

Predicting Air Quality at First Ingress into Vehicles Visiting the International Space Station

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- INTRODUCTION:** NASA regularly performs ground-based offgas tests (OGTs), which allow prediction of accumulated volatile pollutant concentrations at first entry on orbit, on whole modules and vehicles scheduled to connect to the International Space Station (ISS). These data guide crew safety operations and allow for estimation of ISS air revitalization systems impact from additional pollutant load. Since volatiles released from vehicle, module, and payload materials can affect crew health and performance, prediction of first ingress air quality is important.
- METHODS:** To assess whether toxicological risk is typically over or underpredicted, OGT and first ingress samples from 10 vehicles and modules were compared. Samples were analyzed by gas chromatography and gas chromatography-mass spectrometry. The rate of pollutant accumulation was extrapolated over time. Ratios of analytical values and Spacecraft Maximum Allowable Concentrations were used to predict total toxicity values (T-values) at first entry. Results were also compared by compound.
- RESULTS:** Frequently overpredicted was 2-butanone (9/10), whereas propanal (6/10) and ethanol (8/10) were typically underpredicted, but T-values were not substantially affected. Ingress sample collection delay (estimated by octafluoropropane introduced from ISS atmosphere) and T-value prediction accuracy correlated well ($R^2 = 0.9008$), highlighting the importance of immediate air sample collection and accounting for ISS air dilution.
- DISCUSSION:** Importantly, T-value predictions were conservative 70% of the time. Results also suggest that T-values can be normalized to octafluoropropane levels to adjust for ISS air dilution at first ingress. Finally, OGT and ingress sampling has allowed small leaks in vehicle fluid systems to be recognized and addressed.
- KEYWORDS:** confined spaces, offgas toxicity, air quality, risk determination.

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One of the primary goals of toxicologists supporting NASA's human spaceflight programs is to identify significant risks to astronaut health from air pollution in vehicles or habitats.⁸ Exposure to volatile contaminants during flight have caused a wide range of toxicological responses, from slight irritation of mucous membranes to life-threatening hypoxia.^{2,5,14,21} Other important exposure symptoms include effects such as central nervous system depression and visual disturbances, which are closely monitored to avoid performance decrements.^{6,29} Thus, identification and quantification of compounds known to be detrimental to human health allows for the development of strategies to control them.^{10,25,26} Toxicological risks from air pollutants in space habitats originate from many sources, including entry of external propellants, offgassing from polymeric materials, leakage of systems compounds,

escape of payload materials, and metabolism by microbes, laboratory animals, and humans.⁴ Therefore, information learned via ground-based and in-flight analysis of air samples regarding the identities of chemicals in crew inhabited volumes is important. Many of the compounds detected in NASA's air sampling efforts, such as formaldehyde, carbon monoxide, or siloxanes, arise from offgassing of new materials incorporated into the

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vehicle or module structure.^{9,27} In addition, components of payload materials and materials associated with payload and system operations are common sources of released compounds (offgassed or leaked) that may present a significant crew hazard, such as lubricants, adhesives, cleaning agents, and tissue fixatives.⁷ An historical analysis of air quality data revealed trends in elevated volatile organic compounds (halocarbons) associated with vehicle docking during the NASA-Mir program (1993–1998) and on the International Space Station (ISS; 1998–2006).⁹ In a study at NASA Marshall Spaceflight Center wherein predictive techniques were used to determine contaminant control system performance, it was determined that carryover of air pollutants from attached modules and spacecraft was significant and should be considered when planning vehicle docking for crew exchanges or logistical flights.²⁴ Even a minor offgassed product, such as formaldehyde, can accumulate in the ISS environment, but is controllable using aggregate data from module offgas testing to estimate the rate and amount of chemical release and plan accordingly.²⁷ These studies highlight the importance of accurately predicting air quality at first ingress to prevent detrimental health effects.

The Toxicology and Environmental Chemistry (TEC) group at the Johnson Space Center (JSC) has performed offgas tests (OGTs) on new modules and vehicles scheduled to fly to ISS since 1998. There are two primary reasons for carrying out OGTs. First and foremost is to protect the crew from adverse health effects of accumulated volatile pollutants when they first enter the module/vehicle on orbit. For example, if an OGT reveals an elevated concentration of a specific compound, preflight mitigation, including implementation of an additional breathing air purge, may be recommended. In-flight procedures may also be advisable in response to an elevated OGT result, such as requesting a “hold-out” period to allow ISS air dilution of the docked vehicle before crew initiates unpacking or other activities. The OGTs are also performed to determine the additional pollutant load that ISS cabin atmosphere revitalization systems must handle. This ensures that environmental control and life support systems are appropriately sized to handle expected contaminant loads and support resupply planning for expendable items (e.g., charcoal beds) designed to remove trace contaminants from the habitable environment.

To measure the amount of accumulated pollutants, the module is sealed for at least one-fifth of the worst-case time interval that is expected to occur between the last clean air purge on the ground and the crew's first entry on orbit. This time period can range from a few days to a few months. Typically, triplicate samples are taken at preplanned times throughout the ground-based OGT. Samples are then analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS), and the rate of accumulation of pollutants is then extrapolated over time. The analytical values are divided by compound-specific 7-d Spacecraft Maximum Allowable Concentrations (SMACs). These ratios are then summed, resulting in a predictive total toxicity value (T-value) at the time of first entry.^{11,12} SMACs for approximately 50 compounds have been published on the most relevant compounds for the

spaceflight environment.^{16–20} Interim values are developed for contaminants that do not have published SMAC values. SMACs have been developed for various durations of exposure. A 7-d SMAC protects against compound-specific toxicological effects for 7 d. Although exposure to contaminants introduced from docked vehicles are quickly diluted with the ISS atmosphere, use of 7-d SMACs ensures health protection. T-values and the toxicological effects of specific pollutants that contribute most to the overall toxicity are then used to guide first entry operations. Finally, results can be compared to first entry samples collected on orbit to determine the predictive ability of the ground-based OGT. However, ingress sample collection delay can make prediction a challenge. Delay following hatch opening allows for mixing of vehicle or module air with ISS air, which reliably contains biological waste products and systems chemicals such as volatilized octafluoropropane (Freon 218), a relatively inert on-orbit coolant fluid. Therefore, the presence of such chemicals in ingress samples is indicative of delayed sample collection.

Since OGT analyses are not conducted on orbit prior to first ingress, the safety of ingressing crewmembers relies on the accuracy of the toxicity predictions made based on the preflight OGTs. To determine historical accuracy in predicting air quality at docking, OGT and first ingress data collected from five vehicles [SpaceX-Demo (SpX-D), SpaceX-1 (SpX-1), SpaceX-3 (SpX-3), Orbital-Demo (Orb-D), Orbital-1 (Orb-1)] and five modules [Nodes 1-3, Multi-Purpose Logistics Module (MPLM), U.S. Lab] were compared. Testing of these vehicles occurred over the period from 1998 to 2015. OGTs are not performed on every vehicle and module. Therefore, only those for which both OGT and first ingress data were collected are included in this analysis. In addition, we examined factors, including ingress sample collection delay and compound stability over time, which could affect predictive capability.

METHODS

The OGTs were conducted on sealed modules as they were being added to the ISS and on sealed vehicles that were later launched and docked to ISS (**Fig. 1**). Details for each vehicle and module tested, including sampling dates, percentage loading by mass, hatch closure to ingress interval, primary T-value contributors, carbon dioxide and octafluoropropane values, factors potentially affecting predictive capability, and analytical recoveries are presented in **Table I**.

