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Case Studies in Crewed Spacecraft Environmental Control and Life Support System Process Compatibility and Cabin Environmental Impact

J.L. Perry
Marshall Space Flight Center, Huntsville, Alabama

December 2017

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National Aeronautics and
Space Administration

Marshall Space Flight Center • Huntsville, Alabama 35812

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LIST OF SYMBOLS AND ACRONYMS

Al_2O_3	alumina
ALOHA®	Areal Locations of Hazardous Atmosphere (software developed jointly by NOAA and EPA)
ANT	antifreeze and coolant (trade name)
APM	attached pressurized module
APTS	aminopropyltriethoxysilane
AR	atmosphere revitalization
ATC	active thermal control
ATCS	active thermal control system
ATV	automated transfer vehicle
BMP	Russian acronym for microimpurity adsorption unit
Br	bromine
Br_2	bromine
BTP	bromotrifluoropropene
BXF	Boiling Experiment Facility
CAA	Clean Air Act
CAM	Centrifuge Accommodation Module
CAS	Chemical Abstracts Service
CBA	carbon/charcoal bed assembly (charcoal)
$CBrClF_2$	bromochlorodifluoromethane
CBr_2F_2	dibromodifluoromethane

LIST OF SYMBOLS AND ACRONYMS (Continued)

$CBrF_3$	bromotrifluoromethane
CCAA	common cabin air assembly
CDMK	carbon dioxide monitoring kit
CDRA	carbon dioxide removal assembly
CEA	clean fire extinguishing agent (3M trade name)
CEV	crew exploration vehicle
C_3F_8	octafluoropropane/perfluoropropane
C_3HF_7	1,1,1,2,3,3,3-heptafluoropropane
C_4F_{10}	decafluorobutane/perfluorobutane
C_5F_{12}	dodecafluoropentane/perfluoropentane
C_9F_{16}	hexadecafluorobicyclo[4.3.0]nonane/perfluorobicyclononane
CF_3I	trifluoroiodomethane
CH_4	methane
CIPA	cure in place ablator
CKB	Russian acronym for the humidity control unit (SKV in English)
Cl_2	chlorine
CO	carbon monoxide
CO_2	carbon dioxide
COA	catalytic oxidizer assembly
COF_2	carbonyl fluoride
COS	carbonyl sulfide

LIST OF SYMBOLS AND ACRONYMS (Continued)

CS_2	carbon disulfide
DC	docking compartment
DTO	detailed test objective
EC	European Community (regulation)
ECLS	environmental control and life support
ECLSS	environmental control and life support system
ELM	Experiment Logistics Module
EPA	Environmental Protection Agency
ESA	European Space Agency
EVA	extra-vehicular activity
F_2	fluorine
FGB	Russian acronym for the functional cargo block (Zarya)
FID	flame ionization detection
FOA	Russian acronym for expendable packed bed
FORP	fuel-oxidizer reaction product
FVP	ФВП (Russian); Russian acronym for harmful impurities filter
GAC	granular activated carbon/charcoal
GC	gas chromatography
GCF	Granada Crystallization Facility
GKS	Russian acronym for a second generation solid fuel oxygen generator
GOX	gaseous oxygen

LIST OF SYMBOLS AND ACRONYMS (Continued)

HBr	hydrogen bromide
HCl	hydrogen chloride
HEPA	high-efficiency particulate air
HF	hydrogen fluoride
HFC	hydrofluorocarbon
HFE	hydrofluoroether (3M trade name)
Hg	mercury
H_2O	water
H_3PO_4	phosphoric acid
HT	heat transfer
IMV	intermodule ventilation
ISS	International Space Station
ITCS	internal thermal control system
JAXA	Japanese Aerospace Exploration Agency
JCF	Japanese Crystallization Facility
JEM	Japanese Experiment Module (Kibo)
JSC	Johnson Space Center
LEL	lower explosive limit
Li_2CO_3	lithium carbonate
LiBr	lithium bromide
LiCl	lithium chloride

LIST OF SYMBOLS AND ACRONYMS (Continued)

$LiClO_4$	lithium perchlorate
LiOH	lithium hydroxide
LSI	Life Systems, Inc.
$LiSOCl_2$	lithium thionyl chloride
MIC	microbially induced corrosion
MIT	methyl-isothiazolone
MPLM	multipurpose logistics module
MSDS	material safety data sheets
MSFC	Marshall Space Flight Center
MSG	microgravity science glovebox
$NaClO_4$	sodium perchlorate
NDMA	N-nitrosodimethylamine
NESC	NASA Engineering and Safety Center
NFPA	National Fire Protection Agency
NH_3	ammonia
NOAX	nonoxide adhesive experimental
NO_x	oxides of nitrogen
OPA	ortho-phthalaldehyde
OPF	octafluoropropane
OSHA	Occupational Safety and Health Administration
Pd	palladium

LIST OF SYMBOLS AND ACRONYMS (Continued)

PFA	portable fan assembly
PFE	portable fire extinguisher
PFIB	perfluoroisobutylene/perfluoroisobutene
PKF-T	Russian acronym for thermal catalytic reactor
PM	pressurized module
PMA	pressurized mating adapter
POE	polyolester
PS	pressurized section
Pt	platinum
ROS	Russian On-orbit Segment
SBA	sorbent bed assembly
SF_6	sulfur hexafluoride
SFOG	Russian solid fuel oxygen generator (Russian acronym TGK)
SKV	Russian acronym for the condensing heat exchanger
SM	service module (Zvezda)
SMAC	spacecraft maximum allowable concentration
SNAP	Significant New Alternatives Policy
SO_2	sulfur dioxide
$SOCl_2$	thionyl chloride
SpaceX	Space Exploration Technologies Corporation
SPICE	Smoke Point In Co-Flow Experiment

LIST OF SYMBOLS AND ACRONYMS (Continued)

SPRT	System Problem Resolution Team
STS	Space Transportation System
TCC	trace contaminant control
TCCS	trace contaminant control subassembly/system
TCCS CP	Trace Contaminant Control Simulation Computer Program
TCS	thermal control system
TG-IR	thermogravimetric-infrared
TGK	(Russian acronym) solid-fuel oxygen generation system
THC	temperature and humidity control
TIK	Russian acronym
UPA	urine processor assembly
U.S.	United States
USOS	United States On-orbit Segment
VCD	vapor compression distillation
VOC	volatile organic compound
VUA	volatile usage agreement
WP	water processor
ZBOT	Zero Boil-Off Tank (experiment)

NOMENCLATURE

A	surface area (ft^2); adsorption potential
C	gas phase concentration (g/cm^3); cabin concentration (mg/m^3); free halogen concentration (mg/m^3)
C_A	atmospheric concentration
C_L	liquid phase concentration (mg/L)
C_o	initial concentration (mg/m^3)
C_s	vapor pressure (mg/m^3)
D	diffusion coefficient (cm^2/s)
G	gaseous molar flow rate
g	contaminant generation rate
g_B	generation rate in volume B
$k_H(T)$	Henry's constant at the process operating temperature; Henry's Law constant for the contaminant
L	condensate molar flow rate; adsorption zone length (cm)
M	molecular weight (g/mole)
m	contaminant mass at time
m_A	total mass of contaminant in volume A
m_B	total mass of the contaminant in volume B
m_o	contaminant mass at time equal to zero
n_i	number of moles of the dilute VOC
n_w	number of moles of water

NOMENCLATURE (Continued)

P	pressure (1 atm)
P_V	vapor pressure (mm Hg)
p_i	partial pressure in air
QR	evaporation rate (lb/min)
q	activated carbon loading (cm^3/g liquid)
R	ideal gas law constant
T	absolute/cabin temperature (K)
t	time (s)
u	air velocity (m/s)
V	cabin volume
V_A	free volume of volume A
V_B	free volume of volume B
V_m	liquid molar volume at normal boiling point (cm^3/g mole)
v	flow velocity (cm/s)
$\dot{v}_A$	ventilation flow from the volume A to volume B
$\dot{v}_B$	ventilation flow from volume B to volume A
x	constant; liquid phase molar fraction
x_i	liquid mole fraction
y	vapor/gas phase molar fraction
α	constant; preexponential factor
β	constant; exponential factor

NOMENCLATURE (Continued)

γ	constant
$\sum \eta v$	contaminant removal capacity
η	single-pass decimal removal efficiency; methane oxidation efficiency in decimal form
v	process air flow rate through the condensing heat exchanger core (m^3/hr)

TECHNICAL PUBLICATION

CASE STUDIES IN CREWED SPACECRAFT ENVIRONMENTAL CONTROL AND LIFE SUPPORT SYSTEM PROCESS COMPATIBILITY AND CABIN ENVIRONMENTAL IMPACT

1. INTRODUCTION

Designing for spacecraft cabin trace contaminant control (TCC) requires substantial system-level design activity within the confines of the air quality standard. In the case of crewed spacecraft, that standard is the spacecraft maximum allowable concentration (SMAC). Materials selection and control, hardware design, manufacturing processes, chemical process design, and mission characteristics as well as crew size and activities are only a few of the technical elements that can influence TCC and, therefore, must be considered when developing the crewed spacecraft's active and passive TCC methods.[1]

Passive TCC plays a vital role in minimizing the total trace contaminant load to the spacecraft's cabin environment and provides a component to determining the active TCC equipment size.[2] Elements of passive TCC include materials screening, selection, and control activities to minimize off-gassing load and reduce risk for releasing volatile contaminants, purposely or accidentally, into the cabin. Contaminant releases into the cabin can present acute and chronic health and safety risks to the crew as well as interact with the spacecraft's life support system and cabin environment in a deleterious manner. Technical areas for implementing passive TCC activities to minimize volatile contaminant emissions into the cabin environment include evaluating the following:[1]

- Offgassing characteristics of vehicle structural and systems materials.
- Volatility and containment methods for vehicle systems' working fluids.
- Vehicle system vents into the cabin for composition and rate.
- Offgassing characteristics of experiment payload materials.
- Volatility and containment methods of experiment payload working fluids and reagents.
- Offgassing characteristics, volatility, and procedures of housekeeping materials, solvents, and processes.
- Offgassing characteristics, volatile component content, and application procedures of personal hygiene materials, processes, and products.
- Manufacturing and prelaunch ground processes relative to volatile solvent use.

In the case of vehicle systems and payloads, passive TCC efforts also seek to ensure that fluids—both gases and liquids—used in the equipment are contained. Containment requirements to yield a design for minimum risk relative to fluid leakage are driven more strongly by a fluid's toxic hazard, yet passive TCC plays a role in the overall fluid containment design.

Some volatile contaminants can interact with environmental control and life support system (ECLSS) processes such that they can reduce component service life or degrade system function. This is particularly true for polar volatile organic compounds (VOCs) such as methanol, ethanol, 2-propanol, 2-propanone, and glycol compounds,[3,4] which are commonly used for experiment payload reagents and are found in cleaning fluids used for in-flight housekeeping and prelaunch hardware processing. For this compound class, the cabin concentrations must be maintained far below the individual compound's SMAC to minimize impacts on the ECLSS. Therefore, it is not enough to merely ensure that the SMACs are met. Understanding the interactions that chemicals used in vehicle systems as well as those used by the crew have with the ECLSS and the cabin environment is a vital component of mission safety and success. Further, understanding the fate of chemical contaminants in the cabin environment is an important component to evaluating cabin environmental impact.

Characterizing volatile contaminant emissions into the cabin environment requires information on the contaminant and its use. Contaminant emissions may be in the form of bulk quantity emissions that may occur during fluid system maintenance activities or containment failures and fugitive emissions that may occur during routine vehicle operations. Bulk quantity emissions represent acute circumstances involving a large quantity of material released into the cabin environment over a short time period while fugitive emissions represent chronic circumstances involving a small quantity of material released into the cabin environment over a long time period. While bulk quantity emissions are a difficult challenge for remediation, the risk for such emissions is greatly reduced through designing the fluid-containing equipment according to standards that lead to a design for minimum risk. Fugitive emissions, however, due to the small quantity of material involved, can present a greater challenge because their location and magnitude may vary. Minor fugitive emissions can result from valve and flange leakage, housekeeping operations, payload operations, and personal care product use. System venting into the cabin accounts for larger fugitive emissions that may require special treatment to minimize impacts to the cabin environment. Fugitive emissions by their very nature can be pervasive and diverse. Fugitive emissions are typically controlled adequately through specifying maximum allowable equipment leakage rates and establishing material usage procedures. While most fugitive emissions are small and can be accommodated within the operational margins of the active TCC equipment, the potential for growth in the number, size, and distribution of emission sources aboard a spacecraft over time can reach a point that may overwhelm the active TCC equipment. For this reason, all emissions must be evaluated relative to ECLSS compatibility and cabin environmental impact.

A process for evaluating experiment payload materials and chemicals was introduced by reference 1. This process, illustrated in figure 1, is updated here to address not only payload materials and chemicals but also vehicle systems and processes relating to housekeeping, manufacturing, and prelaunch hardware cleaning. The process begins with identifying material candidates and conducting an initial screening based on heritage flight experience, safety data, and physical properties. Candidates that pass initial screening are then subjected to more detailed assessment relative to thermal and chemical stability, toxicity, flammability, and biohazards. Compatibility with the ECLSS and persistence in the cabin environment in an event of an emission into the cabin are also assessed. The following narrative discusses the motivation for assessing ECLSS compatibility and cabin environmental impact, active TCC design practice, and guidelines for implementing this process. Examples for implementing the process that evaluate various emission types and quantities are presented.

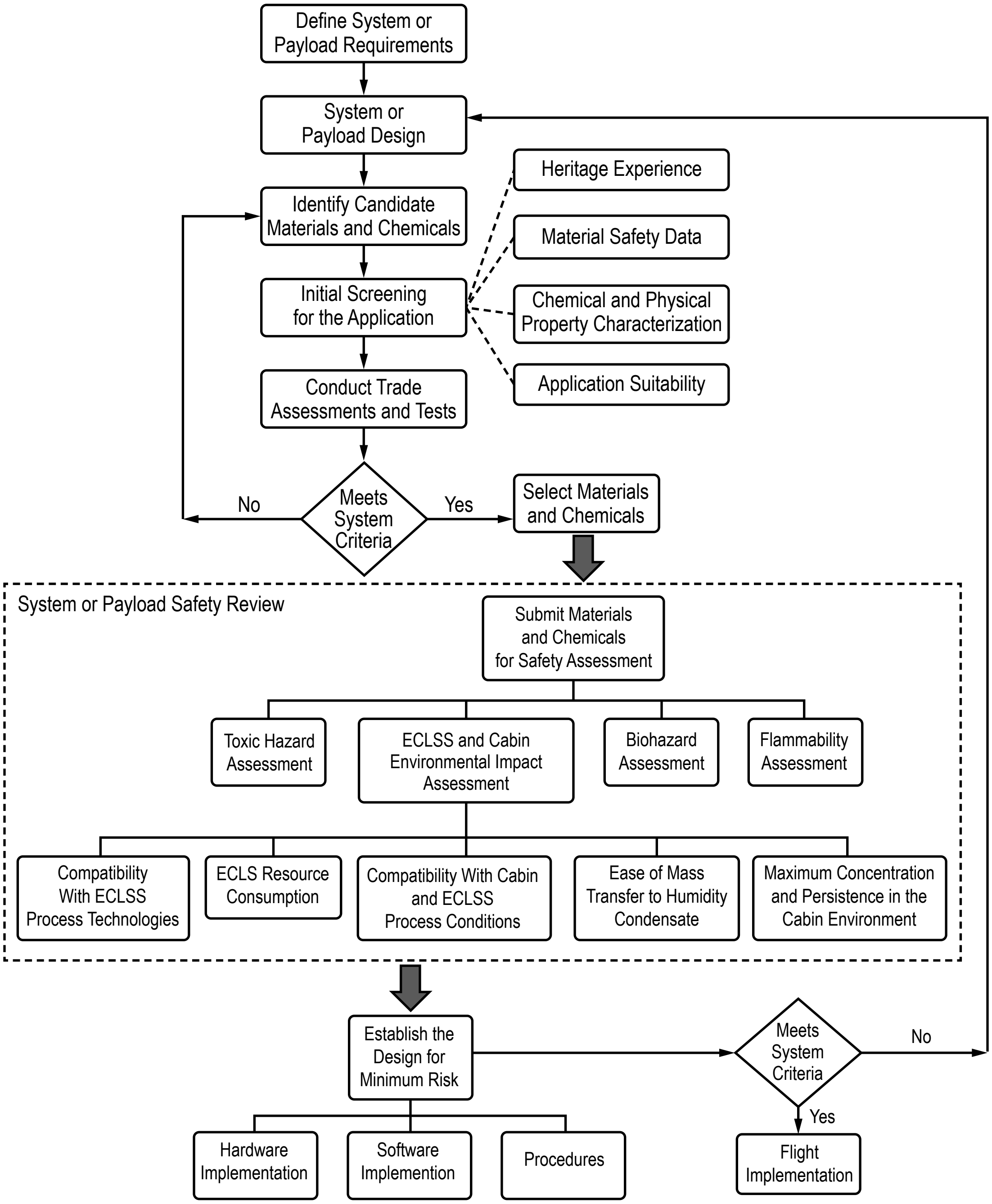


Figure 1. System and experiment payload material and chemical evaluation process.

1.1 Motivation for Evaluating Environmental Control and Life Support System Compatibility and Cabin Environmental Impact

Figures of merit for NASA's space exploration missions include safety, mission success, effectiveness, and affordability.[5] Safety is paramount and all of the other figures of merit flow from safety assurance. Maintaining the highest standard for crew health and safety during all mission phases from launch to landing is the priority for ensuring success for NASA's crewed space exploration programs and missions.

Contamination of the crewed spacecraft cabin environment leading to degradation or loss of ECLSS capability or function can adversely impact crew health, safety, and ultimately mission success. In support of NASA's mission safety and success objectives, vehicle system developers must consider the potential impacts to ECLSSs and the vehicle cabin environment from bulk quantity and fugitive emissions from their equipment. The NASA safety reviews consider all chemicals and materials and their use in a crewed vehicle's habitable volume. Understanding the impact chemicals and materials may have on the ECLSS and the cabin environment early in the payload or system design stage can prevent or mitigate hazards and avoid costly redesigns.

The results from ECLSS compatibility and cabin environmental impact assessment are useful to vehicle system and experiment payload developers as guidance for achieving a design that provides for minimum risk through ensuring adequate containment and developing safe operational protocols supported by flight rules and procedures to ensure ECLSS protection and to minimize the potential for contamination of the cabin environment.

1.2 Spacecraft Active Trace Contaminant Control Design Practice

Because specifying, designing, and sizing the active TCC equipment for a spacecraft precede those data necessary to fully validate its design, standard design practice dictates a conservative approach whereby the active contamination control system performs its function unassisted by any other systems or processes in the cabin.[1] This means that overboard atmospheric leakage and assists provided by other air processing systems such as carbon dioxide (CO_2) removal and humidity control equipment are not considered during the design and validation of the active TCC equipment.

The design point for the active TCC equipment consists of the equipment offgassing load and the crew metabolic load. For vehicles smaller than the International Space Station, the crew metabolic load is the larger design point component.[2] It is also important to note that the active TCC is not designed to accommodate either acute bulk quantity emissions or chronic fugitive emissions, including venting, from other vehicle systems, payloads, or vehicle operations. As well, the active TCC is not to be used as a hazard control for other onboard systems or payloads. In this context, bulk quantity and fugitive emissions into the cabin overlay the active TCC design capacity. By using design safety factors up to 20%, the active TCC design capacity has functional margin. The type and size of additional emissions are evaluated on a case-by-case basis to determine to what extent they utilize the active TCC design's functional margin.

It is informative to expand the assessment beyond the active TCC capability, however, to address the fate of the contamination to address the impact upon all ECLSS processes—both atmospheric and water processing. Therefore, any contamination load that is not found in the active TCC design load is evaluated individually for specific removal routes via the active TCC equipment, humidity control equipment, and other environmental control and life support (ECLS) process equipment as may be indicated. The compatibility with each ECLSS process that may be affected by the contaminant's presence in the cabin environment is evaluated. Processes within the ECLSS of particular interest include those that operate at high temperatures and those that purify humidity condensate to a potable product for crew consumption.

In the event that a vehicle system or process is changed during a vehicle's lifetime, a complete assessment for ECLSS compatibility and cabin environmental impact is necessary to ensure any potential impacts to the cabin environment, as well as the ECLSS equipment, are within acceptable operational margins. The ECLSS hardware and process compatibility and cabin environmental impact assessment approach focuses on assessing the relevant impacts associated with bulk quantity and fugitive emissions into a spacecraft cabin atmosphere. The impact assessment may consider cabin air quality interface requirements, flight rule guidelines, emergency response guidelines, guidelines pertaining to hatch opening and cabin atmosphere exchange between a primary crewed space vehicle and a visiting vehicle, and other guidelines as appropriate for the specific crewed spacecraft configuration.

1.3 Environmental Control and Life Support System and Cabin Environmental Impact Rating Definitions

The definitions for the ECLSS compatibility and cabin environmental impact take guidance from the Occupational Safety and Health Administration's (OSHA's) guidance for hazard classification[6] and the globally harmonized system for classifying and labelling chemicals developed by the United Nations.[7] These guidelines use environmental hazard categories based on aquatic system impacts. A spacecraft's life support system can be viewed as an analogue for the environmental impact hazard category rating method. Using these classification methods as guides, the ECLSS compatibility rating categories were developed as defined in table 1. The ECLSS compatibility ratings are based on functional resource consumption and impact on the equipment maintenance cycle. The cabin environmental impact assesses the time to recover after a contamination emission into the cabin environment. The time to recover considers on the 'natural' means for recovery provided by the ECLSS's operation with no assist to remove 95% of the contamination released into the cabin environment by the emission event. As such, this rating is an indicator of a contaminant's persistence in the cabin environment. The cabin environmental impact categories are provided in table 2.

Table 1. ECLSS compatibility rating definitions.

Compatibility Level	Criteria
Category E0	Functional capacity consumption is <2%. 100% of the functional margin is retained. No ECLS functional performance degradation. No change in scheduled maintenance.
Category E1	Functional capacity consumption is >2% and <10%. >10% of the functional margin is consumed. No ECLS functional performance degradation. No change in scheduled maintenance.
Category E2	Functional capacity consumption >10% and <25%. >25% of the functional margin is consumed. ECLS functional performance is degraded by <10%. Early replacement of consumable components may be necessary within 9 months.
Category E3	Functional capacity consumption >25% and <50%. >50% of the functional margin is consumed. ECLS functional performance is degraded by >10% and <25%. Early replacement of consumable components may be necessary within 6 months.
Category E4	Functional capacity consumption >50% and <75%. >75% of the functional margin is consumed. ECLS functional performance is degraded by >25% and <50%. Early replacement of consumable components may be necessary within 1 month.
Category E5	Functional capacity consumption >75% and <90%. 100% of the functional margin is consumed. ECLS functional performance is degraded by >50% and <75%. System maintenance is required to restore functional performance within 1 week.
Category E6	Functional capacity consumption >90%. 100% of the functional margin is consumed. ECLS functional performance is degraded by >75%. System maintenance is required to restore functional performance within 1 day.

Table 2. Cabin environmental impact rating definitions.

Impact Level	Criteria
Category A	Time to recover <2 hours.
Category B	Time to recover is >2 hours and <24 hours.
Category C	Time to recover is >24 hours and <72 hours.
Category D	Time to recover is >72 hours and <168 hours.
Category E	Time to recover is >168 hours or the ECLSS is unable to remove substance and it persists in the cabin environment.

The ECLS compatibility and cabin environmental impact rating do not define a hazard as it is normally understood but addresses the potential for life cycle cost impact and worst-case functional capacity and/or capability degradation or loss. The ECLS compatibility and cabin environmental impact rating alone are not intended to dictate levels of containment. The ECLS compatibility category indicates the degree of functional degradation or loss that may occur in the worst-case scenario which may dictate early repair and replacement for an ECLS component, leading to increased life cycle costs. The cabin rating provides insight for toxicology regarding the potential persistence in the cabin environment that can be good information for evaluating the toxic hazard associated with the dose the crew may experience. The ECLS compatibility and environmental impact rating are complementary to assessments of toxic hazard, biohazard, and flammability that are vital to conducting the safety review and can serve as a component in failure mode effects and criticality analysis. When considering the failure severity categories listed in table 3,[8–10] the ECLS compatibility and cabin environmental impact rating typically exist in failure severity categories 3 and 4. On rare occasions, a failure such as a bulk leak of anhydrous ammonia into the cabin environment that overwhelms the ECLS capability leading to evacuating the vehicle may rise to failure severity categories 1 and 2. The probability for material emissions typically occurs in the 'remote' to occasional probability range as defined by reference 10 and summarized in table 4.

Table 3. Failure severity categories.

Category	Description
1	Catastrophic—Loss of Mission: Failure modes that may cause death or permanent disabling injury or the destruction of a major system or the vehicle during the mission.
2	Critical—Degraded Mission: Failure modes that may result in loss of one or more mission objectives.
3	Marginal—Loss of Redundancy: Failure modes that may result in degradation of mission objectives.
4	Negligible—Failure modes that may result in insignificant or no loss to mission objectives.

Table 4. Failure probability levels.

Level	Description
A	Frequent—Likely to occur often during the mission.
B	Probable—Likely to occur several times during the mission.
C	Occasional—Likely to occur sometime during the mission.
D	Remote—Unlikely, but possible to occur during the mission.
E	Improbable—So unlikely it can be assumed the event may not occur during the mission.
F	Eliminated—Incapable of occurring during the mission. Applied to failure modes that have been identified and later eliminated.

2. APPROACH

The approach to determining the ECLSS compatibility and cabin environmental impact rating considers the vehicle configuration, cabin ventilation rates, and removal routes for the contaminant. The removal routes include the active TCC equipment and absorption via humidity condensate for gaseous contaminants. Particulate matter removal is provided by the filter elements in the cabin ventilation system. Removal efficiencies for the active TCC equipment are calculated for these removal routes and used in the cabin material balance to evaluate persistence in the cabin environment as well as the dominant removal sink for the contaminant. Volatile liquid contaminants are assumed to evaporate quickly for a worst-case assumption, but for a more rigorous evaluation, the evaporation rate is calculated to use as a generation rate in the cabin material balance.

Thermal and chemical stability are evaluated through literature surveys and reaction products generated are also evaluated relative to ECLSS compatibility and cabin environmental impact. Impurities contained in a material are also evaluated. In some instances, the reaction products or impurities associated with a material can be the main driver for assigning an ECLS compatibility or cabin environmental impact rating. Reaction products may be produced upon the released material's exposure to high temperature processes contained in the ECLSS or upon exposure to the cabin environmental conditions such as decomposition in the presence of humidity or liquid water.

In the case of a mixture of chemicals, the overall ECLSS hardware and cabin environment impact is set by the chemical determined to have the greatest ECLSS hardware and cabin environment impact. If chemicals or mixtures pose different impacts to ECLSS hardware and/or the cabin environment before, during, or after their use, all of the use stages will be assessed. If a liquid is to be mixed with another liquid of a different impact level, then the resultant mixture also is assessed.

2.1 Cases Considered

Cases considered consist of two types. The first type bounds an absolute worst case during which all containment barriers fail and the entire quantity of material is released. The second type is based upon credible release scenarios, when available, provided by the equipment developer. If details on the release scenarios are not available, the release of the entire amount of the material is assumed in the assessment. Additional guidance relating to assessing chemical releases can be found in reference 11.

2.2 Vehicle and Environmental Control and Life Support System Features

The vehicle and ECLSS features are central to conducting ECLSS compatibility and cabin environmental impact assessments. The habitable volume and the atmosphere scrubbing assets available must be well characterized. Vehicle, ECLSS, and ventilation system design and testing documentation serve as the basis for establishing the cabin free volume, cabin environmental conditions, cabin ventilation architecture and flow rates, and contaminant removal device flow rates.

2.3 Cabin Material Balance

Assessing the ECLSS's capability to effectively control material emissions into the cabin atmosphere to below specified limits requires two stages. The first stage assumes the entire primary vehicle cabin is a single, well-mixed volume and that the effective removal term, $\Sigma\eta v$, remains constant with time. This makes the solution of the basic mass balance equation shown by equation (1) fairly simple. The solved form of the equation is shown by equation (2).

$$\frac{dm}{dt} = g - \left(\frac{\sum \eta v}{V}\right) m \tag{1}$$

and

$$m = m_o e^{-\left(\frac{\sum \eta v}{V}\right)t} + \left(\frac{gV}{\sum \eta v}\right)\left[1 - e^{-\left(\frac{\sum \eta v}{V}\right)t}\right], \tag{2}$$

where

m = contaminant mass at time, t
t = time
g = contaminant generation rate
$\sum \eta v$ = contaminant removal capacity
m_o = contaminant mass at time equal to zero
V = cabin volume.

In the event a contaminant release is large, the removal rate is assumed to be much greater than the contaminant generation rate and equation (2) can be simplified to yield equation (3):

$$m = m_o e^{-\frac{\eta v t}{V}} . \tag{3}$$

Solving equation (3) for time (t) can estimate the time required for cabin contaminant removal yields in equation (4). If more than one scrubbing asset is available, the total effective removal rate, ηv, will be the sum of the effective removal rates for each asset. Performance data documenting capability of each removal asset serve as the basis for the total effective removal rate:

$$t = -\left(\frac{V}{\sum \eta v}\right) \ln\left(\frac{m}{m_o}\right) . \tag{4}$$

Approximate removal times can be determined using an average removal efficiency of 50% for adsorption-based removal devices.

The second assessment stage assumes that, in the case of an inadvertent release, conditions approach those of a steady state. At steady state conditions, equation (2) reduces to a very simple form involving only the generation rate, cabin volume, and effective removal terms as shown by equation (5):

$$m = \frac{gV}{\sum \eta v} \ . \tag{5}$$

Equations (1) through (5), for which their derivation is found in reference 1, are suited for a space vehicle consisting of a single, well-mixed habitable volume or for a multivolume vehicle with very efficient ventilation. Even with effective ventilation, the propagation of contamination between two adjacent space vehicle modules may need to be assessed. In the case of a multimodule vehicle or two docked vehicles that exchange cabin atmosphere through forced ventilation leading to contamination propagation between the two volumes, a more rigorous mass balance approach is necessary. This more rigorous mass balance between two adjacent spacecraft volumes helps to examine the duration of a transient event between the volumes. This more rigorous mass balance requires the simultaneous solution of the mass balance equations for each individual volume. The mass balance equations for the two adjacent volumes are provided by equations (6) and (7), respectively.[12] These equations define the change in contaminant mass as a function of time:

$$\frac{dm_A}{dt} = \frac{\dot{v}_B}{V_B} m_B - \frac{\dot{v}_A}{V_A} m_A - \frac{\sum \eta v}{V_A} m_A + g_A \tag{6}$$

and

$$\frac{dm_B}{dt} = \frac{\dot{v}_A}{V_A} m_A - \frac{\dot{v}_B}{V_B} m_B - \frac{\sum \eta v}{V_B} m_B + g_B \ , \tag{7}$$

where

m_A = total mass of contaminant in volume A
$\dot{v}_B$ = ventilation flow from volume B to volume A
V_B = free volume of volume B
m_B = total mass of the contaminant in volume B
$\dot{v}_A$ = ventilation flow from the volume A to volume B
V_A = is the free volume of volume A
$\sum \eta v$ = removal capacity in the respective volume
g_A = generation rate in volume A
g_B = generation rate in volume B.

Simultaneous solution of equations (6) and (7) provide an equation for each volume in the form of equation (8):

$$m = \alpha + \beta e^{x_x t} + \gamma e^{x_3 t} \quad , \tag{8}$$

where

m = total mass of contaminant in the reference cabin volume
α,β,γ = constants calculated from the segment cabin free volume, ventilation flow, removal capacity, and contaminant generation rate
x_2,x_3 = constants.

The integration constants are calculated from the reference cabin free volume, ventilation flow, and removal capacity parameters as detailed in the equation derivation provided in appendix A. Concentration is calculated by simply dividing the contaminant mass by the reference cabin free volume.

If the entire cabin volume is assumed to be well mixed, or each volume is isolated, the total cabin mass balance equation can be defined more simply as equation (2).

The material balance calculations require information on the contaminant emission or generation rate as well as the single-pass efficiencies for each known removal device. The following sections provide guidance for estimating generation rates and removal device efficiencies.

2.4 Generation Rate Estimate

The generation rate is obtained from system leakage test data and system developer analysis results when available. As noted previously, in the absence of detailed information, it is assumed that the entire quantity of the material is released instantaneously during an emission event. For gaseous contaminants, the leakage rate provides the direct estimate for the generation rate; however, volatility must be considered for liquid contaminants.

In the case of an emission event involving liquids, the generation rate can be approximated by estimating the evaporation rate using calculation techniques documented in the literature and employed by the U.S. Environmental Protection Agency (EPA) for assessing environmental impacts of chemical spills. The equation used for this calculation requires information on air velocity, vapor pressure, molecular weight, and leaked surface area. Equation (9) estimates the evaporation rate, QR, in lb/minute:[13]

$$QR = \frac{0.284u^{0.78} M^{2/3} A P_V}{82.05T} \quad , \tag{9}$$

where

u = air velocity (m/s)
M = molecular weight (g/mole)
A = leaked pool surface area (ft^2)
P_V = vapor pressure (mm Hg)
T = absolute temperature (Kelvin).

It should be noted that equation (9) does not take into account effects associated with evaporative cooling such as more rigorous methods employed in the EPA's Areal Locations of Hazardous Atmosphere (ALOHA) software. The results from equation (9), however, are conservative relative to results obtained when using the more complex ALOHA software. Reference 13 indicates that multiplying the result from equation (9) by 0.63 accounts for the conservatism associated with this approach relative to that employed by the EPA's ALOHA software.

For binary liquid mixtures, evaporation rate is evaluated by applying equation (9) to the calculation method described by Blanchard and Hadlock.[14]

2.5 Incidental Removal by Humidity Control Processes

The removal of trace chemical contaminants in air via absorption by humidity condensate is a well-recognized process.[1,15] The assist provided to the active contamination control equipment on board spacecraft that employ a condensing heat exchanger for humidity control, such as is found aboard the International Space Station (ISS) or planned for future space exploration vehicles, is considered only to address potential impacts to water processing systems that might be part of a space exploration vehicle's ECLSS.

This removal method can be quite effective for water-soluble chemicals such as ammonia, alcohols, aldehydes, short-chain esters, and ketones. It is assumed that such contaminants are present at relatively low concentrations and, as such, can be considered to be infinitely dilute. Under this condition, Henry's Law, shown by equation (10), can be applied to relate the partial pressure in air, p_i, to the liquid mole fraction, x_i, and Henry's constant, $k_H(T)$ at the process operating temperature:

$$p_i = k_H(T)x_i \ . \tag{10}$$

By applying Henry's Law to the humidity condensate mass balance, equation (11), the operating curve relating the liquid and vapor phase mole fractions of a contaminant as a function of the gas and liquid flow rates can be obtained:[1,15]

$$x = \frac{y}{\left[\frac{L}{G} + \frac{k_H(T)}{P}\right]} \ , \tag{11}$$

where

x = liquid phase molar fraction
y = vapor phase molar fractions
L = condensate molar flow rates
G = gaseous molar flow rates
$k_H(T)$ = Henry's Law constant for the contaminant
P = total pressure.

Assumptions pertaining to equation (11) are the following:

- Bulk gas phase contaminant concentration is uniform.
- Turbulent mixing in the heat exchanger results in a gas phase interface concentration equal to the bulk concentration making gas phase mass transfer resistance negligible.
- Rapid mass transfer occurs at the gas-liquid interface which is governed by Henry's Law.
- The overall process is characterized by the condensation of moisture followed by co-current absorption.
- Low concentration of contaminants and rapid mixing in the liquid phase makes liquid phase mass transfer resistance negligible.

Equation (11) is the starting basis for equation (12) which is used for calculating the single-pass decimal removal efficiency, η:[15]

$$\eta = \frac{\left(0.004558889\dot{m}_L T\right)}{\left[0.0045559\dot{m}_L TP + k_H(T)v\right]} \,, \tag{12}$$

where

$\dot{m}_L$ = condensate collection rate (kg/hr)
T = condensing heat exchanger operating temperature (Kelvin)
P = cabin total pressure (1 atm)
$k_H(T)$ = Henry's Law constant (atm) adjusted for the condensing heat exchanger's operating temperature
v = process air flow rate through the condensing heat exchanger core (m^3/hr).

It is important that the Henry's Law constant be adjusted for condensing heat exchanger's operating temperature and be in the proper units. The temperature adjustment is accomplished according to equation (13), where k_H is in mol/m^3-Pa and T is in Kelvin:

$$k_H(T) = k_{H,298K} e^{\left\{\left[\frac{d\ln\left(k_H\right)}{d\left(\frac{1}{T}\right)}\right]\left(\frac{1}{T} - \frac{1}{298.15}\right)\right\}} \,. \tag{13}$$

Reference 16 provides an excellent compilation of values for $k_{H,298\mathrm{K}}$ and the temperature dependence, $d\ln(k_H)/d(1/T)$.

As noted previously, the Henry's Law constant must be in the proper units. Equation (14) provides the method for converting the Henry's Law constant from units of mol/m^3-Pa to atmospheres:

$$k_H(T)_{\text{atm}} = \frac{1}{\left[k_H(T)_{\text{mole}/m^3\cdot\text{Pa}} \times 1.83089\right]} \ . \tag{14}$$

Reference 16 contains unit conversion factors for other units commonly encountered in the literature for Henry's Law constants. The Henry's Law constant resulting from the temperature adjustment using equation (13) and unit conversion using equation (14) is used in equation (12) to calculate the single-pass removal efficiency for a condensing heat exchanger. This efficiency is then used with the condensing heat exchanger flow rate in the cabin material balance.

In the event that the temperature dependence, $d\ln(k_H)/d(1/T)$, is not available in the literature, the temperature adjustment can be accomplished by multiplying the Henry's Law constant by the vapor pressure ratio for the condensing heat exchanger temperature to the vapor pressure at 20 °C.[17]

Equation (11) is also useful for estimating the cabin concentration condition that exists in equilibrium with a known humidity condensate loading. Such a calculation is useful for determining concentration conditions in the cabin atmosphere for compounds that are not targeted by air quality analysis methods or for concentrations that may be well below the method detection limits. In such cases, the liquid phase mole fraction is calculated at the measured humidity condensate loading via equation (15):

$$x = \frac{C_L}{\left[M \times 1{,}000 \times 55.494\right]} \ , \tag{15}$$

where C_L is the liquid phase concentration (mg/L) and M is the molecular weight (g/mole):

The result from equation (15) is used to calculate the gas phase mole fraction according to equation (11) solved for the gas phase mole fraction, y. The gas phase mole fraction is then used in the ideal gas law to calculate the gas phase concentration, C, in g/cm^3 according to equation (16):

$$C_i = \frac{My_iP}{RT} \ , \tag{16}$$

where

M = molecular weight (g/mole)
P = cabin pressure (atm)
R = ideal gas law constant (82.06 cm^3-atm/mole-K)
T = cabin temperature (Kelvin).

The concentration units are converted to mg/m^3 by applying the conversion factors 10^3 mg/g and 10^6 cm^3/m^3.

2.6 Removal by Activated Carbon Adsorption

Calculation of activated carbon loading is based upon the Polanyi adsorption potential theory.[1,18] The adsorption potential, as defined by equation (17), is used to calculate the activated carbon saturation capacity:

$$A = \left(\frac{T}{V_m}\right)\log_{10}\left(\frac{C_s}{C}\right) , \tag{17}$$

where

T = temperature (Kelvin)
V_m = liquid molar volume at the normal boiling point (cm^3/g mole)
C_s = vapor pressure expressed in concentration units (mg/m^3)
C = cabin concentration (mg/m^3).

The potential factor is used in a Freundlich-type isotherm equation shown in its general form by equation (18):

$$q = \alpha e^{-\beta A} , \tag{18}$$

where

q = the activated carbon loading (cm^3 liquid contaminant/g charcoal)
α = preexponential factor (2.1 for soluble compounds and 1.41 for insoluble compounds at 50% relative humidity)
β = exponential factor (0.31).

Adsorbent bed efficiency can be estimated by using the adsorption potential, A, to determine the adsorption zone length. The correlation for adsorption zone length is provided by equation (19):

$$L = (0.00275A)(v / 0.66)^{0.88} , \tag{19}$$

where

L = adsorption zone length (cm)
v = flow velocity through the bed (cm/s)
A = calculated using equation (17).[1]

Dividing the bed length by the adsorption zone length provides a rough estimate for the single-pass efficiency which can be used in the cabin material balance.

The preceding factors are correlations for Barnabey Sutcliffe Type 3032 activated carbon used in the active TCC equipment aboard the ISS. These correlations can be used for estimating loading magnitude for other activated carbon products; however, it is highly recommended that correlations specific to a particulate activated carbon product be used when available.

Additional information on trace contaminant removal equipment performance and the fate of trace contaminants in spacecraft cabins that are useful guides is documented by references 15, 19–21.

2.7 Removal by Catalytic Oxidation

Catalytic oxidation approaches used for TCC consist of either ambient temperature processes that target carbon monoxide (CO) or high temperature processes that oxidize methane (CH_4) and VOCs. The efficiency of ambient temperature catalytic processes are highly dependent on contact time. Typically, contact times >0.2 s provide 100% removal efficiency. The efficiency typically decreases linearly below the 0.2-s contact time. High temperature catalytic oxidation processes typically provide high, single-pass efficiencies >98% for CH_4 and VOC oxidation. In general, catalytic oxidation processes can be assumed to provide >95% removal efficiency for the purposes of the cabin material balance.

2.8 Evaluation Sequence for Environmental Control and Life Support Compatibility and Cabin Environmental Impact

The sequence for conducting the ECLS compatibility and cabin environmental impact assessment begins with data gathering. Information must be acquired and compiled for the materials to be evaluated. This information, which may be obtained from literature, on-line sources, or estimated using standard techniques, includes the following:

- Material nomenclature.
- Material quantity.
- Material purity.
- Chemical Abstracts Service (CAS) registry number.
- Molecular weight.
- Phase.
- Color.
- Odor.
- Odor threshold concentration.
- Liquid density.
- Freezing point.
- Boiling point.
- Flash point.
- Thermal decomposition temperature.
- Chemical stability and incompatibilities.
- Critical temperature.
- Critical pressure.

- Critical volume.
- Vapor pressure.
- Henry’s Law constant.
- Solubility in water.
- Solubility of water and oxygen in the material.
- Liquid molar volume.

In addition to the information on the material to be evaluated, the relevant information for the vehicle’s ECLSS configuration must be acquired. This information includes the following:

- Cabin volume.
- Cabin ventilation flow rates.
- ECLSS characteristics.

The ECLSS characteristics include process technology, flow rate, process temperature conditions, and performance data.

Once the information on the material to be evaluated and the vehicle and ECLSS configuration are obtained, detailed calculations involving the contaminant emission rate, cabin material balance, and ECLSS removal routes and impacts are determined using the calculation methods described earlier. These calculations compare adsorbent loading capacity and humidity condensate loading levels to the available resource to determine the ECLSS compatibility rating. As well, compounds are assessed for their chemical stability when exposed to the cabin environment and ECLSS process conditions. The evaluation also determines whether the materials can foul or poison ECLSS components such as catalytic reactors. The result of the ECLS resource consumption, fouling, or poisoning form the basis for the ECLSS compatibility rating.

The time to return the cabin to preevent conditions is calculated using equation (4) for simple assessments. A more rigorous time to recover can be based on calculations using equation (2). Equations (6) through (8) are used to determine dispersion between well-mixed volumes and concentration dynamics under more complex multivolume vehicle configurations. The concentration dynamic calculations serve as the basis for determining the cabin environmental impact rating.

Examples illustrating the ECLSS compatibility and cabin environmental impact assessment methodology are presented by the following narrative. These examples were conducted for the ISS program and address materials such as volatile fluid additives, aqueous thermal working fluids, fluorocarbon thermal working fluids, EVA-associated contamination, fire extinguishing agents, and process vents into the cabin.

3. WATER-BASED INTERNAL THERMAL CONTROL WORKING FLUIDS AND ADDITIVES

The following sections provide assessment results for antimicrobial additives used in water-based thermal control system working fluids used aboard the ISS as well as candidate water-based thermal control working fluids for future crewed space exploration vehicles.

3.1 Glutaraldehyde Antimicrobial Additive Evaluation

The ECLS compatibility and environmental impact associated with glutaraldehyde as a candidate antimicrobial additive to the ISS internal active thermal control system (ATCS) was assessed in 2004 and documented under NASA memorandum FD21(04-086), "Compatibility of a Candidate Internal Thermal Control System Biocide with the International Space Station's Environmental Control and Life Support System," dated June 9, 2004.

3.1.1 Background

The ISS's internal ATCS presently uses silver as a biocidal additive in the internal water working fluid. The silver concentration in the fluid declines within a few days as silver deposits upon metal surfaces, but microbial control is maintained by the specified 9.5 pH. Samples returned from flight have indicated that the internal ATCS fluid chemistry is affected by the on-orbit environment. Decreased pH and other changes have been traced to CO_2 permeation through the Teflon™ flex hoses. Due to the combination of lower pH and lower biocidal additive concentration in the fluid concerns exist that microbially induced corrosion (MIC) rates for internal ATCS wetted components may have increased, particularly for heat exchangers and cold plates.

The concern about MIC has led to a search for an alternative biocidal additive. Beyond periodically injecting more silver biocidal additive, hydrogen peroxide and glutaraldehyde are being considered as candidates.[22,23] Material compatibility testing for glutaraldehyde has been completed while more work is pending for hydrogen peroxide. Since work to evaluate glutaraldehyde's suitability has reached a more advanced stage, a change request, SSCN 008447, was prepared that sought to implement glutaraldehyde on board the United States On-orbit Segment (USOS).

One supporting basis for proceeding with the change request was an assessment of glutaraldehyde's toxicity hazard rating that stated that ECLSS 'charcoal filters should efficiently remove' glutaraldehyde vapors. While a correct statement, it was not quantified and does not address the overall capability to control glutaraldehyde's concentration to below its 180-day SMAC of 0.002 mg/m^3. This SMAC is the lowest documented in Spacecraft Maximum Allowable Concentrations for Airborne Contaminants (JSC 20584. Chemical compounds with a very low SMAC are typically difficult for the ECLSS to control if persistent generation sources exist because the total effective flow rate through the contamination control equipment is limited. That is, active contamination control equipment on board the ISS is accomplished using fixed flow devices. The primary means for maintaining cabin concentration below the SMAC in such cases then becomes source control. With this in mind, an engineering assessment has been conducted to address the ECLSS's capability to accommodate routes by which glutaraldehyde can enter the cabin environment if it is employed as a biocidal additive to the internal ATCS working fluid.

3.1.1.1 Spacecraft Trace Contaminant Control Design Practice. As discussed in section 1.2, designing for spacecraft cabin TCC requires substantial design activity within the confines of the air quality standard. In the case of crewed spacecraft, that standard is the SMAC. Materials selection and control, hardware design, manufacturing processes, chemical process design, mission characteristics as well as crew size and activities are only a few of the elements that must occur within the constraints of the air quality standards. A change to any of these, as is the case of a change in a thermal control system working fluid from a nonvolatile, inorganic silver ion biocidal additive to a semi-volatile, organic additive, can have an impact upon cabin atmospheric quality, to the ECLSS equipment, or both. A complete assessment by ECLS engineering is required when such changes are proposed to ensure any potential impacts to the cabin environment, as well as the ECLSS equipment, are negligible.

Because the specification of the active TCC equipment for a spacecraft precedes those data necessary to fully validate its design, standard design practice dictates a conservative approach whereby the active contamination control system performs its function unassisted by any other systems or processes in the cabin.[1] This means that overboard atmospheric leakage and assists provided by other air processing systems such as CO_2 removal and humidity control equipment are not considered during the design and validation of the active TCC equipment. To maintain consistency, all new contamination loads are assessed in the same manner.

For the ISS, the key design requirements pertaining to TCC design and performance state that trace contaminants shall be controlled to less than their respective SMACs for a normal equipment offgassing and crew metabolic load. More specifically, the trace contaminant control subassembly (TCCS) maintains trace atmospheric component concentrations from normal equipment offgassing and crew metabolic processes to less than 90% of individual contaminant SMACs. These design specifications are for the active contamination control systems operating without assistance from other ECLS processes or overboard leakage. It is also important to note that they do not specify that the active contamination control systems on board the ISS must be designed to accommodate chronic, fugitive leaks from other systems or payloads nor do they specify that these systems' performance must be verified for such an additional contamination loading. Further, these requirements do not authorize using the active contamination control systems as hazard controls for other onboard systems or payloads.

