (mole/m <sup>3</sup> -Pa)	ADJUSTMENT FACTOR	
		14 °C	4.4 °C
D3	5.60E-06	0.4952	0.2522
D4	3.46E-05	0.4137	0.1760
D5	7.40E-05	0.3501	0.1262
TMS	7.00E-02	0.4820	0.2410
DMSD	2.80E+03	0.3180	0.1514

### III. Volatile Methyl Siloxane Stability

Stability of cVMS compounds and TMS has been evaluated in the atmosphere, water, and surface (soil) environmental compartments as an analogy for the ISS cabin environment. Understanding the cVMS and TMS stabilities in the different cabin environmental compartments is vital to developing active TCC strategies for VMS compounds. Stability in each environmental compartment is discussed and considerations for the reaction component basis of the cabin material balance are identified.

#### A. Stability in the Cabin Atmosphere

The reported VMS stability in air typically ranges between 2.5 and 11 days.<sup>4,17-19</sup> Reaction rates with ozone and ultraviolet radiation have been found to be very small in comparison to reaction with hydroxyl radicals in the atmosphere.<sup>4,6,20</sup> Therefore the former reactions are neglected when applying VMS compound gas phase stability considerations to the cabin material balance.

Reaction with the hydroxyl radical is the predominant mechanism for cVMS ring opening to produce oligomer siloxane diols.<sup>1,6,20,21</sup> The overall reaction of VMS compounds with hydroxyl radicals in air occurs via replacement of a methyl group at a silicon atom by a hydroxyl group.<sup>4</sup> The methyl group that has been displaced by the hydroxyl radical interacts with water to yield formaldehyde or formic acid. The reaction with hydroxyl radicals occurs as a repetitive sequence to the final end products which have been reported to consist of DMSD and some TMS which is also reported to react with hydroxyl radicals to form DMSD and methylsilanetriol (MST).<sup>4,18</sup> The TMS reaction with hydroxyl radicals to form DMSD is, therefore, important to understanding the observed correlation aboard the ISS between gas phase TMS in the cabin and DMSD in humidity condensate.<sup>22</sup>

Owing to the role of the hydroxyl radical to VMS compound stability in the atmosphere, understanding hydroxyl radical concentration levels and production mechanisms in indoor environments must be gained. Hydroxyl radical concentration in the troposphere, the atmospheric layer between Earth's surface and up to 20 km altitude, is in the parts per trillion (ppt) range but rises to 1 part per billion (ppb) at 50 km altitude.<sup>23</sup> In comparison, indoor hydroxyl radical concentrations are typically  $\sim 10^{-7}$  to  $10^{-5}$  ppb which can approach outdoor nighttime levels.<sup>24,25</sup> Indoor hydroxyl radical production and concentration maintenance relies on ozone infiltration into the living space via outdoor ventilation exchange<sup>26</sup> and an ultraviolet radiation source in combination with humidity.<sup>27</sup> In sealed indoor chamber tests that use purified facility air, the means to produce hydroxyl radicals is greatly reduced or eliminated because there is no ozone source or ultraviolet radiation source. Therefore, it is unlikely that gas phase VMS compound reaction with hydroxyl radicals would be observed in short duration ground-based tests conducted in indoor facilities. Similarly, the ISS does not have known ozone sources or a sustained ultraviolet radiation source to promote and sustain hydroxyl radical production by typical means. However, aboard the ISS, the ionizing radiation energies at 300 km to 400 km altitude are sufficient to ionize water.<sup>28</sup> Hydroxyl radicals are products of water radiolysis.<sup>29,30</sup> Further, both D3 and D4 are reported to undergo ring opening to form silanol species when irradiated by x-rays and gamma irradiation of silicone elastomers is reported to produce TMS and cVMS species.<sup>4</sup> These observations indicate that the radiation environment may play a role in VMS stability aboard the ISS by contributing to cVMS ring opening, silicone material degradation leading to offgassing, and forming hydroxyl radicals. The gas phase VMS reaction pathway with hydroxyl radicals, therefore, is considered to be plausible aboard the ISS.

The tropospheric half-life for D3 via its reaction with hydroxyl radicals is up to 30 days which is typically about two to three times longer than the half-life for D4 and D5.<sup>10</sup> The half-life for D4 is reported to range between 5.5 days and 10.6 days<sup>2</sup> while the half-life for D5 is reported to range between 5.2 days and 10 days.<sup>3,10,14,31</sup> The D5 half-life in urban areas has been reported to range between 0.6 and 2.6 days.<sup>14</sup> Trimethylsilanol is reported to react with hydroxyl radicals more readily than cVMS compounds with reported half-lives of 2.5 days to 4 days.<sup>18,19</sup> Dimethylsilanediol is also reported to react with hydroxyl radicals to form MST with a half-life of  $\sim 7.5$  days.<sup>18</sup>

In comparison, the time to provide >95% VMS contamination level reduction in the ISS cabin via the primary removal pathways described by Section II is approximately 60 hours (2.5 days). The removal pathways for DMSD which are predominately via absorption in humidity condensate result in an  $\sim 4.8$ -hour dwell time in the cabin. Based on these cabin dwell times and the reported half-lives, the estimated theoretical daily atmospheric degradation could be as high as approximately 4% of D3, 11.8% to 22.8% of D4, 12.5% to 24.1% of D5, 31.3% to 50% of TMS, and 1.3% of DMSD present in the cabin atmosphere. These theoretical daily VMS degradation percentages combined with rapid DMSD scrubbing before it reacts are key considerations for the cabin material balance.