Grab sample containers (GSCs) with passivated (polished, cleaned, and resistant to corrosion) internal surfaces were used to collect samples. GSCs of 500 mL volume were used for all preflight OGTs. GSCs with a volume of 375 mL were used for first ingress sampling through May 2010 (after Node 3 ingress). By August 2010 (before SpX-D ingress), 187-mL GSCs were in use exclusively for on-orbit first entry sampling, replacing the bulkier 375-mL canisters. Before they were used, all GSCs were checked for leaks, cleaned, verified clean (proofed), and injected with known amounts of control compounds (dosed). The leak

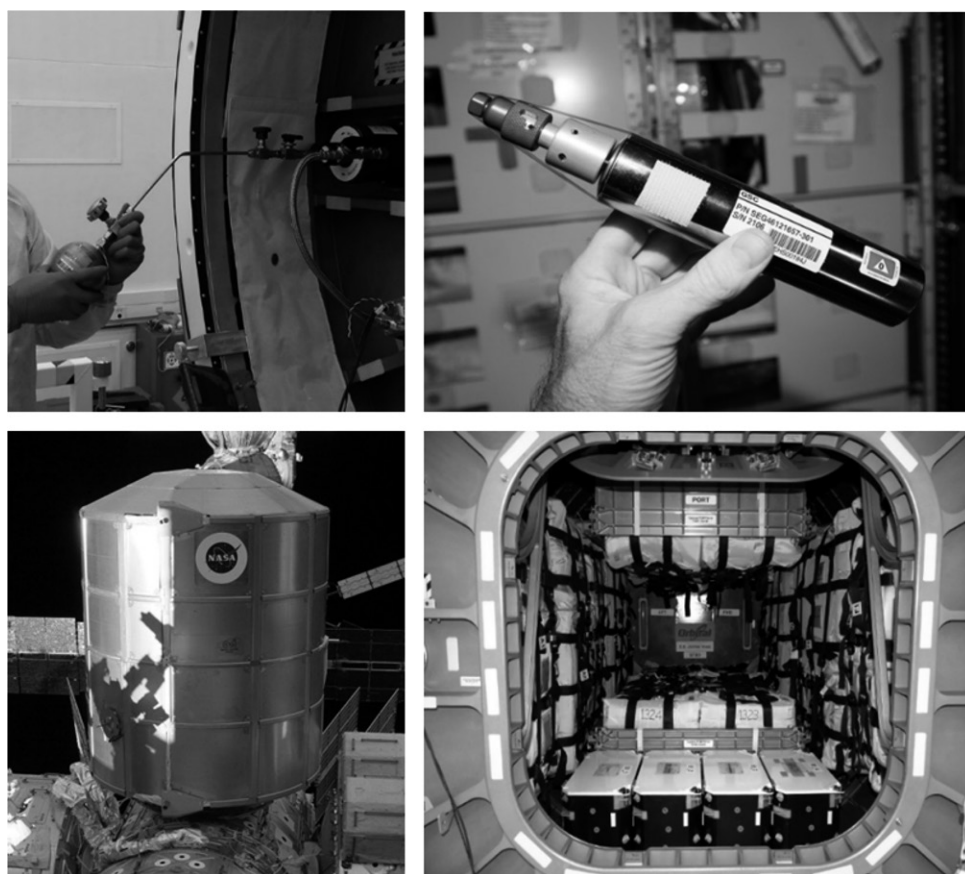


Fig. 1. Top left: ground-based OGT using 500-mL grab sample container (GSC). Top right: mini-GSC (187 mL). Bottom left: Cygnus docked to ISS. Bottom right: docked Cygnus following hatch opening.

check procedure ensured that valves and fittings were not damaged and could maintain a vacuum before sampling. After an initial evacuation to a pressure < 0.05 psia, the GSCs were connected to the pressure monitoring station and evacuated further to allow the pressure in the GSCs to equilibrate to 0.01 mbars. The GSCs were removed from the manifold for at least 96 h and then reattached to the vacuum manifold to determine whether they maintained pressure. The allowable pressure change was ≤ 0.01 mbars (≤ 0.01 cc/mo). After the leak check, canisters were cleaned in an Entech 3100 Canister Cleaning System to remove contaminants to < 5 ppbv for each identified volatile organic compound with an exception of < 10 ppbv for acetaldehyde. The canisters were proofed to be clean by an Agilent GC/MS system. Once the canisters were proofed, they were reattached to the vacuum manifold and evacuated to 0.01 mbars before dosing. Canisters were vapor-dosed (10 cc) with a surrogate standard mixture containing ^{13}C -acetone, fluorobenzene-d₅, and chlorobenzene-d₅ for quality control purposes and to determine sample integrity. Primarily, the surrogate levels are used as a guide to inform TEC scientists when a sample has leaked.

The preflight OGT testing interval was required to be, at a minimum, one-fifth of the planned elapsed time between final vehicle/module closeout and on-orbit crew entry (e.g., a 6-d test would be required for a 30-d flight). We generally required that at least 75% of the cargo be present at the time of the

ground-based OGT. A standard test consisted of three sets of three samples. Of the triplicate samples, the first generally served as a line purge to clear any extraneous contaminants and the other two samples were analyzed as duplicates. Therefore, the time between taking the three samples of a given set did not exceed 5 min. Background samples of facility air were also collected (generally within a few feet of the vehicle or module) before the first sampling set for each vehicle or module.

Samples were placed into certified-clean GSC containers by opening valves for approximately 10 s for collection. GSCs were then returned for analysis to the NASA JSC TEC Laboratory within 3 d of their acquisition. The atmosphere inside the specimen container was analyzed to quantify the offgassed compounds.

Archival first entry samples were collected on-orbit to verify the results of the preflight OGT and to characterize crew exposures. This process involved using

1 GSC to sample the air as quickly as practical after the module hatch was opened to ensure the sample was representative of the atmosphere of the vehicle/module (i.e., mixing with the ISS atmosphere is minimal). The first ingress sample was then returned to the ground for detailed GC and GC/MS analyses. The interval between ingress sample collection and analysis at NASA JSC ranged from 18–38 d.

Sample Analysis

Sample analyses were initiated as soon as practical after receipt of samples into the laboratory (usually the day after receipt). Samples were then pressurized as necessary with ultra-high purity nitrogen to ensure adequate sample volume. First ingress samples were typically pressurized to approximately twice the original volume, whereas vehicle offgas samples did not require pressurization because of their much larger sample volume. Aliquots of the samples were then used to quantify several analytes using GC, and then the remainder of the sample was used to perform analysis of volatile organic compounds (VOCs).

Vehicle/module OGT samples were analyzed for carbon monoxide using a GC with a pulsed discharge helium ionization detector. Additionally, these samples were analyzed for VOCs with a GC-flame ionization detector. The GC-flame ionization detector method was used for the reporting of high levels (above 0.3 ppm) of methanol, ethanol, isopropanol,

2-butanone, and acetone. Reported concentrations were quantified using a minimum of 4-point calibration curves. On-orbit first entry samples were analyzed using the same methods described above, except they were also analyzed for methane, hydrogen, and carbon dioxide.

The VOC analysis was based on EPA Method TO-15,³ which was modified to enable the analysis of numerous polar compounds known to be present in cabin atmospheres.²² The analysis included concentrating the VOCs and then separating the mixture into its components for subsequent identification and quantitation. This process was accomplished by introducing samples into an integrated analytical system consisting of an automated inlet system, a GC, a mass selective detector, and a data system. The GSC was first connected to an automated inlet device containing a series of traps for the management of water and carbon dioxide present in the samples. The concentrated sample was then refocused using liquid nitrogen to achieve better chromatography and injected onto the GC capillary column where the sample components were separated and resolved. Resolved sample components were then transferred into a mass selective detector operating in the scan mode where their specific electronic signatures (mass spectra) were stored for subsequent identification and quantification. If, during data reduction, unidentified peaks with an area larger or equal to 10% of the peak area of the internal standard were found, all efforts were made to identify them by comparing their spectrum to the National Institute of Standards and Technology library. For unidentified VOCs, published reference values were used for quantitation.¹ For those compounds having more than one reference value, an average value was used.

Acceptance limits for quality control checks were defined in the work instruction for each analytical method. When quality control criteria could not be achieved, corrective action and troubleshooting of instrumentation was required and documented.

During canister preparation, a minimum of one laboratory control was prepared for every five GSCs dosed. After sample canisters were received into the TEC Laboratory, the canisters were logged into a sample logbook and laboratory tracking numbers were generated. For sample analysis, instrumentation was demonstrated to be linear over a wide range of concentrations and determined to be stable as shown by daily calibration verifications using standard mixtures. To assess the accuracy of sampling and GC/MS analysis process, air samples were measured as the percentage recovery of a minimum of three surrogates spiked in the GSCs during preflight preparation. These results were compared to laboratory surrogate controls, prepared during both preflight and postflight processing. Finally, analytical results were verified by use of an independent computer calculation routine and the Internal Quality Representative conferred with analytical chemists, when necessary, to ensure that all data generated were scientifically sound and of acceptable precision and accuracy. All documentation was maintained by the Internal Quality Representative in hardcopy and/or electronic form.