Within the context of requirements, an additional loading of a chemical compound not contained in the design listing provided in the ISS design specifications constitutes a new, specific verification case. As such, this verification must assume that only the active contamination control systems on board the ISS remove the added contamination load. This maintains consistency with the equipment's certification. It is informative to expand the assessment, however, to address the fate of the contamination to ensure that the impact upon all ECLSS processes—both atmospheric and water processing—are addressed.

3.1.2 Approach

Two basic assessments comprise the evaluation of glutaraldehyde's compatibility with the ISS's ECLSS. Concentrated aqueous solutions will be injected into the internal ATCS if glutaraldehyde's use as an alternative biocidal additive is implemented. Therefore, the first is an assessment of a bulk release of candidate stock solutions containing either 5% or 50% glutaraldehyde by mass. An additional subset of the first assessment, a case that considers a bulk release of 0.025% aqueous solution, is considered as a gross leak from an internal ATCS failure. Second, is an assessment of the ISS ECLSS's capability to handle chronic, fugitive leaks from the internal ATCS for various concentrations of glutaraldehyde. This second assessment considers the ability of the ECLS atmospheric quality control equipment to accommodate chronic emissions from a range of internal ATCS leakage rates and glutaraldehyde concentrations. The equations and calculation techniques found in section 2.3 are used to address these assessment cases.

3.1.2.1 Cases Considered. Cases considered include several scenarios involving substantial leaks of stock solution as well as a range of fugitive emissions encompassing the range of leakage from the internal ATCS by specification. Effects upon the ability to maintain cabin air quality for the specified range of internal ATCS fluid leakage presented by normal operation of the TCC equipment on board the ISS and failure scenarios of this equipment are also considered.

3.1.2.1.1 Evaporation Rate. Evaporation rates were evaluated from a 1-L spill of 5% aqueous glutaraldehyde, 100 mL of 50% aqueous glutaraldehyde, and 3.8 L of 0.025% glutaraldehyde. All cases were evaluated using equation (9) at 20 °C. The last case was also evaluated at 4.4 °C because that case represents leakage from the internal ATCS while operating and the fluid would initially be at a lower temperature before warming to the cabin temperature. In all cases, it is assumed that the spill takes the form of a sphere as the minimum energy shape.

3.1.2.1.2 Control of Fugitive Emissions. Initial screening was conducted using equation (5) to understand the effects of not only internal ATCS fluid leakage rate but also the glutaraldehyde concentration and available active contamination control capacity upon cabin atmospheric quality. The assessment bounds the capability dictated by specification documents and also assists in evaluating the potential impacts upon water processing systems. The leakage rates and concentrations listed in table 5 were investigated. In addition, leakage rates of 0.2 and 2.7 mg/hr were investigated because actual fluid leaks of these magnitudes have been experienced. Additional details on internal ATCS fluid leakage specifications defined by the internal ATCS System Problem Resolution team (SPRT) are provided in table 6 for which the total combined leakage rate is 14.71 mL/hr. Operational notes on internal ATCS operations relating to leakage rates are the following:

- The combined specification leakage for the on-orbit configuration at present in single-loop mode: 4.8 mL/hr.
- Threshold leakage to initiate an item for investigation (<1%/month): 0.16 mL/hr.
- Threshold leakage at which an internal ATCS loop will be shut down (<1% /day): 3.88 mL/hr.
- Normal leakage at station assembly complete: 1.62 mL/hr.
- Leakage rate at which a loop will be shut down at assembly complete: 5.33 mL/hr.

Table 5. Internal ATCS leakage rates and candidate biocide concentrations investigated.

Parameter	Magnitude					
Leakage rate (mL/hr)	0.16	1.6	3.9	4.8	5.3	14.7
Biocide concentration (mg/L)	25	50	100	150	200	250

Table 6. Internal ATCS specification leakage rates.

ISS Module	Low Temperature Loop (mL/hr)	Moderate Temperature Loop (mL/hr)
U.S. Laboratory	0.8	0.8
Airlock	0.8	0.8
Node 1	0.8	0.8
Node 2	1.09	0.86
Node 3	1.5	2
Centrifuge Accommodation Module	0.48	0.48
Multipurpose Logistics Module	0.275	N/A
Cupola	N/A	0.026
Columbus Attached Pressurized Module	0.8	0.8
Japanese Experiment Module	0.8	0.8
Total	7.345	7.366

The initial concept involved using 250 mg glutaraldehyde/L; however, subsequent review focused upon either 100 mg or 50 mg glutaraldehyde/L in the internal ATCS fluid. These latter concentrations are the focus for cases that consider a more rigorous cabin mass balance based upon equations (6) and (7). Using the appropriate numerical values for the system variables in the solved form of equation (8) for the USOS and Russian On-Orbit Segment (ROS), the effects of various leakage rates of internal ATCS fluid containing either 100 mg/L or 50 mg/L glutaraldehyde on cabin atmospheric quality and humidity condensate loading were assessed.

3.1.2.2 Vehicle Configuration. Two vehicle configurations are considered—the configuration as of flight 4R and the ISS assembly complete six-person crew capability. Estimated total cabin free volume for the 4R configuration is 371 m^3 comprised of the USOS free volume of 190.4 m^3 and the ROS free volume of 180.6 m^3. The U.S. assembly complete configuration expands the USOS volume to include the Japanese Experiment Module (JEM), Columbus Laboratory Attached Pressurized Module (APM), Centrifuge Accommodation Module (CAM), Node 2, and Node 3. It is assumed that the ROS volume will not change appreciably to accommodate the six-crew capability; therefore, the total ISS free volume will increase to approximately 928 m^3 as a result of the USOS free volume increasing to approximately 747.4 m^3. The Flight 4R configuration cases consider the present crew size of two people while the ISS assembly complete six-crew capability cases consider only a crew of three. Using only a crew of three for the assembly complete case is considered a greater challenge to overall TTC because the crew latent load is smaller than for the six-person crew size. It is anticipated that a checkout period during assembly complete will have a three-person crew.

In both the flight 4R and assembly complete configurations, the TCCS and Russian microimpurity adsorption unit (Russian acronym BMP) provide the active contamination control on board the ISS. During both ISS assembly stages, the TCCS and BMP operate in parallel with each other to maintain the cabin atmospheric quality. The TCCS removes glutaraldehyde at 100% efficiency in its charcoal bed assembly. If the charcoal bed assembly becomes saturated, then the TCCS will remove the glutaraldehyde via its catalytic oxidizer assembly. The flows through the charcoal bed assembly and catalytic oxidizer assembly are 15.3 and 4.6 m^3/hr, respectively. The BMP removes glutaraldehyde at 100% efficiency at 27 m^3/hr flow. This performance is estimated based upon activated charcoal's capacity for glutaraldehyde. Net intermodule ventilation (IMV) flow between the ROS to the USOS is typically 180 m^3/hr. No attempt is made to account for the effects of IMV flow short circuiting. The challenges presented by failures of the TCCS and BMP, either individually or at the same time, are considered.

3.1.2.3 Absorption by Humidity Condensate as a Removal Device. In addition to removal by the active contamination control equipment, water soluble contaminants are also removed by absorption in humidity condensate. As noted earlier, the assist provided to the active contamination control equipment on board the ISS is considered only to address potential impacts to water processing systems. Absorption via humidity condensate is not considered when evaluating the capability for the active control systems to accommodate a new contaminant loading.

The primary condensate removal for the flight 4R configuration is provided by the condensing heat exchanger (Russian acronym SKV) in the ROS. Typical flow rate through the heat exchanger core is 144 m^3/hr. The condensate loading normally ranges between a three- and two-person latent load, depending upon the crew size. Removal efficiency via absorption by humidity condensate is 86% for a two-person latent load and 91% for a three-person latent load. The calculation technique for estimating condensate absorption efficiency is documented by reference 15. An average latent load is defined as 1.4 L/day/person.

For the ISS assembly complete six-person crew capability, the most challenging case exists during the time when the crew is limited to three people. The combination of added internal ATCS fluid loops and limited TCC scrubbing capacity are most severe during this time. It is assumed for these cases that a two-person latent load is removed by the SKV and a one-person latent load is removed by a common cabin air assembly (CCAA) in the USOS. At this rate of humidity condensate collection, the single-pass removal efficiency is approximately 55% for the CCAA. Removal efficiency for the SKV is 86%, as noted previously.

It must be noted that temperature adjustments to ideal Henry's Law behavior, as reported by references 1, 3, 15, and 19 are not accounted for in this assessment because specific data on glutaraldehyde are not available. For this reason, this aspect of the assessment is not conservative.

3.1.3 Results and Discussion

The following discussion presents and discusses results for estimated evaporation rates from stock solutions, basic control of cabin atmospheric quality under varying internal ATCS fluid leakage conditions, and effects upon humidity condensate loading. Guidelines are presented for maintaining two-failure tolerance with respect to ECLS atmospheric quality and water quality control functions.

3.1.3.1 Evaporation From Bulk Leakage. Evaporation rates from 1 L of 5% aqueous solution, 100 mL of 50% aqueous solution, and 3.8 L of 0.025% aqueous solution were calculated using equation (9). The elapsed time to reach the 180-day SMAC is also calculated, assuming no removal during the period of release. This is a standard, conservative approach to evaluating the time to reach the 180-day SMAC.

For the first case, the calculated evaporation rate is 3.5 mg/hr. At this rate, the time to reach the 180-day SMAC in the USOS is 6.6 min. If allowed to disperse throughout the entire ISS cabin, the 180-day SMAC is reached in 13 min. As expected, the second case shows that the more concentrated solution gives the crew less time to react. The calculated evaporation rate from the 100-mL release of 50% aqueous solution is 9.9 mg/hr. At this rate, the 180-day SMAC can be reached in the USOS within 2.3 min and for the entire ISS cabin within 4.5 min. Evaporation from the dilute solution containing 0.025% glutaraldehyde is 0.054 mg/hr. At this rate, the 180-SMAC is reached within 7 hr in the USOS and 14 hr for the entire ISS.

Based upon the evaluation of evaporation rate, appropriate containment is required for any operation that involves handling aqueous glutaraldehyde solutions in the cabin. Also, depending upon the prevailing glutaraldehyde concentration in the internal ATCS fluid, evaporation from fugitive emissions is considered to be a concern, making the rapid detection and remediation of any leak highly important to maintaining the ISS's cabin air quality. Evaporation from a 3.8 L release of fluid (0.01 mg/hr) is equivalent to the amount of glutaraldehyde introduced into the ISS cabin by a continuous 0.2 mL/hr leak. Leaks of approximately 0.2 and 2.7 mL/hr have been experienced on board the ISS.

3.1.3.2 Control of Fugitive Emissions. The ability to maintain cabin air quality in the presence of fugitive emissions must first consider the available equipment for actively removing the contamination. Figures 2 and 3 illustrate the overall scrubbing flow required to accommodate a range of internal ATCS fluid leakage containing 50 and 100 mg/L glutaraldehyde, respectively. These glutaraldehyde concentrations are considered to be the most likely implemented if approved by the ISS program. Leakage rates of 3.9 and 5.3 mL/hr most likely can be sustained for about 1 month while deliberating the need to shut down an internal ATCS fluid loop. For these leakage rates, figures 2 and 3 show that effective removal flow rate ranges of 95 to 130 m^3/hr and 195 to 265 m^3/hr are necessary to maintain the concentration in the cabin below the 180-day SMAC for 50 and 100 mg/L glutaraldehyde in the fluid. This is far greater than the 15.3 m^3/hr provide by the TCCS alone. The BMP provides an additional 27 m^3/hr and removal via absorption by humidity condensate can vary.

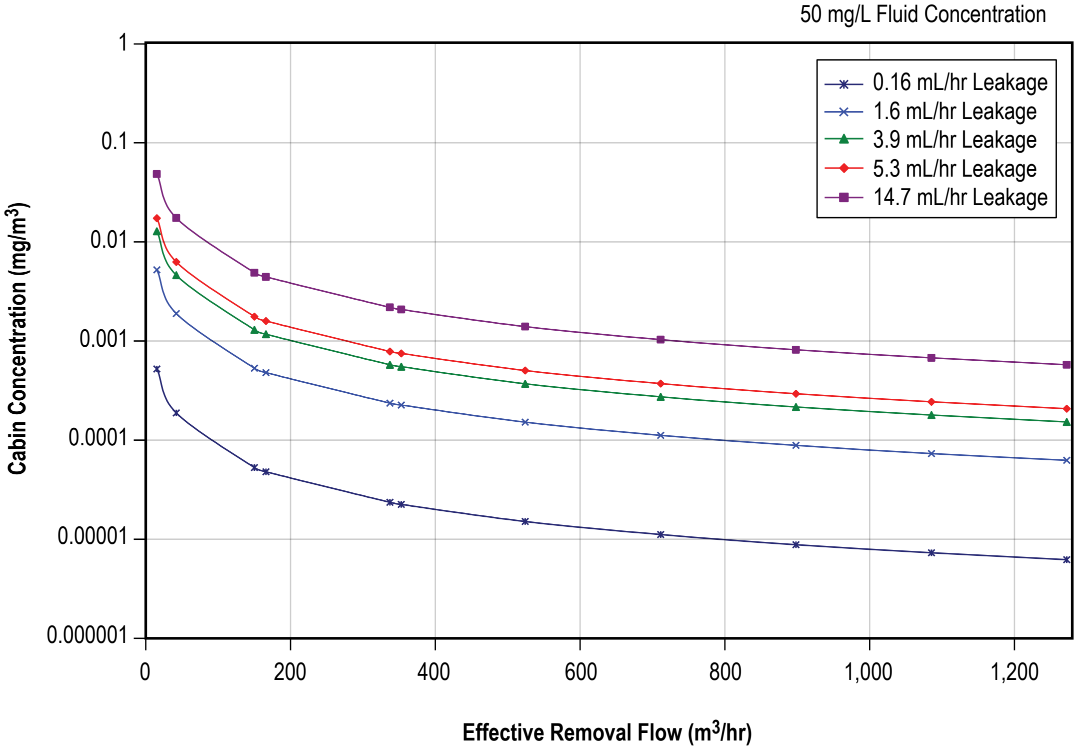


Figure 2. Effective removal flow to maintain SMAC for 50 mg/L glutaraldehyde.

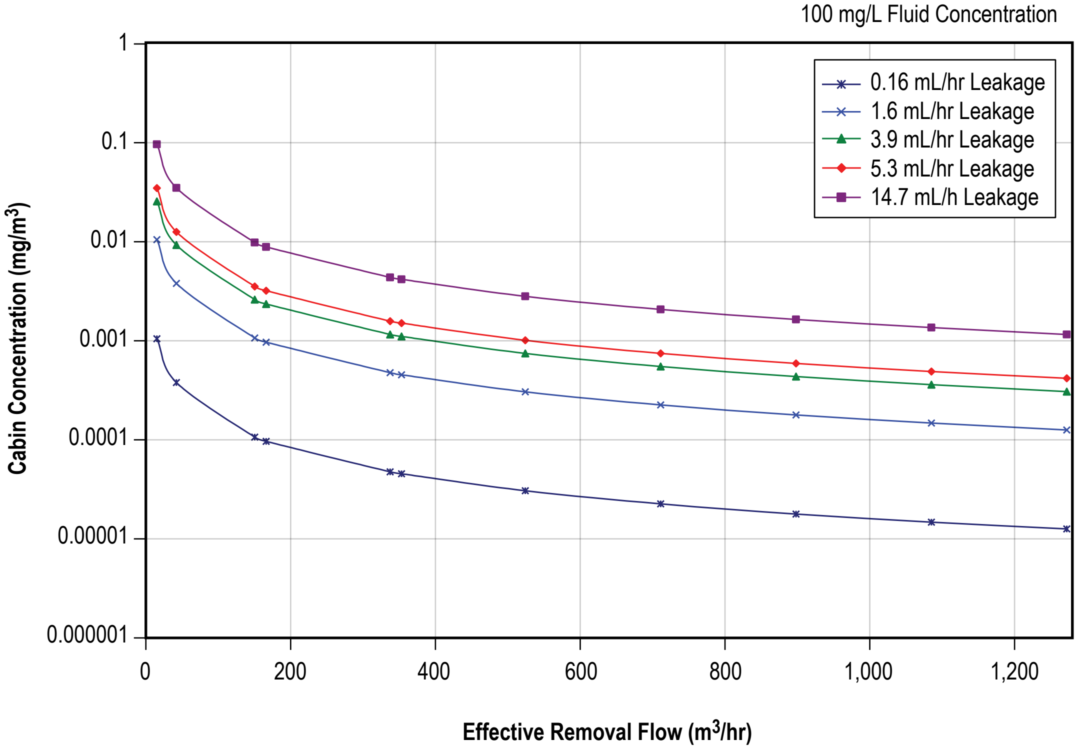


Figure 3. Effective removal flow to maintain SMAC for 100 mg/L glutaraldehyde.

TCC for the ISS USOS was certified by engineering analysis using the constraint that the TCCS, with no assist from the Russian BMP or removal via absorption in humidity condensate, provides active control. Because any new contamination source represents an extension of the specified TCC design load, each new source is evaluated using the same criterion. This ensures that the same levels of safety apply for any known increase in the trace contaminant load. For information, the assist provided to the TCCS by both the BMP and removal via absorption in humidity condensate are included. The additional cases allow the potential impact upon ECLSS water processing systems to be estimated; however, they do not serve as the primary basis for assessing TCC capacity for normal operations.

3.1.3.2.1 U.S. On-Orbit Segment Trace Contaminant Control Subassembly Capability. A range of internal ATCS working fluid leakage rates and glutaraldehyde concentrations were evaluated. Figure 4 shows the steady state concentration that results when the TCCS provides the sole active removal. The TCCS, when operating alone, can provide effective control for a glutaraldehyde source of no greater than 0.03 mg/hr and still maintain the cabin concentration below the 180-day SMAC. This capability is equivalent to a sustained leakage from the internal ATCS up to 1.1 mL/hr for 25 mg/L glutaraldehyde in the fluid. As the fluid's glutaraldehyde concentration increases, the magnitude of the sustained leak accommodated by the TCCS decreases to as low as 0.11 mL/hr for 250 mg/L glutaraldehyde in the fluid. These rates are much lower than those allowed for the internal ATCS by specification. Also, these rates are lower than the nearly 0.2 and 2.7 mL/hr leakage rates that have been experienced on board the ISS.

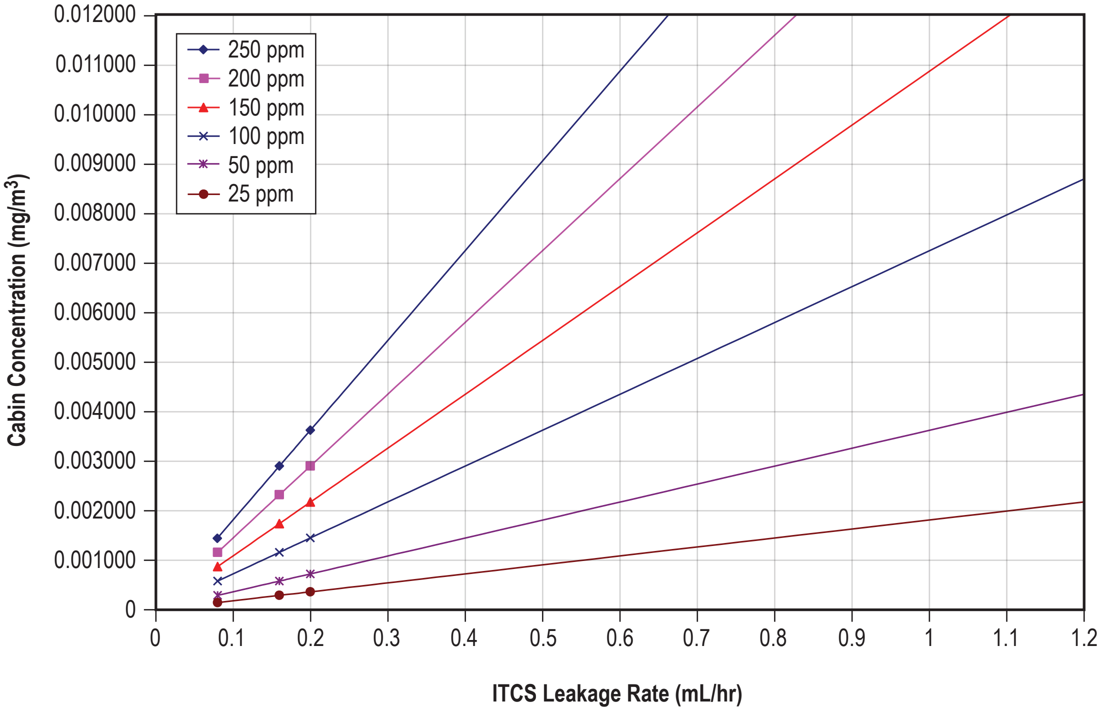


Figure 4. Leakage accommodated by the USOS TCCS.

3.1.3.2.2 Trace Contaminant Control Subassembly and BMP Dual Capability. For the TCCS operating with an assist from the ROS's BMP, the range of leakage accommodated increases by nearly a factor of 3. Figure 5 shows that up to 3 and 0.3 mL/hr fluid leakage can be accommodated for 25 and 250 mg/L glutaraldehyde in the fluid, respectively. This range of leakage rates is comparable to that observed on board the ISS.

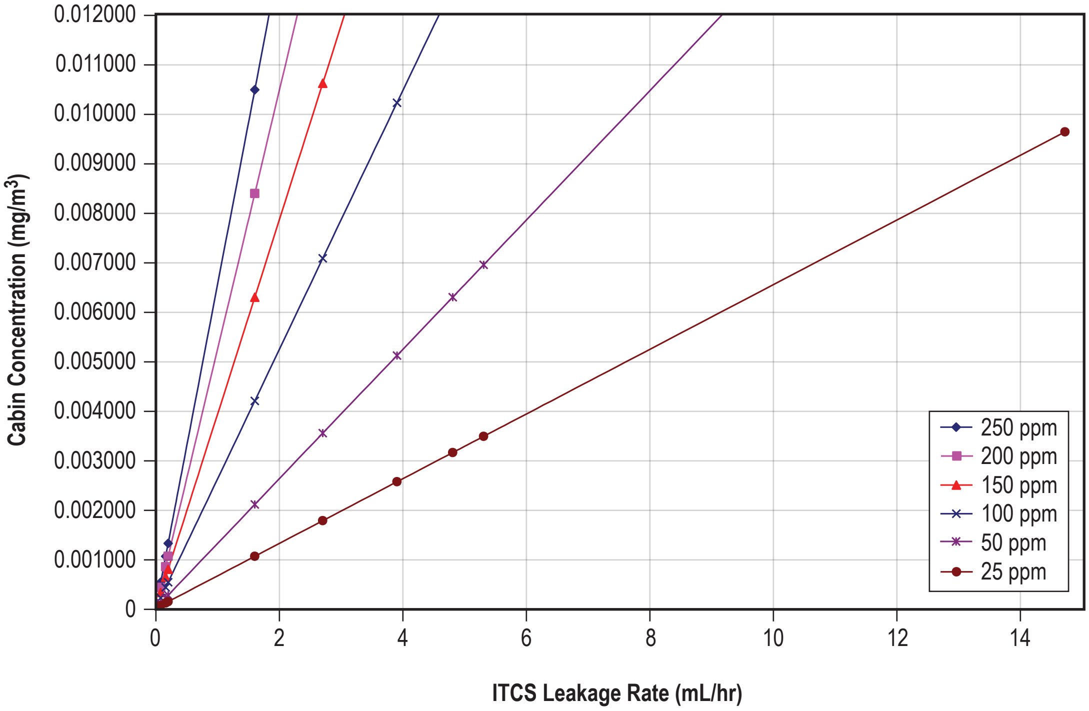


Figure 5. Leakage accommodated by the USOS TCCS and ROS BMP.

3.1.3.2.3 Absorption Via Humidity Condensate and Impacts to Water Processing Equipment. Figure 6 shows the additional capability that absorption via humidity condensate provides. A single CCAA heat exchanger removing condensate at a one-person-equivalent latent load can remove glutaraldehyde via absorption at 55% efficiency. Similarly, the SKV heat exchanger on board the ROS can remove glutaraldehyde at 75% efficiency while removing condensate at a one-person-equivalent latent load. This increases to 86% for a two-person-equivalent latent load. Leakage ranging from 2.5 mL/hr to nearly 13 mL/hr leakage can be accommodated for 250 and 50 mg/L glutaraldehyde loading in the fluid, respectively. The 25 mg/L glutaraldehyde concentration is accommodated across the full range of specified and observed leakage.

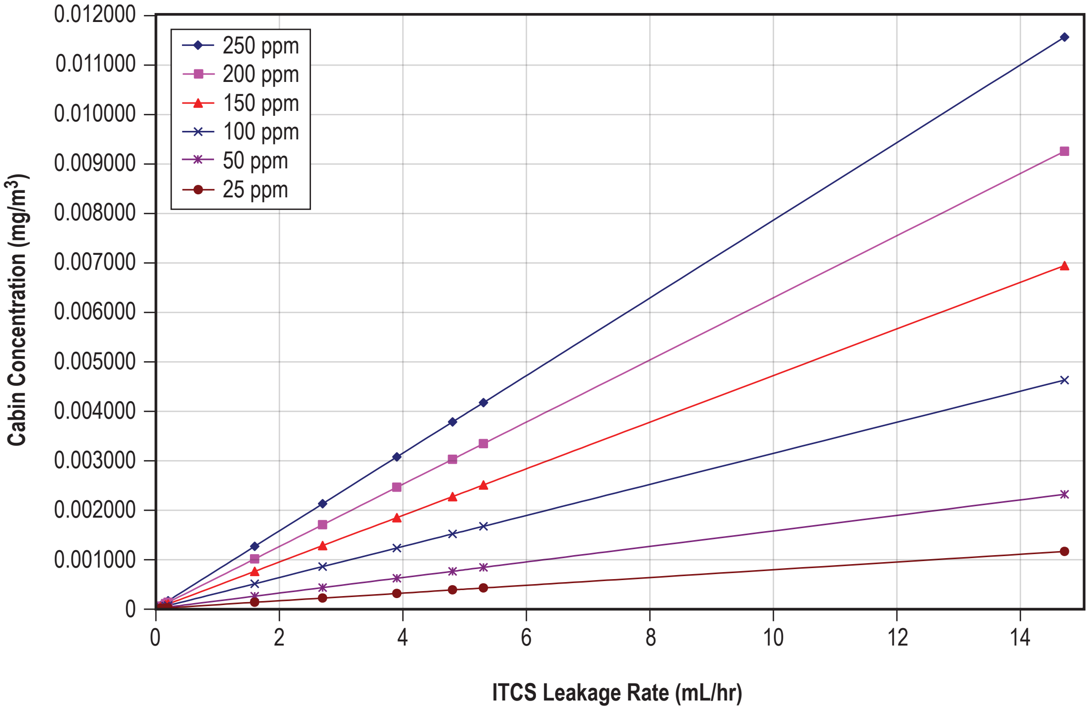


Figure 6. Leakage accommodated by the USOS TCCS and ROS BMP assisted by humidity condensate absorption at assembly complete for a crew of three.

It is evident that removal via absorption by humidity condensate provides an effective assist to the active contamination control equipment. This is vividly illustrated in figure 7 where the capabilities for the TCCS and BMP operating alone and when assisted by varying removal via absorption in humidity condensate are compared. The removal via absorption provided by a two-person latent load can increase the capacity by more than a factor of 5 and a latent load equivalent to three people more than doubles that. While obviously effective, the impacts to water processing equipment must be accounted for. Water processing equipment engineers from both NASA and RSC Energia have indicated glutaraldehyde in humidity condensate must not exceed 5 mg/L. Figures 5 and 6 show the effect that varying cabin concentration and crew latent load can have upon humidity condensate loading for the CCAA and SKV units.

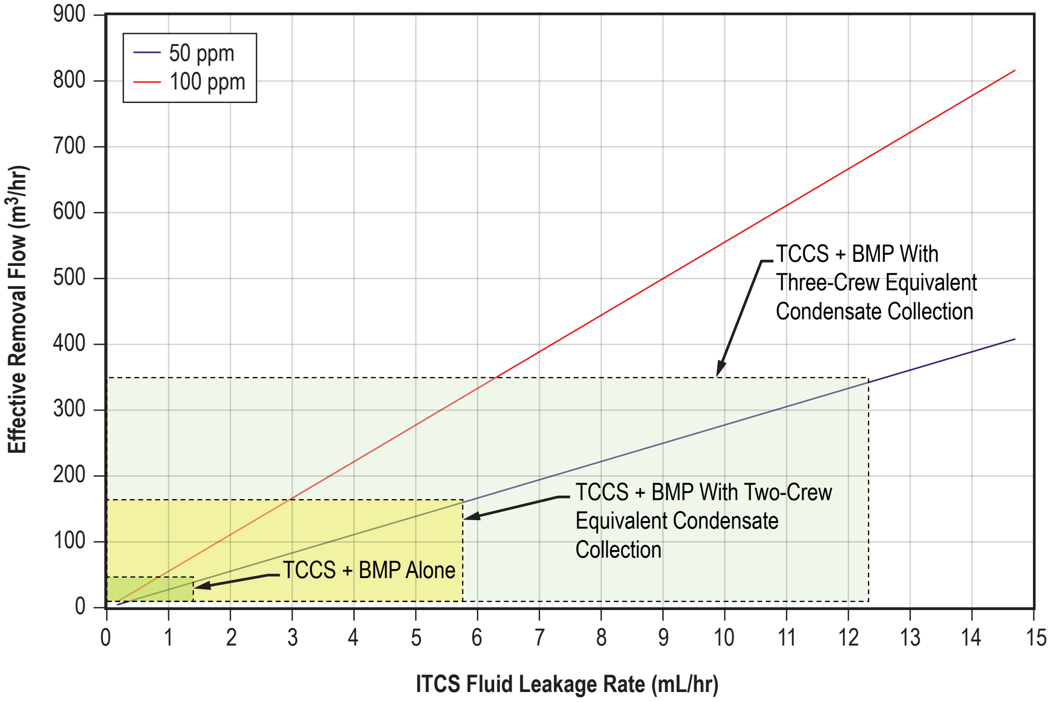


Figure 7. Comparison of assisted and unassisted contamination control capacity.

While removal via absorption by humidity condensate is a potentially effective removal route, the potential impact to the water processing systems can be significant and must be considered. Figures 8 and 9 show how the condensate loading varies when the latent load and the cabin concentration change. For the CCAA, figure 8 shows the cabin concentration that can contribute up to 5 mg/L glutaraldehyde in the condensate ranging from 0.0015 to 0.0032 mg/m^3 for latent loading up to three people. Similarly, figure 9 shows that a cabin concentration ranging from 0.0027 to 0.0066 mg/m^3 can contribute up to 5 mg/L glutaraldehyde in the condensate collected by the SKV for latent loads up to three people.

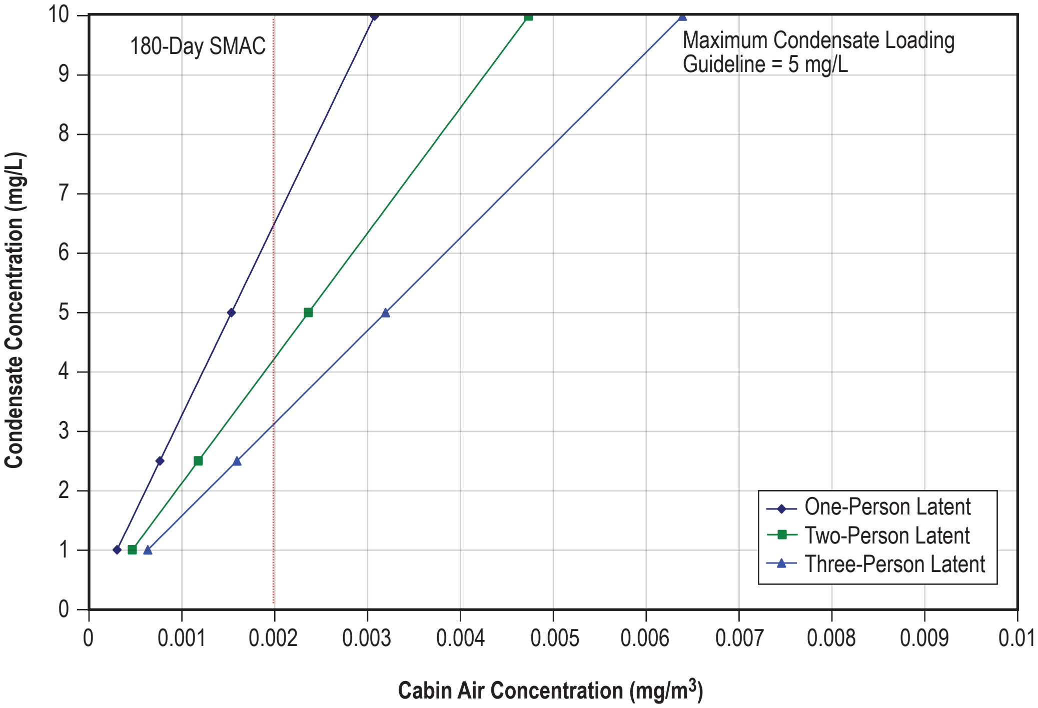


Figure 8. Effect of cabin glutaraldehyde concentration upon condensate collected by the CCAA.

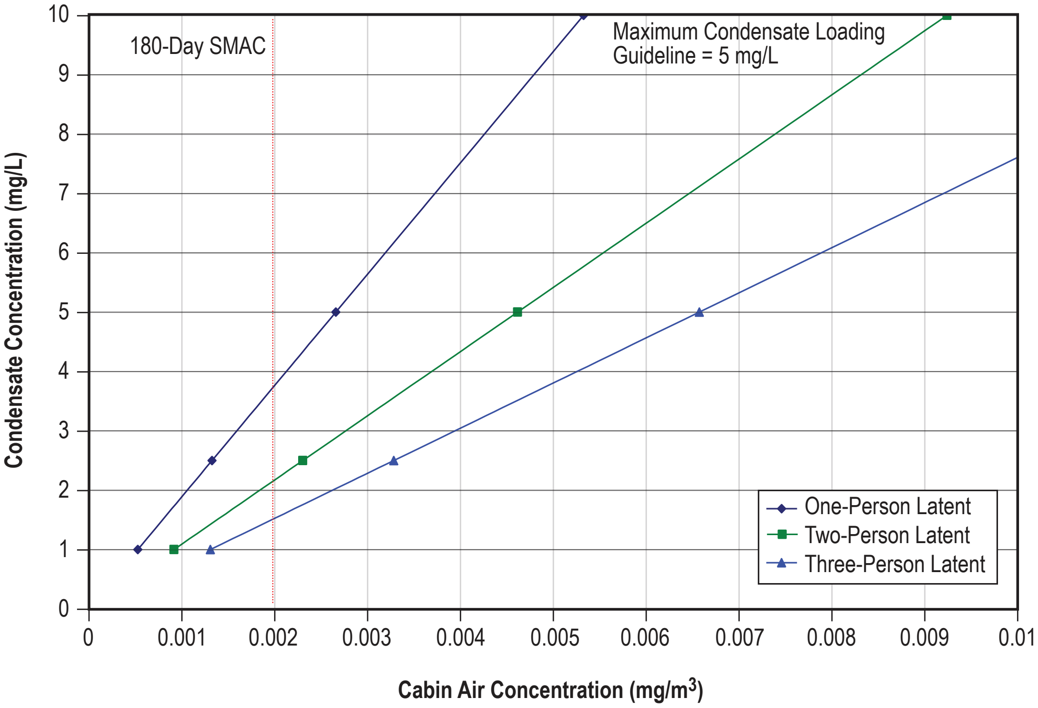


Figure 9. Effect of cabin glutaraldehyde concentration upon condensate collected by the SKV.

To understand the potential impact upon humidity condensate loading for the flight 4R and assembly complete configurations, the rigorous mass balance based upon the simultaneous solution of equations (6) and (7) is used. Appendix B contains tabular results.

Figure 6 indicates that, with respect to maintaining cabin air quality, fluid containing up to 100 mg/L glutaraldehyde can be used for nearly half the specified range of fluid leakage when all removal routes are considered. However, fluid containing <50 mg/L glutaraldehyde has the least potential impact upon the cabin's atmosphere. Based upon the rigorous mass balance, the cabin concentration for the flight 4R configuration can exceed the lower range for condensate loading acceptability for a CCAA when leakage is >1.8 mL/hr for fluid containing 100 mg/L glutaraldehyde. This increases to >3.6 mL/hr for fluid containing 50 mg/L glutaraldehyde. These leakage rates are within that allowed by specification for the flight 4R configuration. Humidity condensate collected by the SKV will not be overloaded for the flight 4R configuration unless total leakage exceeds 7.7 and 15.4 mL/hr for fluid containing 100 and 50 mg/L glutaraldehyde loading, respectively.

For the assembly complete configuration, leakage >4.7 mL/hr can overload the condensate collected by the CCAA for fluid containing 100 mg/L glutaraldehyde. Similarly, leakage >9.4 mL/hr containing 50 mg/L glutaraldehyde can overload the condensate collected by the CCAA. Leakage much greater than allowed by specification is required to overload condensate collected by the SKV. For fluid containing 100 mg/L glutaraldehyde, leakage >22 mL/hr results in >5 mg/L glutaraldehyde in the condensate. Sustained leakage >44 mL/hr is necessary for fluid containing 50 mg/L glutaraldehyde.

3.1.3.2.4 Consideration for Air Quality Control System Failures. Given glutaraldehyde's very low 180-day SMAC and the fact that fluid leakage from the internal ATCS is expected, it is necessary to understand the potential effects that a failure of the TCCS and BMP either individually or simultaneously may have upon the ISS's overall TCC capability. The rigorous mass balance provided by simultaneous solution of equations (6) and (7) was used to evaluate the effects. Internal ATCS fluid containing 100 mg/L and 50 mg/L glutaraldehyde was considered for both the flight 4R and assembly complete configurations. Results are tabulated in appendix B.

The worst-case situation occurs when both the TCCS and BMP fail simultaneously. For such a situation, internal ATCS fluid leakage >1.9 mL/hr for fluid containing 100 mg/L glutaraldehyde and >3.8 mL/hr for fluid containing 50 mg/L glutaraldehyde result in cabin concentration exceeding the 180-day SMAC. These leakage rates are within the range allowed by specification. For assembly complete, leakage >5.6 mL/hr and >11.2 mL/hr result in cabin concentration greater than the 180-day SMAC. Again, these leakage rates are within the range allowed by specification.

For individual failures of the TCCS and BMP for the ISS flight 4R configuration, leakage rates >2.1 mL/hr and >4.2 mL/hr for fluid containing 100 mg/L and 50 mg/L glutaraldehyde, respectively, can result in cabin concentration greater than the 180-day SMAC. At assembly complete, the leakage rates increase to >5.9 mL/hr for fluid containing 100 mg/L glutaraldehyde and >11.8 mL/hr for fluid containing 50 mg/L glutaraldehyde.

If internal ATCS fluid leakage can be adequately controlled and monitored, leakage no greater than 1.8 mL/hr for the flight 4R configuration and 4.7 mL/hr for the assembly complete configuration for internal ATCS fluid containing 100 mg/L glutaraldehyde can achieve acceptable results. Likewise, for ATCS fluid containing 50 mg/L glutaraldehyde, rates no greater than 3.6 mL/hr for the flight 4R configuration and 9.4 mL/hr for the assembly complete configuration achieve acceptable results.

When considering the concentration threshold of 0.0015 mg/m^3 for avoiding adverse impacts upon humidity condensate loading in the USOS combined with a single TCC failure, leakage rates for the 4R configuration >1.6 mL/hr and >3.2 mL/hr for fluid containing 100 mg/L and 50 mg/L glutaraldehyde, respectively, exceed the threshold. Similarly, at assembly complete, leakage of fluid containing 100 mg/L and 50 mg/L glutaraldehyde exceeds the threshold at >4.4 mL/hr and >8.8 mL/hr, respectively. The range of leakage in both cases is within the range of internal ATCS leakage allowed by specification.

3.1.3.3 Summary. Overall, measures must be taken to minimize the risk to human health and maintaining the ISS's cabin air quality as well as protecting the water processing systems. Although the TCCS and BMP have proven themselves reliable, they are designed specifically to control the contamination loading from equipment offgassing and human metabolic processes alone. Further, cabin air quality monitoring techniques are not sensitive enough to monitor glutaraldehyde's concentration at or below the 180-day SMAC. Therefore, it is not possible to verify cabin air quality maintenance via existing monitoring techniques. Therefore, as shown in figures 5 and 7, and presented earlier, to ensure that the risk to human health presented by potentially overwhelming the active air quality control systems and overloading humidity condensate, the internal ATCS fluid should contain <25 mg/L glutaraldehyde. For the entire range of specified internal ATCS fluid leakage, this concentration protects against all human health and ECLS equipment performance impacts as well as accommodates for the potential for air quality control equipment failures.

3.1.4 Conclusions

Based upon evaluation of glutaraldehyde as a candidate biocidal additive to the internal ATCS working fluid, conclusions are the following:

- Evaporation rates from concentrated aqueous solutions of glutaraldehyde are such that appropriate containment and personal protective equipment must be used when injecting the solution into the internal ATCS.

- Basic, unassisted TCC capability as defined by ISS program specification cannot accommodate the range of internal ATCS leakage rates for any glutaraldehyde concentration in the fluid.

- If no suitable alternative can be found, internal ATCS fluid must contain <25 mg/L glutaraldehyde to ensure that long-term hazards to human health and operability of ECLS air quality control and water processing systems are acceptable.

3.1.5 Recommendations

Based upon ISS ECLS engineering evaluation, it is recommended that other candidate biocidal additives be evaluated. The overall challenges and risks associated with using glutaraldehyde as a biocidal additive are significant and present long-term operational issues to the ISS program if implemented.

The USOS ECLSSs cannot be certified for glutaraldehyde concentration >25 mg/L in the internal ATCS fluid. If no other suitable additive can be found, however, glutaraldehyde concentrations <25 mg/L may be used within the range of internal ATCS fluid leakage specification to ensure long-term hazards to human health and ECLSS air quality control and water processing equipment are acceptable.

Further, any decision by the ISS program to use glutaraldehyde as a biocidal additive to the internal ATCS fluid in the USOS must be reviewed by the International Partners within the Common Environments team forum. This is necessary because fugitive emissions from the internal ATCS affect the common cabin environment.

3.2 Methyl-Isothiazolone Antimicrobial Additive Evaluation

The ECLS compatibility and environmental impact associated with methyl-isothiazolone as a candidate antimicrobial additive to the ISS internal ATCS was assessed in 2005 and documented under NASA memorandum EV50(05-004), "Compatibility of the Candidate Methyl-Isothiazolone Internal Thermal Control System Antimicrobial Additive with the International Space Station's Environmental Control and Life Support System," dated September 14, 2005.

3.2.1 Background

The ISS active internal thermal control system (ITCS) presently uses silver as an antimicrobial additive in the internal water working fluid. The silver concentration in the fluid has been found to decline within a few days as silver deposits on internal wetted surfaces, but microbial control is maintained by the specified 9.5 pH. Samples returned from flight have indicated that the ITCS fluid chemistry is affected by the on-orbit environment. Decreased pH and other changes have been traced to CO_2 permeation through the Teflon flex hoses. Due to the combination of lower pH and lower antimicrobial additive concentration in the fluid, concern about microbiologically-induced problems, such as fouling, plugging, or corrosion of ITCS wetted components, may increase, leading to degraded performance and shorter service life.

These concerns have led to a search for an alternative antimicrobial additive. Beyond periodically injecting more silver antimicrobial additive, several candidate antimicrobial additives are being considered.[22,23] Glutaraldehyde was an early promising candidate; however, the assessment in section 3.1 found significant issues relating to its environmental impact on board the ISS, limiting its allowable concentration in the ITCS fluid to <25 mg/L. Additional evaluation by the NASA Engineering and Safety Center (NESC) concluded that glutaraldehyde was not suitable for use on board the ISS.[24] Therefore, further work has been conducted to find more suitable candidates. Among these new candidates is 2-methyl-isothiazolone (MIT). Relevant physical properties of MIT are summarized in table 7.

Table 7. 2-methyl-isothiazolone properties.

Property	Value
CAS number	2682-20-4
Molecular weight (g/mole)	115.15
Melting point (°C)	47.48
Boiling point (°C)	237.75
Water solubility	Infinite
Henry's Law constant (atm/mole fr.)	0.00161
Vapor pressure (mm Hg)	0.031
Solubility	Water, methanol, toluene, ethyl acetate
Odor	Pungent aromatic

The primary challenge for applying any ITCS antimicrobial additive is the ability to maintain the cabin concentration below its SMAC under a range of allowable ITCS leakage rates and ECLSS operational configurations. MIT does not have an officially designated SMAC; therefore, the default SMAC of 0.1 mg/m^3 is used for the purpose of the ECLS engineering assessment. To maintain margin, a concentration <75% of the default SMAC or 0.075 mg/m^3 is preferred. Chemical compounds with SMACs <1 mg/m^3 are typically difficult for the ECLSS to control if the compound is volatile and persistent generation sources exist because the total effective flow rate through the contamination control equipment is limited. That is, active contamination control equipment on board the ISS is accomplished using fixed flow devices. The primary means for maintaining cabin concentration below the SMAC in such cases then becomes source control. With this in mind, an engineering assessment has been conducted to address the ECLSS's capability to accommodate routes by which MIT can enter the cabin environment if it is used as an antimicrobial additive in the ITCS working fluid.

3.2.2 Approach

Two basic assessments comprise the evaluation of MIT's compatibility with the ISS's ECLSS. Depending on the method that MIT may be introduced into the ITCS in flight, evaporation rate from bulk solutions must be considered. One concept, however, employs a resin to introduce the antimicrobial chemical into the ITCS. This latter concept eliminates concern with handling concentrated bulk liquids. Conservatively, the first assessment is to determine the evaporation rate and equivalent amount of pure MIT that contributes to short-term air quality concerns. The second assessment is the ISS ECLSS's capability to handle chronic, fugitive leaks from the ITCS for various concentrations of MIT. This assessment considers the ability of the ECLS atmospheric quality control equipment to accommodate chronic emissions from a range of ITCS leakage rates and MIT concentrations. The equations and calculation techniques in section 2.3 are applied to these assessment cases.

3.2.2.1 Cases Considered. Cases considered include determining the evaporation rate from pure MIT as well as a range of fugitive emissions encompassing the range of leakage from the ITCS allowed by specification. Effects on the ability to maintain cabin air quality for the specified range of ITCS fluid leakage during normal operation of the TCC equipment on board the ISS and failure scenarios of this equipment are also considered.

3.2.2.1.1 Evaporation Rate. Since the working concentration of MIT in the ITCS fluid has not yet been determined, evaporation rate was evaluated using equation (9) to determine the volumes of pure MIT and of a dilute, ideal aqueous solution containing 0.1% MIT by mass at 21 °C that will exceed the TCCS's capability to maintain the cabin concentration below 75% of the default SMAC.

3.2.2.1.2 Control of Fugitive Emissions. Initial screening was conducted using equation (5) to understand the effects of not only ITCS fluid leakage rate but also the MIT concentration and available active contamination control capacity upon cabin atmospheric quality. The assessment bounds the capability dictated by specification documents and also assists in evaluating the potential impacts upon water processing systems. The leakage rates and MIT concentrations listed in table 5 were investigated. In addition, leakage rates of 0.2 and 2.7 mg/hr were investigated because actual fluid leaks of these magnitudes have been experienced. Additional details on ITCS fluid leakage specifications defined by the ITCS SPRT are provided in table 6.

Using the appropriate numerical values for the system variables in the solved form of equations (6) and (7) for the USOS and ROS, the effects of various leakage rates of ITCS fluid containing 25 mg/L up to 250 mg/L on cabin atmospheric quality and humidity condensate loading were assessed.

3.2.2.2 Vehicle Configuration. Two vehicle configurations are considered—the configuration as of flight 4R and the ISS assembly complete six-person crew capability. Estimated total cabin free volume for the 4R configuration is 371 m^3 comprised of the USOS free volume of 190.4 m^3 and the ROS free volume of 180.6 m^3. The U.S. assembly compete configuration expands the USOS volume to include the JEM, Columbus APM, Centrifuge Accommodation Module (CAM), Node 2, and Node 3. It is assumed that the ROS volume will not change appreciably to accommodate the six-crew capability; therefore, the total ISS free volume will increase to approximately 928 m^3 as a result of the USOS free volume increasing to approximately 747.4 m^3. The flight 4R configuration cases consider the present crew size of two people while the ISS assembly complete six-crew capability cases consider only a crew of three. Using only a crew of three for the assembly complete case is considered a greater challenge to overall TCC because the crew latent load is smaller than for the six-person crew size. It is anticipated that a checkout period during assembly complete will have a three-person crew.