#### B. Stability in Humidity Condensate

The half-life of cVMS compounds in water is highly dependent on pH and temperature. The humidity condensate pH is typically nearly neutral averaging 7.2. At neutral pH and 25 °C, the half-life for D5 is reported to be 71

days.<sup>14</sup> At the same conditions, the half-life for D4 is reported to be similar at 70.4 days.<sup>31</sup> As the temperature decreases at neutral pH the half-life increases.<sup>2</sup> The reported half-life for D5 is 315 days at 12 °C,<sup>14</sup> which is close to the 4.4 °C U.S. Common Cabin Air Assembly (CCAA) operating temperature and 14 °C Russian condensing heat exchanger assembly (Russian acronym SKV) operating temperature. Although hydrolysis to DMSD products does occur in water, the CCAA and SKV operating conditions appear to be incompatible with liquid phase hydrolysis.

In addition to operating conditions within the condensing heat exchanger process equipment that are incompatible with cVMS hydrolysis, the cVMS compounds' very low solubility in water further demotes wet deposition to a very minor contributor to the observed DMSD in the humidity condensate. On further evaluation, if liquid phase decomposition is hypothetically considered significant then the typical average DMSD condensate loading of 35.7 mg/L (3.3 mole/L) requires 1.1 mole/L of total cVMS in the condensate. Yet the cVMS Henry's Law partitioning between the gas and liquid phases and the observed cVMS concentration in the cabin indicates the maximum cVMS loading in the condensate is  $2.4 \times 10^{-8}$  mole/L. Therefore, while it is expected that the cVMS absorbed into humidity condensate will undergo hydrolysis, this quantity is insufficient to account for the observed DMSD loading in the humidity condensate and this route can be neglected for the overall material balance.

### C. Stability on Surfaces

The interaction of cVMS compounds with soil is an approximate analogue for their interaction with the coated surfaces in the CCAA's condensing heat exchanger. Soil half-lives for D4 have been reported to range between 3.5 and 5.3 days at 32% relative humidity and 93% relative humidity conditions, respectively.<sup>2,9</sup> The D5 half-life is reported to range between 9 days and 13 days.<sup>9</sup> Hydrolysis is reported to be rapid under low moisture conditions <1%.<sup>13</sup> Additional reports describe rapid hydrolysis in dry soils in equilibrium with air at relative humidity conditions up to 90%.<sup>14</sup> However, under high moisture conditions, hydrolysis rates decrease substantially, particularly as the moisture condition rises above 3.56%.<sup>13</sup> Observations also report that the hydrolysis rate in soils is unmeasurable at water content >8%.<sup>32</sup> As well, rewetting soil to a saturated condition quenches the hydrolysis reaction.<sup>33</sup>

This information indicates that it is very plausible for cVMS compound hydrolysis to occur on dry heat exchanger surfaces in equilibrium with the cabin humidity level which typically ranges between 35% and 45%. These observations also indicate the potential role that rewetting the condensing heat exchanger surfaces after a dryout period may play in producing volatile siloxane diols, including DMSD. As cVMS compounds adsorb onto the dry surfaces within the condensing heat exchanger under the gas phase humidity conditions produced within the heat exchanger core, they hydrolyze to volatile siloxane diols, including DMSD, which then evaporate from the surface. Volatilization rates for DMSD from soil have been reported to range between ~1% and 7% per week.<sup>9</sup> The volatilization rate from heat exchanger surfaces is unknown; however, for purposes of analysis it is assumed that the volatile siloxane diols completely evaporate as they are formed. These volatile siloxane diols then absorb into the humidity condensate in the wetted sections of the condensing heat exchanger. Once in the humidity condensate, the volatile siloxane diols can hydrolyze further. During heat exchanger dryout periods, the dry surface area is much greater leading to a greater potential for hydrolysis products to be produced. However, upon rewetting, those surfaces possess a water content that is incompatible to sustain the hydrolysis reaction. Therefore, maintaining a humidity condensate film on large percentage of the heat exchanger surfaces may serve to minimize DMSD production via this route.

The fraction of the heat exchanger surfaces that remain dry at all times are assumed to retain their activity for promoting the hydrolysis reaction. Based on reported half-lives for D4 and D5, hydrolysis of cVMS compounds in contact with the dry heat exchanger surfaces may range between 4% and 14% per day. While a likely source of DMSD, this pathway is smaller in magnitude compared to the gas phase hydrolysis pathway. The potential for TMS to react via this pathway is unknown.

### D. Interaction with Surfaces

Siloxane chemical reactions with surfaces of oxidized silicon (Si), titanium (Ti), aluminum (Al), and nickel (Ni) show reactions leading to covalently-attached monolayer of siloxane polymer chains that cause a surface to become hydrophobic. Water assists in the equilibrium.<sup>33</sup> Inorganic oxide surfaces can also become hydrophobic from interaction with DMSD. Water is the only byproduct in these reactions between siloxanes and inorganic oxide surfaces.<sup>34</sup> Such interactions are consistent with observations of the ISS CHx surfaces losing their hydrophilic properties over their lifetime. Upon installing a new heat exchanger, the surfaces must load with cVMS compounds to reach a condition where DMSD production becomes significant. Other compounds such as phthalates, long-chain fatty acids, and long chain hydrocarbons may also play a role in CHx surface property changes; however, their contribution relative to that of siloxanes is unknown. Given that siloxanes are routinely observed in cabin air quality measurements, their contribution to changes in CHx surface hydrophilic character is considered to be dominant.