Toxicological Evaluation

Toxicologists at NASA JSC, in collaboration with the National Research Council, establish SMACs, which are exposure limits intended to provide guidance for nominal and emergency situations.¹⁵ Short-term (1 h and 24 h) SMACs apply to off-nominal or emergency situations and allow for minor health effects. SMACs of 7-d, 30-d, 180-d, and 1000-d duration apply to various past, present, and future mission durations and are expected to protect against all health effects. All contaminants found in the preflight OGT and in-flight ingress samples were compared to their respective 7-day SMACs,¹² which is conservative considering the short exposure duration that occurs before mixing with the ISS atmosphere, but ensures that exposures are health protective. Using the SMAC for each offgassed compound, the overall toxicity rating was determined by dividing the measured concentration by the 7-d SMAC, resulting in a compound-specific T-value. T-values for compounds that increased over the course of the test, indicating products generated from offgassing, were summed to provide a total T-value and divided by the number of days over which the increase occurred to establish a rate of T-value increase per day. This rate of increase during the OGT is then used to predict the T-value ($T_{\text{predicted}}$ or T_p) at hatch opening on-orbit (T_{actual} or T_a) based on the number of days between final prelaunch hatch closure and hatch opening on-orbit and the percentage by mass of cargo present in the vehicle at the time the test occurred. The general method for calculating T_p involves determining the amount of T accumulated during each of the OGT sampling intervals using the equation

$$T_p = \frac{\text{\# of days module sealed} \times \text{rate of T increase per day}}{\% \text{ cargo present at test by mass}}$$

We assumed that the rate of accumulation during each of the OGT intervals would provide an upper bound on the T accumulated during intervals of equal duration following final hatch closure and air purge. We further assumed that during that portion of the interval between hatch closure and ingress that exceeds the sum of the OGT intervals that a worst case estimate of the rate of accumulation of T during that time would be obtained by assuming that the rate was the same as that of the last OGT interval. Thus, for example, if OGT samples were collected on 3 consecutive days (days 0, 1, and 2):

$$T_p = (R1 \times L1) + \frac{R2(Lci - L1)}{\% \text{ Cargo}}$$

In which:

R1 and R2 = Daily accumulation rate for OGT interval 1 and 2, respectively;

L1 = Length of OGT interval 1; and

Lci = Length of the interval between hatch closure and ingress.

Background, measured from samples of facility air that were collected within a few feet of the vehicle or module, was not included in the calculations because it was determined to be

Table I. Configurational, Sampling, and Analytical Details for Vehicles and Modules.

	N1	N2	N3	LM	MP1	SXD	SX1	SX3	OD	O1
Vehicle/Module	ISS	ISS	ISS	ISS	ISS	Dragon	Dragon	Dragon	Cygnus	Cygnus
Free Volume (m ³)	55	62	62	98	45	10	10	10	13	13
Preflight	10/1/1998- 10/6/1998	6/11/2007- 7/5/2007	12/19/2008- 1/21/2009	6/23/2000- 7/1/2000	12/27/2000- 1/5/2001	4/7/2012- 4/11/2012	9/26/2012- 9/28/2012	2/14/2014- 2/16/2014	3/25/2013- 3/30/2013	10/23/2013- 10/28/2013
OGT Dates	10/6/1998- 10/14/1998	7/31/2007	2/20/2009- 3/17/2009	6/28/2000- 8/14/2000	1/8/2001- 1/18/2001	4/14/2012- 4/17/2012	10/1/2012- 10/2/2012	2/19/2014	4/1/2013- 4/4/2013	not available
OGT Sample Analysis Dates	10/14/1998	10/27/2007	2/13/2010	2/11/2001	2/28/2001	5/26/2012	10/9/2012	4/21/2014	9/30/2013	1/12/2014
Ingress Sampling Date	12/10/1998	10/27/2007	2/13/2010	2/11/2001	2/28/2001	5/26/2012	10/9/2012	4/21/2014	9/30/2013	1/12/2014
Ingress Sample	12/29/1998	11/19/2007- 11/21/2007	3/5/2010- 3/23/2010	3/1/2001	4/6/2001	6/12/2012- 6/21/2012	not available	not available	not available	not available
Analysis Dates	100	100	100	80	100	100	67	81	71	68
% Loaded During OGT	64	125	61	60	20	33	3	4	13	9
Interval Hatch Closure to Ingress (d)										
Primary T-Value Contributors Preflight	Methanol	Propenal, 1,2-dichloroethane	Propenal, 1,2-dichloroethane, fluoromethylsilane, trimethylsilanol	Acetaldehyde, propenal, methanol, 2-methylfuran	Fluorotrimethylsilane	Trimethylsilanol, fluorotrimethylsilane	Trimethylsilanol	Trimethylsilanol, fluorotrimethylsilane	Acetaldehyde, hexamethyltrisiloxane, trimethylsilanol	Trimethylsilanol, acetaldehyde, fluorotrimethylsilane, hexamethylcyclotrisiloxane
Primary T-Value Contributors First Ingress	Propenal, carbon dioxide	Propenal, 1,2-dichloromethane, fluorotrimethylsilane	Propenal, 1,2-dichloroethane, trimethylsilanol	Octamethylcyclotetrasiloxane, hexamethylcyclotrisiloxane	Dichloromethane, benzene, hexamethyltrisiloxane	Trimethylsilanol, fluorotrimethylsilane	Trimethylsilanol	N/A (full mixing occurred)	Hexamethyltrisiloxane, trimethylsilanol, acetaldehyde	Trimethylsilanol, acetaldehyde, hexamethylcyclotrisiloxane
Ingress CO ₂ T-val/Octafluoropropane T-val	0.15/-	0.24/not quantitated	0.28/0.00055	0.38,0.51/0.00016, 0.00013 (AFT,FWD)	0.17/0.00003	0.12/0.00005	0.4/0.00003	0.53/0.00003	0.12/0.00000	0.24/0.00001
Ingress [CO ₂]/[Octafluoropropane] (mg/m ³)	1900/not analyzed	3200/not quantitated	3600/46	4960.6632/13,11(AFT,FWD)	2223/2.7	1600/4.3	5200/24	6900/2.5	1600/0.4	3200/0.5
Known Factors Affecting Predictive Capability	None	Delayed sample collection (assumed)	Delayed sample collection (assumed)	Delayed sample collection. Fluorotrimethylsilane excluded from preflight OGT T-values, came from outside module	Delayed sample collection (assumed), low hydrogen in ingress sample	None	Delayed sample collection (assumed)	Delayed sample collection (known)	None	Delayed sample collection (assumed)

Continued

Table I. Continued

	N1	N2	N3	LM	MP1	SXD	SX1	SX3	OD	O1
Preflight OGT	88	98	113	91	102	103	101	110	101	114
Avg % Recovery	103	99	120	93	93	100	102	105	98	105
(¹³ C-acetone, fluorobenzene, and chlorobenzene)	100	92	119	111	89	98	82	106	94	105
First Ingress Avg %	88	100	91	70-104	70-130	131	130	119	112	103
Recovery	92	95	83			112	129	109	115	99
(¹³ C-acetone, fluorobenzene, and chlorobenzene)	100	97	74 (low recovery due to high interference from octafluoropropane)			91	132	98	117	93

insignificant. Also not included in the calculation of T_p were any compounds that did not increase during the OGT (slope < 0.00001) and decreased in concentration over the last interval.

Statistical Analysis

A linear regression analysis was performed to evaluate the relationship between T-values ($T_p - T_a$, or ΔT) and octafluoropropane levels. The significance of the association was assessed via an independent samples ANOVA test where $P < 0.05$ was considered significant.

RESULTS

As expected, the predicted T-values were conservative (higher than the actual ingress values) for SpX-D, SpX-1, SpX-3, Orb-1, Lab, MPLM-1, and Node-1; however, the actual T-values for Orb-D, Node 2, and Node 3 were underpredicted (Fig. 2). No clear trends were apparent when ΔT was plotted by number of days between OGT and hatch opening. Likewise, there was no significant association between ΔT vs. time between sample collection or percentage vehicle loading (data not shown).