In both the flight 4R and assembly complete configurations, the TCCS and BMP provide the active contamination control on board the ISS. During both ISS assembly stages, the TCCS and BMP operate in parallel with each other to maintain the cabin atmospheric quality. The TCCS removes MIT at 100% efficiency in its charcoal bed assembly. If the charcoal bed assembly becomes saturated, then the TCCS will remove the MIT via its catalytic oxidizer assembly. The flows through the charcoal bed assembly and catalytic oxidizer assembly are 15.3 and 4.6 m^3/hr, respectively. The BMP removes MIT at 100% efficiency at 27 m^3/hr flow. This performance is estimated based on activated charcoal's capacity for MIT. Net IMV flow between the ROS to the USOS is typically 180 m^3/hr. No attempt is made to account for the effects of IMV flow short circuiting. The challenges presented by failures of the TCCS and BMP, either individually or at the same time, are considered.

3.2.2.3 Absorption by Humidity Condensate as a Removal Device. In addition to removal by the active contamination control equipment, water soluble contaminants are also removed by absorption in humidity condensate. As noted earlier, the assist provided to the active contamination control equipment on board the ISS is considered only to address potential impacts to water processing systems. Absorption via humidity condensate is not considered when evaluating the capability for the active control systems to accommodate a new contaminant loading.

The primary condensate removal for the flight 4R configuration is provided by the SKV condensing heat exchanger in the ROS. Typical flow rate through the heat exchanger core is 144 m^3/hr. The condensate loading normally ranges between a three- and two-person latent load, depending upon the crew size. Removal efficiency via absorption of MIT by humidity condensate is 39.2% for a two-person latent load and 49.3% for a three-person latent load. The calculation technique for estimating condensate absorption efficiency is documented by reference 15. An average latent load is defined as 1.4 L/day/person.

For the ISS assembly complete six-person crew capability, the most challenging case exists during the time when the crew is limited to three people. The combination of added ITCS fluid loops and limited TCC scrubbing capacity are most severe during this time. It is assumed for these cases that a two-person latent load is removed by the SKV and a one-person latent load is removed by a CCAA in the USOS. At this rate of humidity condensate collection, the single-pass removal efficiency is approximately 11.9% for the CCAA. Removal efficiency for the SKV is 39.2% as noted previously.

It must be noted that temperature adjustments from ideal Henry's Law behavior, as reported by references 1, 3, 15, and 19 are not accounted for in this assessment because specific data on MIT relative to nonidealities that may affect strict Henry's Law behavior are not available. For this reason, this aspect of the assessment is not conservative.

3.2.3 Results and Discussion

The following discussion presents and discusses results for estimated evaporation rates from stock solutions, basic control of cabin atmospheric quality under varying ITCS fluid leakage conditions, and effects upon humidity condensate loading. Guidelines are presented for maintaining single-failure tolerance with respect to ECLS atmospheric quality and water quality control functions.

3.2.3.1 Evaporation From Bulk Leakage. The generation rate that equals the TCCS's capability to maintain MIT at 75% of the default SMAC is 1.15 mg/hr. The volume of pure MIT from which 1.15 mg/hr generation is expected was calculated using equation (9). For pure MIT, the total leaked volume that can contribute to this production rate is 18 cm^3. Assuming an ideal solution exists, a 0.1% MIT by mass aqueous solution can be expected to exert approximately 17 mm mercury (Hg) vapor pressure. The leaked fluid volume, in this case, that contributes to 1.15 mg/hr MIT introduction into the cabin atmosphere is 3.3 L. This is within the 3.8-L maximum leaked amount allowed during normal ITCS operation before the system automatically shuts down.

3.2.3.2 Control of Fugitive Emissions. The ability to maintain cabin air quality in the presence of fugitive emissions must first consider the available equipment for actively removing the contamination. Figures 10 through 12 illustrate the overall scrubbing flow required to accommodate a range of ITCS fluid leakage containing up to 250 mg MIT/L. Leakage rates of 3.9 and 5.3 mL/hr most likely can be sustained for about 1 month while deliberating the need to shut down an ITCS fluid loop. For these leakage rates, figures 10 through 12 show that effective removal flow rates >20, >30, and >40 m^3/hr are necessary to maintain the concentration in the cabin below 75% of the default SMAC for 100, 150, and 200 mg MIT/L, respectively. This is greater than the base 15.3 m^3/hr provided by the USOS TCCS alone. Therefore, the TCCS must be supplemented to maintain the cabin concentration below 75% of the default SMAC.

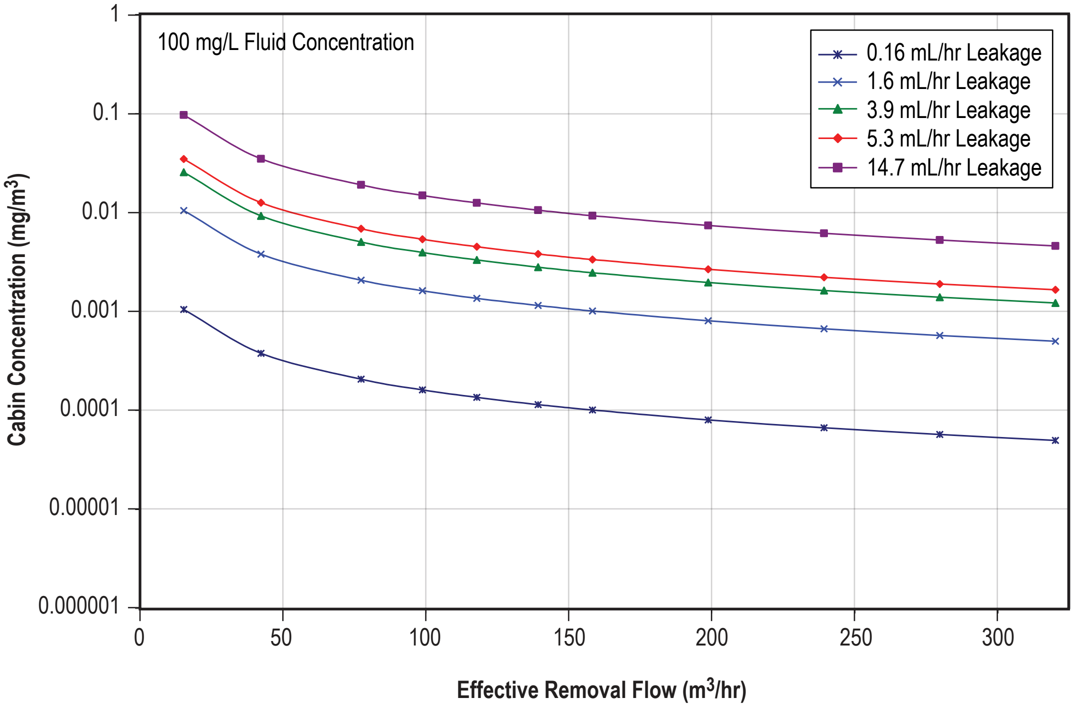


Figure 10. Effective removal flow to maintain SMAC for 100 mg MIT/L.

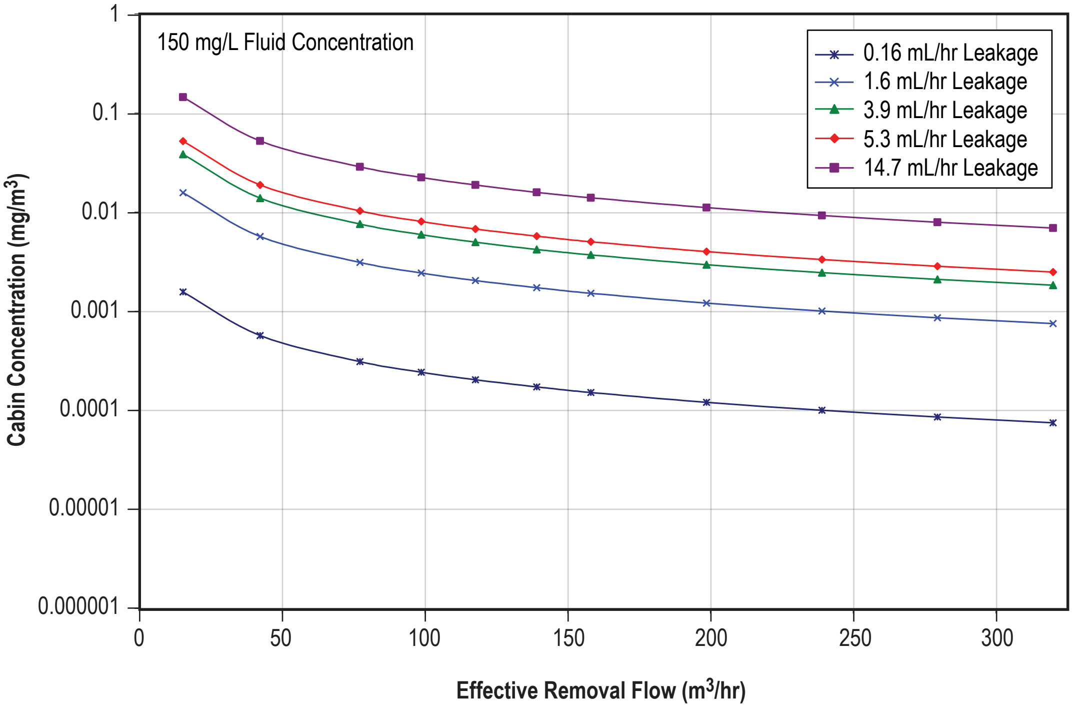


Figure 11. Effective removal flow to maintain SMAC for 150 mg MIT/L.

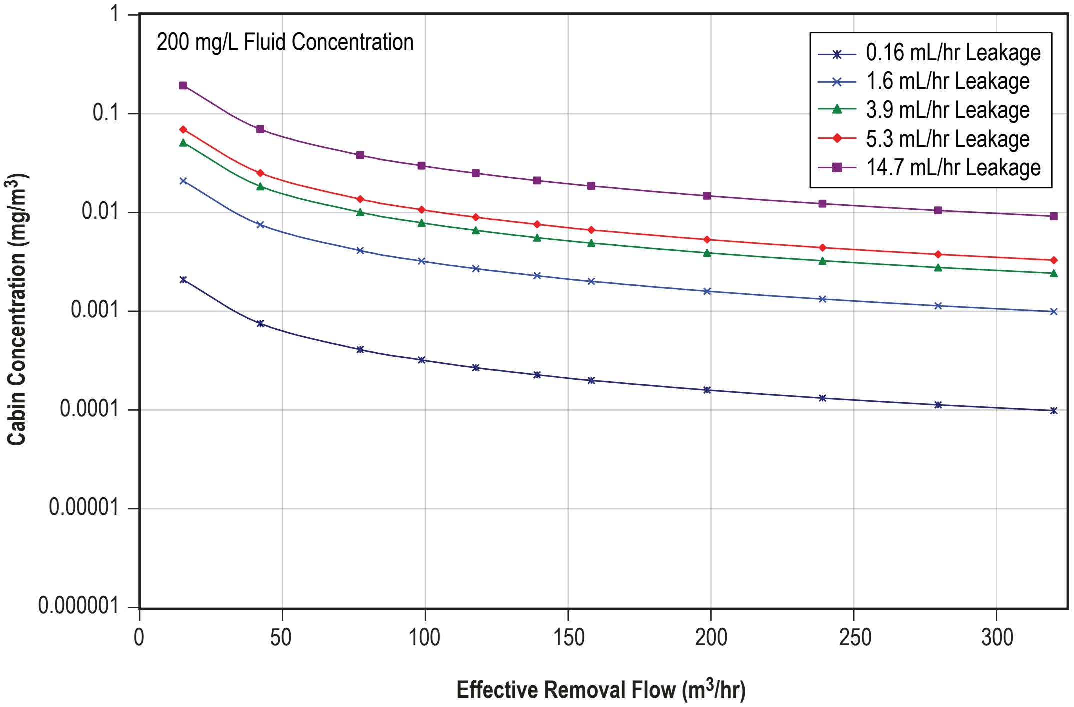


Figure 12. Effective removal flow to maintain SMAC for 200 mg MIT/L.

TCC for the ISS USOS was certified by engineering analysis using the constraint that the TCCS, with no assist from the Russian BMP or removal via absorption in humidity condensate, provides active control. Because any new contamination source represents an extension of the specified TCC design load, each new source is evaluated using the same criterion. This ensures that the same levels of safety apply for any known increase in the trace contaminant load. For information, the assist provided to the TCCS by both the BMP and absorption in humidity condensate is included. The additional cases allow the potential impact on ECLSS water processing systems to be estimated; however, they do not serve as the primary basis for assessing TCC capacity for normal operations.

3.2.3.2.1 U.S. On-Orbit Segment Trace Coontaminant Control Subassembly Capability. A range of ITCS working fluid leakage rates and MIT concentrations were evaluated. Figure 13 shows the steady state concentration that results when the TCCS provides the sole active removal. The TCCS, when operating alone, can provide effective control for an MIT source of no greater than 1.4 mg/hr and still maintain the cabin concentration below the default SMAC. This capability is equivalent to a sustained leakage from the ITCS >14.7 mL/hr containing 95 mg MIT/L of fluid. As the fluid's MIT concentration increases, the magnitude of the sustained leak accommodated by the TCCS decreases to as low as 5.5 mL/hr for 250 mg MIT/L of fluid. These rates span the range of ITCS leakage allowed by specification and are greater than the nearly 0.2 and 2.7 mL/hr leakage rates that have been experienced on board the ISS.

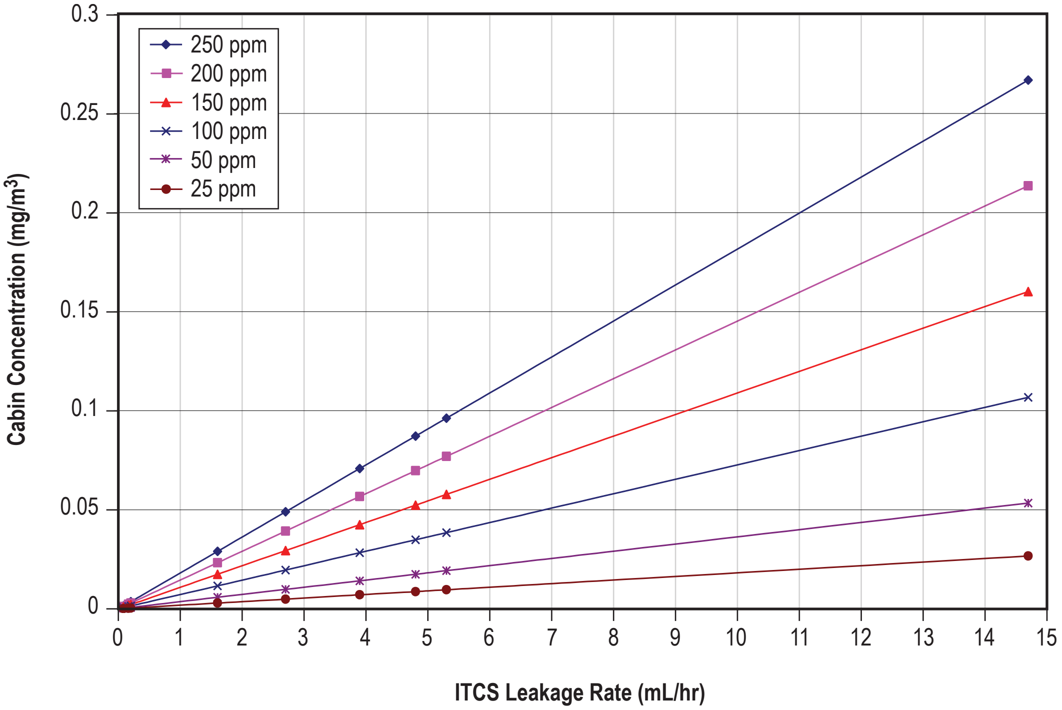


Figure 13. Leakage accommodated by the USOS TCCS.

3.2.3.2.2 Trace Contaminant Control Subassembly and BMP Dual Capability. For the TCCS operating with an assist from the ROS's BMP, the range of leakage accommodated increases to 3.2 mg/hr. Figure 14 shows that up to 250 mg MIT/L of fluid can be accommodated across the entire specification range of ITCS fluid leakage while maintaining the cabin concentration below the default SMAC. To maintain the concentration below 75% of the default SMAC, the full fluid leakage range is accommodated by using 217 mg MIT/L of fluid.

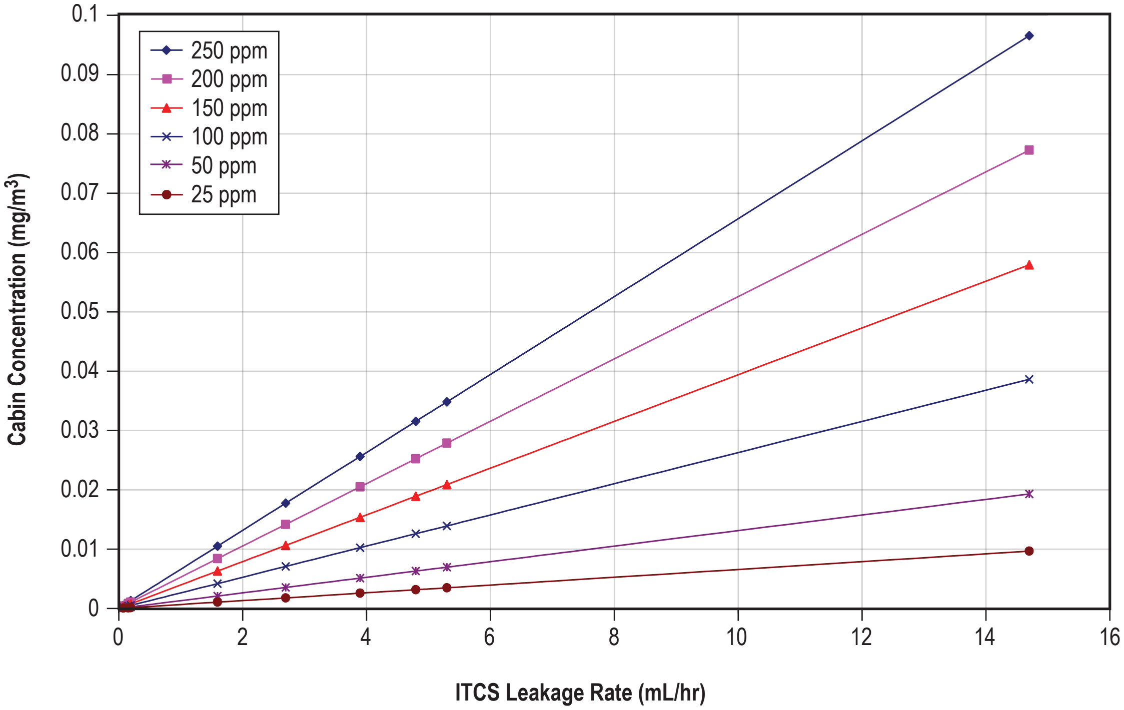


Figure 14. Leakage accommodated by the USOS TCCS and ROS BMP.

3.2.3.2.3 Absorption via Humidity Condensate and Impacts to Water Processing Equipment. Figure 15 shows the additional capability that absorption via humidity condensate provides. A single CCAA heat exchanger removing condensate at a one-person equivalent latent load can remove MIT via absorption at 11.9% efficiency. Similarly, the SKV heat exchanger on board the ROS can remove MIT at 24.3% efficiency while removing condensate at a one-person equivalent latent load. This increases to 39.2% for a two-person latent load. The entire range of specification leakage can be accommodated for concentrations to >250 mg MIT/L of fluid with substantial margin relative to the default SMAC. Therefore, to actually obtain the desired margin supported by the NASA toxicology assessment, absorption via humidity condensate must be considered as a supplemental control mechanism. Accounting for humidity condensate absorption, 75% of the default SMAC can be maintained for the entire range of leakage allowed for fluid 640 mg MIT/L.

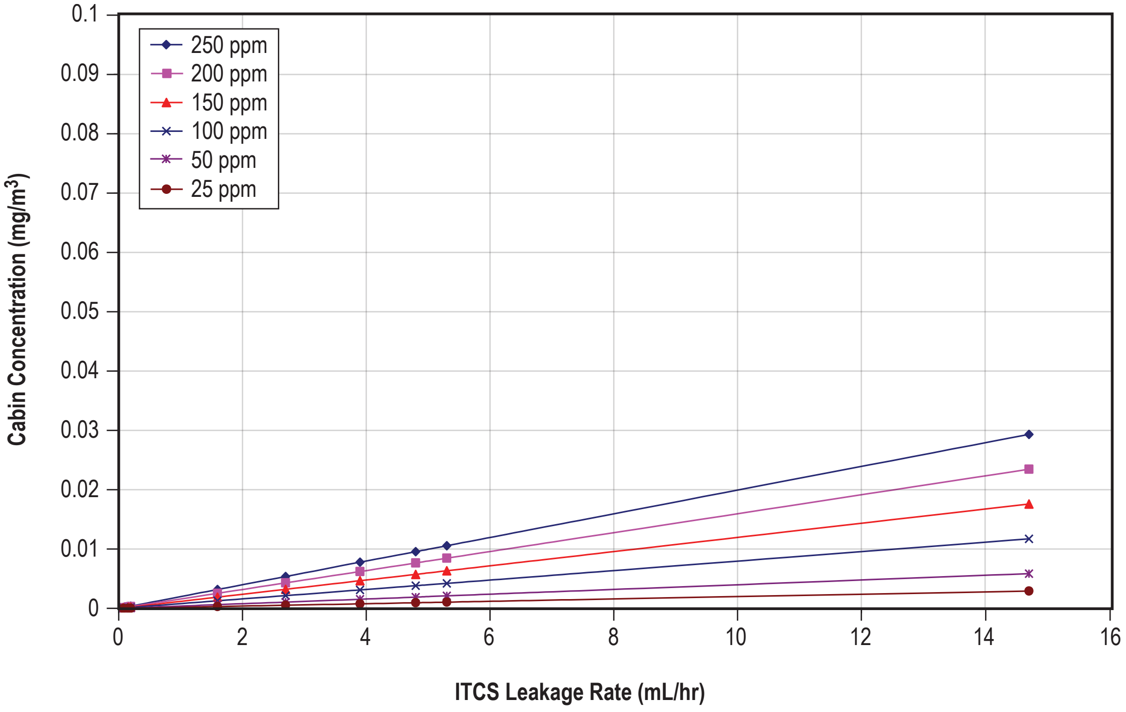


Figure 15. Leakage accommodated by the USOS TCCS and ROS BMP assisted by humidity condensate absorption at assembly complete for a crew of three.

Comparing figures 14 and 15 demonstrates that removal via absorption by humidity condensate provides an effective assist to the active contamination control equipment. This assist is necessary to meet the desired margin relative to the default SMAC. While effective with respect to airborne contamination control, there are impacts to water processing equipment that must be recognized and accounted for. Water processing equipment engineers from both NASA and RSC Energia have indicated supplemental VOC loading in humidity condensate resulting from ITCS fluid leakage must not exceed 5 mg/L.

Figures 16 and 17 illustrate the sensitivity of humidity condensate loading to cabin MIT concentration and condensate collection rate by the CCAA and SKV, respectively. For the CCAA, figure 16 shows the cabin concentration that can contribute to 5 mg MIT/L of condensate begins at approximately 0.007 mg/m^3 for latent loading up to three people. Similarly, figure 17 also shows approximately 0.008 mg/m^3 results in 5 mg MIT/L of condensate for latent loads up to three people collected by the SKV. It should be noted that these concentrations are well below the 0.05 mg/m^3 threshold of detection for archival air quality monitoring methods used on board the ISS. Therefore, it is not possible to detect MIT in the cabin atmosphere in the concentration range where deleterious effects on ECLSS performance may begin. Essentially, the MIT concentration that is likely deleterious to the ECLSS performance is undetectable by any air quality monitoring method employed by the ISS program.

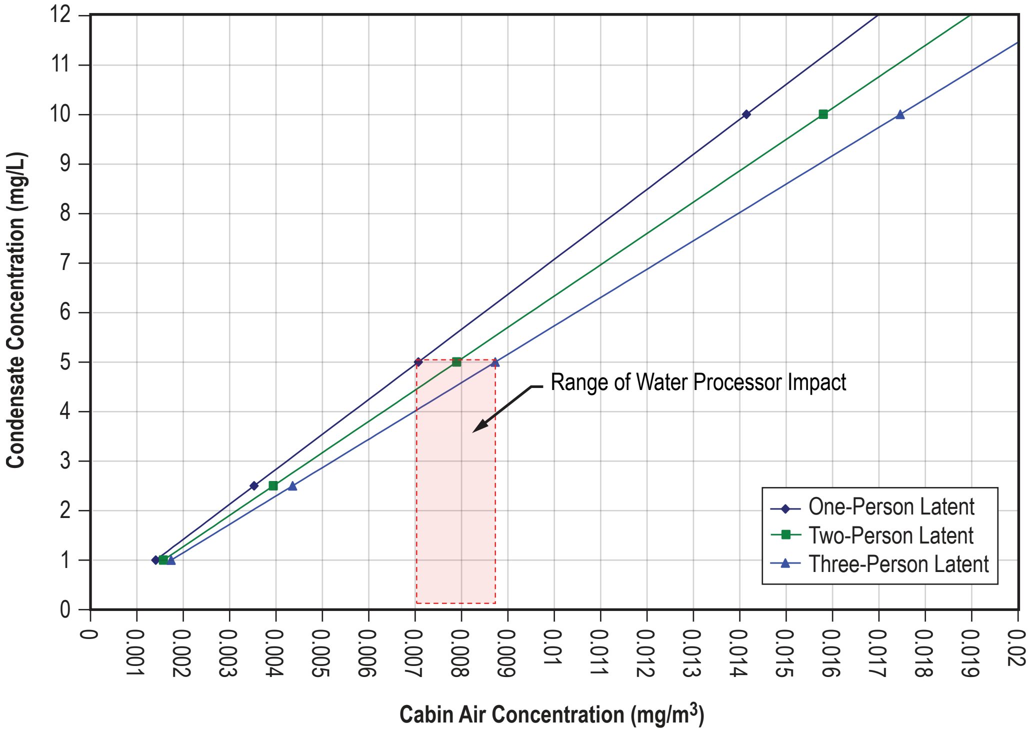


Figure 16. Effect of cabin MIT concentration on condensate collected by the CCAA.

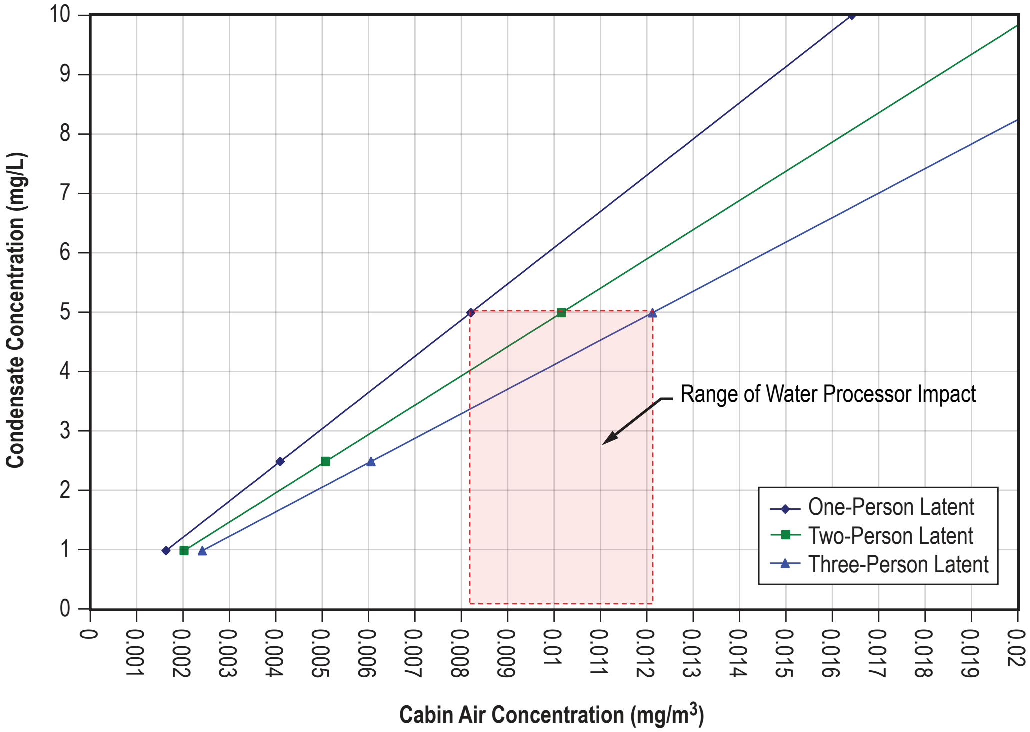


Figure 17. Effect of cabin MIT concentration on condensate collected by the SKV.

3.2.3.2.4 Consideration for Air Quality Control System Failures. To understand what ITCS fluid leakage rates present potential impacts on humidity condensate loading for the flight 4R and assembly complete configurations, the rigorous solution of mass balance equations (6) and (7) is used. This assessment includes the range of potential TCCS and BMP operational combinations to account for potential failures. The desire is to maintain single-failure tolerance with respect to contamination control equipment operation and the humidity condensate loading limit. Appendix C contains tabular results.

Figure 15 indicates that, with respect to maintaining cabin air quality, fluid containing >250 mg MIT/L can be used across the entire range of fluid leakage allowed by specification when all removal routes are considered. However, fluid containing <100 mg MIT/L has the least potential impact on the cabin's air quality as shown in figures 13 and 14. Examining figures 16 and 17, however, indicate that much lower concentration in the fluid is necessary to protect ECLS water purification system performance.

Using the rigorous mass balance and accounting for the combinations of TCCS and BMP operational modes, it is found that the cabin concentration for the flight 4R configuration can exceed the lower range for condensate loading acceptability for both the CCAA and SKV when leakage is >5.3 mL/hr for fluid containing 94 mg MIT/L. For the assembly complete configuration, leakage >14.7 mL/hr can overload the condensate collected by the CCAA and SKV for fluid containing 49 mg MIT/L. Thus, to protect for all possible ECLS failure ISS assembly phases, the MIT concentration in the ITCS fluid should not exceed 49 mg/L.

3.2.3.3 Summary. Overall, measures must be taken to minimize the risk to human health and maintaining the ISS's cabin air quality as well as protecting the water processing systems. Although the TCCS and BMP have proven themselves reliable, they are designed specifically to control the contamination loading from equipment offgassing and human metabolic processes alone. Further, cabin air quality monitoring techniques are not expected to be able to isolate MIT in archival air quality samples at the concentrations that can adversely affect water processing system performance. The method detection limit is typically 0.05 mg/m^3 for most VOCs. In summary, findings of the engineering assessment are the following:

- Evaporation rates from concentrated and dilute aqueous solutions of MIT are such that basic contamination control capability may be exceeded for fluid concentrations >100 mg/L.

- Basic, unassisted TCC capability as defined by ISS program specification can accommodate the full range of ITCS leakage rates for MIT concentration in the fluid <100 mg/L.

- Assisted TCC capability with allowance for ECLS water processing system protection and contamination control single failure tolerance can accommodate the full range of ITCS leakage rates for <49 mg MIT/L of fluid.

3.2.4 Conclusion and Recommendation

Based on ISS ECLS engineering evaluation, ITCS fluid containing <49 mg MIT/L of fluid is compatible with the ECLSS. Because there is no air quality monitoring method presently available to the ISS program to monitor MIT's concentration below 0.02 mg/m^3, using a less volatile antimicrobial candidate that is not infinitely soluble in water is recommended.

3.3 Ortho-Phthalaldehyde Antimicrobial Additive Assessment

The ECLS compatibility and environmental impact associated with ortho-phthaldehyde as a candidate antimicrobial additive to the ISS internal ATCS was assessed in 2005 and documented under NASA memorandum EV50(05-005), "Compatibility of the Candidate Ortho-Phthalaldehyde Internal Thermal Control System Antimicrobial Additive with the International Space Station's Environmental Control and Life Support System," dated September 14, 2005.

3.3.1 Background

The ISS's active ITCS presently uses silver as an antimicrobial additive in the internal water working fluid. The silver concentration in the fluid has been found to decline within a few days as silver deposits on internal wetted surfaces, but microbial control is maintained by the specified 9.5 pH. Samples returned from flight have indicated that the ITCS fluid chemistry is affected by the on-orbit environment. Decreased pH and other changes have been traced to CO_2 permeation through the Teflon flex hoses. Due to the combination of lower pH and lower antimicrobial additive concentration in the fluid concern that microbiologically-induced problems, such as fouling, plugging, or corrosion of ITCS wetted components, may increase, leading to degraded performance and shorter service life.

These concerns have led to a search for an alternative antimicrobial additive. Beyond periodically injecting more silver antimicrobial additive, several candidate antimicrobial additives are being considered.[22,23] Glutaraldehyde was an early promising candidate; however, significant issues relating to its environmental impact on board the ISS limited its allowable concentration in the ITCS fluid to <25 mg/L. Additional evaluation by the NESC concluded that glutaraldehyde was not suitable for use on board the ISS.[24] Therefore, further work has been conducted to find other, more suitable candidates. Among these new candidates is ortho-phthalaldehyde (OPA). Relevant physical properties of OPA are summarized in table 8.

Table 8. Ortho-phthalaldehyde properties.

Property	Value
CAS number	643-79-8
Molecular weight (g/mole)	134.14
Melting point (°C)	53.2
Boiling point (°C)	236
Water solubility @ 25 °C (mg/L)	5,346
Henry's Law constant (atm/mole fr.)	0.0122
Vapor pressure (mm Hg @ 21 °C)	0.0052
Solubility	Soluble in water, alcohol, and ether
Odor	Odorless

The primary challenge for any ITCS antimicrobial additive is the ability to maintain the cabin concentration below the SMAC under a range of allowable ITCS leakage rates and ECLSS operational configurations. OPA does not have an officially designated SMAC; therefore, the default SMAC of 0.1 mg/m^3 is used for the purposes of the ECLS engineering assessment. To maintain margin, a concentration <75% of the default SMAC or 0.075 mg/m^3 is preferred. This is consistent with evaluation of comparative toxicity data conducted by NASA Toxicology experts. Chemical compounds with SMACs <1 mg/m^3 are typically difficult for the ECLSS to control if persistent generation sources exist because the total effective flow rate through the contamination control equipment is limited; i.e., active contamination control equipment on board the ISS is accomplished using fixed flow devices. The primary means for maintaining cabin concentration below the SMAC in such cases then becomes source control. With this in mind, an engineering assessment has been conducted to address the ECLSS's capability to accommodate routes by which OPA can enter the cabin environment if it is used as an antimicrobial additive in the ITCS working fluid.

3.3.2 Approach

Two basic assessments comprise the evaluation of OPA's compatibility with the ISS's ECLSS. Depending on the method that OPA may be introduced into the ITCS in flight, evaporation rate from bulk solutions must be considered. A more recent concept, however, employs a resin to introduce the antimicrobial chemical into the ITCS. This latter concept eliminates concern with handling concentrated bulk liquids. Conservatively, the first assessment is to determine the evaporation rate and equivalent amount of pure OPA that contributes to short-term air quality concerns. The second assessment is of the ISS ECLSS's capability to handle chronic, fugitive leaks from the ITCS for various concentrations of OPA. This assessment considers the ability of the ECLS atmospheric quality control equipment to accommodate chronic emissions from a range of ITCS leakage rates and OPA concentrations. The equations and calculation techniques in section 2.3 are applied to the assessment cases.

3.3.2.1 Cases Considered. Cases considered include determining the evaporation rate from pure OPA as well as a range of fugitive emissions encompassing the range of leakage from the ITCS allowed by specification. Effects on the ability to maintain cabin air quality for the specified range of ITCS fluid leakage during normal operation of the TCC equipment on board the ISS and failure scenarios of this equipment are also considered.

3.3.2.1.1 Evaporation Rate. Since the working concentration of OPA in the ITCS fluid has not yet been determined, evaporation rate was evaluated using equation (9) to determine the volume of pure OPA and 0.55% aqueous OPA at 21 °C that will exceed the TCCS's capability to maintain the cabin concentration below 75% of the default SMAC.

3.3.2.1.2 Control of Fugitive Emissions. Initial screening was conducted using equation (2) to understand the effects of not only ITCS fluid leakage rate but also the OPA concentration and available active contamination control capacity upon cabin atmospheric quality. The assessment bounds the capability dictated by specification documents and also assists in evaluating the potential impacts upon water processing systems. The leakage rates and OPA concentrations listed in table 5 were investigated. In addition, leakage rates of 0.2 and 2.7 mg/hr were investigated because actual fluid leaks of these magnitudes have been experienced. Additional details on ITCS fluid leakage specifications defined by the ITCS SPRT are provided in table 6.

Using the appropriate numerical values for the system variables in the solved form of equations (6) and (7) for the USOS and ROS, the effects of each ITCS fluid leakage rate containing 25 mg OPA/L up to 250 mg OPA/L on cabin atmospheric quality and humidity condensate loading were assessed.

3.3.2.2 Vehicle Configuration. Two vehicle configurations are considered—the configuration as of flight 4R and the ISS assembly complete six-person crew capability. Estimated total cabin free volume for the 4R configuration is 371 m^3 comprised of the USOS free volume of 190.4 m^3 and the ROS free volume of 180.6 m^3. The U.S. assembly complete configuration expands the USOS volume to include the JEM, Columbus Module, CAM, Node 2, and Node 3. It is assumed that the ROS volume will not change appreciably to accommodate the six-crew capability; therefore, the total ISS free volume will increase to approximately 928 m^3 as a result of the USOS free volume increasing to approximately 747.4 m^3. The flight 4R configuration cases consider the present crew size of two people while the ISS assembly complete six-crew capability cases consider only a crew of three. Using only a crew of three for the assembly complete case is considered a greater challenge to overall TCC because the crew latent load is smaller than for the six-person crew size. It is anticipated that a checkout period during assembly complete will have a three-person crew.

In both the flight 4R and assembly complete configurations, the TCCS and BMP provide the active contamination control on board the ISS. During both ISS assembly stages, the TCCS and BMP operate in parallel with each other to maintain the cabin atmospheric quality. The TCCS removes OPA at 100% efficiency in its charcoal bed assembly. If the charcoal bed assembly becomes saturated, then the TCCS will remove the OPA via its catalytic oxidizer assembly. The flows through the charcoal bed assembly and catalytic oxidizer assembly are 15.3 and 4.6 m^3/hr, respectively. The BMP removes OPA at 100% efficiency at 27 m^3/hr flow. This performance is estimated based upon activated charcoal's capacity for OPA. Net IMV flow between the ROS to the USOS is typically 180 m^3/hr. No attempt is made to account for the effects of IMV flow short circuiting. The challenges presented by failures of the TCCS and BMP, either individually or at the same time, are considered.

3.3.2.3 Absorption by Humidity Condensate as a Removal Device. In addition to removal by the active contamination control equipment, water soluble contaminants are also removed by absorption in humidity condensate. As noted earlier, the assist provided to the active contamination control equipment on board the ISS is considered only to address potential impacts to water processing systems. Absorption via humidity condensate is not considered when evaluating the capability for the active control systems to accommodate a new contaminant loading.

The primary condensate removal for the flight 4R configuration is provided by the SKV in the ROS. Typical flow rate through the heat exchanger core is 144 m^3/hr. The condensate loading normally ranges between a three- and two-person latent load depending upon the crew size. Removal efficiency via absorption of OPA by humidity condensate is 8% for a two-person latent load and

11% for a three-person latent load. The calculation technique for estimating condensate absorption efficiency is documented by reference 15. An average latent load is defined as 1.4 L/day/person.

For the ISS assembly complete six-person crew capability, the most challenging case exists during the time when the crew is limited to three people. The combination of added ITCS fluid loops and limited TCC scrubbing capacity are most severe during this time. It is assumed for these cases that a two-person latent load is removed by the SKV and a one-person latent load is removed by a CCAA in the USOS. At this rate of humidity condensate collection, the single-pass removal efficiency is approximately 2% for the CCAA. Removal efficiency for the SKV is 8% as noted previously.

It must be noted that deviations from ideal Henry's Law behavior, as reported by references 1, 3, 15 and 19 are not accounted for in this assessment because specific data on OPA relative to nonidealities that may affect strict Henry's Law behavior are not available. For this reason, this aspect of the assessment is not conservative.

3.3.3 Results and Discussion

The following discussion presents and discusses results for estimated evaporation rates from pure OPA, basic control of cabin atmospheric quality under varying ITCS fluid leakage conditions, and effects on humidity condensate loading. Guidelines are presented for maintaining single-failure tolerance with respect to ECLS atmospheric quality and water quality control functions.

3.3.3.1 Evaporation From Bulk Leakage. The generation rate that equals the TCCS's capability to maintain OPA at 75% of the default SMAC is 1.15 mg/hr. The volume of pure OPA and 0.55% aqueous OPA from which evaporation at 1.15 mg/hr is expected was calculated using equation (9). For pure OPA, the total leaked volume that can contribute to this production rate is 234 cm^3. Literature reports that for 0.55% aqueous OPA, the vapor pressure is 7.6×10^{-7} mm Hg. If the OPA concentration selected for the ITCS fluid is 0.55% or less, then nearly 133,000 L (~35,000 gal) will have to leak before creating an air quality control problem on board the ISS. Vapor pressure for 1% to 1.5% aqueous OPA ranges between 10^{-5} to 10^{-4} mm Hg. These more concentrated solutions require at least 88 L to be released to result in an air quality problem on board the ISS. The volumes of fluid that contribute to a cabin air quality control challenge are well beyond what is expected during any credible leakage scenario associated with OPA's introduction to and use in the ITCS fluid.

3.3.3.2 Control of Fugitive Emissions. The ability to maintain cabin air quality in the presence of fugitive emissions must first consider the available equipment for actively removing the contamination. Figures 18 through 20 illustrate the overall scrubbing flow required to accommodate a range of ITCS fluid leakage containing up to 250 mg OPA/L. Leakage rates of 3.9 and 5.3 mL/hr most likely can be sustained for about 1 month while deliberating the need to shut down an ITCS fluid loop. For these leakage rates, figures 18 through 20 show that effective removal flow rates >20, >30, and >40 m^3/hr are necessary to maintain the concentration in the cabin below 75% of the default SMAC for 100, 150, and 200 mg OPA/L, respectively. This is greater than the base 15.3 m^3/hr provided by the USOS TCCS alone. Therefore, the TCCS must be supplemented to maintain the cabin concentration below 75% of the default SMAC.

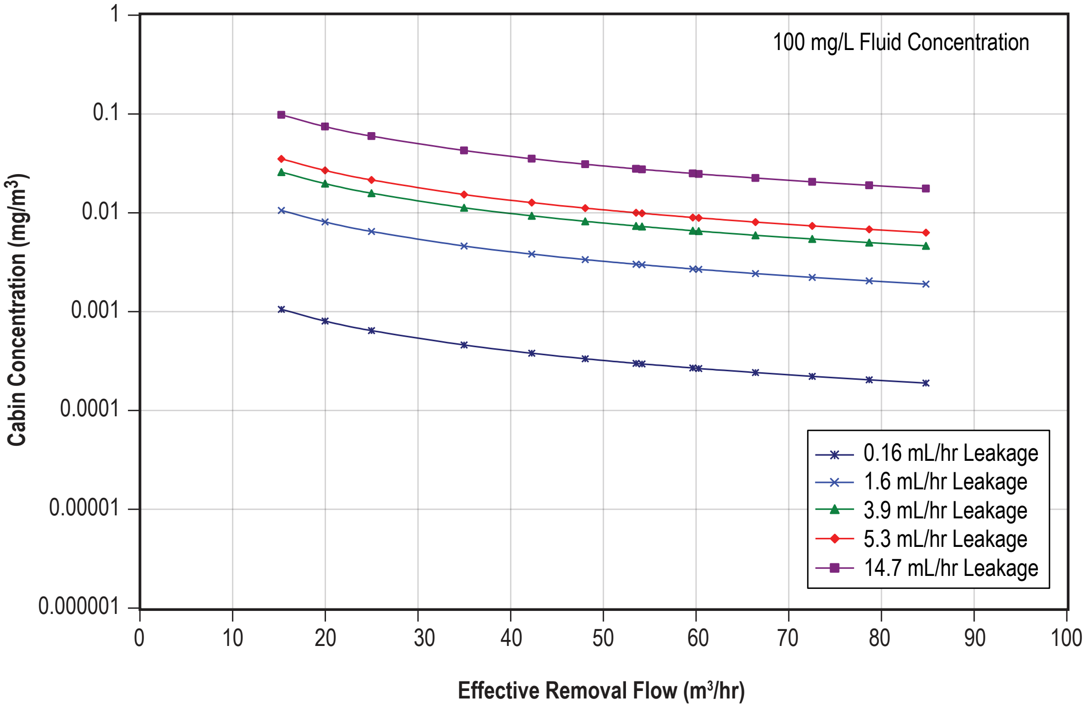


Figure 18. Effective removal flow to maintain SMAC for 100 mg OPA/L.

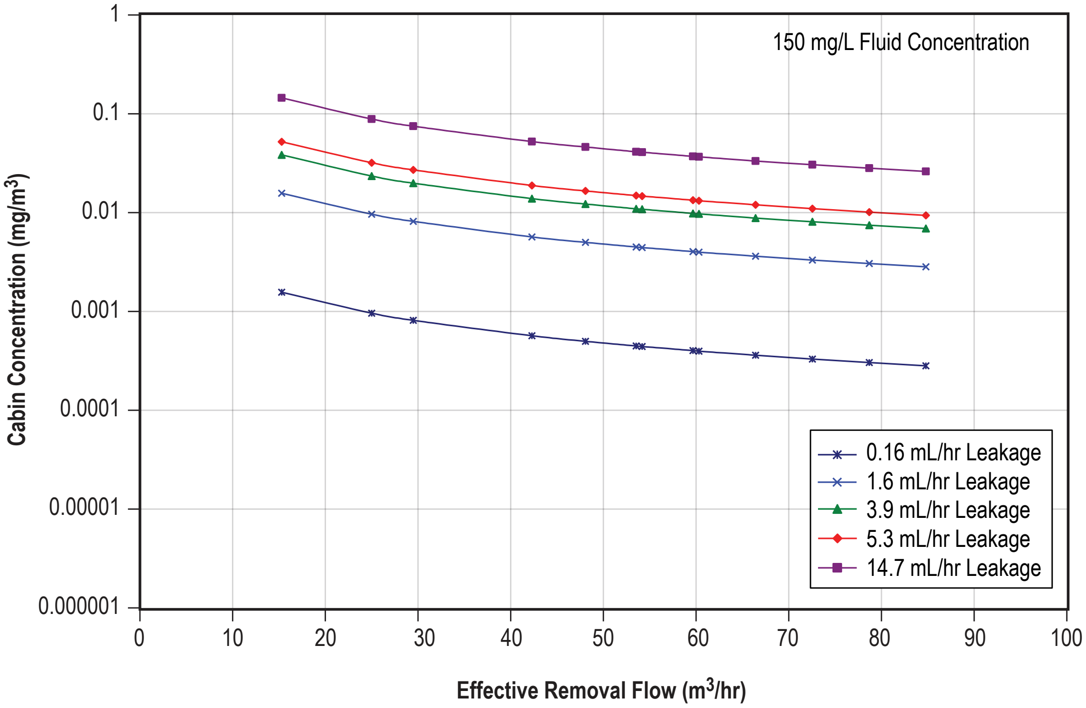


Figure 19. Effective removal flow to maintain SMAC for 150 mg OPA/L.