#### IV. Evidence for a Dominant Volatile Methyl Siloxane Decomposition Pathway

On evaluating the gas phase and surface interaction stabilities by comparing the range of half-lives reported for the different environmental compartments it is estimated that approximately 88% to 94% of the volatile silicon diol load may originate from hydroxyl radical-induced gas phase reaction and approximately 6% to 12% may originate from surface-catalyzed hydrolysis. This indicates a dominant gas phase VMS decomposition pathway. Observations that are consistent with a dominant atmospheric decomposition pathway have been made during ground-based testing and aboard the ISS. These observations are presented and discussed.

##### A. Evidence from Ground Testing

The effect of various linear (L2-L5) and cyclic (D3-D6) siloxane cabin atmosphere concentrations on humidity condensate DMSD loading was studied on the ground by utilizing a flight-like, hydrophilic coated CHx. Testing was performed in the Regenerative Environmental Control and Life Support Module Simulator (REMS) facility at the Marshall Space Flight Center (MSFC) as described by Ref. 35. Test conditions were maintained to mimic operations aboard ISS and featured two wet CHx phases and a cabin VMS load of equivalent magnitude and of half-magnitude of the levels aboard ISS. At the end of each wet phase, a 3-day CHx dryout was maintained. Humidity condensate sampling post-dry out was analyzed for DMSD and revealed a unique condensate volume dependent washout profile. No correlation between atmospheric siloxane levels and DMSD condensate levels was observed. Furthermore, it was shown that DMSD could be produced post CHx dryout with no atmospheric siloxane loading indicating the impact of adsorbed VMS residues which partition with the surface treated CHx despite their inherent hydrophobicity. Remarkably, DMSD concentrations in the condensate were consistently measured at only a few mg/L (i.e.  $10^0$  mg/L order of magnitude). The observed levels were also consistent with ground testing conducted in 2013 at MSFC in both the REMS and Environmental Chamber utilizing cyclic and linear siloxane doses as well as personal care products such as hand lotion, hair shampoo and conditioner, and antiperspirant, containing primarily dimethicone.

##### B. Evidence Aboard the ISS

Trace constituent concentrations in the ISS cabin atmosphere are typically uniform across the habitable cabin. The VMS compounds are no exception with a total VMS concentration ratio of 0.93 between the U.S. Lab and the Russian Service Module for grab sample pairs collected between June 2011 and August 2016. Humidity condensate samples collected from the Service Module in November 2010 indicate a gas phase DMSD concentration of approximately  $0.016 \text{ mg/m}^3$ . The U.S. humidity condensate sample collected near this time period in October 2010 indicates a gas phase DMSD concentration of approximately  $0.015 \text{ mg/m}^3$ . The resulting concentration ratio between the U.S. Laboratory Module and the Russian Service Module is 0.94 which is consistent with the typical ratio for the VMS compounds. This is an important observation because the condensing heat exchanger in the Russian Service Module does not contain a coating suspected of promoting VMS hydrolysis. While it is unfortunate that more paired sample sets are not available for analysis, the indication that DMSD is present at a uniform concentration in both the ISS U.S. and Russian segments points toward the plausibility of a gas phase DMSD source.

A cabin grab sample was collected in the Service Module within 48 hours of the November 2010 Russian humidity condensate sample. This humidity condensate-cabin grab sample pair also exhibits the strong correlation between DMSD and TMS reported elsewhere.<sup>22</sup> Including this additional sample pair in the previous correlation analysis results in a stronger positive Pearson correlation by increasing the coefficient magnitude from 0.8 to 0.83. On further analysis of this correlation using the Spearman's Rank analysis technique,<sup>36</sup> the correlation's likelihood for occurring by chance is found to be  $\sim 0.9\%$ . This additional correlation analysis indicates that the link between DMSD in humidity condensate and VMS compounds in the cabin atmosphere is not mere coincidence.

Additional evidence supporting the plausibility for a gas phase DMSD production mechanism is indicated by the DMSD concentration reported in humidity condensate sample analyses being unaffected by reducing the VMS concentration in the cabin by  $>50\%$ . The nearly 3.25 theoretical moles of DMSD produced by one mole of mixed VMS compounds contributes to this stubborn challenge. If a gas phase mechanism were not occurring, then reducing the cabin's VMS concentration would have a greater impact on the slower surface reaction as indicated by the difference in half-lives between the surface and atmospheric environmental compartments.

According to this evidence, the combination of observed DMSD loading in both the Russian and U.S. humidity condensate samples, the correlation between gas phase VMS-condensate DMSD correlation, and the DMSD loading's persistence all support gas phase hydrolysis as a plausible and dominant VMS reaction mechanism aboard the ISS.