Data for SpX-D illustrate the importance of an appropriate test duration. The original predicted button-up period (hatch closed) was 10 d, so the OGT was conducted for 4 d. However, unexpected launch delays resulted in an actual button-up period of 33 d, and our short test and linear extrapolation method for calculating T_p significantly over-predicted the T_a at first ingress. This result is expected as offgassing rates tend to decrease over time. Data for Node 3 indicated the presence of propenal (acrolein) at first ingress that was not detected during the OGT. Even a trace amount of this compound will drastically affect the T-value, as the SMAC is set at a very low ceiling limit ($0.03 \text{ mg} \cdot \text{m}^{-3}$) to protect against mucosal irritation. The source of propenal, a compound that is relatively ubiquitous in

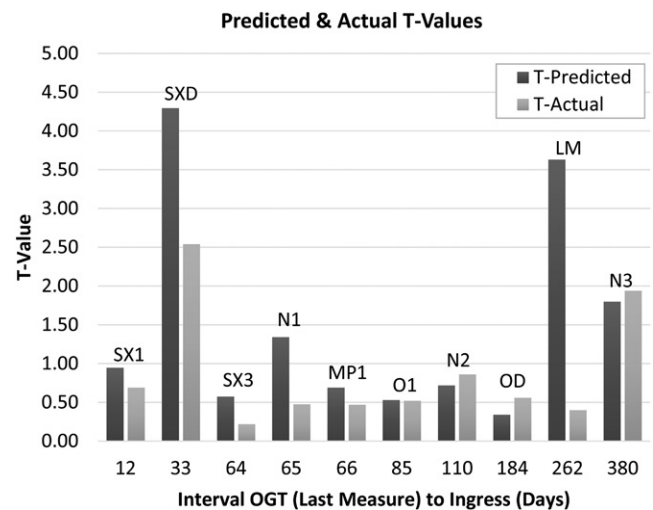


Fig. 2. Predicted T-values at first ingress (dark gray) and actual T-values at first ingress (light gray) from five commercial vehicles (SpX-D, SpX-1, SpX-3, Orb-D, and Orb-1) and five ISS modules (Lab, MPLM-1, Node-1, Node-2, and Node 3) as a function of the OGT-to-ingress interval.

foods and the environment, was not identified. The primary contributors to preflight and ingress T-values are listed in Table I.

Analytical recovery in samples collected at first ingress was slightly greater than in OGT samples collected for SpX-1, and the opposite was true for Node 3. Recovery for Node 3 ingress samples was determined to be low due to high interference from octafluoropropane during analysis. However, evaluation of prediction trends observed for SpX-1 and Node 3 (Fig. 2) did not indicate that recovery percentage had any substantial impact on T-value predictive capability. The average recoveries for the surrogates were within the normal range expected for our method.

To evaluate the effect of sample collection delay on prediction accuracy, the percentage change in overall T-value was compared to the carbon dioxide T-value at first ingress (T_a) (Fig. 3A). Results indicate that carbon dioxide concentration did not correlate well with ΔT values ($R^2 = 0.0034$, $P = 0.9015$). Carbon dioxide varies considerably on ISS. Levels are associated with scrubbing efficiency at the time of sampling and factors that result in fluctuating generation of carbon dioxide, such as the amount of time the crew exercises each day. There was also no relationship between ΔT and methane or hydrogen, other compounds frequently detected at ingress only. This detailed information can be viewed online (auxiliary Table A; <https://doi.org/10.3357/AMHP.4702.2017>). However, a fairly strong association ($R^2 = 0.9008$, $P = 0.0038$) was observed between octafluoropropane concentration and the ΔT (Fig. 3B), indicating that this compound may serve as an excellent normalization factor to adjust for ISS air dilution of samples (e.g., sample collection delay). Unlike carbon dioxide, there are no metabolic sources of octafluoropropane on ISS that would potentially confound results. Thus, the octafluoropropane concentration is generally more stable on ISS, except during the infrequent event of a leak.²⁸ Furthermore, this compound is not efficiently scrubbed from the air, so the primary loss mechanism is through nominal, low level ISS air leakage and dilution as vehicles dock.

The percentage change in overall T-value at first ingress was plotted against carbon dioxide (Fig. 3C) and octafluoropropane (Fig. 3D) T-values at first ingress to visualize the effect of sample collection delay. When a known or suspected sample collection delay occurred for a vehicle or module, based on either actual reports or high carbon dioxide and octafluoropropane values, T-values tended to occupy a smaller area of the graph in the case of octafluoropropane. However, octafluoropropane

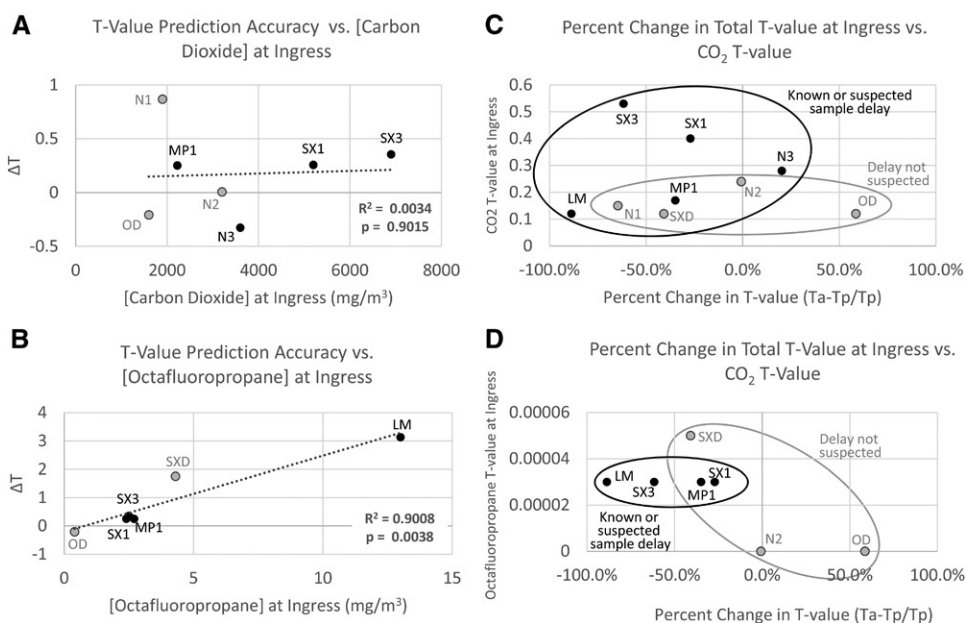


Fig. 3. Change in overall T-value (ΔT) was plotted against A) carbon dioxide and B) octafluoropropane concentrations at first ingress. Percentage change in the overall T-value at first ingress as a function of C) carbon dioxide and D) octafluoropropane T-value at first ingress was also plotted to examine the effect of sample collection delay. Vehicles and modules having a known or suspected sample collection delay based on actual reports or high carbon dioxide and octafluoropropane values are represented in black. Vehicles and modules for which no known or suspected delay occurred are represented in gray. Note: The Node 3 octafluoropropane level has been excluded as an outlier (disproportionately high due to a leak on ISS).

does not affect T-values to the extent that a more toxic volatile would, so it is not surprising that a consistently low T-value was calculated for cases in which there was a known or suspected delay in sample collection. The Node-3 octafluoropropane level was excluded as an outlier in Figs. 3B and 3D due to disproportionately high levels following a leak on ISS.