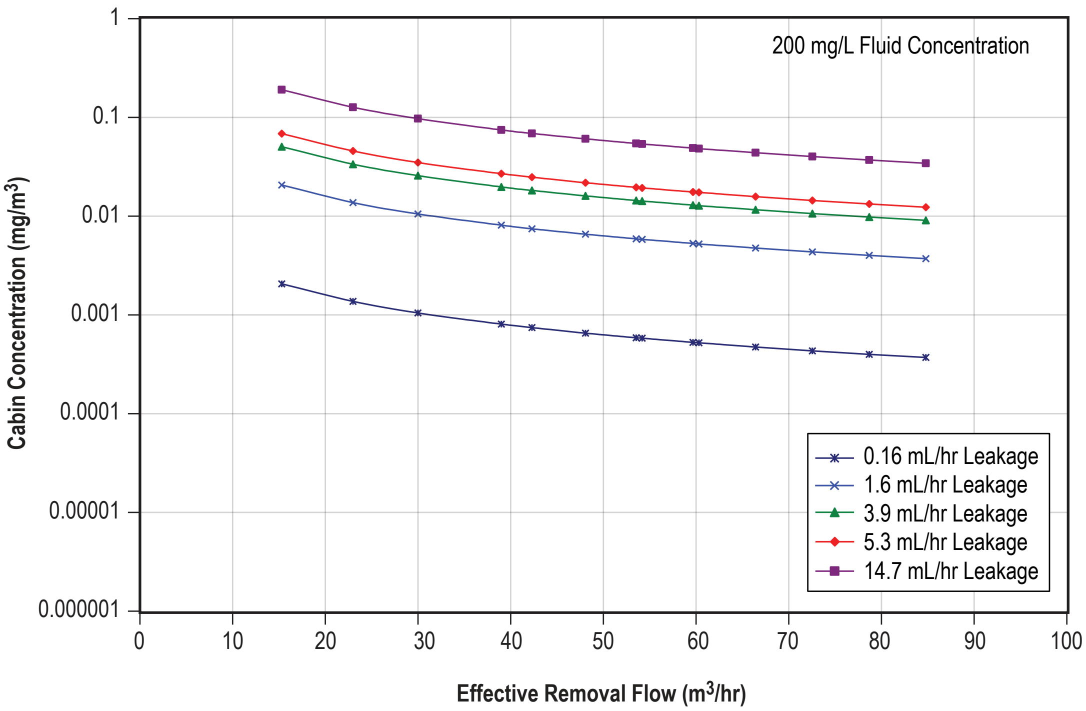


Figure 20. Effective removal flow to maintain SMAC for 200 mg OPA/L.

TCC for the ISS USOS was certified by engineering analysis using the constraint that the TCCS, with no assist from the Russian BMP or removal via absorption in humidity condensate, provides active control. Because any new contamination source represents an extension of the specified TCC design load, each new source is evaluated using the same criterion. This ensures that the same levels of safety apply for any known increase in the trace contaminant load. For information, the assist provided to the TCCS by both the BMP and absorption in humidity condensate is included. The additional cases allow the potential impact on ECLSS water processing systems to be estimated; however, they do not serve as the primary basis for assessing TCC capacity for normal operations.

3.3.3.2.1 United States On-Orbit Segment Trace Contaminant Control Subassembly Capability. A range of ITCS working fluid leakage rates and OPA concentrations were evaluated. Figure 21 shows the steady state concentration that results when the TCCS provides the sole active removal. The TCCS, when operating alone, can provide effective control for an OPA source of no greater than 1.4 mg/hr and still maintain the cabin concentration below the default SMAC. This capability is equivalent to a sustained leakage from the ITCS >14.7 mL/hr containing 95 mg OPA/L of fluid. As the fluid's OPA concentration increases, the magnitude of the sustained leak accommodated by the TCCS decreases to as low as 5.5 mL/hr for 250 mg OPA/L of fluid. These rates span the range of ITCS leakage allowed by specification and are greater than the nearly 0.2 and 2.7 mL/hr leakage rates that have been experienced on board the ISS.

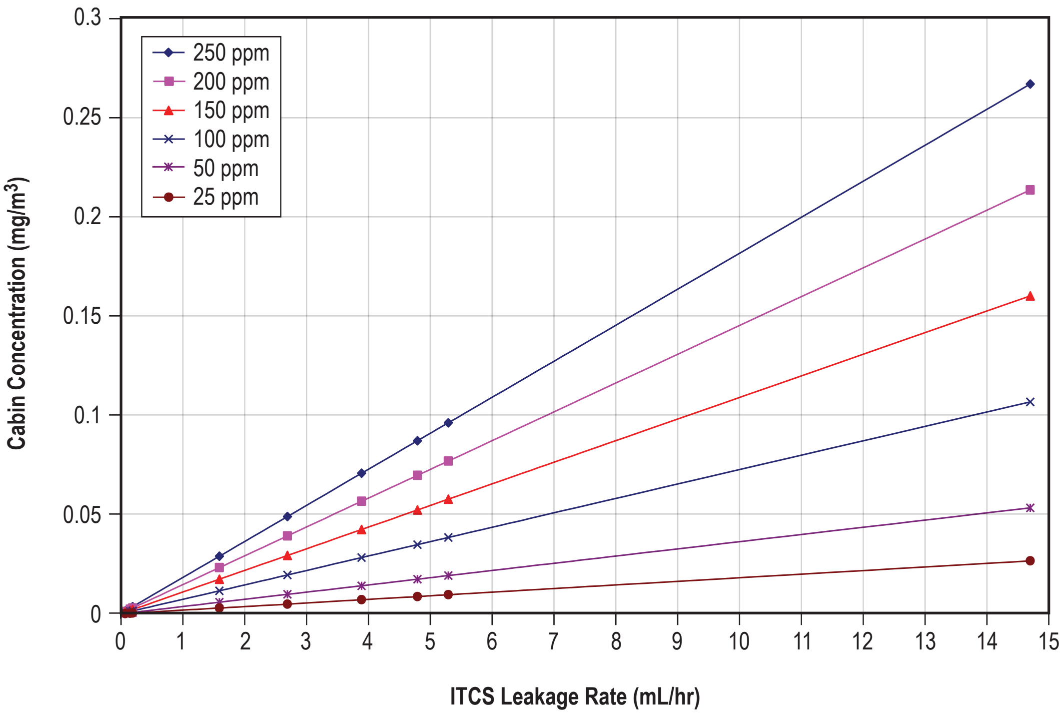


Figure 21. Leakage accommodated by the USOS TCCS.

3.3.3.2.2 Trace Contaminant Control Subassembly and BMP Dual Capability. For the TCCS operating with an assist from the ROS's BMP, the range of leakage accommodated increases to 3.2 mg/hr. Figure 22 shows that up to 250 mg OPA/L of fluid can be accommodated across the entire specification range of ITCS fluid leakage while maintaining the cabin concentration below the default SMAC. To maintain the concentration below 75% of the default SMAC, the full fluid leakage range is accommodated by using 217 mg OPA/L of fluid.

3.3.3.2.3 Absorption Via Humidity Condensate and Impacts to Water Processing Equipment. Figure 23 shows the additional capability that absorption via humidity condensate provides. A single CCAA heat exchanger removing condensate at a one-person-equivalent latent load can remove OPA via absorption at 1.8% efficiency. Similarly, the SKV heat exchanger on board the ROS can remove OPA at 4% efficiency while removing condensate at a one-person-equivalent latent load. This increases to 7.8% for a two-person-equivalent latent load. The entire range of specification leakage can be accommodated for concentrations to 250 mg OPA/L of fluid with margin relative to the default SMAC. The cabin concentration is also maintained below 75% of the default SMAC for all leakage and ITCS fluid concentrations considered. Therefore, to actually obtain the desired margin supported by the NASA toxicology assessment, absorption via humidity condensate must be considered as a supplemental control mechanism of OPA concentration in excess of 200 mg/L is required.

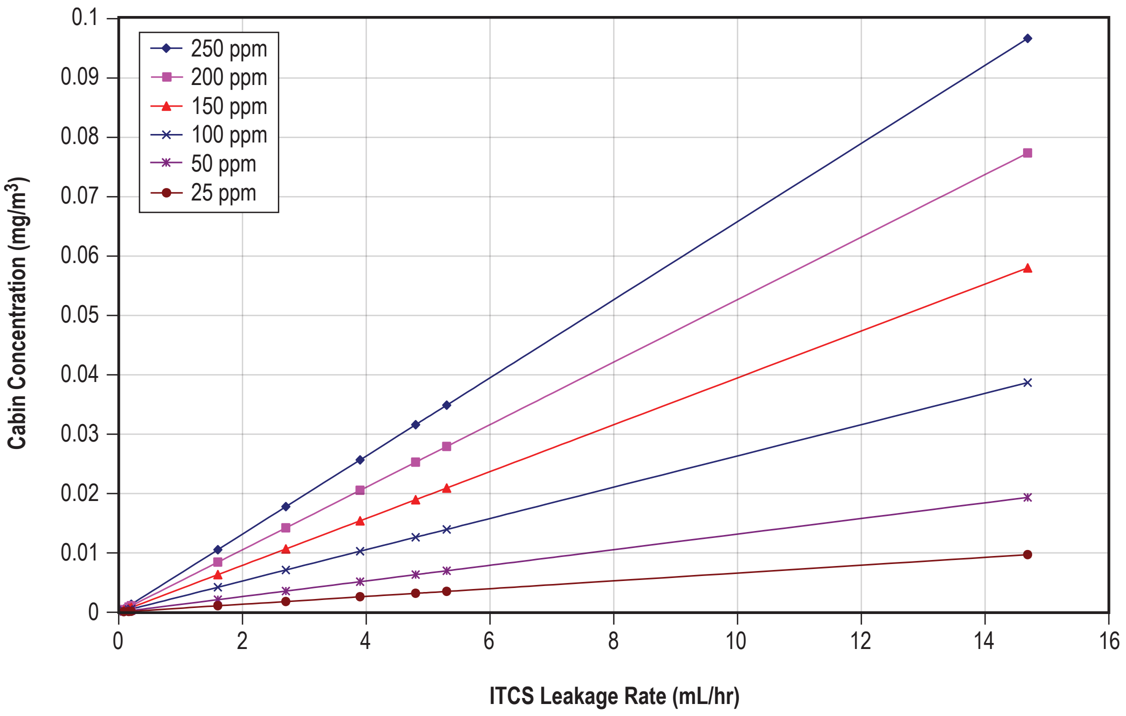


Figure 22. Leakage accommodated by the USOS TCCS and ROS BMP.

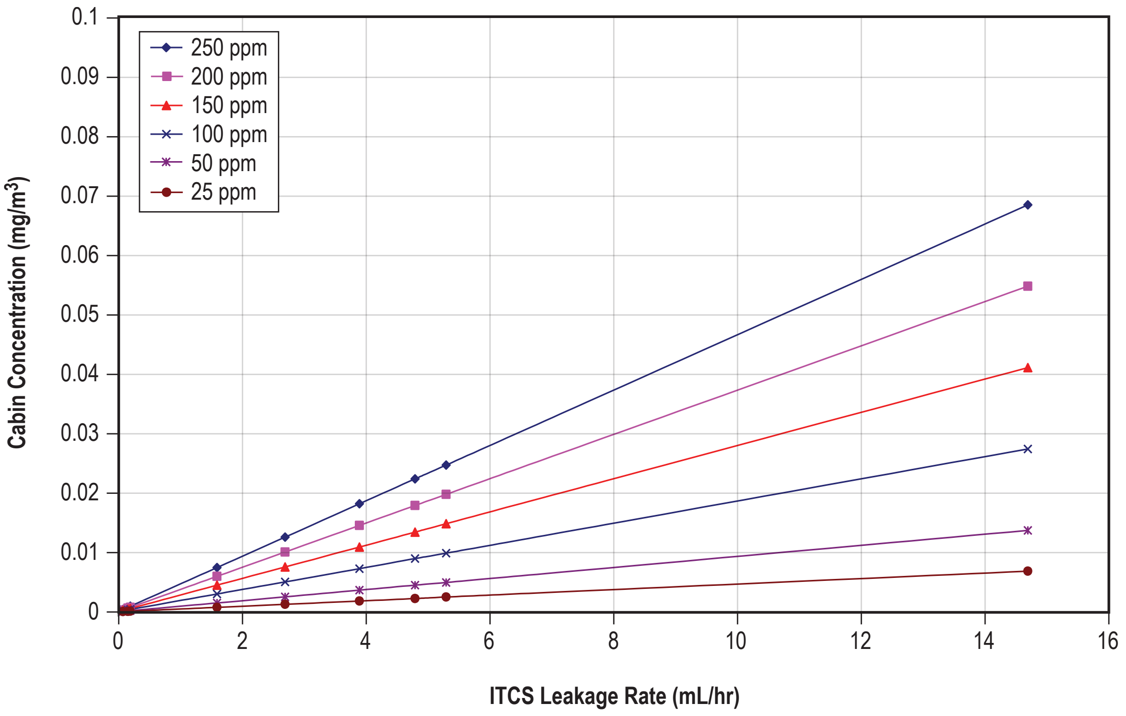


Figure 23. Leakage accommodated by the USOS TCCS and ROS BMP assisted by humidity condensate absorption at assembly complete for a crew of three.

Comparing figures 22 and 23 demonstrates that removal via absorption by humidity condensate provides an effective assist to the active contamination control equipment. This assist is necessary to meet the desired margin relative to the default SMAC. While effective with respect to airborne contamination control, there are impacts to water processing equipment that must be recognized and accounted for. Water processing equipment engineers from both NASA and RSC Energia have indicated supplemental VOC loading in humidity condensate resulting from ITCS fluid leakage must not exceed 5 mg/L.

Figures 24 and 25 illustrate the sensitivity of humidity condensate loading to cabin OPA concentration and condensate collection rate by the CCAA and SKV, respectively. For the CCAA, figure 24 shows the cabin concentration that can contribute to 5 mg OPA/L of condensate is approximately 0.05 mg/m^3 for latent loading up to three people. Similarly, figure 25 also shows approximately 0.05 mg/m^3 results in 5 mg OPA/L of condensate for latent loads up to three people collected by the SKV. It should be noted that 0.05 mg/m^3 is on the threshold of detection for archival air quality monitoring methods used on board the ISS. Therefore, it is possible to detect OPA in the cabin atmosphere in the concentration range where deleterious effects on ECLSS performance may begin. Attention to tuning the air quality sample analytical method for OPA is required to provide this capability. Even so, no in-flight analytical technique is available for OPA and it may be necessary to determine whether the formaldehyde monitoring method can be affected by the presence of OPA in the cabin atmosphere.

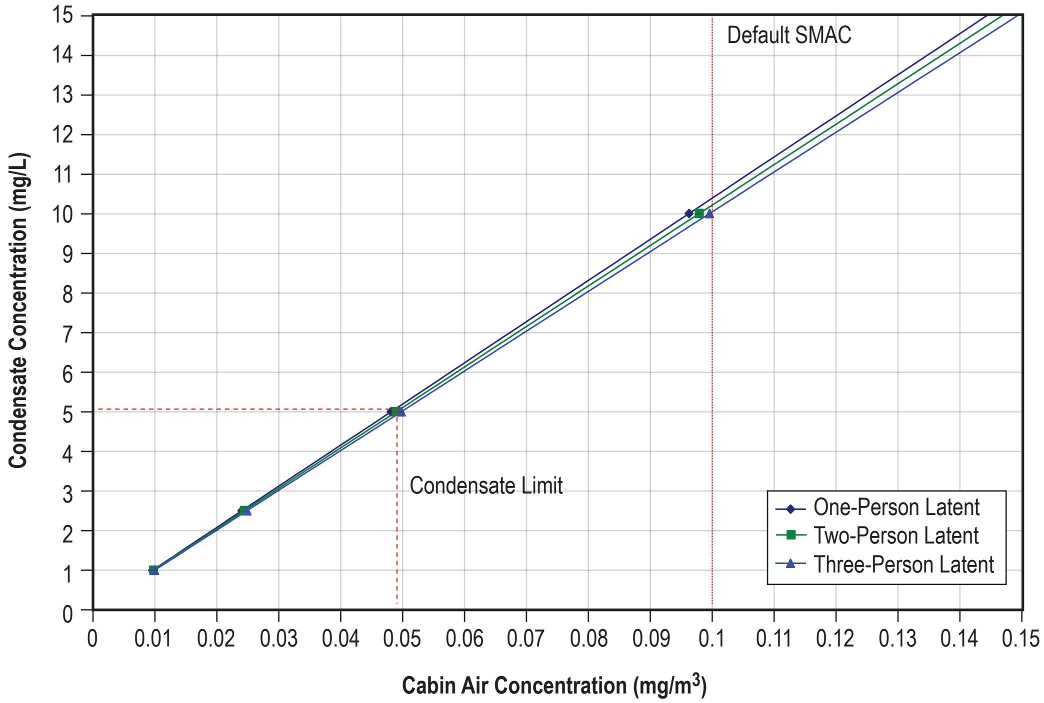


Figure 24. Effect of cabin OPA concentration on condensate collected by the CCAA.

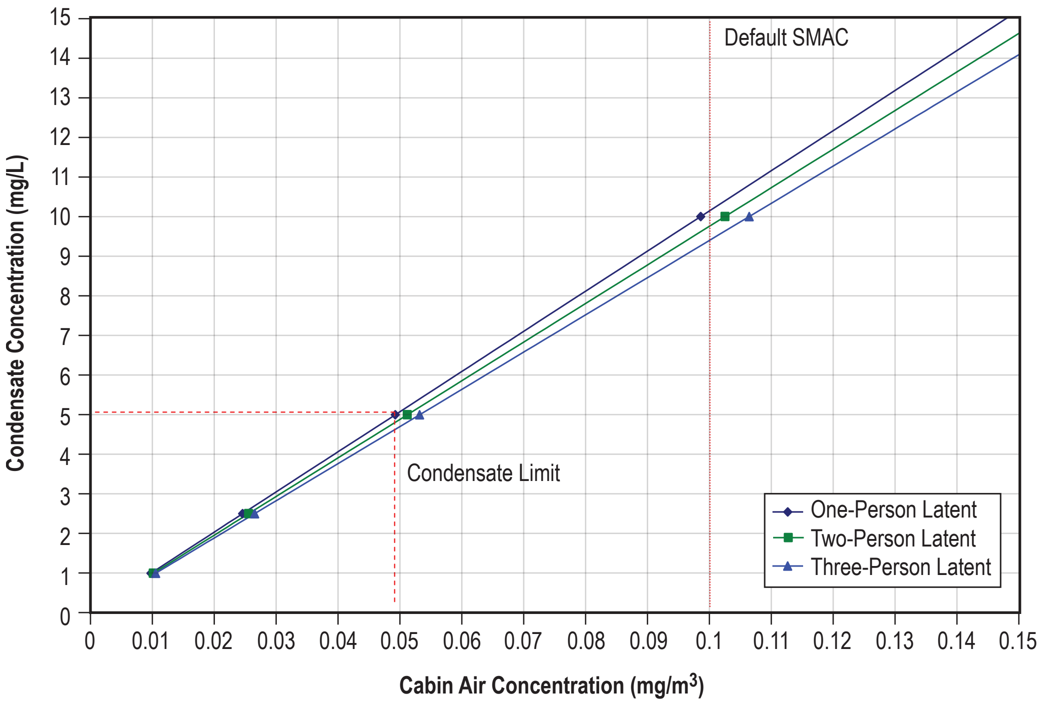


Figure 25. Effect of cabin OPA concentration on condensate collected by the SKV.

3.3.3.2.4 Consideration for Air Quality Control System Failures. To understand what ITCS fluid leakage rates present potential impacts on humidity condensate loading for the flight 4R and assembly complete configurations, the rigorous solution of mass balance equations (6) and (7) are used. This assessment includes the range of potential TCCS and BMP operational combinations to account for potential failures. The desire is to maintain single-failure tolerance with respect to contamination control equipment operation and the humidity condensate loading limit. Appendix D contains tabular results.

Figure 23 indicates that, with respect to maintaining cabin air quality, fluid containing up to 219 mg OPA/L can be used across the entire range of fluid leakage allowed by specification when all removal routes are considered. However, fluid containing <100 mg OPA/L has the least potential impact on the cabin's atmosphere as shown in figures 21 and 22.

Using the rigorous mass balance and accounting for the combinations of TCCS and BMP operational modes, it is found that the cabin concentration for the flight 4R configuration can exceed the lower range for condensate loading acceptability for both the CCAA and SKV when leakage is >5.3 mL/hr for fluid containing 300 mg OPA/L. For the assembly complete configuration, leakage >14.7 mL/hr can overload the condensate collected by the CCAA and SKV for fluid containing 109 mg OPA/L. Thus, to protect for all possible ECLS failure ISS assembly phases, the OPA concentration in the ITCS fluid should not exceed 109 mg/L.

3.3.3.3 Summary. Overall, measures must be taken to minimize the risk to human health and maintaining the ISS's cabin air quality as well as protecting the water processing systems. Although the TCCS and BMP have proven themselves reliable, they are designed specifically to control the contamination loading from equipment offgassing and human metabolic processes alone. Further, cabin air quality monitoring techniques may be able to isolate OPA in archival air quality samples. The method detection limit is typically 0.05 mg/m^3 for most VOCs. Aldehydes can be challenging for the analytical methods employed for monitoring cabin air quality so work will be necessary to demonstrate that OPA can be detected. Further, interference with the existing formaldehyde monitoring method must be considered.

The following conclusions are based on the evaluation of OPA as a candidate antimicrobial additive to the ITCS working fluid:

- Evaporation rates from concentrated and dilute aqueous solutions of OPA are such that the ISS air quality control equipment can handle all credible leakage scenarios and maintain the cabin concentration below 75% of the default SMAC for fluid containing >1% OPA by mass.

- Basic, unassisted TCC capability as defined by ISS program specification can accommodate the full range of ITCS leakage rates for OPA concentration in the fluid <100 mg/L.

- Assisted TCC capability with allowance for ECLS water processing system protection and contamination control single-failure tolerance can accommodate the full range of ITCS leakage rates for <109 mg OPA/L of ITCS fluid.

3.3.4 Conclusion and Recommendation

Based on ISS ECLS engineering evaluation, ITCS fluid containing <100 mg OPA/L is determined to be the most compatible with ECLSS processes and contributes to the least overall impact to the ISS's cabin environment. It is recommended that potential interference with the existing in-flight formaldehyde air quality monitoring method and enhancement of the archival air quality sample analytical method to target OPA should be considered and investigated.

3.4 Aqueous Propylene Glycol Fluid Assessment

The ECLS compatibility and environmental impact associated with aqueous propylene glycol as a candidate thermal working fluid for the Orion crew exploration vehicle (CEV) was assessed in 2009 and documented under NASA memorandum ES62(09-11), "ECLSS Compatibility Assessment of an Aqueous Propylene Glycol Thermal Working Fluid for the *Orion* Crew Exploration Vehicle," dated December 14, 2009.

3.4.1 Introduction

The design and operation of crewed spacecraft require identifying and evaluating chemical compounds that may present compatibility risks with the ECLSS. Such risks must be understood so that appropriate design and operational controls, including specifying containment levels, can be instituted or an appropriate substitute material selected.

All spacecraft cabin system design and operation activities occur within the bounds specified by the air quality standard. In the case of crewed spacecraft, that standard is the SMAC. Materials selection and control, hardware design, manufacturing processes, chemical process design, mission characteristics as well as crew size and activities are only a few of the elements that must occur within the constraints of the air quality standards. A change to any of these, whether for a spacecraft system or a payload, can negatively impact cabin atmospheric quality, the ECLSS equipment, or both. An assessment of spacecraft system and payload fluids by ECLSS engineering ensures that any potential impacts to the cabin environment, as well as the ECLSS equipment, are accounted for and understood.

Because the specification of the active TCC equipment for a spacecraft precedes those data necessary to fully validate its design, standard design practice dictates a conservative approach whereby the active contamination control system performs its function unassisted by any other systems or processes in the cabin.[1] This means that overboard atmospheric leakage and assists provided by other air processing systems such as CO_2 removal and humidity control equipment are not considered during the design and validation of the active TCC equipment. To maintain consistency, all new contamination loads are assessed in the same manner.

For the ISS, the key design requirements pertaining to TCC design and performance state that trace contaminants shall be controlled to less than their respective SMAC for a normal equipment offgassing and crew metabolic load. More specifically, the U.S. Laboratory specification requires that the TCCS maintain trace atmospheric component concentration from normal equipment offgassing and crew metabolic processes to less than 90% of individual contaminant SMACs. These design specifications are for the active contamination control systems operating without assistance from other ECLS processes or overboard leakage. It is also important to note that they do not specify that the active contamination control systems on board the ISS must be designed to accommodate chronic, fugitive leaks from other systems, payloads, or docked vehicles nor do they specify that these systems' performance must be verified for such an additional contamination loading. Further, these requirements do not authorize using the active contamination control systems as hazard controls for other onboard systems, payloads, or docked vehicles.

Within the context of requirements, an additional loading of a chemical compound not contained in the design listing provided in ISS design specifications constitutes a new, specific verification case. As such, this verification must assume that only the active contamination control systems on board the ISS remove the added contamination load. This maintains consistency with the equipment's certification. It is informative to expand the assessment, however, to address the fate of the contamination to ensure that the impact upon all ECLSS processes—both atmospheric and water processing—are addressed.

Operational experience acquired during the ISS program has found that understanding ECLSS and environmental impact presented by chemicals contained in other ISS systems, payloads, and docked vehicles is imperative to safely executing any crewed space exploration mission. This experience provides the opportunity to address ECLSS and cabin environmental impacts for the Orion CEV early in the conceptual design phase.

3.4.2 Background

Selecting an ATCS working fluid for a spacecraft is a critical step for developing future vehicles that will enable future crewed space exploration initiatives. NASA traditionally uses single-phase, ATCSs comprised of separate internal and external circulating fluid loops. Vehicles presently operated by the NASA use water for the internal working fluid. The ISS uses ammonia (NH_3) for the U.S. segment's external ATCS working fluid while the Shuttle uses dichlorofluoromethane (Freon 21).

3.4.2.1 Orion Crew Exploration Vehicle Active Thermal Control System Fluid Selection. Previously, several candidate Orion CEV ATCS working fluids were evaluated for their compatibility with the ISS ECLSS. Perfluorocarbon fluids and polyhydric alcohols, commonly known as glycols, were evaluated as reported in section 6.6. Due to the various thermal decomposition and volatility challenges, among others, associated with perfluorocarbon fluids, the developmental focus shifted to aqueous glycol mixtures. Aqueous glycol mixtures, usually ethylene glycol (1,2-ethanediol), have been used as thermal working fluids on board early NASA spacecraft and the Russian Space Station, Mir. More recent experience was gained with aqueous ethylene glycol used on board Mir. The fluid leaked into the cabin, producing a persistent background concentration that approached ethylene glycol's 13 mg/m^3, NASA's SMAC maximum allowable concentration in the cabin atmosphere. This experience led Russian designers to select aqueous glycerol (1,2,3-propanetriol), a trihydric alcohol, for use on board the ISS ROS. Glycerol is much less toxic than ethylene glycol yet possesses the necessary thermal working fluid properties for that particular application.

As Orion CEV ATCS development has progressed, the thermal working fluid trade assessment has recommended an aqueous dihydric alcohol mixture manufactured by Amsoil, Inc. and marketed under the trade name, Amsoil ANT. Propylene glycol (1,2-propanediol) is the primary component in Amsoil ANT. Technical evaluations conducted by NASA identified aqueous propylene glycol as a candidate working fluid for future vehicles, including the Orion CEV, for a variety of reasons. Propylene glycol has characteristics similar to ethylene glycol such as low corrosiveness and low volatility. Unlike propylene glycol, propylene glycol is nontoxic and is commonly used in consumer products such as foodstuffs and cosmetics, among many others. Propylene glycol, however, is more viscous and exhibits poorer heat transfer film coefficients compared to ethylene glycol.[25]

3.4.2.2 Considerations for Environmental Control and Life Support Sysystem Compatibility. A challenge for ATCS design exists with selecting a working fluid that possesses the desired performance characteristics, yet is compatible with onboard ECLSSs, and demonstrated to present a minimal health risk to the crew. The Orion CEV's ATCS designers determined that an aqueous 51% by weight propylene glycol fluid provides the best thermal control performance while exhibiting good compatibility with system wetted surfaces. A commercial product manufactured by Amsoil, Inc. and marketed as Amsoil ANT is the recommended basis for the Orion CEV's ATCS working fluid.

Table 9 lists the components of concentrated Amsoil ANT fluid. Amsoil ANT includes an additive package that contains various stabilizers and anticorrosive agents. Independent NASA toxicology evaluation has assigned a toxic level of 1 based on the fluid's potential for irritating the eyes, skin, and respiratory system. This rating is based on the finding by NASA toxicology evaluation that leaked ATCS fluid could produce a concentration in the Orion CEV cabin that exceeds the 102 mg/m^3 1-hr SMAC and that the irritation effects could last longer than 30 min. Table 10 lists the SMACs for propylene glycol from JSC 20584. All units are in mg/m^3.

Table 9. Amsoil ANT concentrate composition.

Trade Name	Constituent	Weight %	CAS Number
Amsoil ANT	Propylene glycol Water	92 6.52–6.68	57-55-6 7732-18-5
	Additive package	1.30–1.43	N/A

Amsoil, Inc.

Table 10. Propylene glycol SMACs.

1 Hour	24 Hours	7 Days	30 Days	180 Days
102	54	29	9.6	4.8

The ECLSS compatibility and cabin environmental impact assessment complements the NASA toxicology assessment. This assessment considers the following:

- Chemical composition of the fluid, including additives, and impacts to ECLS atmosphere revitalization processing systems.
- Water solubility and impacts to ECLS water processing systems.
- Volatility and ease of removal from the cabin atmosphere.
- Thermal stability and decomposition products.
- Reactivity under ECLSS process conditions.

Water solubility, volatility, and ease of removal from the cabin atmosphere address the potential impacts to ECLS equipment performance including their ability to maintain a cabin environment suitable to support the crew in the presence of leaked ATCS working fluid. Such ATCS leaks may be gross leaks or fugitive emissions resulting from slow leaks from fluid couplings, valves, pumps, or other potential leak paths. Likewise, thermal stability and decomposition products along with reactivity are evaluated to determine whether a particular fluid is compatible with ECLS equipment process conditions. Some ECLS equipment may operate at high temperature and the potential for leaked ATCS fluid to thermally decompose to hazardous products must be understood. Reactivity addresses compatibility with ECLS equipment employing reactive adsorbents such as lithium hydroxide (LiOH). Relative toxicity is evaluated by NASA toxicologists who set SMACs. The toxicologists' evaluation is used by engineers to assess the TCC challenge that the fluid may present to a future spacecraft or space habitat active TCCS design.

3.4.2.3 Crew Exploration Vehicle Active Thermal Control Fluid Characteristics. The candidate aqueous propylene glycol ATCS fluid consists of commercially available Amsoil ANT diluted with deionized water. Diluted Amsoil ANT is the sole subject of the compatibility assessment. The Orion CEV ATCS will contain 11–15 L (3–4 gal) of fluid. The predicted maximum leaked quantity that precipitates ATCS shutdown is approximately 4.9 L (1.3 gal). This quantity serves as the basis for the compatibility assessment. The Orion CEV ATCS operating temperature ranges from 7 °C (45 °F) to 40.5 °C (105 °F). The ECLSS compatibility and environmental impact assessment considers cases for the range of operating temperatures.

The Orion CEV ATCS working fluid consists of two primary components—propylene glycol and water. A proprietary additive solution containing stabilizing, corrosion inhibiting, and antimicrobial compounds is included in Amsoil ANT. Table 11 lists the components of the diluted Amsoil ANT fluid. Evaluation of the Amsoil ANT additive compounds finds that all exist naturally in a solid state and possess very low vapor pressures. Therefore, as leaked ATCS fluid evaporates, it is expected that a solid residue will be left on contacted surfaces. Because the additive compounds are nonvolatile, the scope of the ECLSS compatibility and environmental impact assessment can be narrowed to propylene glycol only. Table 12 contains relevant physical properties of propylene glycol.

Table 11. Diluted Amsoil ANT fluid constituents.

Constituent	Weight %	CAS Number
1,2-propanediol	49–51	57-55-6
Water	6.52–6.68	7732-18-5
Proprietary additive No. 1	0.637–0.729	N/A
Proprietary additive No. 2	0.02–0.03	N/A
Proprietary additive No. 3	0.009–0.012	N/A
Proprietary additive No. 4	0.004–0.009	N/A
Proprietary additive No. 5	0.0007–0.0012	N/A

Table 12. Propylene glycol properties.

Property	Value
CAS number	57-55-6
Molecular weight (g/mole)	76.096
Melting point (°C)	–60
Boiling point (°C)	187.6
Flash point (°C)	99
Autoignition temperature (°C)	415
Liquid density (g/mL @ 20 °C)	1.036
Water solubility (mg/liter @ 20 °C)	1×10^{6}
Henry's Law constant (atm/mole fraction)	3.46×10^{-3}
Vapor pressure (mm Hg @ 25 °C)	0.129
Critical volume (cm^3/mole)	237
Critical pressure (mm Hg)	45,600
Critical temperature (°C)	352
Critical compressibility	0.2768
Antoine coefficient A	20.5324
Antoine coefficient B	6,091.95
Antoine coefficient C	–22.46

Sources: Condensed Chemical Dictionary, 10th Edition; The Properties of Gases and Liquids, 3rd Edition; U.S. EPA Estimation Programs Interface Suite™; Korea Thermophysical Properties Databank (http://www.cheric.org/kdb/); The Chemical Engineers' Handbook, 6th Edition

3.4.3 Purpose

The technical assessment summarized by the following discussion addresses the compatibility of an aqueous propylene glycol thermal working fluid with ECLSSs typically found on board crewed spacecraft and outposts. Potential hazards associated with aqueous propylene glycol fluids are evaluated with specific attention given to ECLSS compatibility and spacecraft cabin environmental impact in the event of fluid leakage. ECLS compatibility considers the ISS as the worst-case basis because the Orion CEV's early mission objectives include transportation to and from the ISS as well as extended docked periods when compatibility with the ISS's cabin environment and life support systems is necessary. Future long-term space exploration outposts may use ECLS process technologies and architectures that operate similarly to those found on board the ISS. Therefore, compatibility with future closed-loop ECLSSs is implied.

3.4.4 Objective

The impacts of a 4.9-L leak of Orion CEV ATCS fluid into the combined CEV and ISS cabin as well as the CEV cabin alone are assessed. The primary objective of the assessment is to address interactions with ECLSS equipment and process conditions and to recommend appropriate actions, if any, necessary to ensure ISS cabin environmental conditions comply with relevant specifications and guidelines in the event of an Orion CEV ATCS fluid release into the cabin.

3.4.5 Assumptions

Basic assumptions pertaining to background offgassing rates and cabin atmospheric conditions for the ECLSS compatibility and cabin environmental impact assessment are the following:

- Offgassing rates are derived from ground-based offgassing test results and in-flight cabin atmospheric quality sample analyses reported by NASA. The background propylene glycol generation rate is 5.97 mg/hr.
- Atmospheric leakage from the ISS and Orion CEV cabins is zero.
- The Orion CEV free volume is approximately 15 m^3.
- The ISS free volume is represented by assembly stage 20A and is estimated to be 849 m^3.
- Atmospheric conditions are on average 20 °C (68 °F), 50% relative humidity, and 1 atm.
- Background offgassing rates are constant with time. This has been shown to be conservative because experience shows rates decay with time.
- NASA SMACs documented by JSC 20584 apply.
- Ventilation flow between the ISS cabin and the Orion CEV cabin is maintained at ~187 m^3/hr minimum during docked operations.

3.4.5.1 International Space Station and Orion Crew Exploration Vehicle On-Orbit Configuration. At the completion of ISS assembly stage 20A, the on-orbit configuration consists of PMA-1, PMA-2, Unity (Node 1), Destiny (U.S. Laboratory), Quest (U.S. airlock), Harmony (Node 2), the Columbus APM, the Kibo Experiment Logistics Module (ELM) pressurized section (PS) and pressurized module (PM), Jules Verne automated transfer vehicle-1 (ATV-1) cargo vehicle, heat transfer vehicle-1 cargo vehicle, Zarya functional cargo block (FGB), Zvezda (service module), Pirs docking compartment, Poisk mini research module-1, two Soyuz spacecraft, and a Program cargo vehicle. The ISS's total habitable volume is approximately 849 m^3, including the cargo and crew transport vehicles. The USOS is approximately 554 m^3 and the ROS is approximately 295 m^3.

3.4.5.2 International Space Station and Orion Crew Exploration Vehicle Trace Contaminant Control Assets. Active TCC is provided for the ISS by the USOS TCCS located in Destiny and the BMP located in Zvezda. Previous analysis has shown that both the TCCS and BMP have sufficient capacity to control the Station's trace contaminant load.[26] The previous analysis did not investigate performance for removing propylene glycol. A second USOS TCCS unit located in the Tranquility Node 3 provides operational margin. Incidental trace contaminant removal occurs in condensing heat exchangers that are located in several ISS modules via absorption by humidity condensate. Additional incidental removal may occur via co-adsorption with CO_2 in the CO_2 removal units. The Orion CEV active TCC assets include an activated carbon bed, an ambient temperature catalyst bed, and incidental removal via the CO_2 removal process.

3.4.6 Approach

The ECLSS engineering assessment addresses the evaporation rate from a 4.9-L leaked quantity of Orion CEV ATCS fluid during the period while docked with the ISS and during free flight. Concentration dynamics are determined as the available TCC assets act on the fugitive emission rate that may be accommodated by the ECLSS.

3.4.6.1 Governing Equations. The equations in section 2.3 serve as the calculation basis covering evaporation rate, humidity condensate loading, and cabin mass balance. The evaporation rate calculation is adapted to determine evaporation from a binary liquid mixture using the method of reference 14.

3.4.6.2 Assessment Cases Considered. Cases considered by the ECLSS engineering assessment address contamination resulting from an Orion CEV ATCS fluid leak into the cabin. Dynamics of evaporation rate and dispersion through the cabin are considered. Impacts to and compatibility with ECLSS equipment are determined. The following discussion provides summary details for the principle areas for assessment.

3.4.6.2.1 Maximum Leaked Quantity and Evaporation Rate of Fluid Components. The maximum leaked amount is determined by the Orion CEV ATCS's ability to sense fluid loss and enter a safe mode to prevent further losses. Consultation with Orion CEV ATCS experts determined the maximum leaked quantity to be approximately 4.9 L. All ECLS assessment cases consider this maximum quantity as the starting basis for evaporation rate calculations.

3.4.6.2.2 Dispersion of Leaked Fluid Components in the International Space Station Cabin and Cleanup Duration. Dispersion through the combined ISS and Orion CEV cabins is based on mass balance equations defined by equations (6) through (8). Average evaporation rate is determined from a transient analysis of the propylene glycol evaporation rate under varying fluid temperature conditions.

3.4.6.2.3 Cabin Atmospheric Quality Impacts and Trace Contaminant Control Resource Consumption. The concentration dynamic calculations are based on the time-dependent evaporation rate and well-mixed cabin mass balance defined by equation (2). An average evaporation rate determined from a transient analysis of propylene glycol evaporation is used as the point generation source term. The peak concentrations are compared to the NASA SMACs.

3.4.6.2.4 Humidity Condensate Loading. Propylene glycol is miscible in water. When absorbed into humidity condensate, propylene glycol may contribute to excessive ISS water processing equipment resource consumption leading to more frequent maintenance and higher logistics costs. The ISS water processing system's propylene glycol design loading is 35 mg/L. However, water processor designers have determined that humidity condensate loading up to 100 mg/L. To preserve operational margin, a threshold of 50 mg/L loading is established as the assessment basis. Available data on propylene glycol's solubility in water serve as the basis for this aspect of the assessment.

3.4.6.2.5 Thermal Stability and Decomposition. Understanding thermal stability and decomposition of candidate ATC fluids is necessary to ensure safety. Lower explosive limit (LEL) and thermal decomposition products are of most concern.

3.4.7 Results and Discussion

The following discussion presents and discusses results for the evaluation of a 4.9-L leak of aqueous propylene glycol into the combined ISS and Orion CEV cabin and notes the effects on humidity condensate loading and ECLSS performance.

3.4.7.1 Maximum Leaked Amount and Evaporation Rate Dynamics. The evaporation rate assessment considers evaporation of propylene glycol and water from 4.9 L of the binary fluid. The presence of the stabilizing additives is assumed to have a negligible effect on vapor pressures. Using the technique described by reference 14 and employing equation (9) as well as assuming ideal solution behavior, an evaporation rate dynamic profile is determined for three fluid temperatures: 7, 21, and 40 °C. These temperatures represent the range of expected Orion CEV ATCS operating conditions. Figures 26 through 28 illustrate the expected evaporation rate dynamics. Water is the dominant component driving the overall evaporation in all cases. The propylene glycol evaporation rate remains under 1 g/min in all cases. As expected, the peak propylene glycol evaporation rate is reached more rapidly for the warm fluid condition of 40 °C. Even under this condition the peak propylene glycol evaporation rate of 0.68 g/min is not reached for more than 18 hr. The elapsed time to reach the peak propylene glycol evaporation rate triples to nearly 56 hr at 21 °C. At this condition, the peak rate is 0.169 g/min. At 7 °C, the peak rate is not reached even after 80 hr elapse. At that time, the 0.047 g/min rate is significantly lower than for the other temperature conditions.

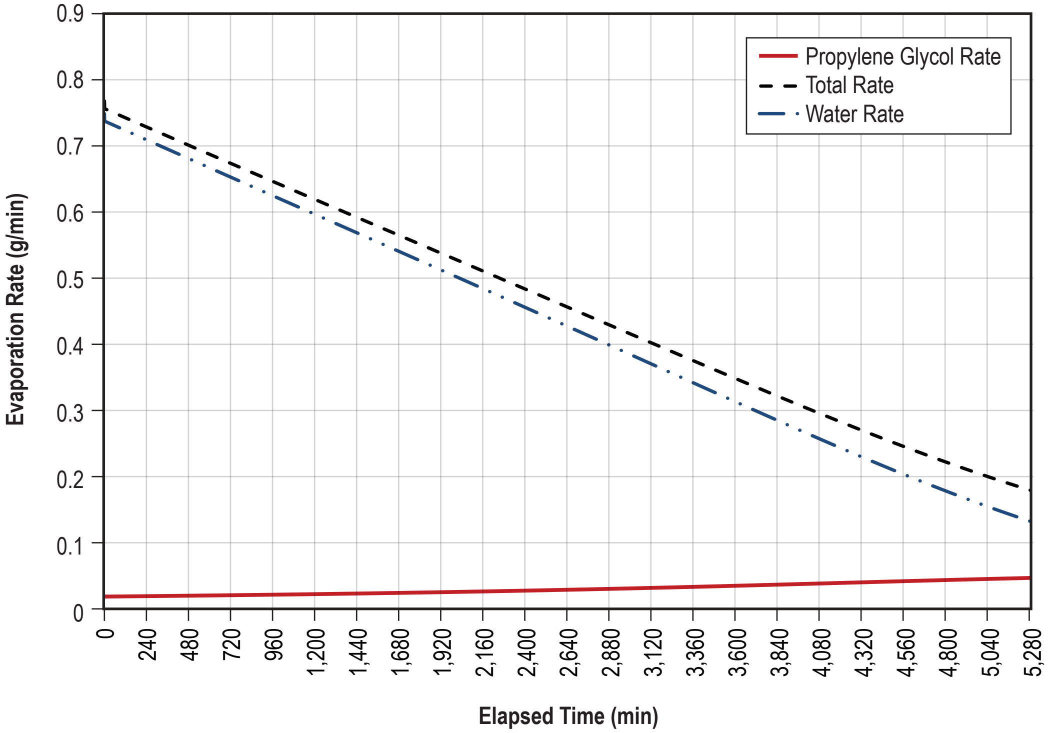


Figure 26. Evaporation rate at 7 °C.

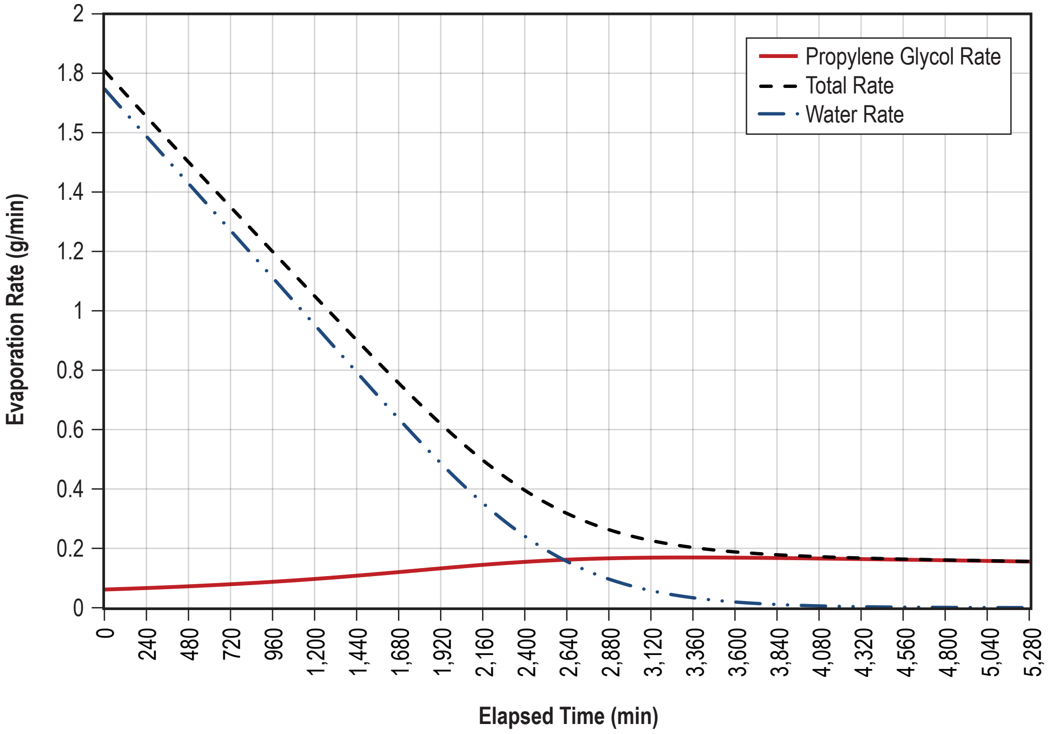


Figure 27. Evaporation rate at 21 °C.

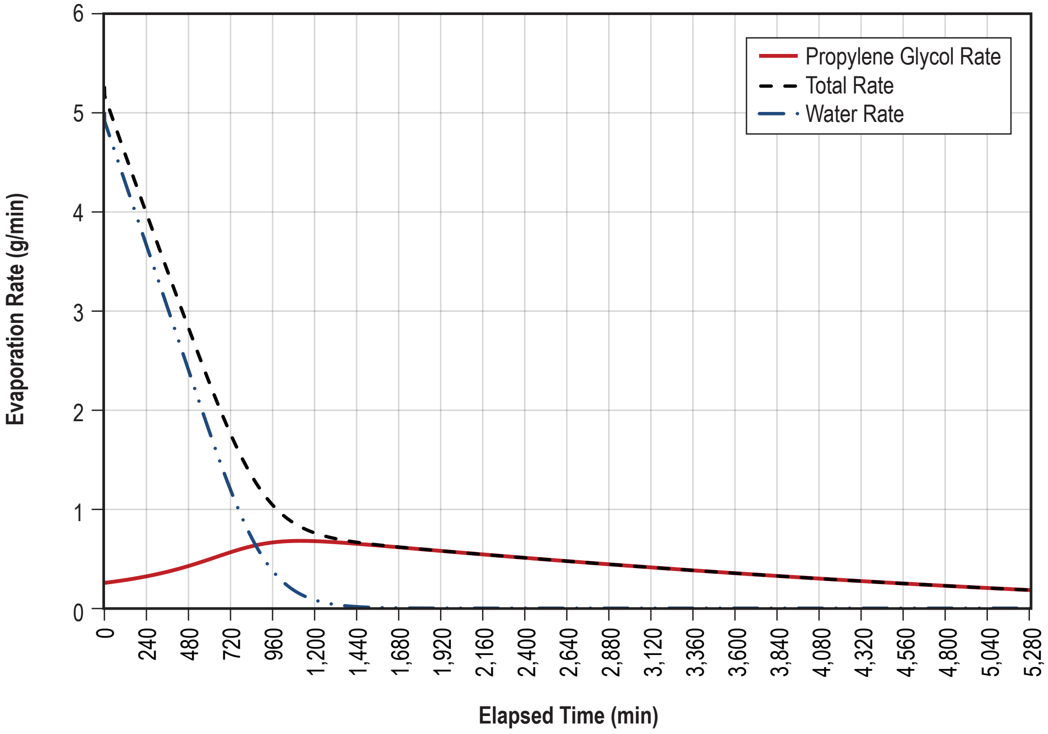


Figure 28. Evaporation rate at 40 °C.

Figures 29 through 31 illustrate the concentration dynamics in the entire ISS cabin and for the case where the USOS is isolated to prevent dispersion into the ROS. Consistent with the more rapid evaporation rate resulting from higher temperature, the peak cabin concentration is reached more rapidly for fluid held at 40 °C than for fluid at 21 or 7 °C. The peak concentrations in the entire ISS cabin range from 10 mg/m^3 for evaporation from a 7 °C source to nearly 150 mg/m^3 for evaporation from a 40 °C source. Isolating the USOS from the ROS results in the peak concentrations increasing to >20 mg/m^3 for evaporation from a 7 °C source to nearly 300 mg/m^3 for evaporation from a 40 °C source. Evaporation from a 21 °C source produces a peak ISS cabin concentration of approximately 36 mg/m^3, while isolating the USOS from the ROS produces a peak concentration of approximately 77 mg/m^3.