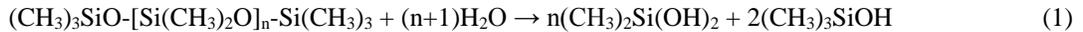
## V. Volatile Methyl Siloxane Stability Applied to the Cabin Material Balance

Based on the literature and supporting evidence from ground-based testing and aboard the ISS, the hydrolysis to volatile oligomer silicon diols in the ISS cabin atmosphere and on the dry fraction of the heat exchanger surfaces are the most plausible mechanisms for producing DMSD in the ISS cabin environment. Of these two mechanisms, the atmospheric mechanism appears to be the dominant route for VMS reaction to yield DMSD. To apply these observations to the material balance, the atmospheric decomposition pathway must be understood. The following discussion presents the characteristics of the primary reaction pathway and the implications for the cabin material balance.

### A. Volatile Methyl Siloxane Decomposition Pathways

Decomposition of linear and cyclic VMS compounds by hydrolysis to yield DMSD consists of multiple steps.<sup>21</sup> Sequential reaction with water by Si-O-Si bond scission yields volatile oligomeric siloxane diols which are soluble in water. With each successive hydrolysis reaction, the resulting diol oligomers become increasingly soluble in water allowing their removal from the atmosphere by wet deposition.<sup>6</sup> This sequential hydrolysis reaction ultimately yields DMSD and small quantities of MST.

For linear VMS compounds, TMS is also formed from terminal trimethyl groups.<sup>13</sup> The multi-step hydrolysis mechanism for linear VMS compounds is best described according to the following chemical equation.<sup>32</sup>



In Eq. 1,  $n$  equals 1, 2, and 3 for octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), and dodecamethylpentasiloxane (L5), respectively. Using this reaction sequence, for each mole of L3 that reacts, one mole of DMSD and two moles of TMS are produced. Similarly, for each mole of L4 that reacts, two moles of DMSD and two moles of TMS are produced while for each mole of L5 that reacts, three moles of DMSD and two moles of TMS are produced. An equimolar mixture of L3, L4, and L5 can theoretically yield two moles of DMSD and two moles of TMS for each mole of the mixture that completely reacts. This pathway may occur in air, in water, or on surfaces as illustrated by Fig. 3.<sup>9</sup> Determining in which environmental compartment the degradation is dominant is important to evaluating mitigation options. As indicated by Fig. 3, DMSD continues to react via oxidation pathways to eventually form silica ( $\text{SiO}_2$ ) and carbon dioxide ( $\text{CO}_2$ ). Section III notes that MST may be formed as an intermediate product.

The reaction pathway for cVMS compounds begins with molecular ring opening followed by sequential hydrolysis reactions. In the case of cVMS compounds, Eq. 1 simplifies to produce only DMSD according to Eq. 2 by which



the moles of DMSD produced by the hydrolysis of a single mole of the cVMS compound is equal to the number of  $\text{Si}(\text{CH}_3)_2\text{O}$  units in the cVMS molecule. Thus, one mole of D3 can theoretically produce three moles of DMSD while D4 and D5 can theoretically produce four and five moles of DMSD, respectively. An equimolar mixture of D3, D4, and D5 can theoretically yield four moles of DMSD for each mole of the mixture that completely reacts. Therefore, the hydrolysis of cVMS compounds is theoretically a greater source of DMSD compared to linear VMS decomposition. However, TMS produced by linear VMS decomposition can ultimately decompose to DMSD. If TMS produced by linear VMS hydrolysis further decomposes to DMSD, then an equimolar mixture of linear VMS compounds may theoretically yield six moles of DMSD for each mole of the mixture that completely reacts.

### B. Experimental Program Development to Confirm VMS Decomposition Pathways

The VMS reaction pathways are complex and the conditions aboard the ISS are difficult to simulate in ground-based laboratories. Experimental protocols and methods must be developed to test these reaction pathways.

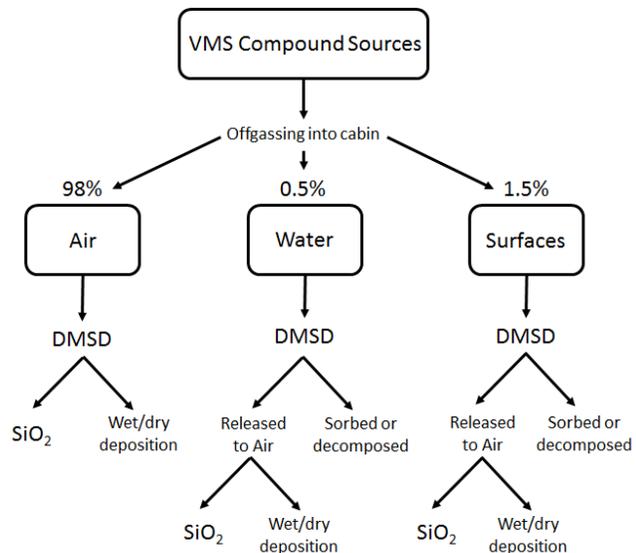


Figure 3. VMS compound environmental compartment partitioning and decomposition. Adapted from Ref. 9.