Consistent with NASA Environmental Control and Life Support Systems engineering analysis of OGT and in-flight contaminant concentrations from July to October 2009,²³ evaluation of our results by compound collection revealed that, of the compounds that contributed to T-values, 2-butanone was typically over-predicted ($T_p > T_a$) in all but Node 2, whereas others, including ethanol, methanol, acetone, and hexamethylcyclotrisiloxane, were frequently underpredicted ($T_p < T_a$) (refer to auxiliary Table A online). Octafluoropropane was consistently present at ingress only, indicating that it was present only in ISS air that had begun to mix with vehicle or module air following hatch opening. Compounds that were present during the OGT only were either assumed to have degraded to molecular species not analyzed or, in the case of more polar compounds (e.g., acetaldehyde, methanol, and siloxanes), lost as a result of adhesion to inner surfaces of the GSCs. The percentage contribution of compounds detected in air collected from each vehicle and module is represented in Fig. 4. In some cases (i.e., MPLM, Node 1, SpX-D), a larger number of offgassed compounds that were toxicologically relevant only during the OGT were detected, suggesting that molecular degradation occurred. In other samples, particularly SpX-1 and SpX-3, a substantial percentage of compounds detected were only found in the ingress

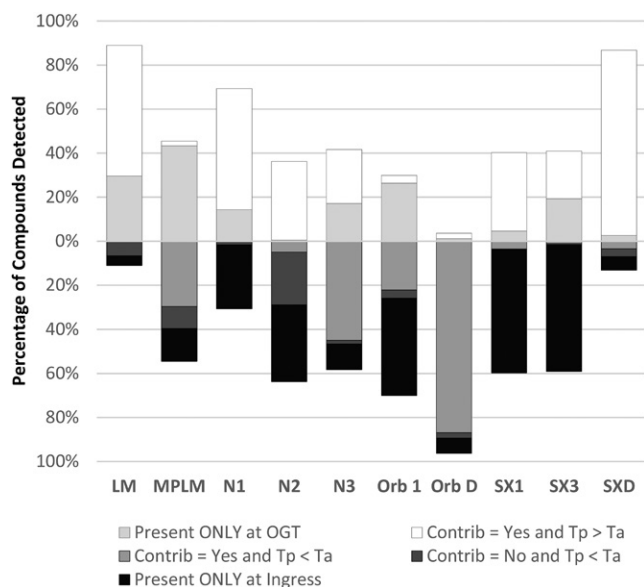


Fig. 4. Relative comparison of the compounds detected during different stages of testing for each vehicle and module and their contribution to the T-value. Values above 0% indicate percentage of compounds for which the prediction was conservative ("Contrib = Yes and $T_p > T_a$ ") or the percentage of compounds that were detected during the OGT only ("Present ONLY at OGT"), which was also considered to be conservative. Compounds that were detected in greater amounts at ingress than in the OGT or only at ingress ("Present ONLY at Ingress") are represented by bars under 0%. Compounds detected in greater abundance at ingress than the OGT are separated into groups indicating whether or not they added to the toxicity of the air (contributed to the T-value). These groups are labeled as "Contrib = Yes and $T_p < T_a$ " and "Contrib = No and $T_p < T_a$ ".

sample, indicating that the contribution likely originated either from ISS air or from cargo added after the OGT was performed.

DISCUSSION

It would be reasonable to assume that the closer the percentage loaded mass is to actual mass at docking, the more accurately first ingress T-values could be predicted. However, we did not observe any correlation between percentage of loaded mass and predictive accuracy, possibly because there was a known or suspected delay in sample collection four out of five times that the amount of cargo loaded was less than 100% (refer to Table I). As expected though, compounds detected at OGT tended to be the same compounds detected at first ingress. This was especially true for trimethylsilanol, a volatile siloxane that originates from the degradation of silicone-based materials. Of the compounds that were detected in either the OGT or first ingress samples for a vehicle or module, only an average of 19% were not detected in both samples.

Delaying collection of the first ingress sample after hatch opening on orbit will depress first ingress T-values as a result of sample dilution with cleaner ISS air. As time passes, contaminants from docking vehicles disperse into ISS air, which has been observed with intermodule ventilation following Space

Shuttle contaminant carryover.²⁴ Due to air mixing, carbon dioxide produced by ISS crew will infiltrate the docked vehicle, therefore carbon dioxide T-values are expected to be low in samples taken immediately after hatch opening and higher if there is a delay. High carbon dioxide in the ingress U.S. Lab sample indicates that the module had been open for an extended time, allowing air mixing to occur before the ingress sample was taken. This is the most plausible explanation for the large difference between predicted and actual T-values for the U.S. Lab. However, using the octafluoropropane concentration to correct for ISS air dilution will produce a more accurate estimate of air pollutant concentration at first ingress since this compound is only found on the ISS and does not fluctuate as frequently or to the degree that carbon dioxide does (refer to Fig. 3). Carbon dioxide concentration is also likely to differ depending on the distance between the GSC and the sample collector, who is exhaling approximately 4% carbon dioxide. For these reasons, carbon dioxide is a less suitable indicator of ISS air mixing. Octafluoropropane should not be used as a normalization factor if a leak has recently occurred on the ISS, as was the case for Node 3 ingress.

The type of cargo loaded and postoffgassing chemical stability are also factors that may result in differences between predicted and actual T-values.^{23,24} Previous VOC long-term stability test results in the TEC laboratory indicated that significantly lower concentrations of reactive polar compounds could be expected after 20 wk of sample storage in the mini-GSC containers (Beck S, Cheng P. Internal NASA report; 2009). In that internal study, eight compounds (four aldehydes, two ketones, one ester, and one ether) were identified as exhibiting significant losses. They included propenal, acetone, butanal, 2-butanone, ethyl acetate, 2-butenal, 1,4-dioxane, and 2-pentanal. In this study, we found that 2-butanone was overestimated ($T_p > T_a$) in all but one case (Node 2), but did not observe a similar consistent trend with the other compounds from the previous study. While the number of days between ingress sample collection and analysis ranged from 19 to 38 d, the amount of time passing between OGT sample collection and analysis ranged from 4 to 55 d, suggesting that OGT T-values could have been underestimated in the case of Node 3. This serves as another potential explanation for one of the two underpredictive scenarios represented in Fig. 2.

There have been several instances during recent spaceflight history in which air concentrations of chemicals measured during first ingress were significantly higher than predicted by preflight OGTs. However, NASA TEC and others have been able to identify specific events that are believed to have been responsible for discrepancies between the predicted and measured first ingress T-values. For example, after the Japanese Aerospace Exploration Agency's (JAXA) HTV1 offgassed a substantially greater amount (52 ppm) of carbon monoxide during ground-based OGT than on first ingress (6 ppm), it was speculated that the foam used for dummy packing material (nonflight item) was the source and could be baked in advance to prevent discrepancies between ground testing and first ingress results (JAXA; internal JAXA report; Sept. 2011). When the Minicel-type

foam was baked at 60°C for 48 h before ground-based OGTs, carbon monoxide levels were sufficiently reduced. This discovery led to a recommendation that all foam materials, including flight and nonflight cargo foams, undergo baking before packing for HTV2. Although carbon monoxide was reduced at first ingress on HTV1, the crew developed headaches after detecting a formaldehyde-like odor, presumably due to a different (unidentified) offgassed compound.

Inconsistency between ground OGT and first ingress sampling results also occurred with the SpaceX Demo vehicle. During the 4-d ground-based OGT, the concentration of perfluoro(2-methyl)pentane increased from 1.2 to 3.3 mg/m³, which was suggestive of material offgassing from inside the module.¹³ At the time of the ground test, the vehicle was 100% loaded. Analysis of the first-entry sample yielded a concentration of 1300 mg/m³, an increase too substantial to be explained by offgassing alone. Through follow-up investigation, we determined that this compound was being used as a heat-exchange fluid in the SpaceX vehicle and probably leaked from the coolant system, releasing increased amounts with launch vibration and perhaps docking. Given that the free volume of the Dragon capsule is about 10 m³, the amount of perfluoro(2-methyl)pentane that escaped from the system was approximately 13,000 mg or 13 g. Since the compound is virtually nontoxic, there was no appreciable effect on the T values (0.009 units); however, the providers of the capsule were asked to investigate the possibility of a small leak in their system. The problem was then resolved by tightening a bolt in the thermal exchange system and leaks did not occur to any great extent on future SpaceX Dragon missions.

In general, there is good agreement between predicted and actual first-entry T-values, and, importantly, our predictions are typically conservative. Factors such as sample collection delay and compound stability can affect expected concentrations at first ingress. Also, understanding how the prediction of offgassed material concentrations can be affected by factors and parameters that can either be controlled or adjusted for mathematically will improve spaceflight safety operations.