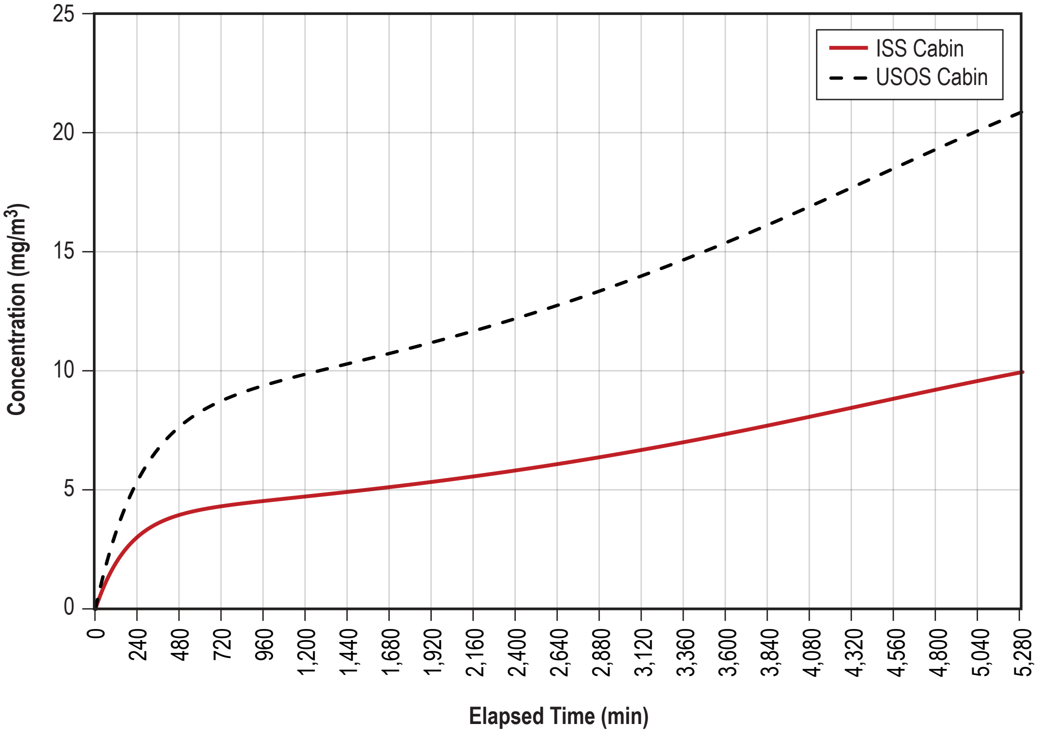


Figure 29. Concentration dynamics from a 7 °C source.

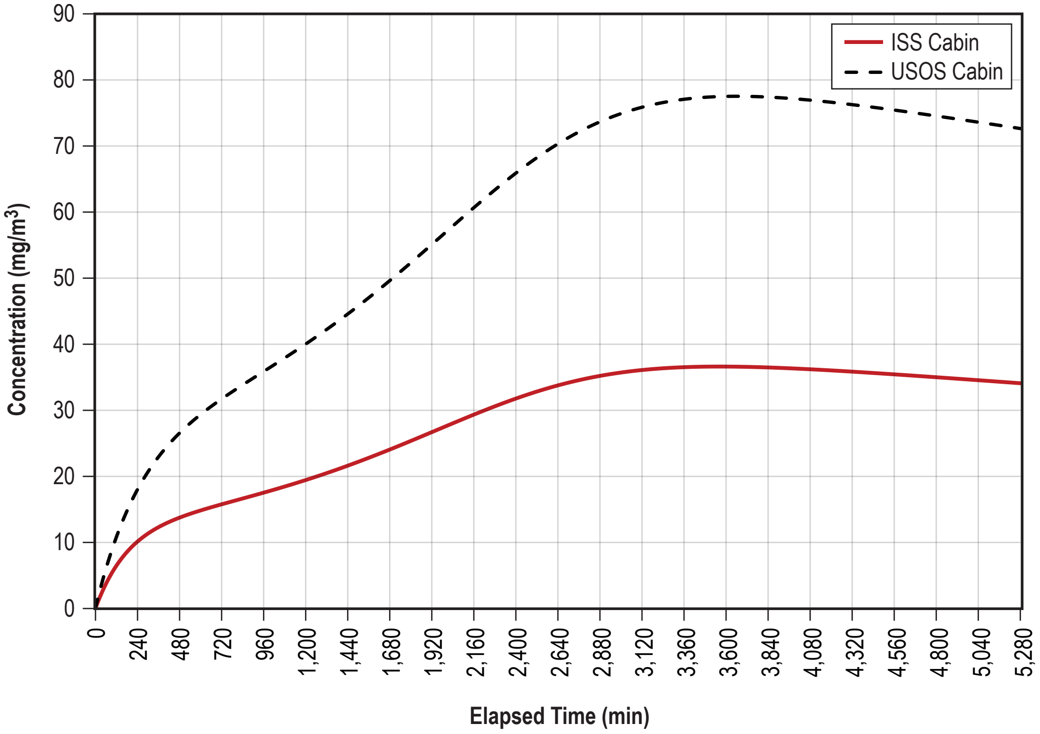


Figure 30. Concentration dynamics from a 21 °C source.

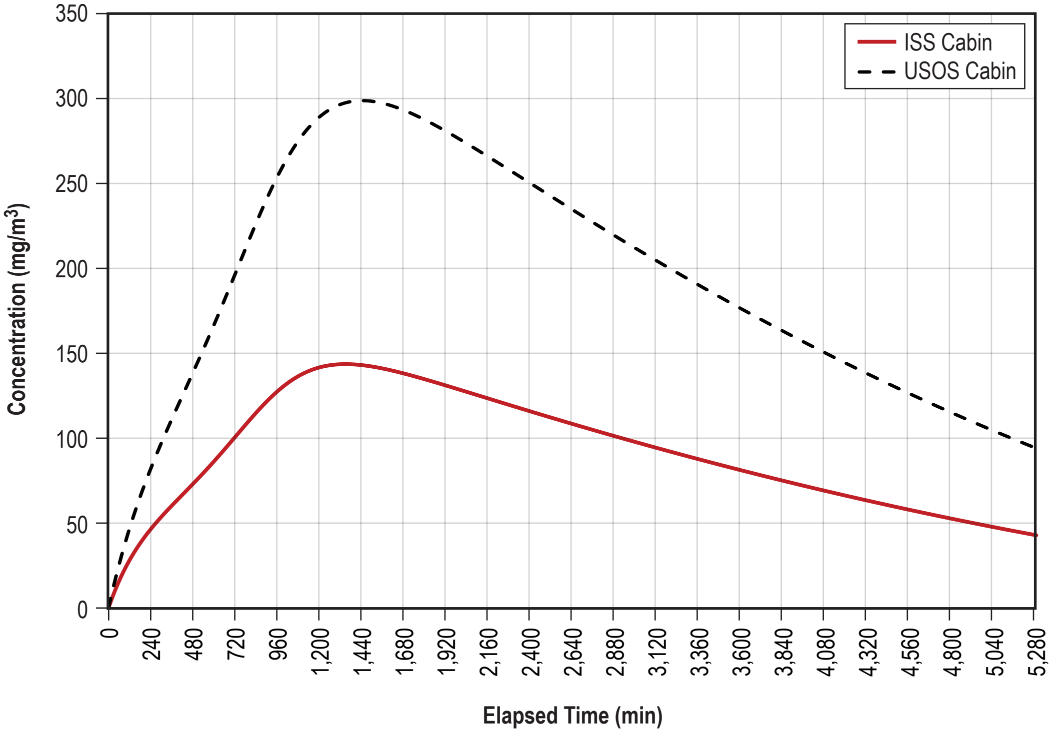


Figure 31. Concentration dynamics from a 40 °C source.

3.4.7.2 Dispersion of Fluid Components Into the International Space Station Cabin and Cleanup Duration. Using a constant time-averaged rate for the 21 °C source, figure 32 indicates that dispersion throughout the ISS cabin is complete within approximately 10 hr. Under such a condition, it is noted that the NASA 180-, 7-, and 30-day SMACs are exceeded in less than 5 hr. If the leaked fluid is not located quickly and isolated from the cabin, a persistent concentration is likely and cabin atmosphere quality restoration may require a significant elapsed time. With a persistent generation source, it is likely that cabin atmospheric quality restoration would take ≫80 hr as figures 29 through 31 indicate. After reaching a peak concentration of 150 mg/m^3—the worst predicted case, it is estimated that, when accounting for all ISS contaminant removal routes, the concentration reduction will take <20 hr as indicated in figure 33.

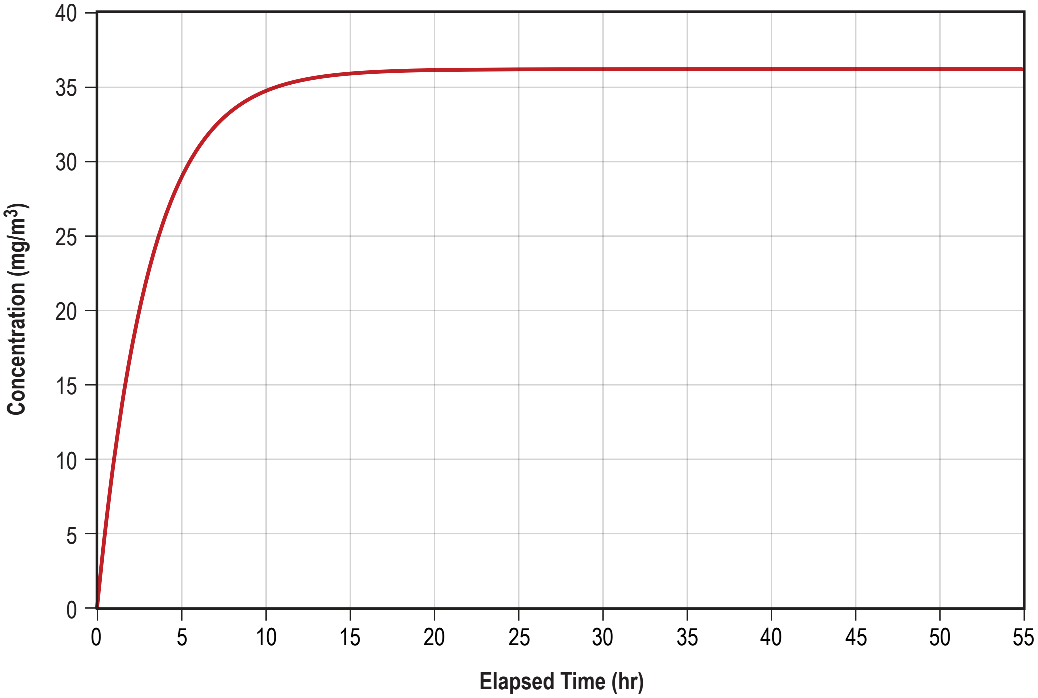


Figure 32. Propylene glycol dispersion in the ISS cabin using a time-averaged rate at 21 °C.

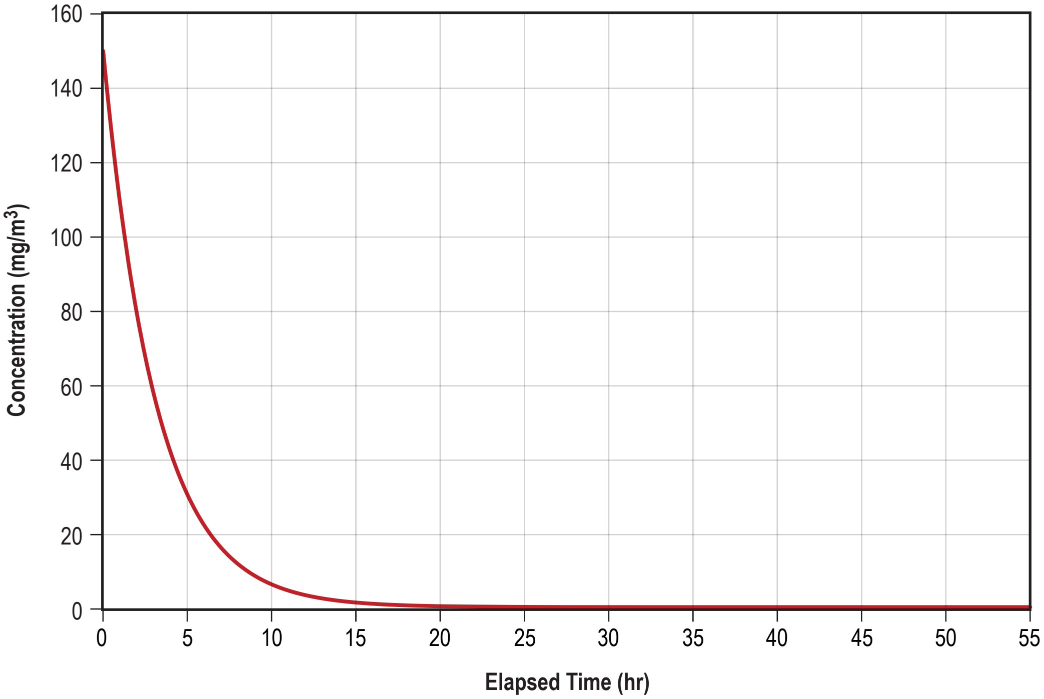


Figure 33. Estimated ISS concentration reduction rate.

3.4.7.3 Cabin Atmospheric Quality Impacts and Trace Contaminant Control Resource Consumption. Table 10 lists the SMACs for propylene glycol. Based on the assessment cases, it is considered likely that a 4.9-L leak of the Orion ATCS fluid that is not located and cleaned up within 8 hr could produce conditions that exceed NASA toxicology cabin atmospheric quality guidelines for all continuous exposure durations during docked and Orion CEV free-flight cases.

3.4.7.3.1 Orion Crew Exploration Vehicle Trace Contaminant Control Resource Impacts During Free Flight. In the case where fluid leakage occurs while the Orion CEV is in free flight, predicted cabin concentrations may reach 50, 181, and 727 mg/m^3 for the 7, 21, and 40 °C sources, respectively. These concentrations are near or exceed the NASA 24-hr SMAC of 54 mg/m^3 and 1-hr SMAC of 102 mg/m^3. All of the Orion CEV TCC and atmosphere revitalization system assets are assumed to be effective in remediating the propylene glycol concentration even though specific testing with the amine-based atmosphere revitalization equipment has not been conducted. It is likely that additional assets may be required to fully recover from an ATCS fluid leak while the Orion CEV is in free flight.

3.4.7.3.2 International Space Station Trace Contaminant Control Resource Impacts During Orion Crew Exploration Vehicle Docked Operations. Evaluation of the available ISS TCC assets indicates that equilibrium loading of granular activated carbon (GAC) with propylene glycol is approximately 0.38 g/g of activated carbon. Each USOS TCCS unit contains approximately 22.7 kg of GAC. Loading to the equilibrium capacity requires the total mass of propylene glycol present in approximately 16.7 L of fluid. Given the likely maximum 4.9-L leaked quantity considered to be credible, any given leakage would be expected to consume no greater than 30% of the available TCC resource in the USOS.

Similarly, the BMP in the ROS contains an expendable packed bed (FOA unit) containing 2 kg GAC and two regenerable-packed beds (ZPL-1M units) containing 2.8 kg GAC combined. These beds represent additional capacity that may accommodate propylene glycol contained in 3.5 L of the Orion CEV ATC fluid.

In total, when considering the normally operating USOS and ROS TCC assets, the quantity of propylene glycol contained in a 4.9-L leak of the Orion ATCS fluid would consume approximately 24% of the available assets. When considering the operational margin that exists in the USOS with a second TCCS unit, the available ISS TCC resource consumption is no greater than 13%.

For the Orion CEV in free flight, the expendable TCC resources are capable of accommodating the propylene glycol contained in approximately 6.3 L of fluid. Therefore, a credible 4.9-L fluid leak would consume approximately 78% of the available expendable resource capacity. It is not known whether propylene glycol will adversely affect the performance of the amine-based vacuum swing atmosphere revitalization system. It is known that desorption kinetics are poor for compounds possessing low vapor pressures. Therefore, there is unquantified risk that propylene glycol could foul the vacuum swing system causing humidity and CO_2 control performance losses. Testing to investigate whether any incompatibilities exist with the Orion CEV's amine-based vacuum swing atmosphere revitalization process is considered prudent to address this knowledge gap.

3.4.7.4 Humidity Condensate Loading. Propylene glycol's solubility in water is a particular issue. Engineering assessment of the impacts that polar organic compounds can have on the ISS's water purification systems finds that a propylene glycol concentration in the cabin atmosphere above 0.02 mg/m^3 loads humidity condensate in excess of the 35 mg/L water processing system design point when a condensing heat exchanger removes humidity condensate at a one-person equivalent rate. This is equivalent to approximately 5.5 mg/hr generation in the cabin. Likewise, a cabin concentration exceeding 0.03 mg/m^3, equivalent to approximately 8.3 mg/hr generation in the cabin, loads humidity condensate to 50 mg/L. If the cabin concentration exceeds 0.07 mg/m^3, equivalent to approximately 19.3 mg/hr generation, the condensate may load to 100 mg/L. Threshold concentrations increase to 0.05, 0.08, and 0.15 mg/m^3 for condensate removal at a three-person equivalent rate. These concentrations are indicative of propylene glycol generation rates of 13.8, 22.1, and 41.4 mg/hr, respectively. To preserve operational margin, it is most desirable to keep the introduction of propylene glycol into the cabin under 20 mg/hr. This rate is equivalent to the expected evaporation rate of propylene glycol from a 193-cm^3 spill at 21 °C.

3.4.7.5 Thermal Stability and Decomposition. Because propylene glycol will readily decompose to CO_2 under typical high temperature ECLS process conditions, emphasis is placed on the perfluorcarbon fluids in this discussion. However, it must be noted that propylene glycol vapors are flammable and the LEL is 2.6% by volume in air, equivalent to ~82,000 mg/m^3 in the cabin atmosphere. Higher oxygen partial pressure will lower the LEL evaluation of volatility, indicating that the greatest cabin atmospheric concentration that can be expected is <0.001% of the LEL. In this regard, thermal stability and decomposition is not a significant issue for aqueous propylene glycol.

3.4.8 Summary

The candidate Orion CEV ATCS fluid has been evaluated for ISS and CEV ECLSS compatibility as well as environmental impact. The maximum 4.9-L credible leaked quantity served as the basis for assessment. Depending on the fluid's temperature, ISS cabin concentrations ranging from 10 to 150 mg/m^3 may result in the event of fluid leakage during Orion CEV docked operations if the fluid leak is not found and isolated within 8 hr. Concentrations may be higher if the dispersion is limited to the ISS USOS only. Exceeding all SMAC exposure levels is also likely if the fluid leak is not found and isolated quickly. The smaller Orion CEV cabin will experience much higher concentrations in excess of the SMAC in all cases.

The expected time to cleanse the ISS cabin atmosphere after isolating the leaked fluid is <20 hr with up to 24% TCC resource consumption, not including operational margin. Expected Orion CEV cabin atmosphere recovery is expected to require <3 hr with 78% TCC resource consumption. The impact on the Orion CEV vacuum swing atmosphere revitalization system performance is unknown, representing unquantifiable operational risk.

Minimizing impacts on the ISS water processing system is the greatest challenge. Leakage in excess of 193 cm^3 may result in excessive humidity condensate loading leading to increased water processing system operating costs.

According to the rating definitions contained in the tables 1 and 2, the fluid's ECLS equipment impact is E2/minor and the environmental impact is level B for ISS. The ISS ECLS equipment impact rating may be in the category E3 range for large, persistent leakage due to excessive humidity condensate loading. The ECLS equipment rating for the Orion CEV ranges from category E4 up to category E5, depending on whether propylene glycol fouls the vacuum swing atmosphere revitalization beds. The environmental impact is level B for the Orion CEV during free flight.

3.4.9 Conclusions

Based on the engineering assessment of the Orion CEV ATCS fluid, conclusions and recommendations regarding the fluid are the following:

- The credible maximum leakage may result in temporarily exceeding propylene glycol's long- and short-duration SMAC levels.
- Aqueous propylene glycol presents a potential risk to ISS water purification systems in leaked amounts >193 cm^3.
- The maximum credible 4.9-L leakage may consume up to 24% of the ISS TCC assets.
- The maximum credible 4.9-L leakage may consume up to 78% of the Orion CEV TCC assets.
- Propylene glycol's interaction with the Orion CEV vacuum swing atmosphere revitalization system is unknown and should be investigated.
- The fluid presents negligible thermal decomposition or chemical stability concerns.
- The fluid additives exist naturally in the solid state and will deposit as a residue on surfaces as the fluid evaporates. The fluid additives are considered to be no impact to the ECLSS or cabin environment.

- Fluid leakage should be located and remediated within 8 hr to prevent excessive cabin environmental impacts.
- Recovery from a leakage event on board the ISS is expected to require <20 hr after the leaked fluid is isolated from the cabin atmosphere.
- Recovery from a leakage event during Orion CEV free flight is expected to require <3 hr after the leaked fluid is isolated from the cabin atmosphere.
- Temperature of the leaked fluid has a significant effect on evaporation rate.

3.4.10 Recommendations

The candidate aqueous propylene glycol fluid presents a significant ECLSS challenge. Two actions are recommended to reduce the magnitude of this challenge. First, the Orion CEV ATCS design should consider operational and control protocols that limit the maximum credible leaked quantity to <200 cm^3. This not only reduces the maximum cabin concentration that might result from the leaked fluid but also minimizes the risk to ISS water processing systems during docked operations. Second, the impact on the Orion CEV's vacuum swing atmosphere revitalization system is unknown and fouling by low volatility compounds such as propylene glycol is possible. Testing to investigate potential vacuum swing bed fouling by propylene glycol should be conducted.

4. EXTRA-VEHICULAR ACTIVITY-RELATED EVALUATIONS

The following assessments address compatibility assessments for contaminants associated with extra-vehicular activity (EVA) operations.

4.1 Cure-in-Place Ablative Materials

In the aftermath of the Shuttle Columbia accident and the subsequent return to flight, shuttle orbiter thermal protection system repair kits containing various cure-in-place materials were developed. The following assessment evaluates a cure-in-place ablative material for ECLSS compatibility and cabin environmental impact in support of the repair kit development and in-flight demonstration efforts. A baseline assessment was conducted on January 5, 2005, and second evaluation case was considered and added to the assessment on April 27, 2005. These assessments were refined and released as a final version on June 27, 2005. This assessment was released under NASA memorandum EC-05-089, "International Space Station Environmental Control and Life Support Systems Compatibility Evaluation of Tile Repair Materials for STS-114 (LF-1): Non-Oxide Adhesive Experimental Crack Repair Material and Cure in Place Ablative Applicator Materials," dated June 28, 2005.

4.1.1 Baseline Assessment

Based on testing data, documented physical property data for the STA-54A and STA-54B components, and levels of containment provided by the CIPA USA, Inc. equipment, an ECLSS assessment has been conducted. Available physical properties of the STA-54A and STA-54B components are summarized in table 13. Of these components, the A-1100 contained in STA-54B is of most concern.

This assessment considers up to 10-mm-deep STA-54B covering 25,935 mm^2 area (40.2 in^2) estimated from photos of the CIPA equipment failure in a test chamber. Using mass loss data from crucible experiments conducted at 50 °C and 35%–50% relative humidity, the estimated flux from exposed material is 1×10^{-5} mg/mm^2/min/mm of material depth. For the hypothetical case, 155.6 mg A-1100/hr is released. Assuming that all the A-1100 hydrolyzes to a stable, crusty product and ethanol, the conservatively ethanol production rate is estimated to be 97 mg/hr.

ECLSS removal capacity for ethanol on board the ISS during Orbiter docked operations is equivalent to 46.1 m^3/hr flow rated at 100% single-pass removal efficiency. This effective removal capacity includes the TCCS catalytic oxidizer, carbon dioxide removal assembly (CDRA), and absorption via humidity condensate removal in the U.S. Laboratory and Airlock modules of the USOS. Removal in the ROS is provided by the BMP and absorption in humidity condensate removed by the SKV. Incidental contaminant removal by the Vozdukh is unknown and no attempt is made to account for it. If the 97-mg ethanol/hr rate is maintained over the 8-hr mass stabilization period documented by testing, the average cabin concentration will rise by approximately 0.3 mg/m^3. This amount of ethanol production is not an impact to ISS air quality control equipment. However, consideration must be given to water processing equipment.

Table 13. CIPA material characteristics.

Component	Composition %	Properties
STA-54A (11,657 g)		
RTV 511	77.3	Ethyl silicate 40 (1%–5%) Vapor pressure = 1 mm Hg Molecular weight = 208.33 Boiling point = 168.1 °C
SF96-50 silicone oil	2.03	Vapor pressure = negligible
Solid Components-Silica Ferric oxide Silica fibers Silica ecospheres	20.23	Nonvolatile
STA-54B (607 g)		
SF-96 50 silicone oil	6.1	Vapor pressure = negligible
A-1100	61.1	3-aminopropyltriethoxysilane Vapor pressure = 1 mm Hg Molecular weight = 221.37 Boiling point = 217 °C Specific gravity = 0.94
Solid components-silica Silica ecospheres	32.8	Nonvolatile

The ethanol is removed by the SKV in the ISS ROS at an estimated 1.7% efficiency single pass. At this rate, approximately 5.3% of the total ethanol released is likely to get into humidity condensate collected in the ROS. For a two-person latent load being removed by the SKV, this will increase the condensate loading by an estimated 6.5 mg/L—a 6% increase over predicted condensate loading in the SKV and 17% of the observed 61.6 mg ethanol/L loading from samples collected in the USOS and returned on board Soyuz flight 8S. This impact can be significantly minimized by quickly isolating the leaked material from the cabin atmosphere by placing the contaminated equipment in bags and sealing them. If this can be accomplished within 1 hr, the cabin concentration rise estimate can be held to <0.05 mg/m^3 and diluting the increase in humidity condensate loading to <1 mg/L or <1% increase. The time to remove the additional ethanol from the cabin atmosphere is <0.5 hr.

All other components of STA-54B are sufficiently nonvolatile to be deemed to have no impact on ECLSS air and water processing systems. Likewise, the components of STA-54A are nonvolatile and considered to have negligible impact to ISS ECLSS equipment functional maintenance.

Based on the available information on the CIPA STA-54A and STA-54B materials and their stability, the maximum ECLSS equipment impact is category E1 and the environmental impact is level A (<2 hr to recover).

4.1.2 A-1100 Phase Separation Case

Recent observation of stored CIPA STA-54B material has found that the A-1100 component separates from the other components under ground-based storage conditions. Because the components are not miscible, this most likely results from specific gravity differences between the components while stored under ground-based conditions. While agitating the material or extruding it through the CIPA application device may remix the components, the most conservative assessment is for separated A-1100. In this case, it is estimated approximately 95 g (101 cm^3) maximum of A-1100, essentially pure 3-aminopropyltriethoxysilane (APTS), may be released if containment is lost under pressurized conditions. Under unpressurized conditions, the estimated amount released is 19 g (20.2 cm^3).

The APTS reacts readily with water and moisture according to the GE Silicone's material safety data sheet for Silquest A-1100 silane. Thermogravimetric analysis documented by reference 27 indicates that, in a humid atmosphere representative of the ISS cabin (34%–50% relative humidity and 21 °C), approximately 38% mass loss of the A-1100 material is observed in 48 hr. This is consistent with hydrolysis to ethanol. Three molecules of ethanol are expected to be produced for every molecule of APTS that reacts.

The vapor pressure of APTS is <1 mm Hg according to the material safety data sheet. Other undocumented sources indicate a vapor pressure of approximately 0.1 mm Hg based on calculation from the Clapeyron equation. At saturation, the concentration in air will be at least 1,211 mg/m^3 (134 ppm). Therefore, in theory, the entire 95 g of A-1100 could be dispersed evenly throughout the ISS cabin without reaching saturation. The evaporation rate, however, estimated using EPA techniques from reference 13, can range from 17.8 to 178 mg/hr at prevailing ISS cabin conditions and maximum leaked volume (101 cm^3). At the most rapid evaporation rate, 9% of the APTS will be expected to evaporate in 48 hr. Considering that APTS has a high molecular weight and low vapor pressure, removal by the U.S. and Russian segment air quality control systems will be expected to be nearly 100% efficient. The estimated cabin concentration is expected to be no more 4.2 mg/m^3 if the highest estimated evaporation rate is sustained. At this concentration, the anticipated ECLS equipment impact is low. Estimated time to remove 90% of the material from the cabin atmosphere is 20 hr regardless of the leaked amount.

Reaction with moisture in the air then becomes the greater concern. Assuming a 100% yield to ethanol, mass stability data for pure A-1100 indicate 0.075 mg ethanol-h^{-1}production rate for each milligram of A-1100 that reacts. For 95 g of separated A-1100, the estimated theoretical ethanol production rate is 7,125 mg/hr. This is 40 times higher than the predicted A-1100 evaporation rate, so some rate limitation must be taken into account. Thus, using the highest predicted A-1100 evaporation rate, 178 mg/hr, and assuming 100% ethanol yield, the predicted ethanol production from pure A-1100 is 111 mg/hr. This is 10% greater than if the mixed STA-54B material is released, and forms a crusty residue. If this generation rate is sustained over the observed 8-hr mass stabilization period documented by testing, the average cabin ethanol concentration may rise by 0.5 mg/m^3. This estimated increase is approximately 10% over prevailing ethanol concentration in the ISS cabin atmosphere. There is no impact to air quality control equipment. Humidity condensate loading in the ISS ROS can be expected to increase by 10.8 mg/L, an estimated 10% increase over loading predicted by prevailing conditions on board the ISS.

For the lower, 19-g release under unpressurized conditions, the ethanol production rate is 38 mg/hr assuming 100% yield. Sustained generation at this rate results in the cabin concentration increasing by 0.2 mg/m^3. Such an increase can be expected to cause humidity condensate loading to increase by 4.1 mg/L or 3.5% over the loading predicted by prevailing conditions on board the ISS.

For all leaked amounts, the impact to water processing equipment can be minimized substantially by rapidly isolating the leaked material and contaminated equipment from the cabin atmosphere. Accomplishing isolation within 1 hr limits the average cabin concentration rise to <1 mg/m^3 and humidity condensate loading increase to <2 mg/L.

Based on all considerations, the ECLS environmental impact is level B (2 to 24 hr to recover) and the ECLS equipment impact is rated category E1.

4.2 Nonoxide Adhesive Experimental Crack Repair Material

This assessment was prepared on April 27, 2005, revised on May 13, 2005, and released under NASA memorandum EC-05-089, "International Space Station Environmental Control and Life Support Systems Compatibility Evaluation of Tile Repair Materials for STS-114 (LF-1): Non-Oxide Adhesive Experimental Crack Repair Material and Cure in Place Ablative Applicator Materials," dated June 28, 2005.

A reinforced carbon-carbon repair detailed test objective plans to fly three Semco tubes containing 5 fluid ounces (~363 g) each of crack repair material. The material, designated nonoxide adhesive experimental (NOAX), consists of Starfire SMP-10 (allylhydridopolycarbosilane), silicon carbide, silicon hexaboride, zirconium diboride, and yttrium oxide. All components, with the exception of the Starfire SMP-10 component, are solid crystalline or powdered materials. The Starfire SMP-10, manufactured by Starfire Systems (Malta, NY) is a clear, amber liquid. It is insoluble in water. Testing indicates that 0.1% mass loss can be expected in a 24-hr period. For a single tube of material, the estimated generation rate into the cabin atmosphere is 15 mg/hr. Organosilicone compounds are well removed by the air quality control equipment located in the U.S. and Russian segments of the ISS. An increase of 15 mg/hr represents a cabin concentration rise of approximately 0.4 mg/m^3. Prevailing organosilicone concentration is typically 1 mg/m^3. After isolating the leaked material, air quality recovery will take an estimated 3 hr.

Organosilicone compounds are suspected to contribute to condensing heat exchanger hydrophilic coating degradation. Concentrations above 7 mg/m^3 are considered to be a risk to the condensing heat exchanger hydrophilic coatings. Release of an entire tube of NOAX material is not expected to approach this concentration.

If released, a single tube of the NOAX material represents an ECLSS equipment impact of E0 (no impact on ECLSSs) and the environmental impact is rated B (2–24 hr for ECLSSs to recover to acceptable levels).

4.3 Fuel-Oxidizer Reaction Products

This assessment was conducted in response to concerns related to EVA-related contamination whereby contamination may be brought into the ISS after contamination with fuel-oxidizer reaction products (FORPs). Contamination risk existed for EVA operations near ISS attitude control thruster locations. The assessment was conducted in 2006 and documented under NASA memorandum EI12-06-015, "Environmental Control and Life Support System Compatibility and Remedial Response for Fuel-Oxidizer Reaction Products," dated June 14, 2006.

4.3.1 Background

An assessment of ECLSS compatibility and remedial response to FORP contamination has been conducted to address EVA scenarios where contamination risk exists. FORP is a vacuum-stable residue resulting reaction with unsymmetrical dimethylhydrazine and nitrogen dioxide and is potentially hygroscopic. FORP residue has been observed in the vicinity of attitude control thrusters on the ROS. FORP contamination is most likely to be introduced into the ISS's cabin when an EVA occurs near or around attitude control thrusters on the ROS. Complicating factors may exist if the EVA is aborted quickly, leaving the crew little time to clean potentially contaminated parts of the suit or equipment before returning to the safety of the Station's cabin. To address the range of potential scenarios, an engineering assessment has been conducted to address ECLSS compatibility and remedial responses involving isolation to the docking compartment (DC) and service module (SM) as well as the case where contamination spreads throughout the Station's cabin.

FORP's average composition is summarized in table 13.[27] Specific properties for the potentially volatile chemical components that may be evolved from FORP are provided in table 14. Note that the other uncharacterized components of FORP are assumed to present no risk to either the crew or vehicle. Volatile components may be evolved as dimethylamine, methylamine, and ammonia on exposure to moisture in the cabin atmosphere. The extent of volatile component evolution is dictated by the ionization constant at 25 °C. Beyond the primary components of FORP, an area of concern is the interaction of FORP with moisture in the cabin atmosphere to form N-nitrosodimethylamine (NDMA). Properties of NDMA are also provided in table 15.

Table 14. Averaged FORP composition.

Component	Formula	Weight Percent
Volatile Components		
Dimethylammonium	$(CH_3)_2NH_2^+$	13.6
Methylammonium	$CH_3NH_3^+$	1.6
Ammonium	NH_4^+	0.3
Nonvolatile Components		
Nitrate salts	NO_3^-	31
Nitrite salts	NO_2^-	6.9
Other uncharacterized	Unknown	46.6

Table 15. Volatile component properties.

Property*	Value
Dimethylamine ($(CH_3)_2NH$)	
Molecular weight (g/mole)	45.08
Specific gravity	0.6865
Boiling point (°C)	–6.88
Liquid molar volume (cm^3/g-mole)**	68.5
Henry's Law constant (atm/mole fr.)***	0.88
Vapor pressure (mm Hg @ 25 °C)	1,277
Solubility	Soluble in alcohol and ether
Odor	Ammoniacal
Methylamine (CH_3NH_2)	
Molecular weight (g/mole)	31.06
Specific gravity	0.703
Boiling point (°C)	–6.79
Liquid molar volume (cm^3/g-mole)**	50.58
Henry's Law constant (atm/mole fr.)***	0.49
Vapor pressure (mm Hg @ 25 °C)	2,226
Solubility	Soluble in H_2O, alcohol, and ether
Odor	Strong ammoniacal
Ammonia (NH_3)	
Molecular weight (g/mole)	17.03
Specific gravity	0.639
Boiling point (°C)	–33.5
Liquid molar volume (cm^3/g-mole)**	25.38
Henry's Law constant (atm/mole fr.)†	0.996
Vapor pressure (mm Hg @ 20 °C)	6,460
Solubility	Very soluble in H_2O, alcohol, and ether
Odor	Sharp, intensely irritating
N-Nitrosodimethylamine ($(CH_3)_2N_2O$)	
Molecular weight (g/mole)	74.08
Specific gravity	1.006
Boiling point (°C)	152
Liquid molar volume (cm^3/g-mole)*	77
Henry's Law constant (atm/mole fr.)	Estimated ~ 1
Vapor pressure (mm Hg @ 25 °C)	3
Solubility	Soluble in H_2O, alcohol, and ether
Odor	Faint, 'characteristic'

[*] All data from R.C. Reid et al., 3rd Ed., 1977 and G.G. Hawley, *The Condensed Chemical Dictionary*, 10th Ed., 1981, unless otherwise noted.

[**] Estimated using techniques from R.C.Reid et al., *The Properties of Gases and Liquids*, 3rd Ed., pp. 59–60, 1977.

[***] C. Yaws, J. Hopper, S.R. Mishra, and R. Pike, "Solubility and Henry's Law Constants for Amines in Water," *Chemical Engineering*, August 2001.

[†] "Preferred and Alternative Methods for Estimating Air Emissions From Wastewater Collection and Treatment," Vol. II, Chapter 5, Eastern Research Group; Morrisville, NC, March 1997.

4.3.2 Fuel Oxidizer Reaction Product Stability Considerations

In the event of suspected FORP-related contamination, efforts to remove the contamination before entering the ISS cabin must be taken. Because FORP mass stability is achieved within 2 hr of attitude control thruster firing, contact with surfaces in the vicinity of the thrusters can result in contamination of the EVA suit or adjacent equipment. Stability has been observed over a range of temperatures from –40 °C to 25 °C. This stable, dry FORP has the average composition summarized in table 13. Because FORP may be hygroscopic, i.e., it may absorb moisture from the air, it is considered reactive once it is brought inside the ISS cabin. The presence of nitrates and nitrites promotes NDMA formation. After 2 hr of evaluation by researchers at the White Sands Test Facility, as much as 2.1 mg NDMA/g FORP has been observed on average for FORP stabilized at –40 °C. After 7 days of exposure to normal laboratory conditions, the NDMA concentration has been observed to increase by ~1.4×10^{-4} mg NDMA/g FORP/hr.[34] Greater increases in NDMA concentrations have been observed in FORP spiked with sodium nitrate; however, the spiking technique is artificial and not representative of actual ISS cabin conditions. Therefore, the starting average concentration of 2.1 mg NDMA/g FORP is the basis for the ECLSS engineering evaluation.

4.3.3 Environmental Impact

Environmental impact considers the maximum amount of FORP that may be introduced into the cabin, the estimated evaporation rate of volatile components, and estimated maximum concentration in the cabin given various levels of isolation.

4.3.3.1 Maximum Amount of Fuel-Oxidizer Reaction Product Introduced. Compatibility with the ECLSS equipment on board the ISS is based upon the worst-case scenario where a crewmember becomes contaminated and the EVA is aborted, allowing no time to remove the contamination before entering the cabin. The amount of FORP brought into the ISS is derived from the range of estimated surface deposition on 100 cm^2 over a range of distances from the thruster from 0.08 to 0.44 m and under the temperature range noted previously. An elapsed time of 1 and 2 hr is also considered in this estimate. Based on these variables, FORP contamination may range from approximately 2×10^{-2} g/cm^2 after 1 hr at 25 °C at a distance of 0.08 m from the thruster to approximately 5×10^{-4} g/cm^2 after 2 hr at –40 °C at a distance 0.44 m from the thruster. This establishes a maximum basis for the purpose of engineering assessment of approximately 2 g of FORP that may be introduced into the cabin.

For the 2-g FORP basis, approximately 4.2 mg NDMA, 272 mg dimethylamine, 32 mg methylamine, and 6 mg ammonia are expected to enter the cabin. The fraction of the amine compounds that may be evolved in the gas phase is found by considering the ionization constant provided in table 16. For these ionization constants, interaction with water vapor in the cabin atmosphere is most likely to result in 1% of the ammonium remaining ionized, 6% of the dimethylammonium remaining ionized, and 5% of methylammonium remaining ionized for hypothetical 0.2-molar aqueous solutions. Further, considering the Henry's Law constants and aqueous phase equilibrium, the driving force is toward the vapor phase for each of these FORP components. Therefore, most of these components of FORP may be evolved in the gaseous phase when exposed to sufficient moisture. So, for the purposes of the engineering assessment, the adjusted total amount of volatile components evolved are 258 mg dimethylamine, 30 mg methylamine, and 5.9 mg ammonia potentially released from 2 g of FORP. These amounts are considered as the basis for engineering calculations.

Table 16. Ionization constants for ammonia and amines.

Compound	Ionization Constant*
Ammonia	1.8×10^{-5}
Dimethylamine	7.4×10^{-4}
Methylamine	5.0×10^{-4}

* At 25 °C.

4.3.3.2 Evaporation Rate and Dispersal in the Cabin. Estimated evaporation rates for the pure volatile components of FORP are rapid. Using an established method for environmental screening recommended by the EPA, evaporation rates at prevailing cabin conditions for pure dimethylamine, methylamine, and ammonia are 1,120, 927, and 935 mg/s, respectively.[11,13] The estimated evaporation rate for NDMA is 2.9 mg/s. Based on these estimated evaporation rates, complete FORP evaporation is likely within 10 s. It is likely, however, that the rate of interaction of atmospheric moisture serves as the limiting factor in evaporation. For the purpose of engineering calculations, it is conservatively assumed that all the FORP and NDMA evaporate and disperse within the cabin volume within minutes.

4.3.3.3 Estimated Cabin Concentration. Three levels of isolation are considered for the purpose of the engineering assessment. First is isolation to the DC. The DC volume is approximately 12.5 m^3. Complete evaporation in the DC results in an NDMA concentration of 0.3 mg/m^3, dimethylamine concentration of 21 mg/m^3, methylamine concentration of 2.4 mg/m^3, and ammonia concentration of 0.5 mg/m^3. The maximum concentrations in the DC are reduced by a factor of 8 if they are allowed to dilute into the SM volume of approximately 100 m^3. If the contamination disperses throughout the entire ISS cabin, then the concentrations in the DC are reduced by a factor of nearly 30.

Of these compounds, only ammonia has a documented 180-day SMAC. In this case, the ammonia concentration is well below its 7 mg/m^3 180-day SMAC. All other compounds must be assessed relative to a default SMAC of 0.1 mg/m^3 unless toxicology experts provide other guidance.

Odor thresholds for dimethylamine, methylamine, and ammonia are 0.6, 4, and 3.6 mg/m^3, respectively.[28] All of these compounds are characterized by an ammoniacal odor. Given that dimethylamine could be above its odor threshold, suspected FORP contamination may be detected by odor for all isolation levels. Besides visual inspection, odor is the next method for detection as there is no monitoring equipment on board the ISS dedicated to monitoring the volatile components for FORP.

4.3.4 Environmental Control and Life Support System Equipment Impact

Compatibility with ECLSS equipment is considered with respect to the potential to damage or render critical functions inoperable as well as the potential for harmful products to be produced by air scrubbing systems. Primary areas of focus center upon depletion of expendable resources such as adsorbent beds and presenting an excessive challenge to water processing systems.

Using techniques documented by reference 1, activated carbon capacities for NDMA, dimethylamine, and methylamine are 5.25, 0.069, and 0.0018 mg/g, respectively. To remove the entire amount of FORP from the cabin atmosphere, including NDMA, via physical adsorption, requires a maximum of 17 kg of activated charcoal. The TCCS contains nearly 23 kg of activated charcoal. Because all of the volatile FORP components are ammonia derivatives, the likelihood that they react with the phosphoric acid treatment on the TCCS's charcoal bed must be considered. The charcoal bed is an expendable resource and exhausting the acid treatment is the primary basis for its preventive maintenance cycle. For the instance of FORP-related contamination, only 0.3% of the TCCS's capacity is consumed. Overall, there is no risk to the TCCS nor is there risk that any ammonia or ammonia derivatives can enter the catalytic oxidizer assembly to produce NO_2. Therefore, the risk to U.S. air quality control assets is considered negligible.

Ammonia is removed by the Russian BMP unit located in the service module. Testing has shown that ammonia is removed at approximately 58% efficiency.[29] It is anticipated that all other volatile products will be removed at 58% efficiency or better. The BMP employs a thermal catalytic reactor known as the PKF-T. The PKF-T operates at 250 °C to minimize nitrogen dioxide (NO_2) production. To allow for the potential of NO_2 production, the exhaust from the PKF-T flows to the BMP's inlet. Activated charcoal removes NO_2 very well with measured capacities approaching 0.35 g NO_2/g carbon.[30] Given the fact that the BMP's activate carbon beds are regenerated and the fact that the PKF-T is operated in a manner to minimize NO_2 production, the risk for NO_2 evolution into the cabin is considered negligible.

Water solubility for each volatile FORP component has been considered. Based on calculation techniques for determining removal efficiency via absorption in condensing heat exchangers, the SKV, with an air flow of 144 m^3/hr and a two-person latent heat removal rate supplies approximately 0.3% single-pass removal efficiency for NDMA, dimethylamine, and methylamine.[1,3,15] Ammonia is removed at approximately 24% single-pass efficiency. Ammonia typically is not a significant problem for ECLSS water processing systems and the very low single-pass efficiency means that the TCCS and BMP remove 99% of the volatile contamination for this case. Therefore, no impact is anticipated to water processing equipment on board the ISS U.S. Segment. Russian specialists will need to provide an assessment with their recommendations concerning the Russian Segment water processing system configuration.

4.3.4.1 Estimated Remediation Time. Estimated remediation time depends on the level of isolation as illustrated in figure 34. If the contamination is isolated to the DC and the portable Russian emergency contamination control unit (Russian acronym AFOT (F2)) is used for remediation, total elapsed time for 99% removal is less than 1.2 hr. This reduces the dimethylamine concentration to approximately 0.2 mg/m^3 or nearly 2 times the default SMAC of 0.1 mg/m^3. By extending the remediation duration to 1.5 hr, achieving the default SMAC is ensured. To achieve the same degree of contamination removal for isolation to the SM, i.e., to reach the default SMAC, requires 96% concentration reduction over nearly 12 hr. If the contamination is allowed to disperse throughout the entire ISS cabin, then only 90% concentration reduction is necessary to reach the default SMAC. Achieving this condition requires 20 hr of active atmospheric scrubbing.

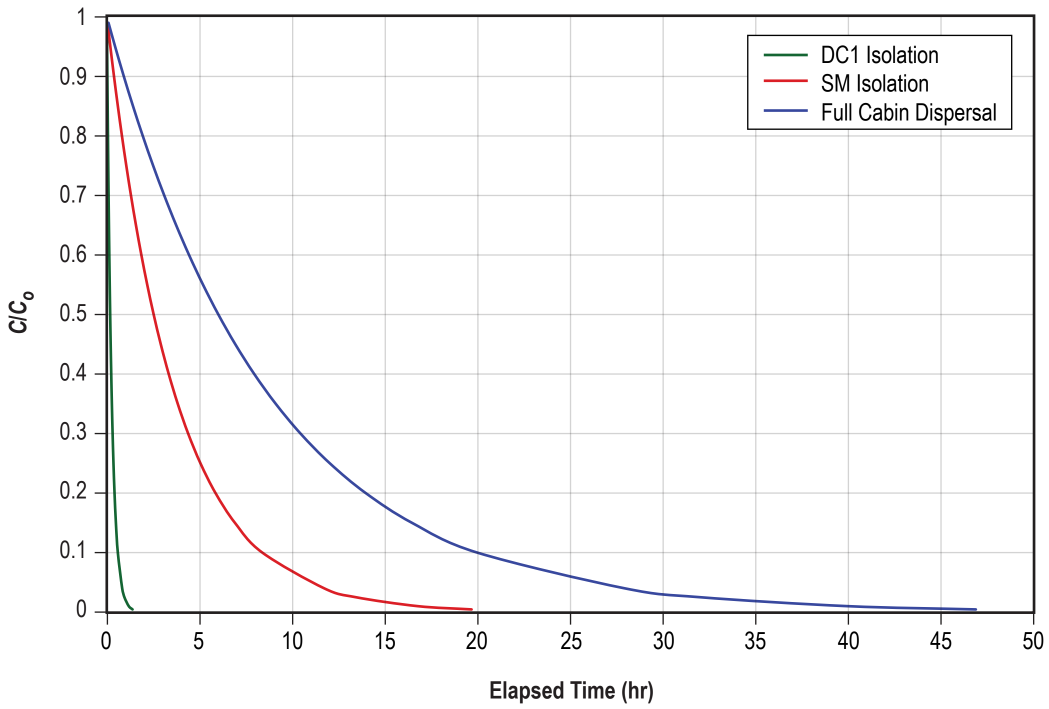


Figure 34. Estimated remediation time using ECLSS equipment.