### C. Cabin Material Balance Incorporating Volatile Methyl Siloxane Reaction

The cabin material balance approach described by Ref. 11 must incorporate a reaction term based on the Eq. 2 stoichiometry to estimate the moles of VMS compounds that react to form DMSD. The quantity of VMS compounds that react are then added to the base load in Table 2 to determine the total VMS generation load. Equation 3 is the simplified material balance on a molar basis.

$$\frac{d\dot{n}_{VMS}}{dt} = \dot{n}_{VMS-generated} - \dot{n}_{VMS-removed} - \dot{n}_{VMS-reacted} \quad (3)$$

At steady state the time dependent term approaches zero yielding Eq. 4. The active removal term is described by

$$\dot{n}_{VMS-generated} = \dot{n}_{VMS-removed} + \dot{n}_{VMS-reacted} \quad (4)$$

Eq. 5 where the term  $\Sigma\eta\dot{v}$  is the total effective flow rate accounting for all active trace contaminant removal routes.

$$\dot{n}_{VMS-removed} = C_{VMS} \Sigma\eta\dot{v} \quad (5)$$

The relationship between the moles of DMSD produced and the moles of each VMS compound that reacts is provided by Eq. 6.

$$\dot{n}_{DMSD} = \dot{n}_{D3,r} \left( \frac{3DMSD}{D3} \right) + \dot{n}_{D4,r} \left( \frac{4DMSD}{D4} \right) + \dot{n}_{D5,r} \left( \frac{5DMSD}{D5} \right) + \dot{n}_{TMS,r} \left( \frac{1DMSD}{TMS} \right) \quad (6)$$

In Eq. 6,  $\dot{n}_{Di,r}$  is the molar reaction rate of each VMS compound to produce DMSD. Each VMS compound's molar reaction rate  $\dot{n}_{Di,r}$  is defined by Eq. 7 where  $y_{Di}$  is the VMS compound mole fraction in the atmosphere and  $\dot{n}_{VMS}$  is the

$$\dot{n}_{Di,r} = y_{Di} \dot{n}_{VMS} \quad (7)$$

total VMS molar reaction rate. Incorporating the theoretical extent of reaction,  $X_i$ , yields Eq. 8. The theoretical extent of reaction is derived from the VMS compound half-life data. By substituting Eq. 8 into Eq. 6 and rearranging,

$$\dot{n}_{Di,r} = y_{Di} \dot{n}_{VMS} X_{Di} \quad (8)$$

the total VMS reaction rate is found using Eq. 9. The term,  $\alpha$ , in Eq. 9 is the overall fractional yield applied to the

$$\dot{n}_{VMS-reacted} = \frac{\dot{n}_{DMSD}}{\left( 3y_{D3}X_{D3} + 4y_{D4}X_{D4} + 5y_{D5}X_{D5} + 1y_{TMS}X_{TMS} \right)} \times \alpha \quad (9)$$

total VMS compound theoretical extent of reaction. Equation 9 is used as the reaction term in the overall cabin material balance. Substituting Eqs. 5 and 9 into Eq. 4 yields the cabin material balance. This balance, Eq. 10, is implicit

$$\dot{n}_{VMS-generated} = C_{VMS} \Sigma\eta\dot{v} + \frac{\dot{n}_{DMSD}}{\alpha \Sigma y_i \dot{n}_{VMS-generated} X_i} \quad (10)$$

in the VMS generation term,  $\dot{n}_{VMS-generated}$ , requiring an iterative approach to obtain the steady state balance for the VMS and DMSD cabin concentration condition based on the extent of VMS compound reaction and the overall fractional yield.

The material balance calculation basis is the DMSD cabin concentration calculated by applying Henry's Law to the reported humidity condensate loading. Considering a dominant airborne hydrolysis pathway and the range of atmospheric half-lives, the material balance for the ISS cabin environment based on the cabin concentrations in Table 2 indicates that between 7% and 8% of the total VMS compound load must react to account for the DMSD load. It is estimated that between ~0.13 grams and ~0.14 grams total VMS per day must react to account for the observed DMSD loading in the humidity condensate. This amount of VMS generation must be added to the base generation in Table 2.

Estimating the relative contribution from each VMS compound must take into account the half-life ranges, the strength of correlation between each VMS compound and the DMSD concentration in humidity condensate, the cabin VMS compound mole fraction, and the approach to theoretical reaction yield. Evaluating the VMS compound half-lives in the atmosphere and in soil indicate that D4, D5, and TMS may be the primary contributors to the DMSD load with D3 contributing to a lesser extent. The order of contribution based on half-lives is TMS>D5>D4>D3. This observation is consistent with correlation assessment of cabin cVMS species and TMS concentrations versus the DMSD level in humidity condensate which indicates the correlation strength between cabin

cVMS species and TMS concentrations and the DMSD level in the condensate as D4>TMS>D5>D3.<sup>22</sup> However, on considering the combination of cabin VMS compound mole fractions in combination with the half-life ranges while also considering a fractional approach to theoretical yield shows that the ISS cabin condition is consistent with a contribution order of TMS>D4>D5>D3. In this condition, D4 exhibits a short half-life while D3, D5, and TMS exhibit long half-lives. An overall fractional yield of 51% results in a balanced condition that agrees best with the conditions observed aboard the ISS.

Upon incorporating the Eq. 2 reaction mechanism and the fractional yield into the VMS material balance via Eq. 10, the total VMS generation in Table 3 is obtained. The total VMS generation in Table 3 is ~6% higher than that obtained by the simple material balance presented by Table 2. This difference accounts for the fraction of the total VMS load that reacts. Examining the total generation rates listed in Table 3 indicate the fraction of the daily molar load that decomposes for each compound is ~2.5% for D3, ~12.8% for D4, ~7.5% for D5, and ~9.2% for TMS.