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REFERENCES

1. Cornu A, Massot R. Compilation of mass spectral data, 2nd ed. London: Heyden; 1975.

2. Davis JR, Johnson R, Stepanek J, Fogarty JA. Fundamentals of aerospace medicine, 4th ed. Philadelphia (PA): Lippincott Williams & Wilkins; 2008.
3. Environmental Protection Agency (U.S.). Compendium method TO-15: determination of volatile organic compounds (VOCs). In: Air collected in specially-prepared canisters and analyzed by gas chromatography/mass spectrometry (GC/MS). (U. S. EPA publication: EPA/625/R-96/010b). Cincinnati (OH): Environmental Protection Agency; 1999.
4. James J. Space toxicology. Space Safety Magazine [Internet]; International Association for the Advancement of Space Safety; 2015. [Accessed 2016 Aug. 29]. Available from: <http://www.spacesafetymagazine.com/spaceflight/space-medicine/space-toxicology/>.
5. James J, Limero T, Beck S, Martin M, Covington P, et al. Toxicological assessment of the International Space Station atmosphere with emphasis on metox canister regeneration. Paper 2003-01-2647 at the International Conference on Environmental Systems; 2003 July 7–10; Vancouver, BC, Canada. Warrendale (PA): SAE International; 2003.
6. James JT, Parmet AJ, Pierson DL. Aerospace toxicology and microbiology. In: NASA Technical Reports Server [Internet]. Houston (TX): National Aeronautics and Space Administration. Document #20070032022. [Accessed 2016 Aug. 23]. Available from: <http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20070032022.pdf>.
7. Khan-Mayberry N, James JT, Tyl R, Lam CW. Space toxicology: protecting human health during space operations. *Int J Toxicol*. 2011; 30(1):3–18.
8. Khan-Mayberry NN, James JT. Space toxicology: toxicological risk management of human health during space exploration. General, Applied and Systems Toxicology [Internet]; John Wiley and Sons, Inc.; 2009. [Accessed 2016 Aug. 25]. Available from: <http://onlinelibrary.wiley.com/book/10.1002/9780470744307/toc>.
9. Macatangay AV, Perry JL. Cabin air quality on board Mir and the International Space Station—a comparison. SAE Technical Paper 2007-01-3219; Society of Automotive Engineers 37th International Conference on Environmental Systems; 2007 July 9–12; Chicago, IL. Warrendale (PA): SAE; 2007.
10. Musgrave GE, Larsen AM, Sgobba T. Safety design for space systems. Oxford (UK): Butterworth-Heinemann; 2009.
11. National Aeronautics and Space Administration. Flammability, offgassing, and compatibility requirements and test procedures. NASA publication: NASA-STD-6001B. Washington (DC): National Aeronautics and Space Administration; 2016.
12. National Aeronautics and Space Administration. Spacecraft maximum allowable concentrations for airborne contaminants. NASA Publication: JSC-20584. Houston (TX): National Aeronautics and Space Administration; 2008.
13. National Aeronautics and Space Administration. Space-X first entry sample analysis. NASA publication: JSC-CN-26767. Houston (TX): National Aeronautics and Space Administration; 2012.
14. National Aeronautics and Space Administration. Apollo 1: the fire [Internet]. 1967. [Accessed 2016 Aug. 25]. Available from: http://history.nasa.gov/SP-4029/Apollo_01a_Summary.htm.
15. National Research Council. Guidelines for developing spacecraft maximum allowable concentrations for space station contaminants. Washington (DC): National Academy Press; 1992.
16. National Research Council. Spacecraft maximum allowable concentrations for selected airborne contaminants, vol. 1. Washington (DC): National Academy Press; 1994.
17. National Research Council. Spacecraft maximum allowable concentrations for selected airborne contaminants, vol. 2. Washington (DC): National Academy Press; 1996.
18. National Research Council. Spacecraft maximum allowable concentrations for selected airborne contaminants, vol. 3. Washington (DC): National Academy Press; 1996.
19. National Research Council. Spacecraft maximum allowable concentrations for selected airborne contaminants, vol. 4. Washington (DC): National Academy Press; 2000.
20. National Research Council. Spacecraft maximum allowable concentrations for selected airborne contaminants, vol. 5. Washington (DC): National Academy Press; 2008.

21. Nicogossian AE, LaPinta CK, Burchard EC, Hoffler GW, Bartelloni PJ. Crew health, In: The Apollo-Soyuz Test Project Medical Report, Chapter 3. Report No.: NASA SP-411. Washington (DC): NASA; 1977:11–24, 44.
22. Palmer PT, Limero TF. Mass spectrometry in the U.S. space program: past, present, and future. *J Am Soc Mass Spectrom.* 2001; 12(6): 656–675.
23. Perry J. A review of International Space Station habitable element equipment offgassing characteristics. Report No.: AIAA 2010-6068. International Conference on Environmental Systems, 40th International Conference on Environmental Systems; 2010; Barcelona (SP). Reston (VA): American Institute of Aeronautics and Astronautics; 2010.
24. Perry J. Predictive techniques for spacecraft cabin air quality control. SAE Technical Paper 2001-01-2398. Society of Automotive Engineers 31st International Conference on Environmental Systems; 2001 July 9–12; Orlando, FL. Warrendale (PA): SAE; 2001.
25. Perry JL. A design basis for spacecraft trace contaminant control. SAE Technical Paper 2009-01-2592: Society of Automotive Engineers 39th International Conference on Environmental Systems; 2009 July 12–16; Savannah, GA. Warrendale (PA): SAE; 2009.
26. Perry JL. Elements of spacecraft cabin air quality control design. Washington (DC): National Aeronautics and Space Administration; 1998. Report No: NASA/TP-1998-207978.
27. Perry JL. Formaldehyde concentration dynamics of the International Space Station cabin atmosphere. SAE Technical Paper 2005-01-3091: Society of Automotive Engineers 35th International Conference on Environmental Systems; 2005 July 11–14; Rome, Italy. Warrendale (PA): SAE; 2005.
28. Perry JL. Octafluoropropane concentration dynamics on board the International Space Station. SAE Technical Paper 2003-01-2651. Society of Automotive Engineers 23rd International Conference on Environmental Systems; 2003 July 7–10; Vancouver, BC, Canada. Warrendale (PA): SAE; 2003.
29. Wong KL. Spacecraft maximum allowable concentrations for selected airborne contaminants, vol. 1. Washington (DC): National Academy Press; 1994:149–167.

Table A. ΔT by Compound for Each Vehicle and Module Tested.