Because ammonia is removed very effectively via absorption by humidity condensate, remediation times for 99% concentration reduction for isolation to the SM volume and for dispersal throughout the entire ISS cabin are approximately 9 and 26 hr, respectively. Twenty hours of scrubbing provides >97% concentration reduction. Ammonia is removed at the same rate if the contamination is isolated to the DC because only the AFOT (A2) unit provides removal.

Overall, the greatest challenge exists for removing the amine-based contaminants that require a longer remediation time, therefore, the remediation times noted in figure 34 are the recommended durations for remediation at the three isolation levels. Total remediation time to achieve concentration reduction to the default SMAC may be reduced to approximately 4 hr for the SM volume and 9 hr for the entire ISS cabin if the AFOT (A2) unit is used to supplement the TCCS and BMP. Figure 35 shows the concentration reduction rates for these two isolation cases when supplemented remediation is used.

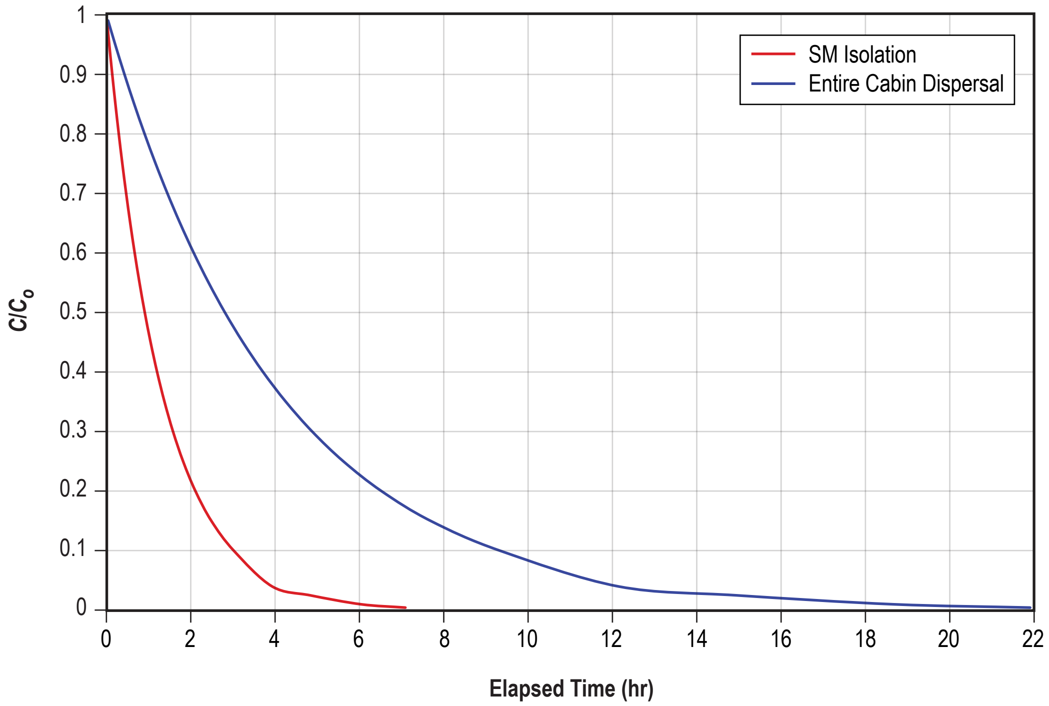


Figure 35. Estimated remediation time with ECLSS equipment and AFOT unit.

It should be noted that all calculations regarding removal provided by the AFOT (A2) unit assume 75% average removal efficiency. Details on the types of adsorbent and catalytic materials used in the AFOT (A2) unit are assumed to be similar to those of the harmful impurities filter (Russian acronym FVP) unit located in the FGB so a 25% margin has been used.

4.3.4.2 Summary Observations. The chemical components associated with a worst-case FORP contamination event have been evaluated with respect to their compatibility with ECLSS equipment. Evaporation and dispersion rate estimates indicate that contamination can be expected to rapidly disperse into the cabin atmosphere. An ammoniacal odor may be the primary indication of FORP contamination beyond visual inspection. All FORP components are expected to be removed from the cabin atmosphere by available air quality control assets. No impact to air quality control or water processing system assets is anticipated. Remediation time for all cases ranges from 1.5 to 20 hr, depending upon the isolation level and degree of supplemental atmospheric scrubbing provided.

4.3.4.3 Environmental Control and Life Support System Compatibility and Remediation Ratings. Based on the worst-case situation, the ECLSS compatibility rating is category E1. At most, 0.3% of a consumable resource will be used and no damage to ECLSS equipment is anticipated. Environmental impact is level B or C, depending on the isolation level and whether the AFOT (A2) unit is used to supplement baseline air quality control assets. ECLSS hardware and environmental impact categories are summarized in tables 1 and 2.

4.3.5 Recommendation

It is recommended that the Russian portable AFOT (A2) unit be deployed in the DC for any EVA where risk of FORP contamination exists. If FORP contamination is suspected, operating the AFOT (A2) unit for 1.5 hr minimum is necessary to minimize the risk of contamination entering the ISS cabin. If an ammoniacal odor is noted in either the DC or the ISS cabin post-EVA, FORP contamination should be suspected and remedial actions taken. Deploying the AFOT (A2) unit to supplement the TCCS and BMP in full cabin remediation is an option but not required. It is further recommended that the rated performance of the AFOT (A2) unit for this application be confirmed by Russian experts.

5. FIRE EXTINGUISHING AGENTS

The following evaluates heritage and candidate fire extinguishing agents used in aviation and aboard crewed spacecraft.

5.1 Bromotrifluoromethane Fire Extinguishing Agent

The ECLSS compatibility and cabin environmental impact of the heritage Halon 1301 fire extinguishing agent used by the Shuttle orbiter program was conducted in late 2007 through early 2008 and documented by NASA memorandum ES22-08-006, "Compatibility of Bromotrifluoromethane with Crewed Spacecraft Cabin Environments and Life Support System Equipment," dated February 8, 2008.

5.1.1 Background

Bromotrifluoromethane ($CBrF_3$), commonly known as Halon 1301, is one among many halogenated compounds used as fire extinguishing agents. Most halogenated fire extinguishing agents are methane derivatives with the hydrogen atoms substituted by iodine, bromine, chlorine, and/or fluorine atoms. Substituting the hydrogen atoms with halogen atoms influences the compound's thermal stability, fire extinguishing effectiveness, toxicity, and other properties.[31]

Halogenated extinguishing agents leave no residue after use because they are applied to a fire as a gas or as a liquid that rapidly vaporizes. They do not conduct electricity and their high liquid densities allow for compact storage containers. On a weight basis, the leading halogenated fire extinguishing agents are more effective than CO_2 by a factor of ~2.5. Halogenated extinguishing agents have found uses in systems designed for protecting electrical and electronic equipment; petroleum production facilities; engine compartments of ships, motor vehicles, and aircraft; and various other applications where minimal equipment damage and/or cleanup after use is desired. They have been demonstrated most effective for extinguishing class B (flammable liquids) and class C (electrical) fires. Halogenated extinguishing agents are effective on class A (ordinary combustibles) fires only if the fire is not 'deep seated.' These agents are not recommended for class D (combustible metals) fires.

Total flooding fire suppressant systems typically employ Halon 1301 because it is the least toxic and second most effective halogenated extinguishing agent. Dibromodifluoromethane (CBr_2F_2), Halon 1202, is considered to be the most effective halogenated fire extinguishing agent; however, it is the most toxic, making it unacceptable for use in portable extinguishers or total flooding systems. Testing during the 1970s found that Halon 1301 is compatible with electronic equipment, making it a good choice for total flooding systems and portable extinguishers designed to protect electronic equipment. Typically, a concentration of 5% Halon 1301 by volume is used.

5.1.2 Physical and Chemical Properties

Halon 1301 is a colorless gas at room temperature and pressure, 21 °C and 1 atm, respectively. Its odor is described as 'ethereal.' Table 17 lists many of Halon 1301's most useful chemical and physical properties. Portable Halon 1301 extinguishers are usually pressurized up to 4,137 kPa (600 psig) to overcome its much lower vapor pressure at low temperature conditions. The vapor pressure decreases from 1,372 kPa (199 psig) at 21 °C (70 °F) to 386 kPa (56 psig) at –17 °C (0 °F). Because Halon 1301 is chemically stable, it does not exhibit corrosive action on metals commonly used for constructing extinguisher bottles or buildings unless free water is present. Halon 1301 does contain some acidic impurities and free water can concentrate these impurities to form a corrosive liquid. Halon 1301 is compatible with most plastics and elastomers such as Teflon, nylon, neoprene, Buna N, and Viton.[32]

Table 17. Bromotrifluoromethane properties.

Property	Value
CAS number	75-63-8
Molecular weight (g/mole)	148.91
Phase	Gas
Color	Colorless
Odor	Ethereal
Boiling point (°C)[*]	–58
Liquid density @ 25 °C (g/cm^3)[**]	1.54
Critical temperature (°C)[***]	67.2
Critical pressure (kPa)[***]	3,972
Critical volume (cm^3/mole)[***]	200
Critical compressibility[***]	0.28
Water solubility @ 25 °C (mg/L)[†]	320
Henry's Law constant (atm/mole fraction)[†,‡]	27,615
Solubility in water @ 25 °C (wt. fraction)[‡]	0.000322
Vapor pressure (kPa @ 21 °C)[§]	1,372

[*] G.G. Hawley: *The Condensed Chemical Dictionary*. 10th Ed., 1981.

[**] Freon 13B1 Refrigerant, MSDS, DuPont, Wilmington, DE, revised April 28, 2004.

[***] R.C. Reid; J.M. Prausnitz; and T.K. Sherwood: *The Properties of Gases and Liquids*. 3rd Ed., 1977.

[†] Estimated Using EPISUITE, U.S. EPA Office of Pollution Prevention and Syracuse Research Corp., 2000.

[‡] C.L. Yaws; J.R. Hopper; X. Wang; et al.: "Calculating Solubility and Henry's Law Constants for Gases in Water," *Chemical Engineering*. pp. 102–105, June 1999.

[§] D.W. Moore: "Halogenated Agents and Systems," Fire Protection Handbook, 16th Ed., NFPA, Section 19/Chapter 2, pp. 19–12, 1986.

Halon 1301 has many desirable fire extinguishing properties. It has a high liquid density, allowing for compact storage, does not conduct electricity, and is nontoxic at the concentrations needed to extinguish a fire. Halon 1301 works by interrupting the chemical chain reaction of a combustion process. Several theories have been proposed to explain how Halon 1301 works. These include releasing bromine (Br) which reacts with the hydrogen and hydroxyl radicals to form HBr in a chain terminating step and Br capturing electrons from activated hydrocarbons before they can activate oxygen.[31,32] Beyond chemically interrupting the combustion process, Halon 1301 also displaces oxygen from the fuel's vicinity, affecting the oxidizer part of the fire triangle.

Although Halon 1301 possesses many desirable properties that make it a desirable fire extinguishing agent, there are limitations to its application. Halon 1301 is not an effective fire extinguishing agent for combustion processes involving reactive metals such as potassium, magnesium, sodium, titanium, and zirconium (class D). Fires involving metal hydrides and petroleum solvents are not extinguished by Halon 1301 either. Likewise, Halon 1301 is ineffective for fires involving materials that decompose rapidly and fuels that contain their own oxygen source such as gunpowder and rocket propellants.[32] The perchlorate materials used in solid oxygen generation canisters formally used on board Mir and now on board the ISS are examples of these latter materials. Materials that undergo autothermal decomposition such as hydrazine and organic peroxides are also not controlled by Halon 1301.

5.1.2.1 Toxicology Considerations. Halon 1301 has been studied extensively and NASA toxicology experts in collaboration with the National Research Council's Committee on Toxicology have developed SMACs documented in JSC 20584. The 1-hr/24-hr SMACs are 21,350 mg/m^3 and the 7-/30-/180-day SMACs are 11,000 mg/m^3. Short- and long-term toxic effects that serve as the basis for the SMACs are cardiovascular effects and central nervous system effects. Halon 1301 commercial products marketed before 1957 contained impurities that apparently caused many toxic responses in humans. Studies on purified Halon 1301 (99.8% purity) reported no toxic effects. Commercial Halon 1301 products on the market after 1957 are high purity.[33]

5.1.2.2 Thermal Stability. Care must be taken when using Halon 1301 on 'deep-seated' class A fires and very hot fires. Exposure to flames or surface temperatures >482 °C cause Halon 1301 to decompose to more harmful chemical compounds. These include hydrogen fluoride (HF), HBr, and bromine (Br_2). Some early stability evaluations reported carbonyl halides among the decomposition products; however, recent evaluations have not supported that observation.[32] Early developmental studies on spacecraft TCC equipment designs for a space station conducted in the mid-1970s cited several studies involving Halon 1301 thermal decomposition under temperature conditions ranging from 700 to 1,100 °C. All cases reported HF, HBr, and Br_2 as the primary decomposition products.[34]

A NASA toxicology assessment of Halon 1301's thermal decomposition products was conducted for the NASA Mir program in 1995. Unfortunately, no guidance for SMACs for the decomposition products was provided. Therefore, the 0.1 mg/m^3 default SMAC applies for all engineering and operational assessments until toxicology experts provide official guidance. Bromine is of most concern because its tolerance in air is reported to be 0.1 ppm$_v$ (0.7 mg/m^3). Both HF and HBr are both reported to have 3 ppm$_v$ ground-based tolerances in air.[35] From this observation, it is likely that the NASA toxicology SMAC guidelines for HF and HBr may be similar in magnitude and lower than the 1-ppm_v spacecraft air quality limit established in JSC 20584 for hydrogen chloride (HCl) which has a ground-based tolerance in air of 5 ppm_v.

5.1.3 Life Support Equipment Testing

5.1.3.1 Catalytic Oxidation Reactor Compatibility Experiments and Predictions. During the ISS TCCS's development, an investigation of poisoning of the 0.5% palladium (Pd) on alumina (Al_2O_3) catalyst by several halocarbon compounds was conducted for NASA by TDA Research Inc. (Wheat Ridge, CO). Halon 1301 was one of the compounds selected for evaluation. The experimental results using a 10-ppm_v (61 mg/m^3) Halon 1301 concentration challenge found that the catalyst's methane oxidation efficiency decreased by 30% within 20 hr. After removing the Halon 1301 challenge, the efficiency recovered; however, the temperature necessary to reach 50% methane oxidation efficiency increased from 250 to 300 °C. The catalyst's activity after Halon 1301 exposure was found to be approximately 4 times lower than fresh catalyst. This lost activity was permanent. Correlation of methane oxidation efficiency and catalyst poison concentration as free halogen found the relationship can be predicted by equation (20) where η is methane oxidation efficiency in decimal form and C is free halogen concentration in mg/m^3:[36]

$$\eta = 0.9373C^{-0.5548} . \tag{20}$$

During the catalyst poisoning investigation, it was reported that 10% of the Halon 1301 entering the reactor decomposed to oxidation products. Chemical analysis found 0.3 ppm_v of Br_2 and 0.4 ppm_v of HF. A concentration for HBr was not reported due to analytical method limitations. The concentrations of Br_2 and HF were lower than stoichiometry might predict. The investigators hypothesized that some of the HF may have interacted with stainless steel components in the test rig and that the analytical method used for Br_2 lacked sensitivity. Even with these limitations, the fact that the ISS TCCS's thermal catalytic oxidizer will decompose Halon 1301 to more toxic products creates an operational hazard. Therefore, hazard controls must be in place.

The results from this evaluation independently confirmed the oxidation efficiency and catalyst poisoning effects reported from experiments conducted by the European Space Agency (ESA).[37] The study conducted by ESA found that a Halon 1301 concentration of 583 ppm_v (3,550 mg/m^3) completely depletes the thermal oxidation catalyst's activity. When the Halon 1301 challenge is removed, the catalyst's activity recovers.

Lockheed conducted an extensive study of low temperature CO catalysts in 1977. During this study, the 2% platinum (Pt) on activated carbon that was ultimately selected for use in the Shuttle and Spacelab programs was challenged with several poisons. A 48-hr challenge using trichlorofluoromethane (Freon 11) and dichlorodifluoromethane (Freon 12) showed no effect on the catalyst's CO oxidation performance.[38] By virtue of Halon's molecular similarity to Freon 11 and Freon 12, it is likely that Halon will also have no effect on the 2% Pt on activated carbon's catalytic activity. The presence of other compounds that may be present during and after a fire, however, may have effects but no experiments have been conducted on this catalyst to determine its performance under such conditions.

5.1.3.2 Adsorption Capacity Experiments and Predictions. In 1977, during the developmental phase of the Shuttle and Spacelab programs, concerns emerged regarding interaction of Halon 1301 and its thermal decomposition products with the atmosphere revitalization system. A study conducted for Dornier System GmbH found that Halon 1301 is difficult to remove from the cabin atmosphere once released. The Halon 1301 challenge was 3% by volume. Only molecular sieve 13X, at 0.6% by weight, and GAC, at 4% by weight or 40 mg/g, exhibited adsorption capacity for Halon 1301. Potential theory calculations predict ~70 mg/g loading at this condition for acid-treated carbon and ~177 mg/g for untreated carbon. Granular LiOH was reported to remove Br_2 and HBr at 24% and 58% by weight, respectively. No evaluation of fluorine (F_2) and HF was conducted.

NASA Marshall Space Flight Center (MSFC) conducted a simple study of activated carbon's ability to retain Halon 1301 from a 25.5-ppm$_v$ (155 mg/m^3) challenge in a recirculating flow loop. After 5 min, the concentration was reduced to 2 ppm$_v$ (12 mg/m^3). The total test volume was ~8.5 L. Therefore, the total amount of Halon 1301 adsorbed by the 40 g of carbon was ~1.14 mg. The activated carbon loading derived from this study, ~0.03 mg/g carbon, is very low. Few details on this study are available so it is difficult to determine if the results are being interpreted absolutely correctly. The capacity derived from potential theory calculations predicts loading at ~0.6 mg/g carbon for treated carbon at this condition. Untreated carbon loading is predicted to be 2 mg/g carbon.

During the first year of crewed operations on board the ISS, a large quantity of octafluoropropane (Freon 218) leaked into the cabin. Evaluation of the observed concentration decay rate indicates that the ability to remove halocarbon compounds from the cabin atmosphere is quite limited and does not exceed 1% efficiency for a regenerable activated carbon-based air quality control process.[39] Halon 1301 has an observed and predicted equilibrium capacity on activated carbon that is much lower than that of Freon 218. Removal assists from other processes such as zeolite-based CO_2 removal equipment, are negligible based on the zeolite 13X loading capacity reported by the Dornier study. It is concluded from these data sources and observations that insignificant Halon 1301 removal is provided by adsorption-based processes and that thermal catalytic oxidation is the only effective removal process on board the ISS.

5.1.4 Environmental Regulations

Halon 1301 is classified as a class I ozone-depleting substance. According to Air Force Research Laboratory documentation, halons account for 23% of ozone depletion.[40] Internationally, the 1987 Montreal Protocol set goals for ceasing production of ozone-depleting chemicals. Developed countries were to cease production by 1993 and developing countries must cease production by 2010. Ten years later, the 1997 Kyoto Protocol set goals for reducing releases of global warming gases. There have been various responses to these international agreements.

5.1.4.1 Foreign Regulatory Responses. European Community Regulation 2037/2000 took effect in October 2000, and has the following stipulations:

- New halons cannot be used to refill existing systems.
- Only recovered, recycled, or reclaimed Halon 1301/1211 can be used to refill existing systems until December 31, 2002, after which no refilling was permitted.

- Mandatory decommissioning of Halon-based fire extinguishing systems must be completed by December 31, 2003.

Effectively, this regulation sought to decommission all Halon-based fire extinguishing systems in Europe. Halon removed from the systems was to be disposed of in an appropriate manner or 'banked' for 'critical uses.' Most critical uses usually are for commercial aircraft, military, petrochemical, and marine applications.

5.1.4.2 Domestic Regulatory Responses. In 1998, the EPA issued a regulation pertaining to the handling and disposal of Halon 1301, Halon 1211, and Halon 2402 (63 FR 11084). The regulation banned the manufacture of new Halon blends and established provisions for handling, release mitigation, and disposal. The regulation did not affect existing Halon stores and included an exemption for manufacturing Halon blends for aviation fire protection applications as long as they are recycled.

Legislation that was introduced in 2007, the Global Climate and Ozone Layer Protection Act of 2007, places additional limits on the importation and production of class 1 ozone-depleting substances. Under this legislation, importing products that contain phased out class 1 ozone-depleting substances is banned effectively on January 1, 2010. The EPA is given the latitude to allow some compounds to be used as fire suppressants in applications where 'they reduce overall risk to human health and the environment compared to alternatives.' A strategy for destroying existing stores of substances is also established whereby anyone seeking an exemption for producing or importing a class 1 ozone-depleting substance must offset their use by destroying 3 times the amount used or produced. This provision takes effect on January1, 2010. Beyond January 1, 2012, the amount that must be destroyed varies between 1.2 and 2 times the amount imported or produced.

It is anticipated that continued regulatory pressures will make Halon 1301 increasingly difficult to acquire and more expensive than alternatives.

5.1.4.3 International Space Station Program Discussions With the Russian Partner. Bilateral discussions between NASA and Russian spacecraft cabin air quality experts have touched on Halon 1301 on a number of occasions. Protocol content pertaining to Halon 1301 dating to January 2000 is the following:

- Flight rules pertaining to the release of Halon 1301 from Shuttle fire extinguishers were reviewed and the Russian position on Halon 1301 is that it is not safe or compatible with the spacecraft cabin environment. A safety review panel assessment was requested (January 2000).

- Russian experts expressed concern about the Shuttle's Halon 1301 fire extinguishers because the Halon 1301 can decompose at temperatures >500 °C and it can displace oxygen in the area where it is used. Also, because of the risk to produce Br_2 and HF after a Halon 1301 discharge, the USOS TCCS is turned off, placing the full atmospheric quality recovery burden on the ROS air quality control equipment (July/August 2001).

- An action was assigned to research the Shuttle fire extinguisher leak rate and Halon 1301 concentration on board the Shuttle and ISS (December 2006).

These discussions highlight the bilateral recognition that the presence of Halon 1301 on board the Shuttle is viewed as an air quality and environmental impact risk to the ISS.

5.1.5 Bromotrifluoromethane and Spacecraft Cabin Air Quality

Given its fire extinguishing effectiveness, favorable toxicity, and compatibility with electronic equipment, Halon 1301 was selected as the fire extinguishing agent for the Space Shuttle and Spacelab programs. Early in the Shuttle and Spacelab programs, measurable Halon 1301 concentrations were reported in cabin atmospheric grab sample analyses. The concentrations reported during the STS-9/Spacelab-1 mission are most noteworthy because they increased from ~11 mg/m^3 early in the mission to >77 mg/m^3 at the end of the mission. Postflight assessment concluded that Halon 1301 was leaking into the cabin at ~333 mg/hr.

5.1.5.1 Spacelab Program. In total, 50 grab samples were collected during flight using the evacuated container method during the Spacelab program. The average Halon 1301 concentration reported was 8.2 mg/m^3 with a maximum of 77.3 mg/m^3 and standard deviation of 16.5 mg/m^3. The 95% confidence interval is bounded by 3.6 mg/m^3 at the lower end and 12.8 mg/m^3 at the upper end.

5.1.5.2 Shuttle Program. Through the STS-90 mission, 107 grab samples were collected on board the Shuttle orbiter during flight. The average Halon 1301 concentration reported from these samples is 1.2 mg/m^3 with a maximum of 43 mg/m^3 and standard deviation of 4.4 mg/m^3. The 95% confidence interval is bounded by 0.3 mg/m^3 on the lower end and 2 mg/m^3 on the upper end. Samples collected from the Shuttle orbiter during preflight preparations also found that Halon 1301 was present. The preflight concentration averaged 0.08 mg/m^3 with a 6.4 mg/m^3 maximum and 0.7 mg/m^3 standard deviation for 77 total samples collected.

5.1.5.3 NASA Mir and International Space Station Programs. Halon 1301 has also been observed on board the Mir Space Station after the Shuttle began docking. Because the Mir Space Station had no Halon 1301 source on board, as one would expect, none was found in grab samples collected before the first Shuttle docking. However, after the first docking and throughout the remainder of the NASA-Mir program, the Halon 1301 concentration was observed to be influenced by the Shuttle's presence. Figures 36 and 37 show the concentration trend observed on board Mir during the NASA-Mir program. Similarly, even though the ISS has no Halon 1301 source on board, the compound has been found routinely in archival grab samples. Figure 38 shows the Halon 1301 trend observed from samples collected from the ISS.

The air quality samples collected during the Shuttle and Spacelab programs establish Halon 1301 as a characteristic compound in their cabin atmosphere. These results also lead to the conclusion that the fire extinguisher bottles leak at slow rates. Further, the observations from the NASA-Mir and ISS programs demonstrate that carryover from the Shuttle orbiter into the Space Station cabin occurs and emphasizes the point that any vehicle that docks to a long-term space habitat will influence the habitat's cabin air quality.

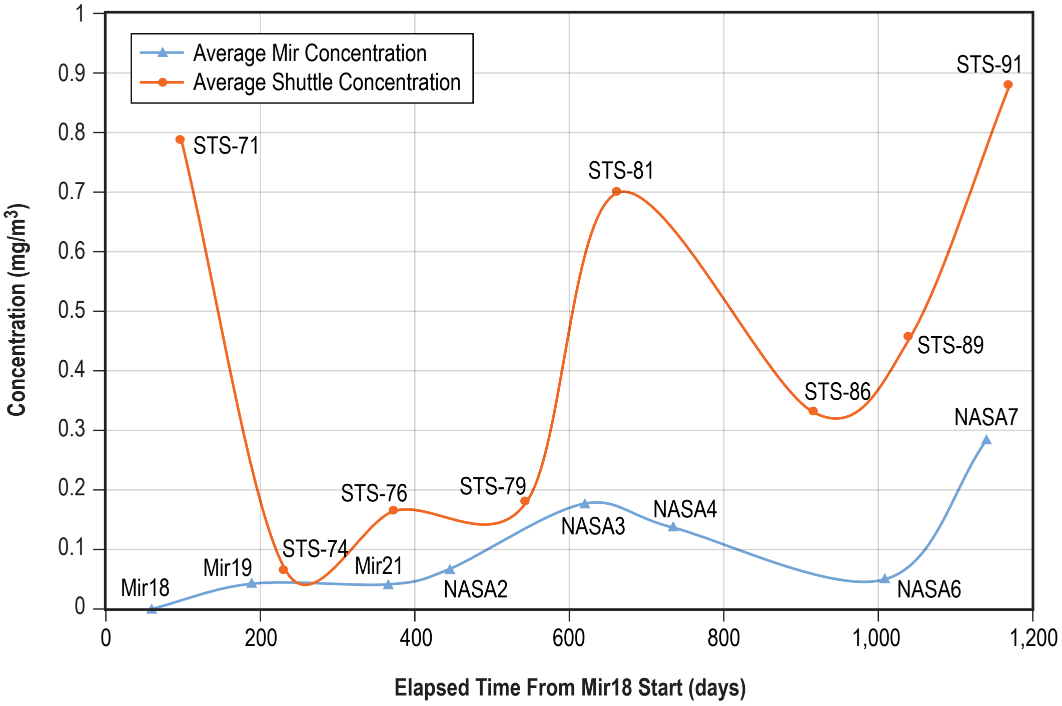


Figure 36. Average halon 1301 concentration on board Mir.

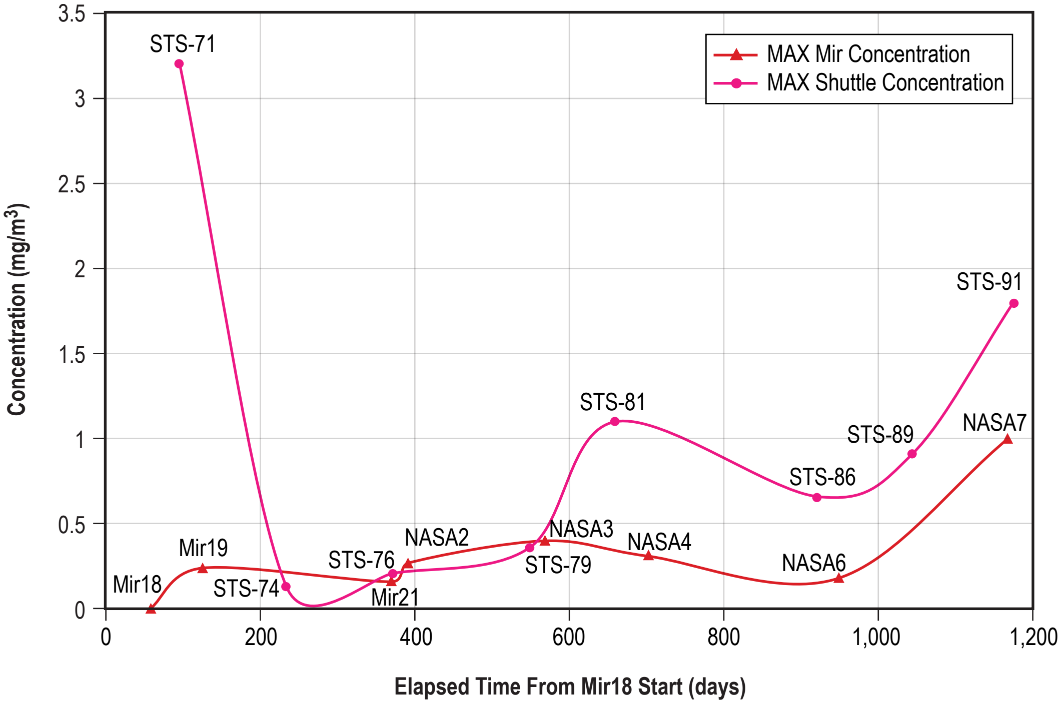


Figure 37. Maximum halon 1301 concentration on board Mir.

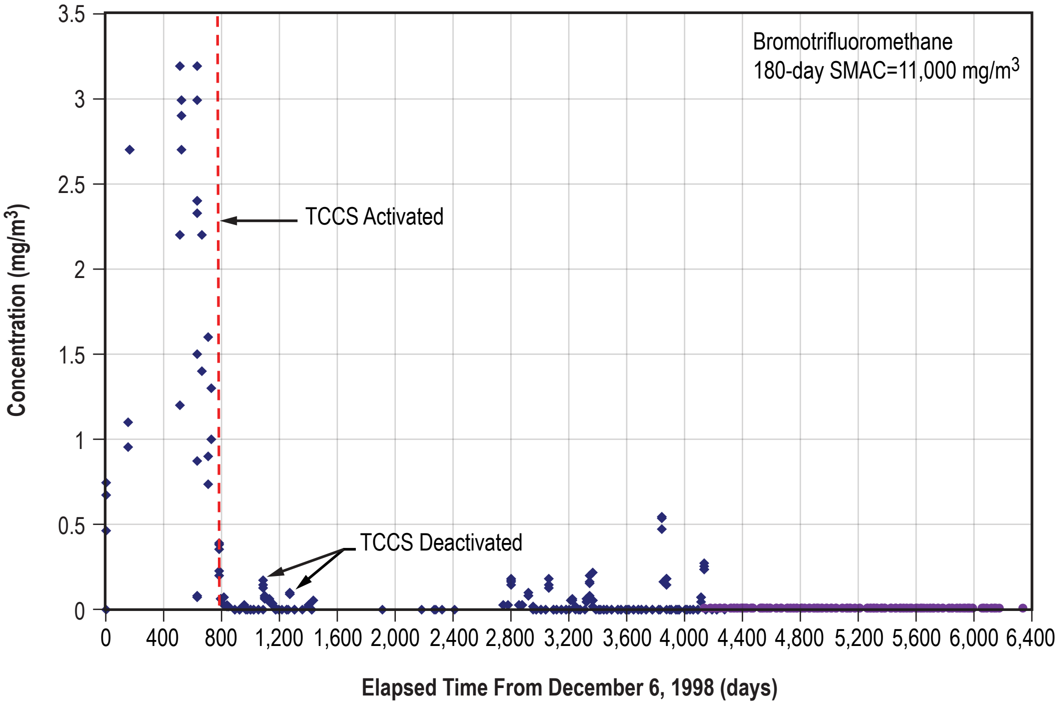


Figure 38. Halon 1301 concentration on board the ISS.

5.1.6 Assessment Approach and Assumptions

The environmental impact and life support system compatibility assessment is conducted within the bounds of standard spacecraft TCC design practice. The following discussion provides details on that practice and the various aspects of the compatibility assessment.

The objective of the compatibility assessment is to understand whether a chemical compound, if released into the cabin environment, can have deleterious effects on life support equipment leading to unscheduled maintenance and/or damage. Also, the assessment investigates the degree of difficulty of removing Halon 1301 from the cabin environment. Life support system and environmental impact ratings are assigned based on the assessment results. Section 1.1 provides a description of the life support system compatibility and environmental impact rating and their rationale in tables 1 and 2, respectively. The calculation techniques described in section 2.3 were applied to the assessment cases as appropriate.

5.1.6.1 Vehicle Configuration. The vehicle configuration assessed is the ISS at assembly complete with either the Shuttle orbiter or the Orion CEV present. The ISS's habitable on-orbit configuration at assembly complete consists of PMA-1, Unity (Node 1), Destiny (U.S. Laboratory), Quest (U.S. airlock), Harmony (Node 2), Columbus APM, Kibo PM and ELM-PS, Zarya (FGB), Zvezda (service module), a Soyuz spacecraft, and a Progress cargo vehicle. The ISS's total habitable volume is approximately 794 m^3. The ROS accounts for 269 m^3 and the USOS for 525 m^3.

Active TCC is provided for the ISS by the USOS TCCS located in Destiny and the BMP located in Zvezda. Previous analysis has shown that both the TCCS and BMP have sufficient capacity to control the Station's trace contaminant load.[26]

The Halon 1301 bottles are assumed to be similar in size to those used on board the Shuttle orbiter. The portable extinguisher contains 1.25 kg Halon 1301 and the avionics bay extinguisher bottles contain 1.72 kg Halon 1301. The Orion CEV architecture plans to consider Halon 1301 for portable extinguisher use only. Another extinguishing agent will be used for the avionics bay fire extinguishing application. The discharge rate from a portable extinguisher is 80% of the total Halon 1301 mass within 4 s.

5.1.6.2 Assumptions. Basic assumptions pertaining to cabin atmospheric conditions for the Halon 1301 compatibility assessment are the following:

- The cabin atmosphere is well mixed.
- Atmospheric leakage from the ISS and all other habitable volumes is zero.
- The ISS habitable free volume is approximately 794 m^3 with 269 m^3 provided by the ROS and 525 m^3 provided by the USOS.
- Atmospheric conditions are on average 21 °C (70 °F), 50% relative humidity, and 1 atm.
- Acceptable risk and zero risk air quality limits as defined by SSP 50260 apply.
- Ventilation flow between the ISS segments is maintained at ~221 m^3/hr.

5.1.7 Results and Discussion

As noted previously, the assessment applies the equations and calculation techniques found in section 2.3 for cabin material balance, evaporation rate, humidity loading, and activated carbon loading to evaluate two primary cases.

5.1.7.1 Cases Considered. The cases evaluated address both long-term leakage and complete extinguisher discharge. The amount of Halon 1301 selected for the basis for each case reflects in-flight experience with the Shuttle orbiter portable fire extinguishers. The cases considered for assessment are the following:

- Control of a sustained leak at a maximum 333 mg/hr rate.
- Recovery from a 1.25-kg discharge from a portable extinguisher.

Beyond evaluating these leakage and bulk discharge cases, the Halon concentration that must be present in the ISS cabin atmosphere to result in hazardous concentrations of thermal decomposition products is also determined.

5.1.7.2 Evaporation From Sustained Leaks and Bulk Discharge. Examination of Halon 1301's physical properties concludes that the release will be in the gas phase. Even if stored as a liquid, any leaked fluid will evaporate so rapidly that it can be considered to be nearly instantaneous. A supporting calculation of a 1.25-kg leaked volume using equation (9), assuming it remained liquid after exiting its container, indicates the evaporation rate magnitude results in the entire amount evaporating in <0.1 s. Therefore, it is reasonable to conclude that any Halon 1301 entering the cabin will be in the gas phase.

5.1.7.3 Controlling a Sustained Leak. A sustained 333 mg/hr leak into the USOS cabin, the largest leak observed from the Shuttle and Spacelab programs, results in the ISS cabin concentration increasing to ~450 mg/m^3 over >4,700 hr (>196 days). The concentration approaches a steady state concentration of ~450 mg/m^3 and, therefore, cannot exceed the 11,000 mg/m^3 SMAC. Even for a 70 m^3 cabin volume, a sustained 333 mg/hr leak requires >97 days to reach the SMAC with no removal. Given that the leakage observed during the STS-9/Spacelab 1 mission is exceptional, the capability to maintain the cabin concentration well below acceptable air quality limits under normal circumstances is considered to be more than sufficient.

In the event that the USOS TCCS carbon bed assembly (CBA) becomes saturated and the full 450 mg/m^3 Halon 1301 concentration enters the catalytic oxidizer assembly (COA), the methane oxidation efficiency is predicted to decay to ~12%, an 88% loss of function.

5.1.7.4 Recovering From a Single Extinguisher Discharge. In the case of a single portable fire extinguisher discharge, any cabin volume <114 m^3 can expect to reach a concentration in excess of the SMAC. This is important to consider for future vehicle designs. In the event of a single bottle discharge that is dispersed into the ISS cabin, 1,574 mg/m^3 is the maximum concentration that may be attained. Seven portable fire extinguisher bottles must discharge into the ISS cabin to reach the SMAC.

Recovering from a single bottle discharge requires ~5,500 hr (~229 days) to reduce the concentration to <10 mg/m^3. This is with both the USOS TCCS and ROS BMP operating. If the ROS BMP is the sole removal device, then ~14,900 hr (621 days) is required to reduce the cabin concentration to <10 mg/m^3.

It is most likely that the ROS BMP will operate alone after a single Halon 1301 bottle discharge to avoid poisoning the TCCS COA's catalyst and generating hazardous thermal decomposition products within the oxidizer. The TCCS may be operated during this time but in the COA 'heater override' mode. Once the cabin concentration is certified to be <10 mg/m^3, the TCCS COA heaters may be restarted. This action avoids unscheduled maintenance for the TCCS COA as well as the downstream sorbent bed assembly (SBA). It should be noted that introducing 1,574 mg/m^3 into the TCCS COA reduces the methane oxidation efficiency to ~6%, a 94% loss of function.

5.1.7.5 Life Support System Capabilities and Impacts. The life support system impacts consider water processing equipment and the cabin atmosphere revitalization systems.

5.1.7.5.1 Absorption Via Humidity Condensate and Impacts to Water Processing Equipment. Halon 1301 is not very soluble in water. When evaluated for the expected single-pass efficiency for removal via absorption by humidity condensate, the result is on the order of 2×10^{-8}, indicating very negligible mass transfer can be expected into humidity condensate. This result indicates that Halon 1301 presents no challenge to water purification equipment on board the ISS.

5.1.7.5.2 Halon 1301 Removal and Disposal by International Space Station Cabin Air Quality Control Systems. Based on estimated activated carbon capacities, the USOS TCCS carbon bed may become saturated by Halon 1301 between 0.45 and 5 hr after a single bottle discharge. The time to reach saturation depends on the amount of Halon 1301 discharged and the rate that it disperses throughout the cabin. At the lower sustained leakage concentration, it is estimated that TCCS carbon bed saturation may occur between ~2 and 17 hr after the leak begins.

Because the USOS TCCS employs expendable activated carbon contained in the CBA, its usefulness for recovering from a Halon 1301 discharge into the cabin is limited. Depending on the cabin concentration, the TCCS's CBA capacity may range from ~12.5 g up to ~119.3 g. All Halon 1301 removed by the CBA is contained in the activated carbon and disposal is accomplished by physically replacing the bed. After depleting the CBA's capacity, the primary removal within the TCCS occurs in the catalytic oxidizer. At 10% single-pass efficiency, the catalytic oxidizer provides an effective 0.46 m^3/hr removal flow. The risks associated with producing HF, Br_2, and HBr by the COA when processing air containing Halon 1301 are considered in the following section.

The capacity and potential safety limitations associated with operating the USOS TCCS after a Halon 1301 event shift the recovery burden more heavily on the ROS BMP. The TCCS and BMP may be able to work together for the first few hours but then it becomes necessary to shut the TCCS down to conserve resources and manage risks associated with forming toxic oxidation products in the catalytic oxidizer.

The BMP's expendable FOA bed, containing ~2 kg of activated carbon, provides for a capacity ranging from ~1.1 g up to ~10.5 g. The Halon 1301 removed by the FOA bed is contained in the activated carbon and disposal is accomplished by physically replacing the bed. The capacity of the BMP's two ZPL-1M regenerable carbon beds, containing ~2.8 kg activated carbon combined, is estimated to range from ~1.5 g up to ~14.7 g. All Halon 1301 removed by the regenerable ZPL-1M beds is vented overboard.

Combined, the TCCS and BMP provide a short-term Halon 1301 removal capacity ranging from ~15 g up to 144.5 g. The short-term capacity is exhausted within 138 min (2.3 hr) after dispersing a single Halon 1301 bottle throughout the cabin. After initial saturation, it is estimated that the BMP will provide approximately 1% single-pass removal efficiency or an effective 0.27 m^3/hr removal flow. The time to reduce the Halon 1301 concentration to <10 mg/m^3 after the initial short-term capacity is exhausted is ~14,900 hr (~621 days) as shown in figure 39. Continuing to operate the TCCS COA, which provides 10% removal efficiency, reduces the cleanup duration to ~5,500 hr (229 days) as shown in figure 40. However, the risk of producing toxic oxidation products by the COA and the potential for release into the cabin must be addressed.

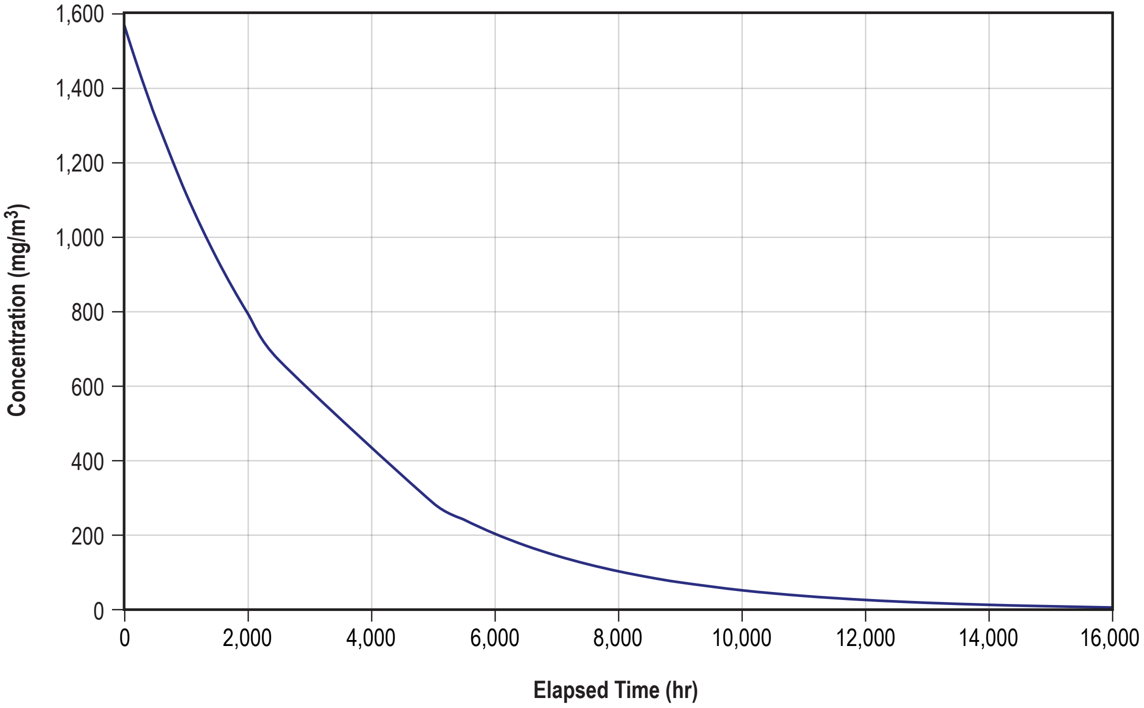


Figure 39. Halon 1301 removal using the BMP.

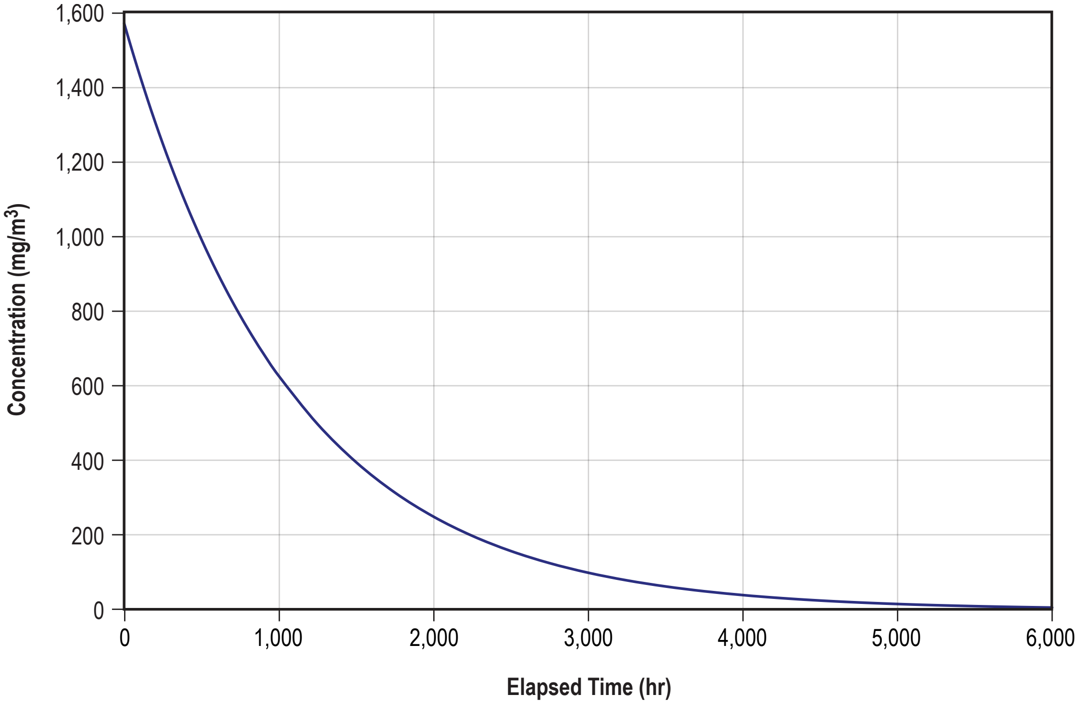


Figure 40. Halon 1301 removal using the BMP and TCCS.

Testing conducted by Lockheed in 1991 on molecular sieves 13X and 5A found that trichlorotrifluoroethane (Freon 113) is removed by a four-bed molecular sieve process at approximately 60% efficiency. Similarly, system-level testing conducted by MSFC in 1998 found that dichloromethane is removed by a four-bed molecular sieve process at approximately 50%.[19] If it is assumed that the CDRA located in the USOS can provide at least 50% removal efficiency, then the total time required to reduce the cabin concentration to <10 mg/m^3 may be no more than 235 hr (~9.8 days) as shown in figure 41. Therefore, it is advantageous to start the CDRA in the event of a Halon 1301 extinguisher discharge. No damage to the CDRA equipment or reduction in its function is anticipated. The CDRA operates below Halon 1301's thermal decomposition temperature.