**Table 3. Total VMS generation compared to base generation.**

VMS COMPOUND	CABIN CONCENTRATION		BASE GENERATION		REACTION		TOTAL GENERATION	
	(mg/m <sup>3</sup> )	(mole/m <sup>3</sup> )	(mole/day)	(g/day)	(mole/day)	(g/day)	(mole/day)	(g/day)
D3	1.12	5.03E-06	5.07E-03	1.13E+00	1.31E-04	2.91E-02	5.20E-03	1.16E+00
D4	0.35	1.19E-06	1.20E-03	3.56E-01	1.75E-04	5.20E-02	1.37E-03	4.08E-01
D5	0.29	7.71E-07	7.78E-04	2.89E-01	6.26E-05	2.32E-02	8.41E-04	3.12E-01
TMS	0.29	3.04E-06	3.08E-03	2.90E-01	3.13E-04	2.95E-02	3.39E-03	3.19E-01
DMSD	0.013	1.41E-07	1.72E-03	1.58E-01	0.00E+00	0.00E+00	1.72E-03	1.58E-01

## VI. Implications for Life Support Systems

The pervasive nature of the VMS contamination control challenge coupled with their potential for degrading the performance of some life support system process equipment presents implications not only for the ISS but also future crewed exploration missions. Approaches for reducing the DMSD load in humidity condensate, VMS compound source control, and future life support system design considerations are presented by the following discussion.

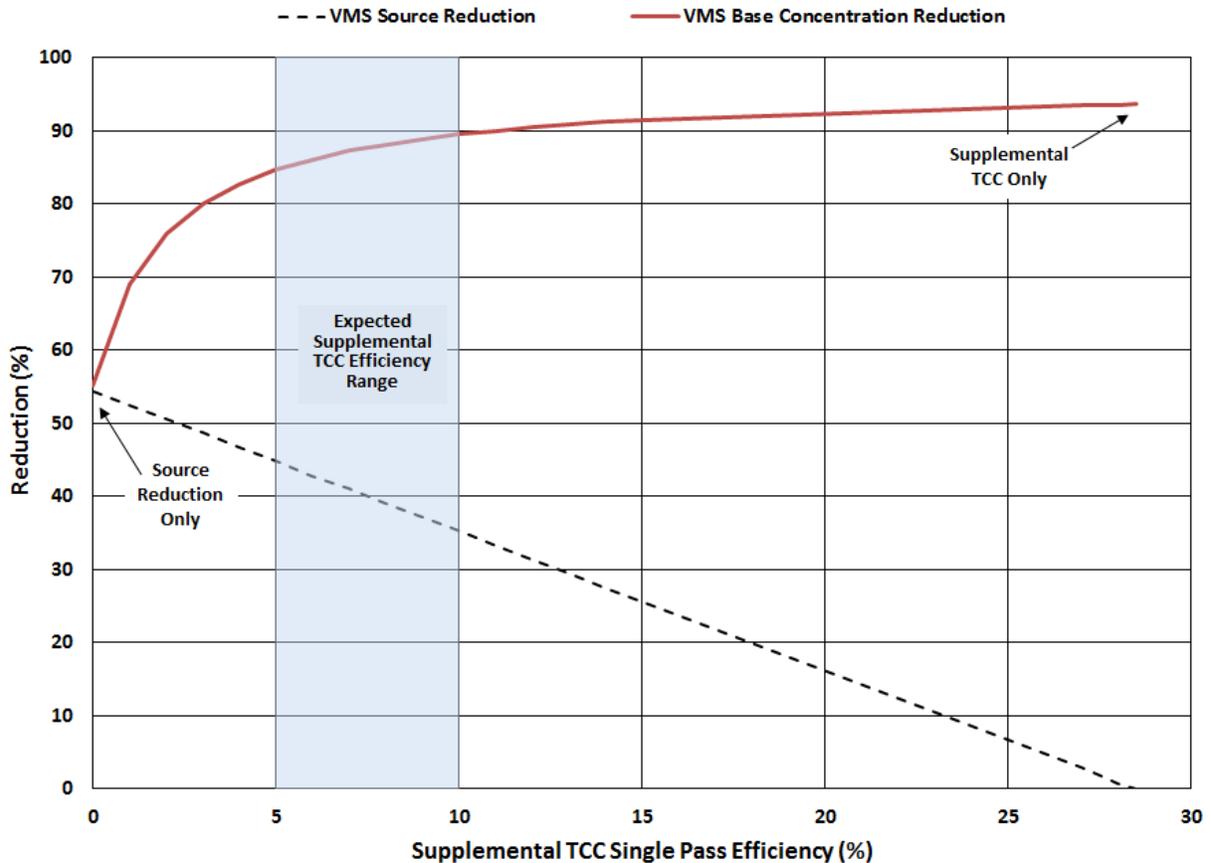
### A. Supplemental Active Trace Contaminant Control

Aboard the ISS the effective process air flow for VMS compound removal provided by the U.S. Trace Contaminant Control Subassembly (TCCS) and the Russian Micropurification Assembly (BMP) supplemented by incidental removal by humidity control equipment and other removal routes is ~42 m<sup>3</sup>/h. High flow, low aspect ratio adsorbent beds installed in the cabin ventilation system have been leading candidates for providing this supplemental capability.<sup>22, 37</sup> An approach for providing supplemental TCC capability aboard the ISS replaces twenty-one particulate filter elements in the cabin ventilation system with a new design that incorporates activated carbon adsorbent media. This approach can provide approximately 2140 m<sup>3</sup>/h total flow. However, high flow, low aspect ratio packed adsorbent bed designs typically provide low single pass removal efficiencies. It is estimated that the filter design for the ISS may provide between 5% and 10% single pass efficiency yielding no more than 214 m<sup>3</sup>/h of effective flow.