Compound	LM	MPLM	N1	N2	N3	Orb 1	Orb D	SX1	SX3	SXD
1,1,1,2-TETRAFLUOROETHANE					-0.00128	-0.00515	-0.00197		ND	
1,1,1-TRICHLOROETHANE	ND	0.00051	-0.00016	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-TETRACHLOROETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE	ND	0.01011	0.00204							
1,1,2-TRICHLOROETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-DICHLOROETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-DICHLOROETHENE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-DICHLOROPROPENE			ND							
1,1-DIFLUOROETHANE						-0.00133	-0.00074		ND	
1,2,4-TRICHLOROBENZENE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,4-TRIMETHYLBENZENE	ND	ND	ND	-0.00083	ND	ND	ND	ND	ND	ND
1,2-DIBROMOETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-DICHLORO-1,1,2,2-TETRAFLUOROETHANE	ND	ND	ND							
1,2-DICHLOROETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-DICHLOROETHENE	0.05879	-0.02500	ND	-0.06190	0.22114	ND	ND	ND	-0.00781	ND
1,2-DICHLOROPROPANE	ND	-0.00196	0.01043	ND	ND	ND	ND	ND	ND	ND
1,2-DIMETHOXYETHANE		-0.00022		-0.00003						
1,2-DIMETHYLCYCLOPENTANE					ND					
1,3,5-TRIMETHYLBENZENE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-BUTADIENE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-DICHLORO-1,1,2,2,3-PENTAFLUOROPROPANE	0.00204						-0.00061			
1,3-DICHLOROBENZENE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-DIOXOLANE		-0.03900		-0.00035					ND	
1,4-DICHLOROBENZENE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,4-DIOXANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-BROMOPROPANE	0.72247									
1-BUTENE				-0.00008	ND					-0.00006
1-FLUORO-1,1-DICHLOROETHANE	0.00953									
1-HEXENE										
1-PENTANOL										
2,2,3-TRIMETHYLBUTANE										
2,3-DIMETHYLPENTANE				ND	ND	ND	-0.01119	ND	-0.00005	ND
2,4-DIMETHYLPENTANE										
2,5-DIMETHYLFURAN	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-BUTANONE	0.04910	0.00447	0.06532	0.00592	0.02451	-0.02548	0.00616	0.00103	0.00972	0.00609
2-BUTENAL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-BUTOXYETHANOL+					ND					
2-ETHOXYETHANOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-ETHYL-1-HEXANOL				ND				0.00089	-0.00266	-0.00441
2-ETHYLHEXANOL					0.00180					
2-HEPTANONE	ND	-0.00109	-0.00106	-0.00054	-0.00054	ND	ND	ND	ND	ND
2-HEXANONE				-0.00030						
2-METHOXY-2-METHYLPROPANE							ND			
2-METHYL-1,3-BUTADIENE				-0.00208				-0.00417		
2-METHYL-1-PROPANOL					-0.00010					
2-METHYL-1-PROPENE						-0.00006	-0.00005		0.00021	
2-METHYL-2-PROPANOL	ND	-0.00021	0.00344	-0.00008	-0.00008	-0.00032	0.00553	0.00001	0.00052	0.00075
2-METHYL-2-PROPENAL	ND	-0.01471	0.25579	-0.00735	-0.00735	ND	ND	0.00175	ND	-0.01471
2-METHYLBUTANE	ND	ND	ND	ND	ND	ND	ND	-0.00008	ND	ND
2-METHYLFURAN				ND	ND	ND	ND	ND	-0.00005	ND
2-METHYLHEXANE				ND	ND	-0.00005	-0.00951			ND
2-METHYLPENTANE								ND		
2-PENTANONE	-0.00036	0.00079	ND	-0.00018	ND	ND	ND	0.00040	ND	ND
2-PENTENAL	0.10714	-0.01190	ND	-0.00595	ND	ND	ND	ND	ND	ND
3,3-DICHLORO-1,1,1,2,2-PENTAFLUOROPROPANE							-0.00063			
3,3-DIMETHYLPENTANE					ND					
3-BUTEN-2-ONE	ND	ND	ND	-0.02907	ND	ND	ND	ND	ND	ND
3-CARENE					ND					
3-CHLOROPROPENE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-DICHLOROPROPENE									ND	
3-HEPTANONE				0.00652						
3-METHYLHEXANE				ND	ND	-0.00012	-0.01627	ND	-0.00019	-0.00010
3-METHYLPENTANAL				ND						
3-METHYLPENTANE					ND					

Continued

Table A, Continued

Compound	LM	MPLM	N1	N2	N3	Orb 1	Orb D	SX1	SX3	SXD
4-METHYL2-PENTANONE	-0.00018	-0.00018		-0.00009	ND	-0.00009	ND	0.00052	0.00056	0.00234
ACETALDEHYDE	-0.02325	0.00228	-0.01806	0.23978	0.03039	-0.02095	-0.00480	0.01650	0.00446	0.08871
ACETIC ACID, 2-METHYLBUTYLESTER								-0.00016		
ACETONE	0.11497	-0.02999	0.07976	0.00968	-0.00026	-0.00696	-0.00548	0.00613	-0.00531	0.00255
ACETONITRILE	ND	ND		-0.00187	ND	ND	ND	ND	ND	ND
ACRYLONITRILE	ND	-0.00893	ND	0.04911	ND	ND	ND	ND	ND	ND
BENZALDEHYDE				-0.00007						
BENZENE	ND	-0.12500	ND	-0.00833	ND	ND	ND	ND	ND	ND
BROMOMETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BROMOTRIFLUOROMETHANE	-0.00004	ND	-0.00004							
BUTANAL	-0.00568	-0.00568	-0.00021	-0.00284	-0.00078	0.00192	-0.00203	0.00794	0.00260	0.01395
BUTANE						ND				ND
BUTYL ACETATE	-0.00013	-0.00013	-0.00013	-0.00016	-0.00017	ND	ND	-0.00014	0.00031	0.00231
C10-ALKANE							-0.00222	-0.00161		
C11-ALKANE						0.00442	0.01909	ND	ND	0.01271
C11-ALKANE						0.00280	0.01256			
C11-ALKANE							0.01187	ND		0.00611
C11-ALKANE							0.01144	-0.00184		-0.00212
C11-ALKANE							0.00592			
C11-ALKANE							0.00561			
C11-ALKANE							0.00068			
C11-ALKANE							-0.00050			
C11-ALKANE							-0.00278			
C12-ALKANE					ND	0.00408		0.00443	0.00308	ND
C12-ALKANE					ND	0.00360		0.00394	0.00298	ND
C12-ALKANE					ND	0.00210		0.00369		-0.00158
C12-ALKANE					ND	0.00191		0.00358		
C12-ALKANE					ND	0.00186		0.00346		
C12-ALKANE						-0.00175		ND		
C12-ALKANE						-0.00205		ND		
C13-ALKANE										0.01364
C2-SUBSTITUTED CYCLOHEXANE								0.00274		
C2-SUBSTITUTED CYCLOHEXANE								0.00083		
C2-SUBSTITUTEDCYCLOPENTANE					ND					
C2-SUBSTITUTEDCYCLOPENTANE					ND					
C2-SUBSTITUTEDCYCLOPENTANE					ND					
C2-SUBSTITUTEDCYCLOPENTANE					ND					
C3-SUBSTITUTED BENZENE								ND		
C3-SUBSTITUTED CYCLOHEXANE								0.00268		
C3-SUBSTITUTED CYCLOHEXANE								0.00223		
C3-SUBSTITUTED CYCLOHEXANE								ND		
C4-SUBSTITUTED BENZENE								ND		
C4-SUBSTITUTED BENZENE								ND		
C4-SUBSTITUTED CYCLOPENTANE								ND		
C5-ALKANE			ND							
C5-ALKANE					-0.00039					
C7-ALKANE			-0.00002		ND	ND				
C7-ALKANE					ND					
C8-KETONE				-0.00048	ND					
C9-ALKANE								-0.00008	ND	ND
C9-KETONE				-0.00775	0.00737					
CARBON DIOXIDE	-0.12017	-0.17100	-0.14677	-0.24309	-0.28012	-0.24380	-0.11960	-0.40345	-0.53154	-0.12084
CARBON DISULFIDE	-0.00156	0.00343	-0.00156	0.00804	0.00600	-0.00192	-0.00078	ND	-0.00078	-0.00156
CARBON MONOXIDE	0.52562	0.01600	-0.05500	ND	0.11947	-0.01763	-0.04417	0.00203	0.00180	-0.05434
CARBON TETRACHLORIDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CARBONIC ACID, DIMETHYLESTER				-0.00001		-0.00004	-0.00003			-0.00007
CARBONYL SULFIDE				0.02418	0.04815	-0.00260	0.00525	-0.00208	0.00385	-0.00208
CHLOROBENZENE	ND	ND	ND	ND	ND	ND	ND	0.00060	ND	ND
CHLORODIFLUOROMETHANE					ND					
CHLOROETHANE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CHLOROFORM	ND	-0.00510	ND	ND	ND	ND	ND	ND	ND	ND
CHLOROMETHANE	-0.00061	-0.00061	-0.00061	-0.00030	ND	ND	ND	ND	ND	ND
CHLOROPROPENE	ND									
CHLOROROPROPENE										
CIS-1,2-DICHLOROETHENE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CIS-1,3-DICHLOROPROPENE	ND					ND				
CYCLOHEXANE		-0.00045	ND		ND			0.00400		
CYCLOHEXANONE	0.00681	-0.00042	0.01322	0.00128	-0.00052	ND	ND	ND	ND	ND
CYCLOPENTANE								ND		