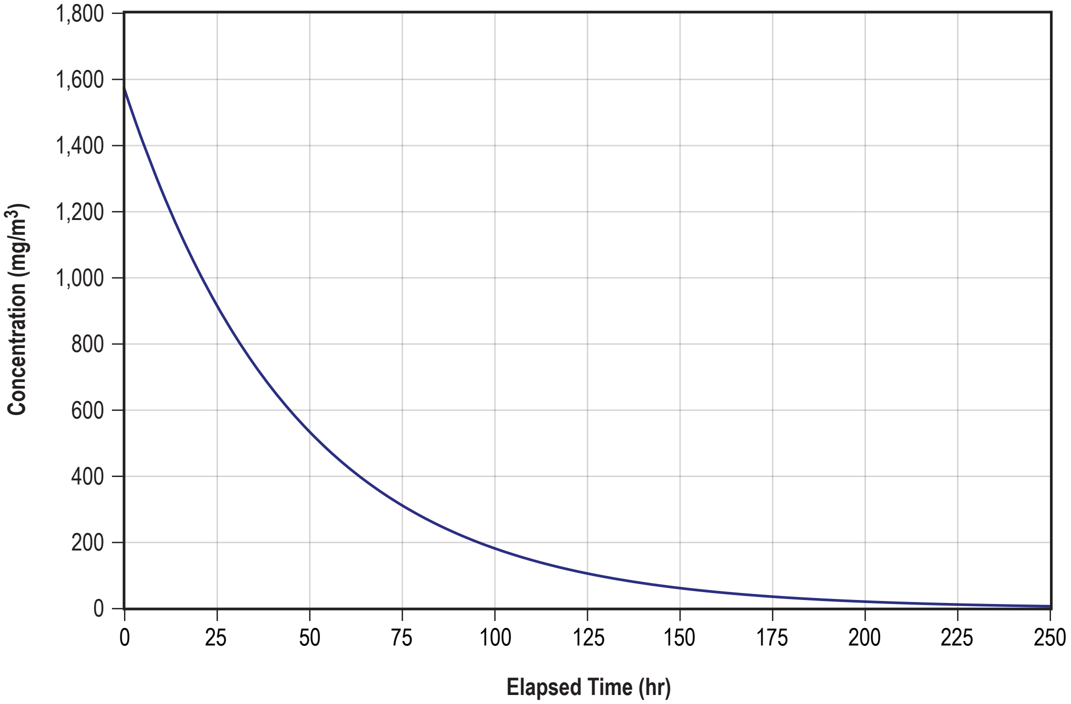


Figure 41. Halon 1301 removal using the BMP and CDRA.

5.1.7.5.3 Trace Contaminant Control Subassembly Sorbent Bed Assembly Resource Consumption. Upon processing by the TCCS COA or contact with deep-seated hot fires, Halon 1301 decomposes to form HF, HBr, and Br_2. Results from specific testing conducted for the TCCS COA catalyst and other related evaluations were discussed earlier. The primary consideration must be given to the potential to deplete the TCCS SBA capacity to remove the acid gases produced in the TCCS COA.

Experience has shown that 3.98 moles (95.25 g) of LiOH contained in the TCCS SBA are available for reaction.[36] This is only 7% of the total 1.36 kg of material contained in the bed. In addition, long-term operational experience gained from the ISS found that lithium chloride (LiCl), the product of the reaction of HCl with LiOH, is deliquescent, and in combination with the warm temperature entering the bed and background humidity, causes size attrition of the LiOH granules. The resulting moist powder increases the flow resistance through the SBA. After approximately the first 10 cm of the bed reacts the ability of the TCCS to maintain proper air flow control becomes compromised.

The total acid gas production, if assumed to be in the form of HF and HBr with no Br_2 production, is 4 moles for every mole of Halon 1301 that decomposes. This means that only 1 mole (~149 g) of Halon 1301 must decompose to saturate a fresh TCCS SBA. It is possible to produce this total load within ~225 hr (~9.4 days) after a single Halon 1301 extinguisher release.

Of Halon 1301's thermal decomposition products, HBr, and potentially Br_2, will form lithium bromide (LiBr) on reaction with LiOH. LiBr, like LiCl, is deliquescent and can be expected to cause an increased flow resistance through the bed over time. LiBr also reacts with ammonia and amines which may be a concern for air quality control equipment that employ amines for CO_2 control. Lithium fluoride, the product from the reaction of LiOH and HF, is a fine white powder that possesses no deliquescent or hygroscopic properties.

The production of LiBr in the first 10 cm of the TCCS SBA is of most concern with respect to flow resistance increase caused by LiBr's deliquescent properties. The quantity of LiOH available for reaction in the first 10 cm of the bed is ~38 g (~1.6 moles). This amount of LiOH is theoretically consumed by processing ~238 g of Halon 1301. For a single extinguisher release, it is predicted that the TCCS SBA will require maintenance approximately 380 hr (16 days) after the activated carbon in the CBA becomes saturated. Given that this time is longer than required to consume the LiOH available for reaction in a fresh TCCS SBA and also does not account for competitive reaction of LiOH with HF, it is likely that TCCS flow control will not be compromised before the TCCS SBA's acid gas removal capacity is depleted.

The possibility that the TCCS SBA may already be nearing its end-of-life at the time of a Halon 1301 discharge event must be considered. Because the normal TCCS SBA service life is limited by flow resistance increase caused by reaction of HCl with the ~1.6 moles (~38 g) contained in the first 10 cm of the bed, this leaves approximately 2.38 moles available for acid gas removal for an aged TCCS SBA bed. This quantity of LiOH is consumed by processing ~89 g of Halon 1301. In the case of a single extinguisher release event, the TCCS SBA function for an aged bed is depleted within ~130 hr (~5.4 days).

5.1.7.6 Conditions Leading to Hazardous Thermal Decomposition Product Buildup. In the event that TCCS operation continues beyond 5 days after a single Halon 1301 extinguisher release event, toxic oxidation products may be introduced into the cabin atmosphere. The HF, HBr, and Br_2 products are not very soluble in water so no significant assist via absorption by humidity condensate can be claimed. Removal via other means is also difficult for these compounds. After a single Halon 1301 extinguisher discharge with combined TCCS and BMP operation for 5 days, the cabin concentration is predicted to be ~1,397 mg/m^3. Processing this concentration by the TCCS COA with no downstream hazardous oxidation product removal due to a saturated SBA bed results in Br_2 reaching the default 0.1 mg/m^3 SMAC within ~15 min. Under this condition, HF and HBr are predicted to reach the default SMAC within ~18 and ~74 min, respectively. This assessment indicates that operating the TCCS longer than 5 days for removing a large amount of Halon 1301 from the cabin atmosphere presents significant risk to the long-term cabin air quality and crew health and safety.

5.1.7.7 International Space Station Contamination Control Equipment Impact Summary. The overall impact to the ISS TCC equipment potentially involves performing maintenance on the TCCS CBA and SBA beds and the BMP FOA bed. Maintenance on the TCCS COA is not necessary because the catalyst activity should recover to an acceptable level once the Halon 1301 concentration in the cabin falls below 10 mg/m^3.

To accommodate all aspects of TCCS resource consumption and appropriately manage the risk for introducing toxic thermal decomposition products into the cabin atmosphere, it is recommended that TCCS operation not exceed 4 days beyond a single Halon 1301 fire extinguisher release. This allows for a 25% operational margin relative to toxic oxidation product release into the cabin atmosphere. Extending the operation to 5 days allows for a 7% operational margin. It is also recommended that, after completing TCCS maintenance, the Halon 1301 concentration in the cabin atmosphere be reduced to <10 mg/m^3 before restarting the TCCS. This avoids excessive logistics requirements that result from using the TCCS to recover from a Halon 1301 release event and maintains a 90% operational margin with respect to introducing hazardous thermal decomposition products into the cabin.

Operating the BMP alone during the recovery period will be necessary. This places an added burden on the BMP that may reduce the service life of its beds, depending on its operational mode. Continuing to operate in its normal 20-day regeneration cycle, however, should preserve the ZPL-1M bed service life. However, the FOA bed will require replacement at the earliest opportunity. As with the TCCS, replacing the FOA bed should be done after the cabin concentration falls below 10 mg/m^3 to avoid excessive future maintenance.

5.1.7.8 Life Support Equipment Impact and Environmental Impact Ratings. Definitions of the life support equipment and cabin environmental impact rating are provided in tables 1 and 2. Based on the assessment of Halon 1301's interaction with life support system equipment, the equipment impact rating ranges between category E4 and E5 and the environmental impact level is E (>168 hr). The TCCS and BMP drive the life support system equipment impact rating. For the TCCS, the equipment impact rating is category E5 based on the need to replace both the CBA and SBA. The equipment impact rating for the BMP is estimated to be category E4 based on the need to replace the FOA bed and the potential for reduced service life for the ZPL-1M beds. The environmental impact level is E (>168 hr) because the shortest time to reduce the cabin concentration to <10 mg/m^3 is 230 hr.

5.1.8 Summary

The physical and chemical properties, environmental regulations, and spacecraft environmental control system and cabin environmental impact of Halon 1301 has been evaluated. Halon 1301, a highly effective fire extinguishing agent for class B and class C fires, has been used routinely on board the Shuttle orbiter and the Spacelab modules in both fixed and portable fire extinguishers. Background Halon 1301 concentrations have been observed on all spacecraft that employ Halon 1301 as a fire extinguishing agent. Carryover into the Mir Space Station and the ISS cabins has been observed and correlated to docking with the Shuttle orbiter. Halon 1301 is regulated as a class 1 ozone-depleting agent. Environmental regulation of Halon 1301 and similar compounds has grown in response to the 1987 Montreal Protocol and the 1997 Kyoto Protocol. Domestic regulation has placed restrictions on importing and manufacturing Halon 1301, leading to challenges with respect to its future availability and cost. Many fire extinguishing systems are replacing Halon 1301 with other agents due to regulatory requirements and pressures. Halon 1301 decomposes to form HF, HBr, and Br_2 at temperature conditions >482 °C. These thermal decomposition products have been observed during tests conducted on the TCCS catalyst. While Halon 1301 is not considered to be toxic, having an official SMAC of 11,000 mg/m^3, the thermal decomposition products are toxic and, having no official SMAC assigned, must conform to the 0.1 mg/m^3 default SMAC. Equipment impact and environmental impact rating are category E4/E5 and level E (>168 hr), respectively. The equipment impact rating is based on Halon 1301's interaction with the ISS TCCS and BMP units. The most rapid recovery, using the BMP and CDRA, is 230 hr. The effectiveness of the TCCS for recovering from a Halon 1301 release event is limited to 4 days to maintain a 25% operational safety margin for introducing toxic thermal decomposition products into the cabin atmosphere. The TCCS should not be operated when the Halon 1301's cabin concentration is >10 mg/m^3.

5.1.9 Conclusions

Conclusions from the detailed evaluation of Halon 1301's compatibility with spacecraft life support equipment and the cabin environment are the following:

- Halon 1301 is an effective fire extinguishing agent for class B (flammable liquids) and class C (electronic and electrical equipment) fires.

- Halon 1301 decomposes to form HF, HBr, and Br_2 at temperature conditions >482 °C.

- Halon 1301 depletes the expendable activated carbon resources of the TCCS and BMP within ~138 min after a single extinguisher discharge event.

- The TCCS COA decomposes Halon 1301 to form HF, HBr, and Br_2 at 10% efficiency.

- The TCCS SBA capacity for removing Halon 1301 thermal decomposition products is depleted within 5 days of a release event.

- Time to effect to reach the default 0.1 mg/m^3 SMAC for Halon 1301 thermal decomposition products produced by the TCCS COA is as short as 15 min in the event of SBA saturation.

- The CDRA may remove Halon 1301 effectively at ~50% single-pass efficiency.

- The elapsed time to remove a Halon 1301 after a single extinguisher discharge into the cabin is >230 hr.

5.1.10 Recommendations

In the case of continued Halon 1301 use through the retirement of the Shuttle orbiter, the prevailing flight rules pertaining to recovery from a Halon 1301 discharge event should be amended to shut down the TCCS and use the CDRA to supplement the Russian BMP to accelerate the recovery rate and minimize life support equipment and cabin environmental impacts.

Due to the difficulty in removing Halon 1301 from the cabin environment, regulatory issues that may lead to low supplies and increased cost, and significant impacts to the ISS cabin air quality control equipment and cabin environment, it is recommended that all future vehicles that dock with the ISS as well as vehicles and outpost habitats under design for lunar surface exploration evaluate and select a more favorable fire extinguishing agent.

5.2 Halon Alternatives Potentially Compatible With International Space Station Environmental Control and Life Support Systems

Halon 1301 is considered to be detrimental to ISS ECLS process equipment and internal process conditions according to findings documented by NASA memorandum ES22-08-006, “Compatibility of Bromotrifluoromethane with Crewed Spacecraft Cabin Environments and Life Support System Equipment,” dated February 8, 2008. As such, ISS ECLSS engineering has recommended that an alternative to Halon 1301, which is compatible with ECLS process equipment and internal process conditions, be employed as a fire suppressant to vehicles docking to the ISS. Halon 1301 alternatives are presented. These alternatives include inert gases, inert gas blends, and perfluoroalkanes. The inert gases should not have any issues with ECLS process equipment and internal process conditions. Perfluoropropane (octafluoropropane or Freon 218) has been shown to be of no issue to the ISS TCCS and to the water processing system (NASA Memo FD21(02-037), “Trace Contaminant Control Subassembly Catalytic Oxidizer Challenge Testing with Octafluoropropane and Estimation of Sorbent Bed Assembly Service Life,” March 4, 2002). However, care must be exercised to prevent contact of perfluoropropane with other ISS systems capable of temperatures >600 °C to prevent decomposition. Perfluorobutane is similar to perfluoropropane and no issues are expected. These alternatives were derived from a list generated by the Significant New Alternatives Policy (SNAP) program established by the EPA. Several other SNAP-approved alternatives to Halon 1301 were not included until a more extensive ISS ECLSS compatibility assessment can be performed.

Generally, two methods exist for the application of fire suppressants—total flooding and local application. Halon 1301 is considered by the EPA as a total flooding fire suppression agent.

Systems applying the total flooding principle apply an extinguishing agent, automatically or manually, to an enclosed space in order to obtain a concentration sufficient to extinguish the fire. This is true for any gaseous total flooding agent irrespective of its mechanism of extinguishment. Total flooding is the most common application of halons and has been employed for the protection of volumes containing essential electronics, machinery spaces on ships, aircraft engines and cargo bays, enclosed process modules in the oil and gas industry, and both crew and engine compartments on military armored vehicles.

The halons most frequently encountered in fire protection applications are bromine-containing compounds which can be generally described as liquefied compressed gases. Of the various halons available in the United States, Halon 1301 (bromotrifluoromethane or $CBrF_3$) and Halon 1211 (bromochlorodifluoromethane or $CBrClF_2$) are the two halons that have reached any commercial significance. The major application of Halon 1301 has been in total flooding systems, whereas the use of Halon 1211 has been limited mostly to local application from hand portable and wheeled extinguishers. Its ease of implementation and favorable economics have contributed a great deal with the wide use of Halon 1301 as a flooding agent. Both agents are effective on classes A, B, and C fires, however, both are considered ineffective for use on class D fires.

The Montreal Protocol was adopted by the U.S. Government in 1987, and in 1990, the President signed into law the Clean Air Act (CAA). With the CAA, the United States banned the production and import of Halons 1211, 1301, and 2402 beginning January 1, 1994, in compliance with the Montreal Protocol. The U.S. Government also imposed excise tax on halons and passed regulations to reduce emissions of halons through training and proper disposal. The fire protection industry readily accepted the challenge to find alternatives to halons and supported the early phase-out of halon production in 1994. Concurrently, industry took actions to minimize halon emissions. As a result, halon recycling emerged as an important initiative both to reduce unnecessary emissions and to ensure supplies of halons during the transition. Fire protection codes and standards were changed to discourage the use of halons for testing and training. Also, substitute techniques such as the door fan test and discharge tests with surrogate agents were developed to preclude the need for discharging halons. In addition, efforts were doubled to improve the fire detection and control systems associated with the halon systems in order to reduce the high occurrence of system discharges from false alarms.

The SNAP program was established by the EPA to evaluate and regulate substitutes for ozone-depleting chemicals being phased out under the stratospheric ozone protection provisions of the CAA. In section 612(c) of the CAA, the EPA is authorized to identify and publish lists of acceptable and unacceptable substitutes for classes I or II ozone-depleting substances. The general purpose of the program is to allow a safe, smooth transition away from ozone-depleting compounds by identifying substitutes that offer lower overall risks to human health and the environment.

Acceptable substitutes for Halon 1301 in total flooding systems are the following:

- Carbon dioxide
  - System design must adhere to OSHA 1910.162(b)(5) and the National Fire Protection Agency (NFPA) Std. 12.

- Water

- Water Mist Systems Using Potable or Natural Sea Water

- Trifluoromethane
  - $6F_3H$

  - Use should be in accordance with safety guidelines in latest edition of NFPA Standard for Clean Agent Fire Extinguishing Systems.
  - Cardiotoxicity no observed adverse effect level is 30% without added oxygen and 50% with added oxygen; lowest observed adverse effect level likely to exceed 50%.
  - Possible for use in normally occupied areas.

- IG-100 (NN100)
  - Nitrogen.
  - IG-1000 systems must include alarms and warning mechanism.
  - Personnel should not remain or reenter area after system discharge without appropriate PPE.
  - Use should be in accordance with safety guidelines in the latest edition of the NFPA Standard for Clean Agent Fire Extinguishing Systems.

- IG-01 (Argotec)
  - Argon.
  - IG-01 systems must include alarms and warning mechanism.
  - Personnel should not remain or reenter area after system discharge without self-contained breathing apparatus.
  - Use should be in accordance with safety guidelines in the latest edition of the NFPA Standard for Clean Agent Fire Extinguishing Systems.

- IG-55 (argonite)
  - 50/50 argon/nitrogen.
  - IG-55 systems must include alarms and warning mechanism.
  - Personnel should not remain or reenter area after system discharge without self-contained breathing apparatus.
  - Use should be in accordance with safety guidelines in the latest edition of the NFPA Standard for Clean Agent Fire Extinguishing Systems.

- IG-541 (Inergen)
  - 40% argon; 52% nitrogen; 8% carbon dioxide.
  - Personnel should not remain or reenter area after system discharge without self-contained breathing apparatus.
  - Use should be in accordance with safety guidelines in the latest edition of the NFPA Standard for Clean Agent Fire Extinguishing Systems.
  - Possible use in normally occupied area.

- Perfluoropropane (PFC-218, CEA-308)
  - C_3F_8.
  - High global warming potential and atmospheric lifetimes.

- Heptafluoropropane (FM-200)
  - C_3HF_7.
  - High global warming potential and atmospheric lifetimes.

- Bromochlorodifluoromethane (Halon 1211)
  - $CBrClF_2$.
  - Reported health risks with use in confined spaces.

- Perfluorobutane (OFC-410, CEA-410)
  - C_4F_{10}.
  - High global warming potential and atmospheric lifetimes.

- 2-bromo-3,3,3-trifluoropropene (BTP)
  - $C_3H_2F_3Br$.
  - Incomplete health risk evaluation.

- Sulfur hexafluoride
  - SF_6.
  - Only used in military applications and civilian aircraft.

- CF_3I
  - Possible use in normally occupied area.

Of these options, Halon 1211, FM-200, and 2-BTP have received the most interest for replacing legacy Halon 1301-based fire extinguishing systems in aviation. These three candidates are evaluated for ECLSS compatibility and cabin environmental impact at an initial screening level here.

First, for Halon 1211, the ISS TCCS and BMP equipment can handle up to 300 g (~160 mL) and minimize impacts to the TCCS SBA. This quantity saturates the TCCS and BMP activated carbon capacities and is category E5 for ECLS compatibility. Quantities of 400 g (~215 mL) can result in SBA resource consumption within ~26 days of the release in addition to the activated carbon capacity saturation. This quantity (400 g) is category E6 for ECLS compatibility. In general, the cabin environmental impact is E (>168 hr to recover). Additional impacts to Russian BMP equipment may be deactivation of the ambient temperature CO oxidation catalyst. Testing of palladium-based CO oxidation catalysts by Lockheed found that Freon 11 and Freon 12, both halo-methane compounds, caused a 30% efficiency loss within 48 hr. The specifics on the catalyst used in the BMP are unknown but it is known that it is a platinum group metal catalyst and, therefore, it must be assumed that it can be susceptible to poisoning by Halon 1211 and similar halo-methane compounds adding to the risk presented by portable fire extinguishers (PFEs) containing Halon 1211. It should be noted that Halon 1211 is not soluble in water so there are no impacts to ISS water processing systems.

The Shuttle/Spacelab program PFEs contained 1,515 g of Halon 1301 and could discharge 80% of that (1,212 g) in 4 s. For a comparable bottle volume, and assuming the extinguishing agent is liquid when in the bottle, there could be 20% more Halon 1211 in a bottle that size. That means that a PFE could contain enough Halon 1211 to exceed the ECLS compatibility category E6 threshold by 3.6 times.

In a smaller cabin, other issues come into play—a documented fatality from accidental Halon 1211 inhalation in a military tank. The publication on this event concluded that Halon 1211 ‘should be used in confined chambers only after evacuation of all personnel.'[41] This publication highlights the need for a detailed toxicology review of candidate PFE agents.

Leading alternative options to Halon-based fire extinguishing agents under evaluation as Halon replacements are FM-200 (heptafluoropropane) and 2-bromotrifluoropropene (BTP). Both FM-200 and BTP have been evaluated as Halon 1301 replacements. BTP has also been evaluated as a Halon 1211 replacement and shown to be a nearly even trade from an efficacy perspective. And, it is interesting to note that on the commercial aircraft side of Boeing that they have been looking at BTP with interest to replace Halon 1301 and Halon 1211.

The ECLSS compatibility of FM-200 finds that 453 g (310 mL) reaches the category E5 level (<75% TCC capacity consumed). Quantities >600 g (410 mL) reach the category E6 level based on saturating the removal capacity of both the TCCS and BMP leading to persistence in the ISS cabin. The quantity of FM-200 in a Shuttle/Spacelab PFE would be comparable to Halon 1301 (about 1,212 g discharge) which is about twice the quantity needed to saturate the TCCS and BMP. Once saturated, using the BMP rapid regeneration mode, it can take over a week to recover which means the cabin impact rating of 'E.' There are no impacts to the TCCS SBA nor are there any impacts to water processing systems. From an efficacy perspective, it takes more FM-200 to extinguish a fire than Halon 1211.

ECLS compatibility of 2-bromotrifluoropropene (BTP) finds that 550 g (326 mL) reaches the category E5 level (<75% TCC capacity consumed). Quantities >735 g (>436 mL) reach the category E6 level based on saturating the removal capacity of both the TCCS and BMP. A PFE containing BTP could discharge 1,327 g. That is about 1.8 times the quantity that would saturate the TCCS and BMP leading to cabin persistence. Operating the BMP in rapid regeneration mode could restore the cabin in about a week, leading to a cabin impact rating of 'E.' There are no impacts to the TCCS SBA nor to the water processing systems. The emerging knowledge on BTP efficacy compared to Halon 1211 looks very promising relative to classes A and B fires.

From these assessments, the order of PFE agent preference relative to ECLS compatibility is BTP > FM-200 >> Halon 1211. Each has drawbacks yet the BTP and FM-200 ECLS impacts are limited to TCCS and BMP removal capability degradation while Halon 1211 has other impacts that may require unscheduled TCCS and BMP maintenance. BTP has the least impact and may actually be as effective as Halon 1211. Beyond the ECLS compatibility assessment, toxicology reviews should also be conducted for all viable PFE agents.

6. FLUOROCARBON FLUID ASSESSMENTS

The following evaluations consider the ECLSS compatibility and environmental impact of several fluorocarbon-based fluids that are used as thermal working fluids in experiment payloads and cargo vehicles.

6.1 Perfluorohexane-Based Fluids

The following assessment was conducted on the perfluorohexane-based FC-72® fluid used in the Boiling Experiment Facility (BXF) and by the Japanese Aerospace Exploration Agency (JAXA) in an external equipment component aboard the ISS. The evaluation was conducted in 2004 and released under NASA memorandum FD21(04-121), "Environmental Control and Life Support System Compatibility and Remedial Response for Perfluorohexane-Based Fluids," dated September 17, 2004.

6.1.1 Background

An assessment of the ISS ECLSS compatibility and remedial response to contamination events involving perfluorohexane- (C_6F_{14}-) based fluids has been conducted. Perfluorohexane is marketed by the 3M Company as FC-72 Flourinert Brand Electronic Liquid. FC-72 has been selected for use by the JAXA and the BXF team as a thermal control working fluid. Use by JAXA is predominantly external. However, periodically equipment may be brought inside the ISS for maintenance and bringing with it the risk that perfluorohexane may escape containment. The BXF is an internal payload containing a large quantity of perfluorohexane.

A clear, colorless liquid, perfluorohexane is manufactured and distributed by the 3M Company as FC-72. It is thermally and chemically stable, nonflammable, nontoxic, and leaves no residue upon evaporation. Highly pure forms of perfluorohexane can be obtained from Aldrich Chemical Company and F2 Chemicals Ltd. For the purpose of this assessment, the fluid is referred to generically as perfluorohexane. Physical properties acquired from EM Specialty Materials, St. Paul, MN, data sheets for Fluorinert™ Electronic Liquid FC-72 are summarized in table 18.

Perfluorohexane is most likely to be introduced into the ISS cabin atmosphere when external components from the JEM external payload thermal control system are brought inside for maintenance. Leakage from a quick-disconnect coupling may result in the release of up to 75 mL of the fluid. Likewise, failure of all three containment levels of the BXF thermal control equipment may release up to 3.5 L. These cases are evaluated with respect to their impact upon ECLSS equipment and the ISS cabin environment. Evaluating the likelihood that these specific leakage events can or will occur are left to the responsible safety and reliability organizations.

Table 18. Perfluorohexane physical properties.

Property	Value
Molecular weight (g/mole)	338.04
Specific gravity	1.68
Boiling point (°C)	56
Liquid molar volume (cm^3/g-mole)*	168.8
Henry's Law constant (atm/mole fraction)	N/A
Vapor pressure (mm Hg @ 25 °C)	231.8
Solubility in water (ppm_w)	<5
Phase	Liquid
Odor	Odorless

* Estimated using method of Tyn and Calus from Reid et al. *The Properties of Gases and Liquids*. 3rd Ed., pp. 59–60, 1977.

6.1.2 Perfluorohexane Stability Considerations

While perfluorohexane is considered to be an inert material under all anticipated normal operational conditions expected to be encountered on board the ISS, cautions concerning thermal decomposition products have been noted. In particular, temperature conditions exceeding 200 °C were identified as a concern because decomposition products may include perfluoroisobutylene (PFIB) and HF. Evaluation of this concern has been addressed by a literature review and laboratory testing.

6.1.2.1 Literature Review. A literature review found that the conditions necessary to form PFIB require a perfluorocarbon-rich environment coupled with a very long exposure time combined with the presence of halogen gases. In the studies indicating decomposition, the experimental conditions involved sealing the perfluorocarbon in a tube by itself or with chlorine or bromine gas followed by exposure to high temperatures for at least 1 hr. These are conditions that are not representative of those found on board the ISS.

On board the ISS, the perflourohexane will be in the presence of excess oxygen in the cabin air and the residence time within both the TCCS COA and solid-fuel oxygen generation system (Russian acronym TGK) is less than 1 s. The maximum estimated TCCS COA residence time is 0.67 s with a process temperature of 400 °C. Residence time for the TGK is 0.76 s with exposed surface temperature on the exterior cartridge (Russian acronym TIK) no greater than 90 °C. Typically, the TIK external surface temperature is 50 °C. The TIK cartridge is designed to withstand a maximum 450 °C external surface temperature. Both units are built from 300-series stainless steel alloys presently; however, a change to the TGK may change its construction to a titanium alloy. Neither alloy possesses catalytic properties under normal equipment operating conditions.

The literature survey finding indicates that oxygen plays a role by suppressing PFIB formation. Oxygen presence may result in other products such as HF, CO, carbonyl fluoride (COF_2), CH_4, and CO_2.

Residence time is also important. For instance, an experiment where perfluoropropene flowed through a tube held at 510 °C at 1 atm and a 10-s contact time found no PFIB was formed. In contrast, a 7-hr exposure in a sealed tube at the same temperature condition found reaction products. PFIB was not found below 700 °C in this experiment.

6.1.2.2 Stability Testing. Overall, this literature survey indicated that PFIB production would not be expected under normal TCCS and TGK operating conditions. To test this hypothesis and also investigate the potential for producing other harmful oxidation products, two testing activities were defined. The first, conducted by the MSFC Chemistry Group (ED36), subjected the candidate perfluorohexane products, FC-72 and 99% perfluoro-n-hexane to a sustained temperature condition of 250 °C in a flowing gas stream in both oxidizing and nonoxidizing environments. The second testing was conducted at Rutgers University by Dr. Thomas Hartman. In this testing, the composition of 3M Company FC-72 and two samples of 99% perfluoro-n-hexane were evaluated for impurities and for decomposition products when exposed to contact time and temperature conditions representative of the TCCS COA and Russian TGK.

6.1.2.2.1 Thermogravimetric-Infrared Testing Results. This test was accomplished through MSFC's Chemistry Group using a coupled thermogravimetric-infrared (TG-IR) analysis technique. The test allowed for the appearance of carbon double bonds that would qualitatively indicate the presence of PFIB. Samples of 3M Company's FC-72 and 99% perfluoro-n-hexane from Aldrich Chemical Co. were exposed to a sustained temperature of 250 °C. Exposure times exceeded 8 min. Results showed no evolution of functional groups containing carbon double bonds for all runs. Also, no signatures indicating other decomposition products were observed.

6.1.2.2.2 Perfluorohexane Purity and Stability Under Trace Contaminant Control Subassembly and TGK Process Conditions. This testing conducted at Rutgers University involved two steps:

(1) An evaluation of the purity of 3M Company's FC-72 and samples of 99% perfluoro-n-hexane from Aldrich Chemical Co. and F2 Chemicals Ltd. was performed.

(2) A series of five flow tests representative of TCCS and TGK process conditions was done. Analytical methods were gas chromatography (GC)/mass spectrometry and GC with flame ionization detection (FID).

The 3M Company's FC-72 was found to contain 73% perfluoro-n-hexane, 18% perfluoro-2-methylpentane, 6% perfluoro-3-methylpentane, 1% perfluorocyclohexane, 2% perfluorodimethylbutane, and 0.1% perfluoromethylcyclopentane. Trace and ultra-trace quantities of other compounds were noted. The sample from Aldrich Chemical Company contained 99.4% perfluoro-n-hexane with some C_6, C_8, and C_{10} perfluorocarbons. The F2 Chemicals Ltd. sample contained 99.7% perfluoro-n-hexane, 0.1% perfluorocyclopentane, and 0.2% perfluoro-2-methylpentane.

Testing under simulated TCCS and TGK process conditions found that the perfluorohexane samples were not degraded under any conditions and no trace PFIB was detected above the method detection limit of 33.17 ppb. This testing included a condition of 450 °C in the presence of TCCS catalyst material. No other oxidation products of concern were noted.

6.1.2.3 Testing Summary. Overall, testing was conducted by two separate methods. In both sets of tests, no evidence of PFIB production was observed after exposure to a 250 °C condition for 8 min or 450 °C in the presence of a TCCS catalyst. Based upon these results, the hypothesis that PFIB is not produced under short exposure times and in the presence of excess oxygen as advanced by the literature survey is supported. Also, no other oxidation products of concern were observed.

6.1.3 Environmental Impact

Environmental impact considers the maximum amount of perfluorohexane that may be introduced into the cabin, its estimated evaporation rate, and the estimated maximum cabin concentration.

6.1.3.1 Maximum Amount of Perfluorohexane Introduced. Two scenarios are considered for assessment based upon estimated leakage defined by JAXA and the BXF team. JAXA has determined that up to 75 mL of perfluorohexane may be released. The BXF experiment contains approximately 3.5 L of perfluorohexane, and an evaluation that considers failure of all containment levels and release of the full amount into the cabin is considered.

6.1.3.2 Evaporation Rate and Dispersal in the Cabin. Using the vapor pressure documented in table 18 and a minimum cabin air velocity of 0.08 m/s, evaporation rate is estimated using a U.S. EPA technique.[11,13] For perfluorohexane, the evaporation rate at prevailing cabin conditions is 9,800 mg/s. At this rate, a 75-mL leaked volume will evaporate in <15 s. A 3.5-L leaked volume may evaporate in 10 min. Given the highly volatile nature of this material, containing it will be difficult. It must be anticipated that all of a small leak will evaporate before any effort to contain the liquid can be attempted. Likewise, a portion of a larger fluid leak may be contained but it is anticipated that a major percentage will evaporate and disperse throughout the cabin.

6.1.3.3 Estimated Cabin Concentration. Based upon the leaked volumes and material volatility, it is most likely that any leaked perfluorohexane will be dispersed throughout the cabin. The greatest concentration will be associated with the BXF facility because it will be operated while the ISS has a 371-m^3 cabin volume. Leaking the entire 3.5 L contained in the BXF payload results in a maximum 16,000 mg/m^3 (1,160 ppm_v) cabin concentration. This is well below the 11,800 ppm_v SMAC for perfluorocarbons. By comparison, the 75-mL leakage anticipated by JAXA will occur as the ISS nears assembly complete when the cabin volume approaches 930 m^3. The resulting maximum concentration from a 75-mL leak is 137 mg/m^3. Even if this leak is isolated to the USOS, the concentration may rise by no more than 25%.

6.1.4 Environmental Control and Life Support System Equipment Impact

The evaluation of an ECLSS equipment impact considers the consumption of expendable resources, hazardous interactions, and elapsed remediation time.

6.1.4.1 Expendable Resource Consumption. Because it is not likely that a credible leak of perfluorohexane can be contained in its liquid form, atmospheric scrubbing is the primary remediation means. The TCCS in the USOS and BMP in the ROS provides the primary means for atmospheric scrubbing. The TCCS CBA contains 22.7 kg of GAC. Evaluation of predicted charcoal saturation capacity by standard techniques indicates loading may be expected to be approximately 0.2 g perfluorohexane/g GAC.[1] At this capacity, >4,500 g or 2.7 L of perfluorohexane is required to saturate the CBA. Allowing for 20% operational margin, the total leakage leading to a saturated CBA condition is 2.1 L. Similarly, the BMP contains an expendable packed bed (FOA unit) containing 1.3 kg GAC and two regenerable packed beds containing 7.4 kg GAC each (ZPL-1M units). In total, the BMP may accommodate >3,200 g or 1.9 L of perfluorohexane. Its expendable GAC bed, however, can accommodate only 260 g or 153 mL of perfluorohexane. In total, the maximum quantity that may be leaked into the cabin is 3.6 L. This amount includes a 20% operational margin to account for co-adsorption effects on saturation. From a maintenance perspective, however, any leak exceeding 100 mL will require maintenance on the BMP to replace its expendable GAC bed, and any leak exceeding 1.5 L will require maintenance on the TCCS to replace the CBA. Given that perfluorohexane is not water soluble, it should have a minimal impact on elution of previously adsorbed contaminants from GAC beds.

Perfluorohexane is minimally water soluble and single-pass removal efficiency via absorption by humidity condensate is expected to be $<10^{-3}\%$, rendering the impact to water processing systems negligible.

Testing summarized earlier has demonstrated that no hazardous oxidation products are formed when cabin air containing perfluorohexane is processed by ECLSS equipment.

6.1.4.2 Estimated Remediation Time. Remediation time is directly related to single-pass removal efficiency provided by the TCCS and BMP. Flight experience with octafluoropropane (Freon 218) has demonstrated that the BMP removal efficiency is approximately 1%.[39] Compared to Freon 218, perfluorohexane has a 10 times higher GAC equilibrium capacity. Therefore, it is reasonable to expect the BMP to remove perfluorohexane at up to 10% efficiency. The TCCS, in comparison, by virtue of its much larger fixed GAC bed, can provide nearly 100% removal efficiency for up to 50% of its rated capacity. Beyond 50% capacity, removal efficiency will be expected to decrease until it reaches zero. Therefore, for any leaked amount up to 2 L, 100% TCCS removal efficiency and 10% BMP removal efficiency are expected.

Based upon the projected TCCS and BMP performance, figure 42 shows the concentration decay rate predicted for leaked perfluorohexane isolated to the USOS (190 m^3), dispersed throughout the entire ISS cabin based upon the flight 4R configuration (371 m^3), and dispersed throughout the cabin at assembly complete (930 m^3). For these different levels of contamination dispersion, the time to reduce the concentration by 90% ranges from 30 hr to nearly 120 hr.

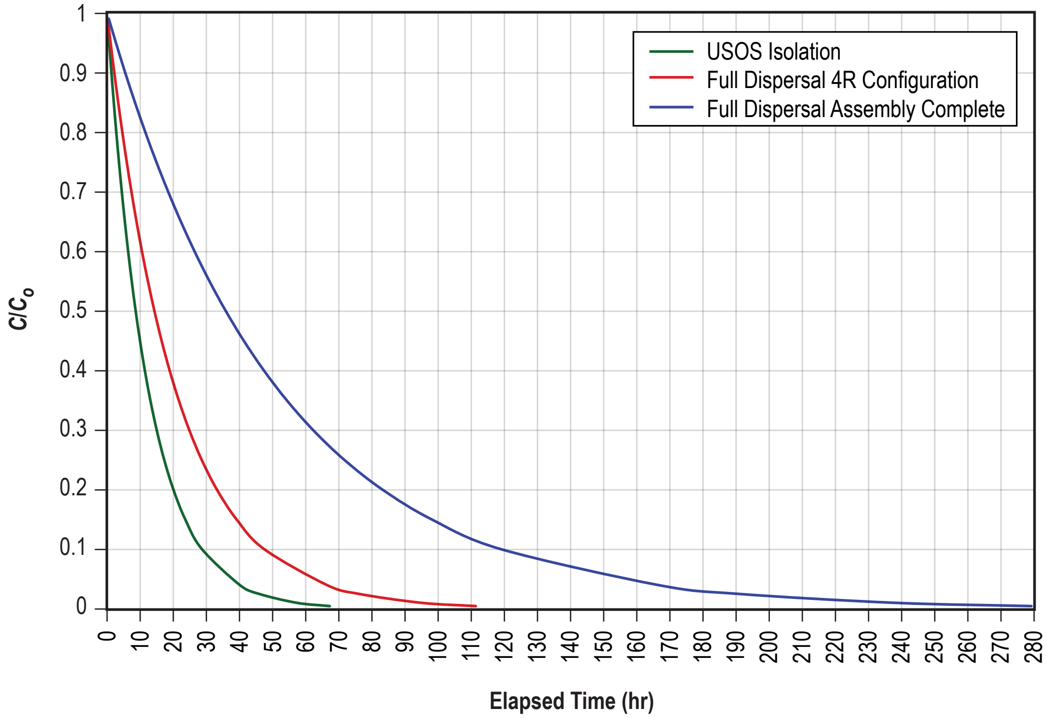


Figure 42. Estimated remediation time using ECLSS equipment.

6.1.4.3 Summary Observations. Evaluation of two scenarios—75 mL and 3.5 L total leaked volume—finds that >2 L of perfluorohexane is necessary to alter the normal TCCS and BMP maintenance cycle. Perfluorohexane is sufficiently volatile to assume that leaked volumes <1 L will fully evaporate and disperse throughout the cabin. It will be very difficult to contain any leaked liquid before it evaporates. The TCCS and BMP working together are expected to be able to remove any contamination resulting from the release of perfluorohexane into the cabin environment. Maximum cabin concentration does not exceed that necessary to protect crew health and safety. No impact is expected with respect to water processing systems because perfluorohexane solubility in water is minimal. The elapsed time to reduce cabin concentration by 90% is as long as 120 hr, depending upon the Station's assembly level.

6.1.4.4 Environmental Control and Life Support System Compatibility and Remediation Ratings. Hardware and environmental impact categories consider the impact upon ECLSS equipment function and consumable resources as well as the rate that the contamination can be removed from the ISS's cabin environment. Categories for both hardware and environmental impact are summarized in tables 1 and 2.

The ECLSS compatibility rating is highly dependent upon the amount of perfluorohexane leaked. The ECLSS compatibility rating for a 75-mL release of perfluorohexane into the ISS cabin is category E0 to E1. A release >2 L has a compatibility rating of E4 because early replacement of the TCCS CBA and the BMP FOA filter unit may be required. Therefore, a 3.5-L leak from the BXF payload is considered E4 for ECLSS compatibility. While replacement of the expendable packed beds from the TCCS and BMP may not be required immediately, such replacement is considered a prudent response to a substantial leaked volume.

Environmental impact is also dependent upon the leaked amount as well as the cabin volume. Isolation to the USOS and dispersal throughout the ISS cabin for the flight 4R configuration are both classified as category C for 90% concentration reduction. As the ISS grows and the cabin volume increases, the time to reduce contamination concentration increases because the basic scrubbing capacity remains static. Therefore, at assembly complete, the environmental impact is classified as category D because 90% concentration reduction takes 5 days or more.

It should be noted that, in all cases, including the release of 3.5 L of perfluorohexane, the maximum cabin concentration does not exceed the allowable for crew health protection. Given this observation, a strong argument can be made that the environmental impact can be classified as category A.

6.1.5 Recommendation

Perfluorohexane is highly volatile and it is expected to evaporate completely for most leakage scenarios. Leakage from the quick-disconnect coupling on the order of <100 mL is considered to be of no impact to ECLSS equipment functional maintenance or the cabin environment. Leaked volumes >2 L are considered an impact to ECLSS requiring early replacement of expendable GAC beds. Replacement does not have to be immediate but at the earliest time logistically possible. While leakage scenarios investigated do not result in cabin concentration exceeding that necessary to maintain crew health and safety, all efforts to reduce the concentration as rapidly as possible must be made. Because potential logistical impacts can result from leaks >2 L, any equipment that contains >2 L of fluid must provide appropriate containment to reduce the likelihood that the full amount of perfluorohexane can be released.

6.2 Reaction of Perfluorinated Compounds Under Environmental Control and Life Support Process Conditions

The following assessment was conducted as a supplement to the work reported in September 2004 on FC-72. The supplemental evaluation was conducted in 2005 and released as NASA memorandum EV50(05-008), "Evaluation of Extent of Reaction of Perfluorinated Compounds Under International Space Station Environmental Control and Life Support System Atmosphere Revitalization Process Conditions," dated December 23, 2005.

6.2.1 Background

The design and operation of the ISS requires identifying and evaluating chemical compounds that may present reactivity and compatibility risks with the ECLSS. Such risks must be understood so that appropriate design and operational controls, including specifying containment levels, can be instituted or an appropriate substitute material selected.

As part of the ongoing effort to ensure ISS ECLSS functionality, flight safety, and minimize environmental impact, ISS system and payload facility designers have asked for evaluation of the 3M Company material, FC-72. Specifically, the JAXA and the BXF project team at NASA's Glenn Research Center requested an evaluation of ECLSS compatibility and environmental impact for FC-72. According to testing and chemical analysis conducted according to NASA ECLSS engineering specifications at Rutgers University, FC-72 is primarily n-perfluorohexane (73.2%) with several branched carbon chain and cyclic perfluorohexane isomers constituting 26.8%. This assay is consistent with information provided by FC-72's manufacturer, the 3M Company. This assessment supplements the ECLSS compatibility and environmental impact assessment documented in section 6.1.

NASA toxicology evaluations for the JAXA and BXF scenarios identified the potential for relatively low temperature (<250 °C) thermal decomposition of some highly branched carbon chain perfluorocarbons to PFIB. Several references are cited in the toxicology assessments in support of the hypothesis that PFIB can be formed from impurities found in FC-72. Of the impurities, perfluorodimethylbutane isomers present the most concern, most notably perfluoro-2,2-dimethylbutane, with respect to the potential for producing hazardous thermal decomposition and thermal oxidation products under some ISS ECLSS process conditions. Specific testing was conducted according to NASA ECLS engineering specifications at Rutgers University to determine whether the hazardous products are indeed produced when cabin air containing FC-72 enters the TCCS COA or the Russian solid oxygen generator (TGK). The detection limit for PFIB used for the experiments and based on an analytical reference standard was originally reported as ~33 ppb_V. However, further evaluation found that the strong signal-to-noise ratio of the PFIB peak in the analytical data indicates the detection is at least 10 ppb_V.[42] No detectable PFIB was noted in any of the experimental runs.

After the evaluation by Rutgers University, the NASA toxicology organization presented critiques of the experimental method. These critiques centered on volume expansion of the injected FC-72 leading to shorter residence time in the reactor and cooling effects associated with evaporating the 1-mL FC-72 test sample. The criticisms have been evaluated by ECLSS engineering personnel, found to be inconsequential to the experimental result of no detectable PFIB, and communicated to the NASA toxicology organization. Unfortunately, the NASA toxicology organization continues to insist that the ECLSS testing is flawed, and therefore, refuses to recognize the validity of the ECLSS testing result despite the weight of evidence presented that fully supports that result. Further, evaluation of the literature citations contained in the NASA toxicology organization's evaluations finds that experimental conditions used in those citations differ significantly from conditions that exist within ECLSS processes. Most specifically, the literature citations indicate very long contact times on the order of hours and pressures to 35 atm under static conditions compared to the dynamic ECLSS process conditions where residence time is <1 s and pressure is 1 atm. It should be noted that independent, qualitative testing by NASA using thermogravimetric infrared methods that also showed no measurable presence of species containing carbon double bonds that would be indicative of PFIB formation after >8 min exposure to conditions at 250 °C in both oxidizing and nonoxidizing environments have met with no criticism.

The ECLSS engineering response to the NASA toxicology organization's critiques, an evaluation of the literature experimental conditions, and an evaluation of expected extent of reaction of perfluoro-2,2-dimethylbutane are provided so that the inherent risk associated with using FC-72 for various uses on board the ISS can be best understood and appropriate recommendations regarding its use made.

6.2.2 Response to Environmental Control and Life Support System Testing Critiques

Critiques of the testing conducted for NASA at Rutgers University addressed two primary areas: (1) That the FC-72 injected into the experimental reactor apparatus results in excessive volume expansion leading to inadequate contact time, and (2) that the evaporation of FC-72 causes significant cooling in the experimental process gas stream such that the reactor temperature will not be representative of the ISS TCCS COA and Russian TGK conditions. These critiques are addressed by the following summaries.

6.2.2.1 Effect of Volume Expansion on Experimental Reactor Residence Time. The important parameters in this instance are the effects that the combination of the evaporation rate of the FC-72 sample into the process gas stream and the control of the carrier gas flow rate may have on the residence time through the experimental reactor. The experimental approach isolated the injection point from the heated zone of the experimental apparatus and the carrier gas flow rate was monitored downstream of the reactor and injection point using a National Institute of Standards and Technology (NIST) traceable flow controller. The flow control set point was maintained at 100 mL/min.

At the experimental conditions and assuming that the entire 1-mL FC-72 sample was injected nearly instantaneously and heated rapidly to >300 °C, the process gas flow past the sample promotes an evaporation rate of 0.4 g/min at the injection point. It must be noted that this evaporation takes place before the heated zone where the entire flow stream is heated to the desired temperature. Therefore, the actual temperature at the injection point and the subsequent evaporation rate is actually slower. This, in fact, is supported by thermal analysis of the testing apparatus that shows that the temperature at the injection point is expected to be <50 °C. Using the higher temperature, however, is instructive because it is a conservative assessment of the potential effect on experimental reactor residence time. At this condition, an increase in volumetric flow to 162.7 mL/min is predicted.

Because the process gas flow was being controlled via a feedback loop, any volume expansion would have been compensated for by reducing the process gas flow. Thus, less process air would flow into the experimental apparatus to accommodate the additional 62.7 mL/min volumetric flow. Conservatively, even if process gas flow control compensation did not occur and the full 162.7 mL/min flow passed through the reactor, the net effect is to reduce the residence time in the experimental reactor from 1.9 s (9-mL catalyst volume with 0.35 void fraction) to 1.2 s.

Compared to the TCCS COA residence time of 0.67 s (0.41 s exposed to the catalyst), the testing conditions are conservative by at least 79% when using the full TCCS COA residence time and accounting for worst-case volume expansion. For the catalyst bed residence time, the testing conditions are conservative by 193% when worst-case volume expansion is considered. The case for the Russian TGK is much more conservative. The empty experimental apparatus provides 14.2 s contact time without accounting for a flow spike and 8.7 s when accounting for a flow spike. The Russian TGK residence time is approximately 0.76 s. So, under worst-case conditions, the experimental apparatus contact time condition is >1,000% longer than is experienced within the TGK. Therefore, the

ECLSS engineering conclusion is that conditions provided by the experimental apparatus used by Rutgers University are highly conservative with respect to actual contact time provided by ECLSS processes and FC-72 sample volume expansion effects are inconsequential to experimental results.

6.2.2.2 Effect of Sample Evaporative Cooling on Experimental Reactor Temperature. The total energy required to evaporate a 1-mL sample of FC-72 is 147.8 J (latent heat of vaporization is 88 J/g). A high-power heater was used in the experiment to bring the entire reactor apparatus to a stable thermal condition before sample injection begins. The process gas (air) flowing through the experimental apparatus at 100 mL/min requires 57.1 J/min (~1 W) to heat from 20 to 450 °C. The entire testing apparatus including the tubing, catalyst, and insulating materials at the 450 °C testing condition represents significant thermal capacitance and the heater must be oversized to heat and maintain the apparatus to the experimental conditions as well as accommodate all energy losses. For example, the catalyst itself possesses 5,400 J stored energy at the experimental condition. The stainless steel tubing adds to the stored energy total but is neglected to allow a nonconservative case to be considered.