Based on Henry's Law analysis, reducing the DMSD concentration in humidity condensate by 50% requires maintaining the cabin DMSD concentration to <0.006 mg/m<sup>3</sup>. This DMSD concentration threshold is the basis for the material balance summarized by Table 4 which also uses the 51% theoretical yield factor for total VMS hydrolysis in the cabin environment and accounts for 149.8 m<sup>3</sup>/h supplemental TCC flow—2140 m<sup>3</sup>/h at 7% single pass efficiency. Under such conditions the total cabin VMS concentration of 2.05 mg/m<sup>3</sup> in Table 2 must be reduced by 87.3% to 0.26 mg/m<sup>3</sup>. At the same time, the 1.28 g/day total VMS generation noted in Table 4 is ~41% lower than the 2.19 g/day in Table 3. This observation indicates that adding supplemental TCC capacity alone may be insufficient and efforts to reduce the total VMS generation rate should be included in an overall VMS control strategy.

**Table 4. Steady state material balance yielding a 50% lower DMSD concentration in humidity condensate.**

VMS COMPOUND	CABIN CONCENTRATION		REMOVAL RATES					TOTAL GENERATION	
			TCCS	BMP	CCA	SKV	OTHER		
	(mg/m <sup>3</sup> )	(mole/m <sup>3</sup> )	(mole/day)	(mole/day)	(mole/day)	(mole/day)	(mole/day)	(mole/day)	(g/day)
D3	0.1427	6.41E-07	2.36E-04	3.85E-04	9.25E-11	9.42E-11	2.33E-03	3.02E-03	6.72E-01
D4	0.0450	1.52E-07	5.57E-05	9.09E-05	1.93E-10	1.65E-10	5.51E-04	7.86E-04	2.33E-01
D5	0.0365	9.83E-08	3.61E-05	5.90E-05	1.41E-10	1.02E-10	3.58E-04	4.84E-04	1.80E-01
TMS	0.0365	3.87E-07	1.42E-04	2.32E-04	7.29E-07	7.29E-07	1.41E-03	2.09E-03	1.97E-01
DMSD	0.00592	6.42E-08	2.36E-05	3.85E-05	4.99E-04	2.19E-04	2.34E-04	1.01E-03	9.35E-02



**Figure 4. Total VMS compound source reduction and supplemental TCC performance necessary for 50% DMSD loading reduction in humidity condensate.**

Figure 4 explores the interaction between the supplemental TCC performance based on redesigned ISS filter elements and source reduction necessary to achieve a cabin condition that yields 50% lower DMSD loading in humidity condensate. There are two extremes illustrated by Fig. 4 in this interaction—source reduction only and supplemental TCC only. For the case employing source reduction alone represented by the source reduction curve intersection at the y-axis, the total VMS sources must be reduced by 54% to achieve 50% lower DMSD loading in humidity condensate. At the opposite extreme the supplemental TCC must provide 28.5% single pass efficiency, equivalent to ~610 m<sup>3</sup>/h effective supplemental removal flow if VMS sources are not reduced. Providing such a capability is a difficult technical challenge within existing ISS filter element volume and cabin fan performance constraints because higher single pass efficiency requires greater adsorbent bed depth which cannot be accommodated within the ventilation system’s pressure drop and cabin acoustic noise allocations. The supplemental TCC efficiency for a cabin particulate filter element retrofit as described by Ref. 22 is predicted to fall between 5% and 10%. Therefore, the material balance analysis depicted by Fig. 4 indicates that measures to reduce VMS sources aboard the ISS by 35% to 45% must be undertaken in combination with deploying supplemental TCC capability.

### **B. Volatile Methyl Siloxane Source Control**

Reducing the total VMS concentration in the cabin atmosphere is the objective for strategies based on supplemental cabin TCC to mitigate DMSD loading in humidity condensate yet it may be quite challenging to achieve the necessary concentration reduction without also addressing total VMS source control. As noted in the previous section, achieving a minimum supplemental trace contaminant control performance is necessary to avoid considering VMS compound source control beyond the standard material selection and control program. Yet, as illustrated by Fig. 4, a robust material selection and control program with greater emphasis on VMS sources may be beneficial by reducing the supplemental TCC performance target. As noted in Section I, VMS compounds in personal care products and residues in PDMS-based materials volatilize into the cabin atmosphere. Therefore, a key to source reduc-

tion is understanding aspects of VMS compound physical and chemical properties, particularly their vapor pressures. Such understanding may prove useful for conducting early materials screening assessments.