Continued

Table A, Continued

Compound	LM	MPLM	N1	N2	N3	Orb 1	Orb D	SX1	SX3	SXD
DECAMETHYLCYCLOPENTASILOXANE	ND		-0.00093	ND	ND	-0.00186	-0.02912	-0.00537	-0.00341	0.00959
DECAMETHYLTETRASILOXANE			ND							
DECANE				-0.00005						
DICHLORODIFLUOROMETHANE	-0.00003	-0.00005	-0.00005			ND				
DICHLOROMETHANE	0.00897	-0.20363	0.04552	-0.00026	-0.00154	-0.00026	ND	ND	-0.00234	ND
DIFLUOROCHLOROMETHANE							ND			
DIMETHOXYMETHANE							-0.00004			-0.00013
DIMETHYL DISULFIDE							ND		ND	
DIMETHYL SULFIDE							ND			
DIMETHYLDISULFIDE	ND	ND	ND	ND	ND		ND		ND	ND
DODECAMETHYLCYCLOHEXASILOXANE			-0.00005							
DODECAMETHYLPENTASILOXANE	0.00207									
ETHANOL	0.01211	-0.00195	0.00744	-0.00116	-0.00079	-0.00046	-0.00034	-0.00063	-0.00445	-0.00045
ETHYL ACETATE	ND	-0.00014	ND	-0.00007	-0.00007	-0.00016	-0.00031	-0.00018	-0.00115	0.00028
ETHYLBENZENE	ND	-0.00019	0.00311	-0.00020	ND	ND	ND	0.00121	0.00061	0.00293
ETHYLCYCLOPENTANE					ND					
ETHYLENE	ND	ND	ND							
ETHYLENE OXIDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
FLUORINATED HYDROCARBON	ND	ND	ND							
FLUOROTRIMETHYLSILANE		0.74650		-0.13913	0.42350	0.15000	-0.05000		0.18519	0.42928
FORMALDEHYDE						ND			ND	
FORMIC ACID, ETHYLESTER						ND				
FREON11				-0.00003	-0.00010	ND	ND	ND	ND	ND
FREON113				ND	ND	ND	-0.00093		ND	
FREON114				-0.00011	ND	ND	ND	ND	ND	ND
FREON12				ND	ND	ND	ND	ND	ND	ND
FURAN	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
HEPTANAL	-0.00357	-0.00357	-0.00446	0.00357	ND	ND	ND	0.00134	ND	ND
HEXACHLORO-1,3-BUTADIENE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
HEXAMETHYLCYCLOTRISILOXANE	ND	-0.12191	0.07173	ND	ND	-0.04469	-2.37876	-0.02064	0.03511	-0.06294
HEXAMETHYLDISILOXANE	ND									
HEXANAL	-0.00410	-0.00410	-0.00510	0.00405	-0.00069	ND	0.00488	0.00333	ND	0.00737
HEXANE	ND	-0.00014	0.00000	0.00000	ND	ND	-0.00114	0.00007	ND	-0.00012
HYDROGEN	-0.00633	-0.00268	ND	ND	-0.00475	-0.00422	-0.00281	-0.00180	-0.01391	-0.00061
ISOBUTANE					ND	0.00304	ND	0.00028	0.00672	0.00329
ISOPRENE					-0.00767	ND	ND		-0.01164	
ISOPROPANOL	0.12778	-0.00678	0.06453	-0.00944	-0.02769	-0.01188	-0.01141	0.02938	0.00088	-0.01391
LIMONENE				-0.00002	-0.00040	-0.00070	ND	ND	-0.00063	ND
M/P-XYLENES	ND	-0.00011	-0.00011	-0.00023	0.00096	-0.00084	ND	0.00329	0.00205	0.00850
MESITYL OXIDE	-0.00063	ND	ND	ND	ND	ND	ND	ND	ND	ND
METHANE	-0.05540	-0.00074	-0.00086	-0.00019	-0.00023	-0.00046	-0.00059	ND	-0.00238	-0.00023
METHANOL	1.53400	-0.03784	0.59222	0.04816	-0.00276	-0.00296	-0.01942	0.01445	-0.00115	0.09163
METHYL ACETATE	ND	ND	ND	-0.00010	ND	-0.00010	ND	ND	-0.00052	-0.00021
METHYLCYCLOHEXANE					ND					
METHYLCYCLOPENTANE					ND					
N-BUTANOL	0.01279	-0.01093	0.02264	0.00180	0.01281	-0.00066	-0.00041	0.00104	0.00154	0.00927
N-HEPTANE				ND	ND	ND	-0.00104	0.00011	-0.00005	-0.00010
NONANAL						ND	0.00473			
NONANE				ND	ND		ND	0.00009	ND	ND
N-PROPANOL	0.01650	-0.00040	0.02573	0.00215	-0.00028	-0.00030	-0.00042	-0.00009	-0.00035	-0.00053
OCTAFLUOROPROPANE	-0.00015	-0.00003	ND	ND	-0.00055	-0.00001	ND	-0.00003	-0.00003	-0.00005
OCTAMETHYLCYCLOTRISILOXANE	ND	-0.06153	0.00927	ND	ND	-0.00007	-0.03520	0.00013	-0.00030	0.00062
OCTANAL				-0.00158						
OCTANE				ND	ND	ND	ND	0.00012	ND	0.00155
O-XYLENE	ND	-0.00011	0.00180	-0.00007	-0.00017	-0.00039	-0.00034	0.00157	-0.00035	0.00415
PENTAMETHYL DISILOXANE-1-OL	0.01583							0.00299		-0.00423
PENTANAL	-0.00472	-0.00472	-0.00023	0.00475	-0.00078	ND	0.00471	0.00446	ND	0.01053
PENTANE	ND	ND		0.00000	-0.00023	ND	ND	0.00049	ND	0.00060
PERFLUORINATED ALKANE										-0.000003
PERFLUORO-2-METHYLPENTANE						ND	ND	0.00798	ND	-0.00899
PERFLUORODIMETHYLCYCLOHEXANE	ND		ND							
PERFLUORO-N-PENTANE								ND		
PERFLUORO-N-PENTANE										-0.000043
PINENE					-0.00020					
PROPANAL	0.00283	-0.02493	-0.00026	0.00142	-0.00505	-0.00354	-0.00253	0.00100	-0.00590	0.02565
PROPANE				ND	ND	-0.00023		-0.00023	ND	ND
PROPENAL	-0.22222	ND	-0.33333	-0.27778	-1.12014		ND	ND	ND	ND
PROPENE				-0.00001	-0.00001	-0.00058	ND		-0.00029	0
STYRENE	ND	ND	ND	ND	ND		ND	ND	ND	ND

Continued

Table A, *Continued*

Compound	LM	MPLM	N1	N2	N3	Orb 1	Orb D	SX1	SX3	SXD
SULFURHEXAFLUORIDE				-0.00001	-0.00006		ND	ND		
TETRACHLOROETHENE	0.01331	-0.00074	ND	ND	ND		ND	ND	ND	ND
TETRAHYDROFURAN								ND		
TOLUENE	0.00610	-0.00134	0.01313	-0.00042	0.00014	-0.00256	0.00642	0.02237	0.00583	0.03378
TRANS-1,3-DICHLOROPROPENE	ND	ND	ND	ND	ND		ND	ND	ND	ND
TRICHLOROETHENE	ND	0.00160	ND	ND	ND		ND	ND	ND	ND
TRICHLOROFLUOROMETHANE	ND	ND	ND							
TRIMETHYLSILANOL	0.26846	-0.01150		0.04686	0.15077	-0.00473	-0.01736	0.13998	0.14518	1.14470
UNIDENTIFIED FLUORINATED HYDROCARBON								0.00207		ND
UNKNOWN SILOXANE COMPOUND								-0.01405	ND	
VINYL CHLORIDE	ND	ND	ND	ND	ND		ND	ND	ND	ND

T _p -T _a Category Counts	LM	MPLM	N1	N2	N3	Orb 1	Orb D	SX1	SX3	SXD
Present ONLY at OGT	10	3	2	1	2	3	4	17	4	4
Contribute to T-val = Yes and T _p > T _a	11	6	16	15	11	7	10	26	16	23
Contribute to T-val = Yes and T _p < T _a	0	11	0	2	6	13	11	6	4	4
Contribute to T-val = No and T _p < T _a	12	14	10	14	12	10	8	0	2	5
Present ONLY at Ingress	6	18	12	29	14	16	18	12	19	17
Contribute to T-val = No and T _a = (ND)	0	0	0	0	0	0	0	0	0	1
No data for OGT and Ingress	114	120	120	100	84	101	90	85	99	98
Total	153	172	160	161	129	150	141	146	144	152