The liquid vapor pressures ( $P_L$ ) at 25 °C of cyclic (D4 - D10) and linear (L5 - L13) siloxanes are remarkably linear with additional dimethylsiloxane units ( $M$ , g/mol) as displayed by Eq. 11 and 12, respectively.<sup>38</sup> The increased volatility of cyclic compounds is related both to structural chemical differences as well as reduced intermolecular attraction between cyclic VMS compounds over linear counterparts.

$$\log_{10} P_L(Pa) = -0.0115M + 5.5098 \quad (11)$$

$$\log_{10} P_L(Pa) = -0.0122M + 5.3945 \quad (12)$$

Additionally, the vapor pressure of low  $M$  VMS compounds as well as the critical properties for the VMS compounds of interest have been reported.<sup>39</sup> Note that D3 is unique in that it sublimates from its solid state and is the most volatile of the cyclic siloxanes with a vapor pressure of 570 Pa at 25 °C.<sup>40</sup> Its crystalline nature is likely related to the inflexibility of the three-membered ring. As indicated by the vapor pressure correlations, the volatile nature of VMS compounds may present challenges to source reduction efforts. Yet, screening materials for their VMS offgassing potential based on their VMS content applied to vapor pressure may prove to be a useful material screening method.

### C. Design Considerations for Exploration Missions

Recently, areas of the ECLS architecture most sensitive to VMS and DMSD exposure have been identified. Specifically, these include the multifiltration (MF) beds within the water processor assembly (WPA)<sup>41-43</sup> and the high-temperature catalytic oxidizer (HTCO) within the TCCS.<sup>44</sup>

Protecting the WPA is necessary as DMSD tends to saturate both MF Beds, is oxidized to a limited extent by the WPA catalytic reactor, and eventually is detected in the potable water supply. Resolution of this problem has typically been MF Bed replacement at significant launch mass penalty. Some relief may be realized by pursuing WPA upgrades,<sup>45</sup> such as the recently developed high activity catalyst,<sup>46</sup> but none will ultimately solve the problem of DMSD entering the wastewater stream via the CCAA. As discussed in previous sections, the low single-pass efficiency of the proposed cabin filter element retrofit will be insufficient to address this problem alone and additional remediation steps must be taken in order to protect the WPA.

Protection of the HTCO is currently guaranteed aboard the ISS by the arrangement of the upstream, low-flow activated charcoal adsorption bed. The absolute necessity to protect the HTCO from VMS exposure was demonstrated by the observed loss in VOC oxidation efficiency during concurrent, unintentional oxidation of silicone offgassed products (D4, D5, and D6) in the process stream during 2015 testing at MSFC.<sup>43</sup> As such, ECLS exploration architecture designs must be cognizant of the contents and purity of process inlet streams to prevent irreversible catalytic activity losses from Si deposition or mineralization.

Note that the challenge for exploration missions may not be to the extent of ISS because VMS sources associated with repetitive logistics resupply from Earth as illustrated in Fig. 1 will not be the norm. Trimethylsilanol is likely the greatest challenge due to removal needs and may become a driver for future exploration TCC design to minimize DMSD levels in humidity condensate.

## VII. Conclusion

The dominant VMS compound degradation pathway appears to be in the cabin atmosphere via reaction with hydroxyl radicals and hydrolysis to yield water soluble, volatile oligomeric siloxane diols, including DMSD. A secondary pathway also releases DMSD into the gas phase via VMS compound hydrolysis on dry condensing heat exchanger surfaces. Both the atmospheric and surface catalyzed mechanisms are directly influenced by the total VMS compound concentration in the cabin atmosphere; therefore, the observed strong positive correlation between VMS compound concentrations in the cabin atmosphere and DMSD in the humidity condensate is expected. The total VMS compound concentration in the ISS cabin atmosphere is in large stoichiometric excess as only ~6% of the total VMS compound load in the cabin environment must react on average to produce the amount of DMSD observed in humidity condensate.

Assessing VMS compound half-lives in the atmosphere and in soil indicate that D4, D5, and TMS may be the primary contributors to the DMSD load with D3 contributing to a lesser extent. The order of contribution based on correlation assessment of the cVMS and TMS concentrations reported in cabin grab samples and DMSD in humidity condensate samples is D4>TMS>D5>D3. However, a cabin material balance sensitivity analysis considering VMS compound concentration ranges as well as the variability in half-lives shows that there are plausible conditions for a contribution order of TMS>D4>D5>D3. These observations are consistent given they are within the material bal-

ance sensitivity range. Overall, the in-flight observations and the cabin material balance indicate that D4, D5, and TMS are the most likely contributors to the DMSD load in the humidity condensate.

Reducing the DMSD concentration in humidity condensate requires supplemental TCC capability and other methods to eliminate the excess VMS compound reactant concentration and maintain a cabin concentration closer to a theoretical stoichiometric ratio with the hydrolysis reaction. At prevailing VMS compound cabin generation loads, reducing the cabin concentrations by ~87% is predicted to reduce the DMSD load in humidity condensate by 50%. This requires a combination of supplemental TCC capability aided by reducing VMS compound sources aboard the ISS.

Observations and experience gained aboard the ISS present valuable lessons learned for future exploration mission vehicle and life support system design, particularly the TCC and water processing processes. Vehicle materials and crew preference items will need careful screening and selection to reduce functional impacts from VMS compounds. The TCC and water processing systems will also need to be functionally robust and integrated in a manner that incorporates protective features to prevent resource consumption and fouling by VMS compounds and their decomposition products.

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