To reduce the catalyst's temperature by 1 °C, 12.6 J of energy must be removed above that required to maintain the reactor's temperature condition without making it up. If the sample's liquid temperature rise from ambient to the 56 °C boiling point (57.3 J) plus the latent heat of vaporization (147.8 J) is conservatively assumed to be supplied inside the reactor from energy stored by the catalyst, it is estimated that under this absolutely worst case, the catalyst temperature could decrease by 16.3 °C. Even under this condition, the lowest catalyst temperature, 433.7 °C, is 8.4% higher than the actual TCCS process condition. Given that, in reality, the sample heating and evaporation occurs before entering the reactor and the heater is able to compensate for all energy losses, including sample heating, then the magnitude of any thermal transient resulting from injecting the FC-72 sample into the experimental apparatus is likely much less than the worst-case prediction.

Specifics regarding temperature control employed by the test apparatus must be considered also. For the experimental apparatus, a small hole was drilled through the stainless steel ½-in reactor tube and a Swagelok fitting was welded in place. A J-type thermocouple with a stainless steel sheath, used with the temperature controller, was inserted into this opening and sealed inside the reactor tube within the reactor. The reactor contained catalyst or was open volume, depending on the experimental run. The Swagelok fitting is underneath insulation. The normal flow of air or nitrogen was passed through the tube during measurements. The temperature controller used the J-thermocouple feedback to regulate temperature approximately ±1 °C. This allowed temperature measurement internally in the flow stream. In this way, the true temperature of the catalyst and sample gases was controlled.

Further, thermal modeling shows results consistent with this simple assessment and experimental apparatus temperature control arrangement. Based on these considerations, the ECLSS engineering assessment finds that evaporative cooling effects within the experimental apparatus are inconsequential to the experimental results obtained. Temperature conditions maintained during all experimental runs are conservative relative to the ISS TCCS and Russian TGK.

6.2.3 Predicted FC-72 Impurity Extent of Reaction

The experimental conditions used for assessing the decomposition of the components comprising FC-72 have been established to be conservative relative to ISS ECLSS process conditions. Further, the ECLSS process temperature conditions within the TCCS and Russian TGK exceed the temperature where some branched carbon chain perfluorocarbon compounds may decompose to produce hazardous products such as PFIB according to literature sources cited by the NASA toxicology organization. To understand the extent of PFIB production during contact with heated ECLSS process equipment and to better understand the ECLS testing results, reaction rate data and conditions favorable to PFIB formation must be understood. Therefore, a review of the literature cited by the NASA toxicology organization with regard to its relevance to ISS ECLSS process conditions is necessary. Other literature sources are also reviewed to understand contributing and inhibiting factors associated with PFIB formation under high temperature conditions.

6.2.3.1 Relevance of Cited Literature to International Space Station Environmental Control and Life Support System Conditions. Review of the primary literature sources cited by the NASA toxicology organization finds that the experimental conditions were specifically tailored to form pyrolysis products so that reaction mechanisms could be studied. Specifically, each 10-mmole experimental sample under evaluation was sealed in a 10-mL glass tube and held at a high temperature for 8 to 15 hr. During this time, pressure in the reaction volume could rise to ~34 atm. To promote reaction, other compounds such as halogens or toluene were injected in some instances.[43,44] All experiments were conducted in the absence of air or oxygen. This is a key point of departure from actual ISS ECLSS process conditions. It is also important because studies conducted at Oak Ridge National Laboratories found that PFIB formation is suppressed in the presence of oxygen.[45,46] As well, references 45 and 46 as well as reference 47 indicate PFIB hydrolysis by moisture in the air will occur with HF, CO, COF_2, and CO_2 as the resulting products. Overall, the literature sources cited by the NASA toxicology organization are meaningful only to the extent that reaction rate data are provided for perfluorocarbon compounds similar in structure to perfluoro-2,2-dimethylbutane.

Because the experimental conditions with respect to residence time, pressure, and nonoxidizing conditions are not in any way representative of those of the ISS ECLSS processes reduces the cited references to the level of information only. At most, these reference materials demonstrate that hazardous thermal decomposition products are produced under static conditions over a long contact time. Such conditions are extraordinary compared to those that exist on board the ISS. Even so, the potential for thermal decomposition should not be taken lightly and efforts to best understand the situation presented by the JAXA and BXF scenarios must be undertaken. Therefore, to achieve a complete, conservative assessment, reaction rate data from references 43 and 44 are considered for predictive purposes with appropriate adjustment to eliminate the effects of radical traps. It must be noted that, although highly likely under ECLSS process conditions, further reaction of PFIB with oxygen and moisture to form other products is not considered and, as such, the predictions that follow are considered to be conservative. The degree of conservatism, unfortunately, cannot be fully quantified except to apply the predictive technique as a check of the observed ECLS compatibility testing results.

6.2.3.2 Predicted Extent of Reaction. While review of the available literature on the subject of hazardous thermal decomposition products demonstrates that the documented experimental conditions are not in any way representative of the ISS ECLSS process conditions, it is prudent to consider the reaction rate data contained in these sources as a potentially conservative means to estimate PFIB formation. Of the perfluorohexane isomers present in FC-72, the most likely to thermally decompose to PFIB is perfluoro-2,2-dimethylbutane. Perfluoro-2,2-dimethylbutane, combined with perfluoro-2,3-dimethylbutane, comprise approximately 1.7% of FC-72. Of all the isomers, however, only perfluoro-2,2-dimethylbutane has the potential to thermally decompose at ISS ECLSS process conditions to produce PFIB. All other isomers are not expected to decompose according to the cited literature.[48]

By using, as a basis, a rate constant at 181 °C (0.77×10^{-5} s^{-1}) from data acquired by Rutgers University for a similar compound that may produce PFIB among its three decomposition products, a reasonable rate constant estimate at 400 °C is made using the Arrhenius equation.[49] The result is 0.78 s^{-1}. This is a first order rate constant and does not reflect the enhancement of the rate constant in the presence of radical traps. Pressure effects on the rate constant are not considered because rate constant decrease is typically not observed until pressure falls below 200 torr.[49]

6.2.3.2.1 Predicted Perfluoroisobutene Production by the Trace Contaminant Control System. For the case of the JEM application where 75 mL (0.37 moles) of FC-72 leaks, the predicted cabin concentration of perfluoro-2,2-dimethylbutane is 1.74×10^{-5} moles/m^3. For the purposes of this assessment, it is assumed that the TCCS charcoal capacity is completely consumed and all the FC-72 and its impurities enter the COA. In the TCCS COA, the maximum residence time is 0.67 s. Using a solved form of a first order plug flow reactor mass balance equation, the single-pass extent of reaction is 41%.[50,51] Keeping in mind that three or more different decomposition products result, the extent of reaction to PFIB is 13.5%. If it is assumed that the perfluoro-2,2-dimethylbutane isomer conservatively accounts for all of the 1.7% perfluorodimethylbutane impurity in FC-72, then the maximum PFIB concentration in the TCCS exhaust gases, in the event of a 75-mL release, is 0.14 mg/m^3 (0.02 ppm_v). PFIB is easily removed by activated carbon so the absolute maximum cabin concentration that may result from sustained FC-72 processing via the TCCS COA at an inlet concentration representative of a 75-mL FC-72 leak is 0.05 mg/m^3 (6 ppb_v). Production, of course, is transient as the FC-72 concentration in the cabin is reduced.

6.2.3.2.2 Predicted Perfluoroisobutene Production by the Russian TGK. The rate constant calculated for temperature conditions encountered in the Russian TGK is 0.0016 s^{-1}. For a 0.76-s residence time, the maximum extent of FC-72 impurity reaction to decomposition products is 0.12%. The extent of reaction to PFIB is 0.04%, given the potential for other decomposition products. The maximum PFIB concentration in the Russian TGK effluent gases resulting from a 75-mL release of FC-72 that could occur from exposure to conditions within the TGK is 0.0014 mg/m^3 (0.2 ppb_v). The absolute maximum cabin concentration that could result after a 75-mL release of FC-72 and subsequent contact with the Russian TGK is 0.0026 mg/m^3 (0.3 ppb_v). Again, this is a steady state concentration assuming sustained FC-72 concentration in the cabin. The cabin concentration, of course, is transient so the cabin concentrations will be very low.

6.2.3.2.3 Implications for the Observed Environmental Control and Life Support Compatibility Testing Results. Applying the rate constant data to the ISS TCCS COA testing conducted by Rutgers University, the highest calculated extent of reaction predicts ~0.01 mg PFIB/m^3 (~1.3 ppb$_v$) in the test gas effluent. This is far lower than the analytical method's ~10 ppb$_v$ detection limit. Therefore, the ECLS process experimental results are indeed expected because, even under the most conservative conditions, the maximum amount of PFIB formed is predicted to be far below the analytical method detection limit.

6.2.3.2.4 Considerations for Perfluoroisobutene Reaction in Humid Air. It must be kept in mind that in the presence of oxygen and humidity and under higher temperature conditions encountered in the ISS ECLSS processes, PFIB will very likely react further or its formation may be depressed. Other reaction products expected in humid air include CO, HF, COF_2, and CO_2. These effects are not quantified by available literature sources or ECLS compatibility testing data so cannot be accounted for in any risk assessment. Further testing using analytical methods that target these compounds is necessary to fully understand the role that oxygen and humidity play in PFIB's persistence under high temperature conditions. Also, the perfluoro-2,2-dimethylbutane isomer is present in lower quantities than assumed for this assessment. For example, an assay provided by the 3M Company indicates it is present at 0.74%. Therefore, the calculated results are conservative by approximately a factor of 2. For the conservative assessment, the threshold for FC-72 leakage is 125 mL to maintain local PFIB concentration <0.08 mg/m^3 (0.01 ppm$_v$). Given that there is likely at least a safety factor of 2 associated with the ECLS engineering assessment, then the 150-mL leakage threshold to protect ISS Russian Segment ECLS equipment established by earlier evaluation is within allowable limits for overall vehicle risk.

6.2.3.2.5 Considerations for FC-72 and Perfluoroisobutene Removal by Activated Carbon. Previous ECLS assessment conducted by NASA MSFC found the equilibrium GAC loading for FC-72 is 0.2 g/g GAC. At this capacity, >4,500 g or 2.7 L of perfluorohexane is required to saturate the 22.7 kg of GAC in the USOS TCCS's CBA. Allowing for 20% operational margin, the total leakage required to saturate the CBA is 2.1 L.

Similarly, the micropurification assembly (BMP) in the ROS contains an expendable packed bed (FOA unit) containing 2 kg GAC and two regenerable packed beds (ZPL-1M units) containing 2.8 kg GAC combined. In total, the BMP may accommodate ~960 g or 570 mL of perfluorohexane. Its expendable GAC bed, however, can accommodate only 400 g or ~240 mL of perfluorohexane.

In total, the maximum quantity that may be leaked into the cabin leading to complete saturation of the TCCS and BMP is 2.6 L. This amount includes 20% operational margin to account for co-adsorption effects on saturation. From a maintenance perspective, however, any leak exceeding 120 mL will require maintenance on the BMP to replace its expendable GAC bed and any leak exceeding 1.5 L will require maintenance on the TCCS to replace the CBA. Given that perfluorohexane is not water soluble, it is expected to have minimal impact on elution of previously adsorbed contaminants from GAC beds.

6.2.4 Summary

In summary, critiques of the ECLSS compatibility testing conducted by Rutgers University have been evaluated and found to have no bearing on the observed experimental results. In fact, further review shows the experimental results are consistent with what would be expected. Relevance of experimental conditions of cited literature sources regarding PFIB formation from branched carbon chain perfluorohexane isomers contained in FC-72 have been compared to actual ISS ECLSS process conditions and found to be significantly different with respect to their static contacting scheme, contact duration, lack of oxygen, and pressure. Reaction rate data from the cited literature sources, although considered conservative, have been used to predict PFIB formation within ECLSS processes during FC-72 leakage scenarios. Scenarios for a 75-mL leak defined by JAXA indicate the maximum theoretical PFIB concentration is below allowable limits even when further reaction with oxygen and moisture are not accounted for. The reaction rate data, when applied to the Rutgers University experimental configuration, fully support the observation that PFIB concentration was below the ~10-ppb_V method detection limit and, therefore, the experimental result is credible and expected. Further, the ECLSS engineering evaluation finds that using a 200-mL leakage threshold to protect equipment provides appropriate cabin environmental impact protection. Given the further consideration that ISS ECLSS maintainability impacts are not expected until the volume of leaked FC-72 exceeds 1.5 L, designs for equipment that contain FC-72 that include multiple containment levels and demonstrate design for minimum risk are considered acceptable for use within the ISS cabin.

6.2.5 Recommendations

It is recommended that FC-72 use be allowed in the ISS cabin in limited quantities. Quantities >200 mL and <1 L must provide necessary hazard controls, including multiple containment levels, and demonstrate design for minimum risk. For quantities >1 L, consideration should be given to using highly pure forms of n-perfluorohexane to achieve minimum risk. Further testing to better understand PFIB's stability at ECLSS process conditions in the presence of humid air is recommended for completeness.

6.3 Perfluoromethylpentane-Based Fluids

The following assessment was conducted in 2008 and released under NASA memorandum ES21 08 057, "Compatibility of Perfluoro-2-Methylpentane with the International Space Station's Environmental Control and Life Support System," dated July 2, 2008.

6.3.1 Background

Space Exploration Technologies Corporation (SpaceX) is developing a spacecraft capable of transporting cargo and crew to the ISS. Called Dragon, the spacecraft is scheduled for three demonstration flights. The first flight is targeted for 2009. This 5-hr flight will serve to verify launch, communications, guidance, thermal control, reentry, and recovery systems performance. The second demonstration flight is also planned for 2009. This 5-day flight will demonstrate rendezvous and breakaway operations with the ISS. The final demonstration flight, scheduled for 2010, lasts 3 days. The objective for the third flight is to demonstrate a complete cargo mission profile, including docking with the ISS.

The Dragon spacecraft designers are investigating candidate fluids for the vehicle's thermal control system (TCS). The candidate thermal working fluids, which are in the perfluorocarbon class, are the following:

- FC-72 manufactured by 3M for the second demonstration flight and ground testing operations.

- Flutec PP1® manufactured by F2 Chemicals Ltd. for the third demonstration flight and long-term vehicle cargo mission operations.

- Pure perfluoro-n-hexane manufactured by Aldrich Chemicals as the alternate for the third demonstration flight and long-term cargo mission operations.

Of the three fluids under consideration, the perfluorohexane-based fluids, FC-72 manufactured by 3M and the pure perfluoro-n-hexane manufactured by Aldrich Chemicals, have been evaluated for their ECLSS equipment impacts and environmental impacts as presented in sections 6.1 and 6.2. Key findings from the earlier assessments are the following:

- Thermal stability testing under more rigorous temperature and contact time conditions than those found within USOS and ROS life support equipment, in particular the U.S. TCCS and Russian solid fuel oxygen generator (SFOG), produced no harmful oxidation products.

- Quantities >200 mL and <1 L must provide necessary hazard controls, including multiple containment levels, and demonstrate design for minimum risk as appropriate.

- Quantities >1 L should consider using pure perfluoro-n-hexane to achieve the lowest risk.

- ECLSS equipment impact rating is category E4 (>50% resource consumption) for perfluoro-n-hexane releases >1.5 L.

- Cabin environmental impact rating is category D because concentration reduction by 90% requires between 3 and 7 days.

The ECLSS equipment and cabin environmental impact rating categories are summarized in section 1.3 in tables 1 and 2.

The Flutec PP1 manufactured by F2 Chemicals Ltd. is the preferred fluid. Because it has not yet been the subject of an ECLSS equipment impact and environmental impact assessment, the following assessment focuses primarily on this thermal working fluid candidate. Flutec PP1 has been assessed for its purity and found to be comprised of 99.706% perfluorohexane compounds. The specific composition reported by the purity analysis is summarized in table 19.

As shown in table 19, the Flutec PP1 fluid is ~99.349% perfluoromethylpentane isomers with ~0.65% impurities. Table 20 provides relevant physical and chemical properties for perfluoromethylpentane. Of the impurities, the perfluoro-2,3-dimethylbutane is of most interest because it can be a beginning reactant for producing PFIB, a compound with very low tolerance in air.

Table 19. Flutec PP1 composition.

Compound	Percent Composition
Perfluoro-2-methylpentane	98.103
Perfluoro-3-methylpentane	1.246
Perfluoro-2,3-dimethylbutane	0.357
Perfluoro-2-methylbutane	0.169
n-perfluoropentane	0.107
Perfluoro-2-methylhexane	0.007
n-perfluorobutane	0.005
Perfluoro-2-methylheptane	0.004
C_9F_{16} perfluorobicyclononane isomers	0.002

Table 20. Perfluoro-2-methylpentane properties.

Property	Value
CAS number	355-04-4
Molecular weight (g/mole)	338.04
Melting point (°C)	–119.13
Boiling point (°C)	57.81
Liquid density (g/mL)	1.73
Solubility in water (mg/L @ 25 °C)	0.038
Henry’s Law constant (atm/mole fraction)	5.81×10^8
Vapor pressure (mm Hg @ 20 °C)	173
Critical volume (cm^3/mole)	532
Critical pressure (mm Hg)	14,424
Critical temperature (°C)	182.3
Acentric factor	0.464

6.3.1.1 Spacecraft Trace Contaminant Control Design Practice. The general crewed spacecraft TCC design approach is summarized in section 1.2. As noted in section 1.2, designing for spacecraft cabin TCC requires substantial design activity within the confines of the air quality standard. In the case of crewed spacecraft, that standard is the SMAC. Materials selection and control, hardware design, manufacturing processes, chemical process design, mission characteristics as well as crew size and activities are only a few of elements that must occur within the constraints of the air quality standards. A change to any of these, whether for a spacecraft system or a payload, can negatively impact cabin atmospheric quality, the ECLSS equipment, or both. An assessment of spacecraft system and payload fluids by ECLSS engineering ensures that any potential impacts to the cabin environment, as well as the ECLSS equipment, are accounted for and understood.

Because the specification of the active TCC equipment for a spacecraft precedes those data necessary to fully validate its design, standard design practice dictates a conservative approach whereby the active contamination control system performs its function unassisted by any other systems or processes in the cabin.[1] This means that overboard atmospheric leakage and assists provided by other air processing systems such as CO_2 removal and humidity control equipment are not considered during the design and validation of the active TCC equipment. To maintain consistency, all new contamination loads are assessed in the same manner.

For the ISS, the key design requirements pertaining to TCC design and performance state that trace contaminants shall be controlled to less than their respective SMAC for a normal equipment offgassing and crew metabolic load. More specifically, the U.S. Laboratory requirements state that the TCCS maintain trace atmospheric component concentration from normal equipment offgassing and crew metabolic processes to less than 90% of individual contaminant SMACs. These design specifications are for the active contamination control systems operating without assistance from other ECLS processes or overboard leakage. It is also important to note that they do not specify that the active contamination control systems on board the ISS must be designed to accommodate chronic, fugitive leaks from other systems or payloads nor do they specify that these systems' performance must be verified for such an additional contamination loading. Further, these requirements do not authorize using the active contamination control systems as hazard controls for other onboard systems or payloads.

Within the context of requirements, an additional loading of a chemical compound not contained in the design specification constitutes a new, specific verification case. As such, this verification must assume that only the active contamination control systems on board the ISS remove the added contamination load. This maintains consistency with the equipment's certification. It is informative to expand the assessment, however, to address the fate of the contamination to ensure that the impact upon all ECLSS processes—both atmospheric and water processing—are addressed.

6.3.1.2 International Space Station Trace Contaminant Control Equipment. Active TCC equipment is located in both the USOS and ROS. The USOS TCCS is located in the U.S. laboratory and the ROS BMP is located in the service module. Brief details for the TCCS and BMP are provided by the following summary.

6.3.1.2.1 U.S. On-Orbit Segment Trace Contaminant Control System. Three main components comprise the TCCS. They are an expendable activated CBA, a thermal COA, and an expendable post-SBA. Additionally, the TCCS contains a blower, a flow meter, and an electrical interface assembly. The process flow rate through the CBA is 15.3 m^3/hr. The CBA contains 22.7 kg of granular activated carbon treated with 10% by weight phosphoric acid (H_3PO_4). The H_3PO_4 treatment provides the means to remove NH_3 before the process air enters the downstream thermal catalytic oxidation reactor. Upon exiting the CBA, the process stream splits. Approximately one-third of the air (4.6 m^3/hr) flows through the COA and SBA before rejoining the bypass stream just before the system's exhaust. Principle parts of the COA include a recuperative heat exchanger, an electric heater, and a catalyst bed. The catalyst bed contains approximately 1 kg of platinum group metal catalyst supported on Al_2O_3 pellets. The process temperature in the catalytic oxidizer is 400 °C. After passing through the catalytic oxidizer, the process stream passes through the SBA, a bed of granular LiOH, to remove any acidic oxidation products. Figure 43 shows a simplified TCCS process schematic.

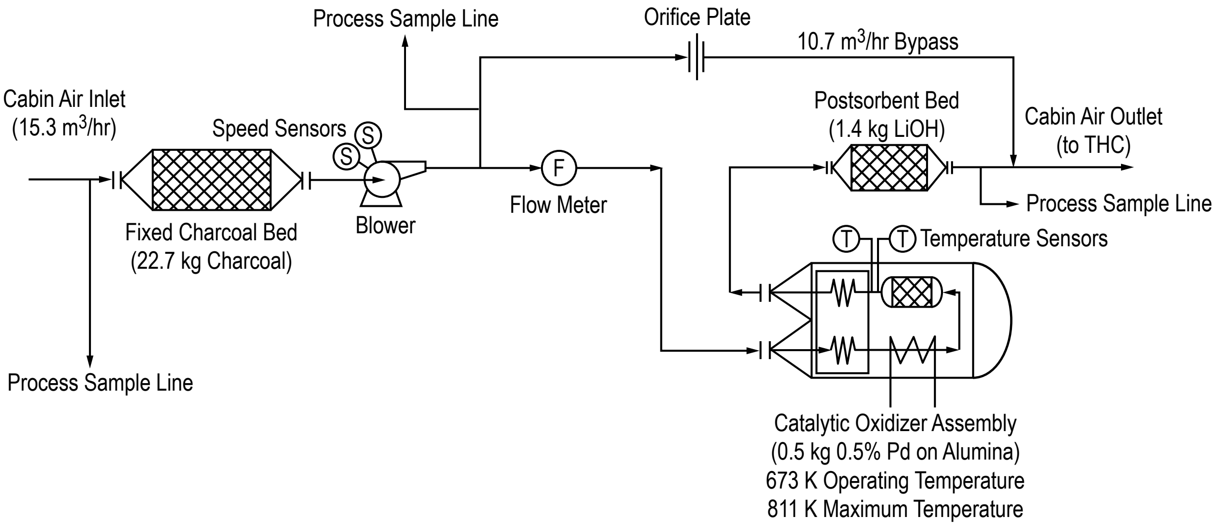


Figure 43. Simplified USOS TCCS process diagram.

6.3.1.2.2 Russian On-Orbit Segment Micropurification System. The ROS BMP unit contains three components—the expendable FOA activated carbon bed, two ZPL-1M regenerable activated carbon beds, and the PKF ambient temperature catalytic oxidation bed. Air flow through the BMP unit is ~25 m^3/hr. The BMP's FOA bed contains 2 kg of granular activated carbon while the two regenerable ZPL-1 beds contain 1.4 kg granular activated carbon each. The ZPL-1M beds are regenerated using a combined thermal-vacuum swing process at a 20-day interval. Figure 44 shows a simplified BMP process diagram.

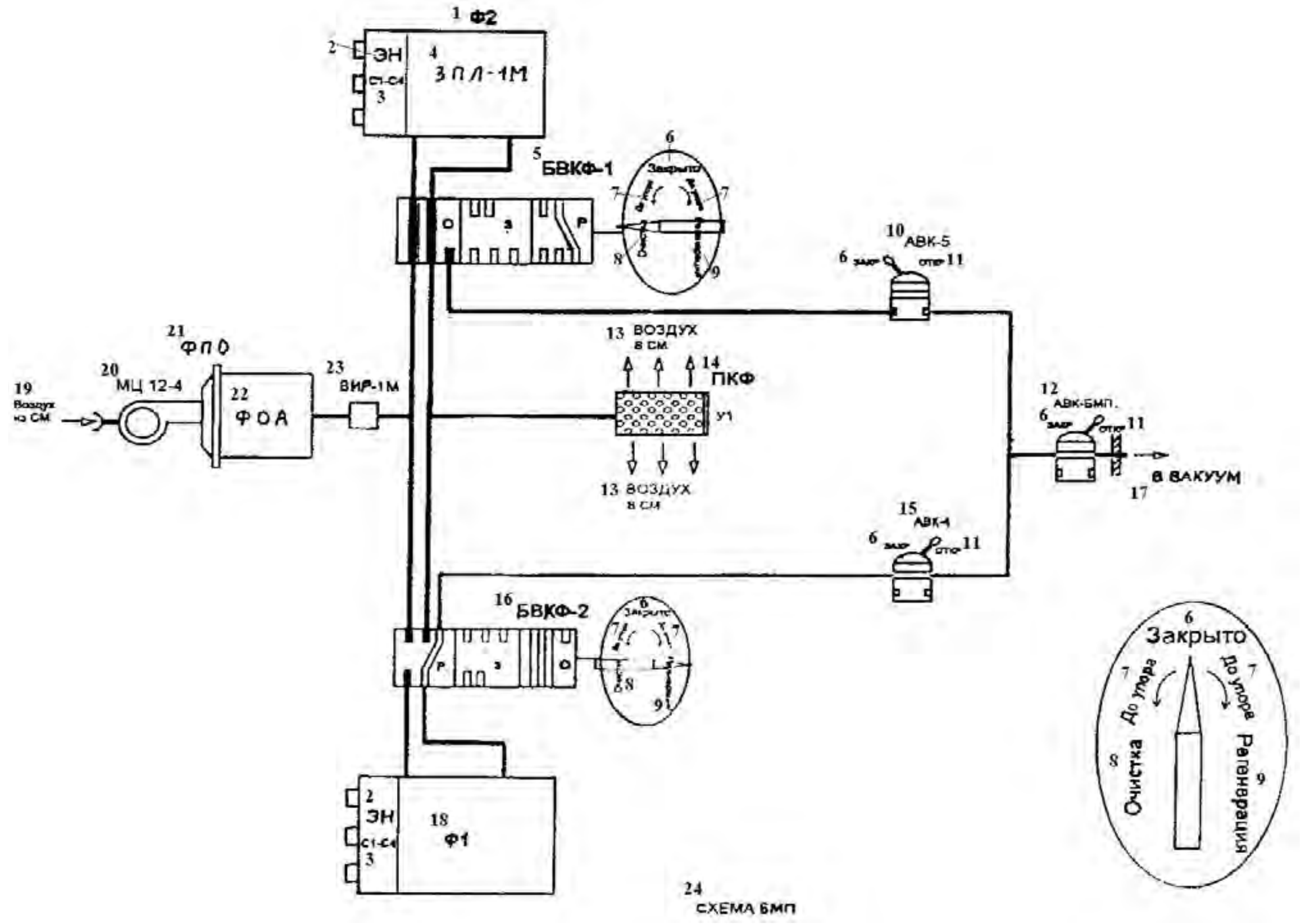


Figure 44. Simplified ROS BMP process diagram.

6.3.2 Purpose

The engineering assessment summarized by the following discussion addresses the compatibility of perfluoro-2-methylpentane with ISS ECLSS equipment and the potential environmental impact.

6.3.3 Objective

The approach to maintaining acceptable cabin air quality in the ISS cabin in the event of a perfluoro-2-methylpentane release is assessed by engineering analysis. The primary objective of the assessment is to address interactions with ECLSS equipment and process conditions and to recommend appropriate actions, if any, necessary to ensure ISS cabin environmental conditions comply with relevant specifications and guidelines in the event of a perfluoro-2-methylpentane release into the cabin.

6.3.4 Assumptions

To conduct the perfluoro-2-methylpentane compatibility assessment, assumptions must be made concerning the cabin atmospheric conditions, payload hardware configuration, and TCC hardware configuration.

6.3.4.1 International Space Station Cabin and Docked Vehicle Conditions. Basic assumptions pertaining to the ISS cabin and SpaceX Dragon vehicle conditions are the following:

- Cabin conditions are on average 21 °C, 50% relative humidity, and 1 atm.
- The ISS habitable volume is the 20A assembly stage with ATV cargo carrier docked, totaling ~834 m^3.
- The SpaceX Dragon vehicle volume 14.5 m^3 empty and 8 m^3 when loaded with cargo.
- The maximum credible leak of perfluoro-2-methylpentane is 1.15 L.
- The 85,000 mg/m^3 perfluoroalkane compound SMAC defined by JSC 20584 applies.

6.3.4.2 On-Orbit Configuration. During the SpaceX Dragon vehicle operations, it is assumed that the ISS will have achieved the 20A assembly stage configuration at a minimum. The 20A stage assembly habitable on-orbit configuration consists of PMA-1, Unity (Node 1), Destiny (U.S. Laboratory), Quest (U.S. airlock), Harmony (Node 2), Tranquility (Node 3), Columbus APM, Kibo ELM-PS, Kibo pressurized module (PM), Zarya (FGB), Zvezda (SM), a Soyuz spacecraft, a Program cargo vehicle, and the Jules Verne ATV. The ISS's total habitable volume is approximately 834 m^3. The USOS contributes 548 m^3 to the Station's total habitable volume while the ROS contributes 286 m^3.

The SpaceX Dragon vehicle is transported to the ISS via the Falcon 9 launch system, also built by SpaceX. The Dragon vehicle may be configured for either cargo or crew transportation. When empty, the Dragon vehicle's free volume is 14.5 m^3. Fully loaded with cargo, the vehicle's free volume is reduced by 6.5 m^3 to 8 m^3 during the transit period from launch to docking with the ISS. The Dragon vehicle's TCS design employs an all-welded construction with its cabin. The bulk fluid quantities are contained in externally mounted accumulators and other system components.

6.3.5 Approach

The ECLSS engineering assessment addresses the impacts from a bulk 1.15-L release of perfluoro-2-methylpentane into the cabin environment. The generation rate into the cabin is governed by the evaporation rate of the bulk fluid. ECLSS impacts are determined by predicting the resource consumption required to remove the contamination from the cabin atmosphere. Impacts on the atmosphere revitalization and water processing equipment and processes are assessed as is the potential for producing hazardous reaction products on exposure to ECLSS process conditions.

6.3.5.1 Governing Equations. The evaluation uses the calculation methods described in section 2.3 for evaporation rate, cabin mass balance, and TCC equipment performance.

6.3.5.2 Assessment Cases Considered. The case considered by the ECLSS engineering assessment addresses a sudden bulk release of 1.15 L of perfluoro-2-methylpentane. The following discussion provides summary details of the assessment.

6.3.5.2.1 Maximum Leaked Amount. The maximum 1.15-L leaked quantity is derived from assessing the maximum operating pressure of the Dragon vehicle's TCS and the quantity of fluid that must be released to cause the system's pressure to decay to 1 atm, the ISS cabin pressure. This assessment was conducted by SpaceX and the result provided to NASA for evaluation purposes.

6.3.5.2.2 Evaporation Rate From a Sudden Bulk Release. Evaporation rate from a sudden bulk release builds on the calculation of the maximum leaked amount. The leaked fluid is assumed to take a spherical shape upon leaking due to surface tension forces becoming dominant in the free-fall environment. Equation (9) serves as the basis for the calculation. A stepwise calculation approach is used with the leaked amount adjusted for 1-min increments. The time for 100% of the initially leaked material to evaporate is determined. The rate of ISS cabin concentration rise is calculated using equation (2).

6.3.5.2.3 Control of Bulk and Fugitive Emissions. The time to reduce the starting concentration produced from a sudden bulk release is calculated using equation (4). The leakage rate corresponding to the 85,000 mg/m^3 perfluoroalkane SMAC is derived from equation (2), assuming steady state conditions apply.

6.3.5.2.4 Absorption by Humidity Condensate as a Removal Device. Perfluoro-2-methylpentane's solubility in water is considered to address its potential for partitioning into humidity condensate. Excessive humidity condensate loading may contribute to excessive water processing equipment resource consumption leading to more frequent maintenance and higher logistics costs. Available data on perfluoro-2-methylpentane's solubility in water serve as the basis for this aspect of the assessment.

6.3.5.2.5 Purity and Thermal Stability. Perfluoro-2-methylpentane's thermal stability is assessed based on available literature and testing results. Some ECLSS equipment process conditions reach 400 °C with contact times ranging between ~0.7 and ~0.8 s. The potential for perfluoro-2-methylpentane, the primary component of the Flutec PP1 product to thermally decompose to HF and lower molecular weight fluoroalkanes or fluoroalkenes that may be more hazardous than the starting material is explored. Ease of removal of any thermal decomposition products, if any, is addressed.

Impurities found in perfluoroalkane fluids must be considered. Trace, branched carbon chain impurities may thermally decompose more readily than the straight carbon chain primary component. Fluid purity testing results are reviewed for the presence of branched carbon chain impurities and worst-case mass balance calculations are conducted to explore the potential for worst-case thermal decomposition.

6.3.6 Results and Discussion

The following discussion presents results for estimated evaporation rates from a 1.15-L release of Flutec PP1 fluid into the ISS cabin atmosphere, basic control of cabin atmospheric quality under varying ITCS fluid leakage conditions and ECLSS resource impacts, effects upon humidity condensate loading, and aspects of thermal decomposition risk.

6.3.6.1 Maximum Leaked Amount. The maximum amount that may leak is 1.15 L or 1,993 g as determined by SpaceX upon assessing the pressure equalization between the Dragon vehicle's TCS working volume and the prevailing ~1 atm pressure of the ISS cabin. This leaked amount serves as the basis for the fluid's ECLSS and cabin environmental impact assessment.

6.3.6.2 Evaporation From a Bulk Fluid Release. The evaporation rate assessment considers a 1.15-L fluid release. Assuming the fluid will coalesce into a spherical shape, a 13-cm-diameter sphere having a 530-cm^3 (0.57-ft^2) surface area. Understanding that the sphere shrinks as the liquid evaporates, a 1-min time increment calculation for evaporation rate over time was employed. Figure 45 shows the evaporation rate decay beginning with a 1.15-L-sized fluid sphere. The initial evaporation rate as calculated from equation (9) is ~6.1 g/min. The calculation predicts that the entire 1.15-L fluid release will evaporate over 16 hr. This evaporation rate allows sufficient time to isolate the leaked fluid from the cabin atmosphere and dispose of it if the leakage rate is sufficiently rapid.

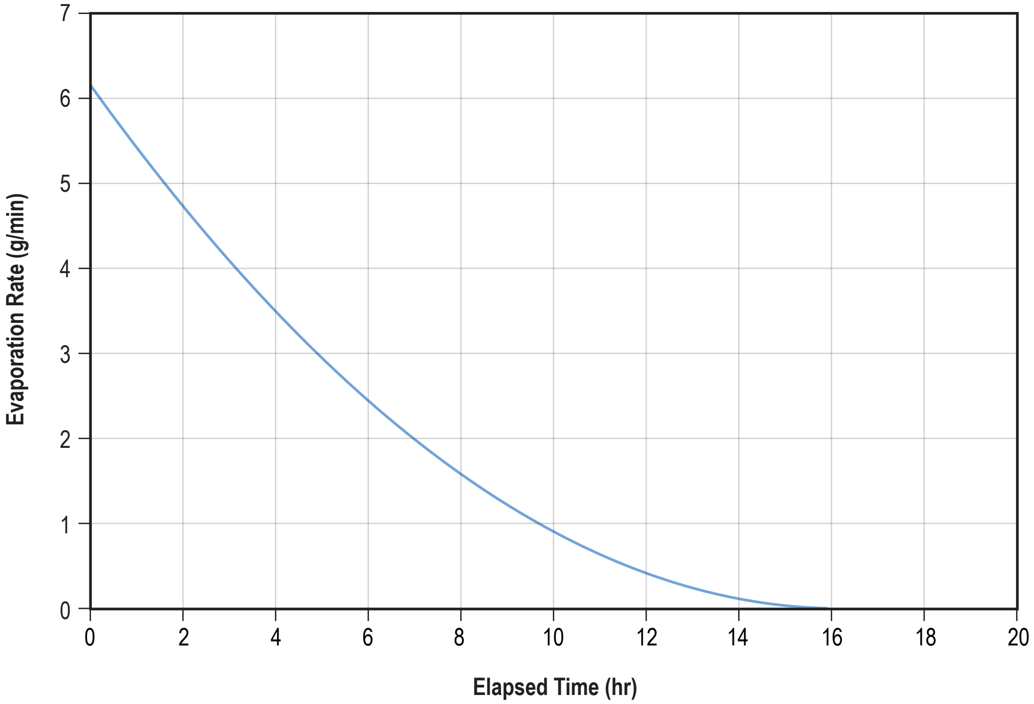


Figure 45. Evaporation rate over time from a 1.15-L Flutec PP1 fluid release.

6.3.6.3 Control of a Bulk Fluid Release and Fugitive Emissions. Activated carbon is predicted to possess a ~0.418 g perfluoro-2-methylpentane/g carbon equilibrium capacity. The 1.15 L of perfluoro-2-methylpentane predicted to be released in the event of a Dragon vehicle TCS leak represents ~21% of the total U.S. Segment's TCCS activated carbon saturation capacity. At this level of resource consumption, none of the perfluorcarbon compounds contained in the Flutec PP1 fluid are expected to break through the TCCS activated carbon bed. This conclusion is supported by the fact that the calculated adsorption zone length is 0.67 cm compared to the total carbon bed length of

63.5 cm which results in a predicted 100% removal efficiency by the carbon bed. Therefore, excellent control is provided by the carbon bed and no breakthrough is expected. Therefore, there is exceptionally low to zero risk that any perfluorocarbon compounds contained in 1.15 L of the Flutec PP1 may enter the downstream catalytic oxidation reactor where there is an equally slight chance they may oxidize to more hazardous compounds.

The calculated activated carbon equilibrium capacity indicates that perfluoro-2-methylpentane will be effectively removed by the activated carbon-based contamination control process equipment on board the ISS. Given the atmospheric scrubbing capabilities on board the ISS and the 85,000 mg/m^3 SMAC, the steady state perfluoro-2-methylpentane vapor-phase generation rate that may be accommodated is nearly 3.6 kg/hr (60 g/min). This rate is ~10 times greater than the absolute maximum vapor-phase generation rate expected from a 1.15-L perfluoro-2-methylpentane bulk fluid release.

In the event of the 1.15-L bulk fluid release, the predicted maximum concentration is 1,650 mg/m^3 and 2,886 mg/m^3 for the U.S. Segment and total ISS cabins, respectively. Figure 46 shows the peak concentration is reached after ~10.6 hr (636 min) in the total ISS cabin. If the U.S. Segment is isolated after a perfluoro-2-methylpentane leak, the peak concentration is reached after 9.7 hr (582 min).

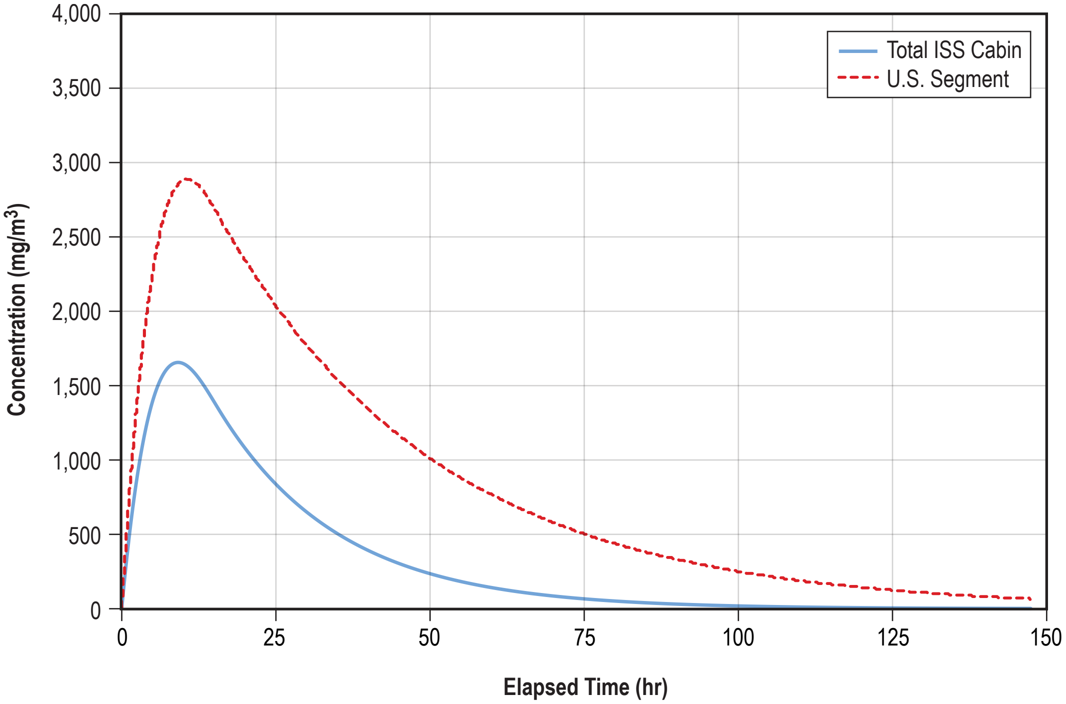


Figure 46. U.S. Segment and total ISS cabin concentration transient.

Continued scrubbing is required to return the cabin concentration condition to as close to its original state as possible. Removing 95% of the total mass of released perfluoro-2-methylpentane is considered a reasonable goal to define a successful cleanup operation. Using this definition, the final target concentration is 82 mg/m^3 in the total ISS cabin and 144 mg/m^3 for the U.S. Segment cabin. Figure 47 shows the concentration reduction dynamics for the total ISS cabin and the U.S. Segment. It is estimated to take approximately 61 to 110 hr beyond the initial ~10-hr period to reach a peak cabin concentration after a 1.15-L fluid release, depending on the cabin volume size and contamination control resources used, to achieve the success criteria defined for perfluoro-2-methylpentane cleanup. In total, the cleanup duration is estimated to require 71 to 120 hr if 1.15 L of perfluoro-2-methylpentane is released and allowed to completely evaporate.

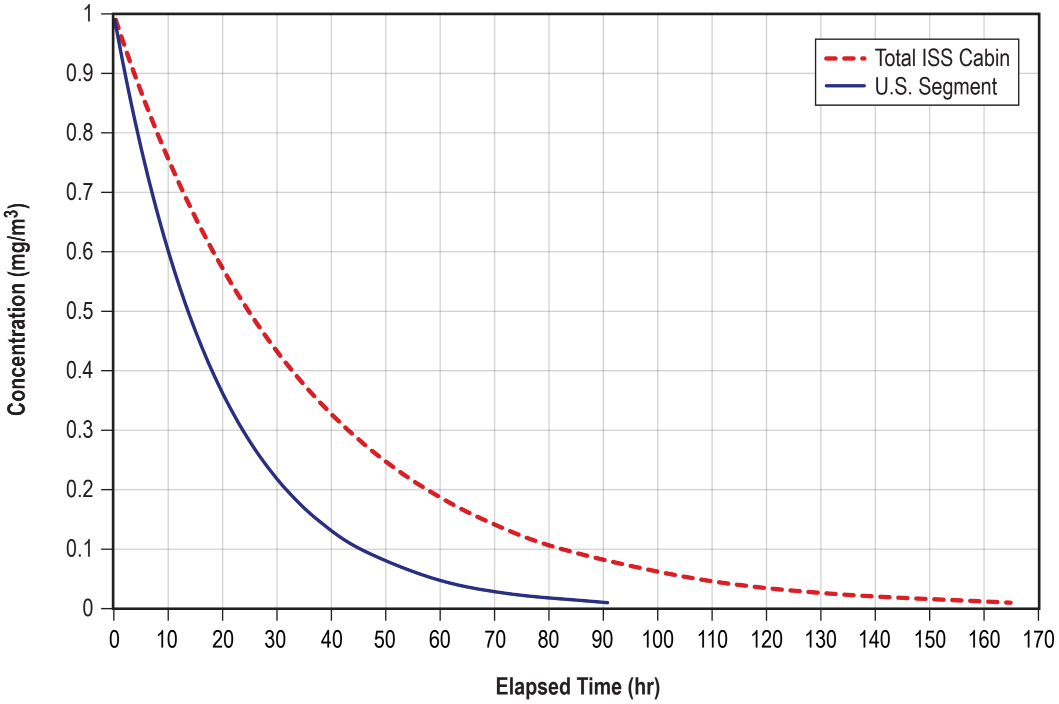


Figure 47. Cabin concentration reduction dynamics.

It should be noted that if the perfluoro-2-methylpentane escapes from its containment during the Dragon vehicle's transit to the ISS, the maximum concentration can reach ~248,700 mg/m^3 or nearly 3 times the SMAC. Therefore, in the event that Flutec PP1 leaks during transit to the ISS, precautions must be made to ventilate the Dragon vehicle's cabin before first entry.

Other cabin air purification systems on board the ISS, such as the CDRA, have been shown to assist the TCC process equipment for some chemical compounds.[19] The CDRA, however, employs molecular sieve 5A adsorbent media that has an average pore size opening of 5 Å. Most perfluorcarbon compounds comprised of more than two carbon atoms in their molecular structure are expected to be too large to enter the zeolite 5A pores, therefore rendering the CDRA ineffective for assisting in the recovery operation. For instance, perfluoropropane (C_3F_8) has approximate molecular dimensions of approximately 3.4 Å × 3.3 Å × 5.9 Å. A perfluoro-2-methylpentane molecule is much larger and not likely to be removed via the CDRA process.

6.3.6.4 Absorption Via Humidity Condensate and Impacts to Water Processing Equipment. According to table 20, perfluoro-2-methylpentane possesses a Henry's Law constant of $\sim 5.8 \times 10^8$ atm/mole fraction. The calculated single-pass efficiency for absorption into humidity condensate is $\sim 10^{-10}$%. Therefore, it is predicted that perfluoro-2-methylpentane will have no effect on ISS water purification processes. This aspect of the assessment was conducted using calculation techniques documented by references 1 and 3.

6.3.6.5 Purity and Thermal Stability. Evaluation of a sample of perfluoro-2-methylpentane acquired as Flutec PP1 found the fluid to contain 99.3% perfluoromethylpentane isomers and 0.357% perfluoro-2,3-dimethylbutane and 0.169% perfluoro-2-methylbutane, and 0.107% n-perfluoropentane as its primary components as reported by an evaluation conducted for NASA by Rutgers University. The remaining 0.018% is composed of perfluorobutane, perfluoroheptane, and perfluorooctane compounds.

6.3.6.6 Environmental Control and Life Support System Process Conditions. The evaluation of perfluormethylpentane stability under ECLSS process conditions follows.

6.3.6.6.1 U.S. On-Orbit Segment. High temperature process conditions within the USOS TCCS are found in the COA and reach 400 °C with a contact time of 0.67 s. As discussed earlier, the TCCS COA is located downstream of a large activated carbon bed. Given the maximum 1.15 L of Flutec PP1 that can leak, the activated carbon bed possesses sufficient capacity to prevent any of the fluid's components reaching the COA. Therefore, the risk for contact with the heated surfaces is considered to be zero.

6.3.6.6.2 Russian On-Orbit Segment. Two backup oxygen generation systems that employ high temperature reactions to liberate gaseous oxygen (GOX) are located in the ROS. Both of these systems operate by initiating a self-sustaining chemical reaction in a perchlorate briquette. One of the SFOG units, known by its Russian acronym TGK, has been on board the ISS since the SM was activated in late calendar year 2000. The second unit, recently transported to the ISS on board logistics flight 24P and known by its Russian acronym GKS, is planned to be used in combination with the TGK unit. Both provide the same function but have some operational differences. The following summary provides details on each unit as described by an ISS program hazard report conducted by Rocket Space Corporation Energia (RSCE-0058-INT).

6.3.6.6.2.1 TGK Solid Fuel Oxygen Generation Unit. The original SFOG unit, known by the Russian acronym TGK passes 80 m^3/hr of cabin air through the unit for a total air flow residence time of 0.76 s. The TGK unit uses a lithium perchlorate ($LiClO_4$) briquette. Evaluation of the TGK equipment schematics, depicted in figure 48, shows the $LiClO_4$ briquette is isolated from the bulk air flow in the unit. The reaction in the briquette can produce internal temperature conditions approaching 560 °C upon initial ignition and sustained reaction. The briquette, however, does not directly contact the cabin air. It is isolated in a sealed, insulated chamber. The air exiting the TGK unit does not exceed 90 °C.

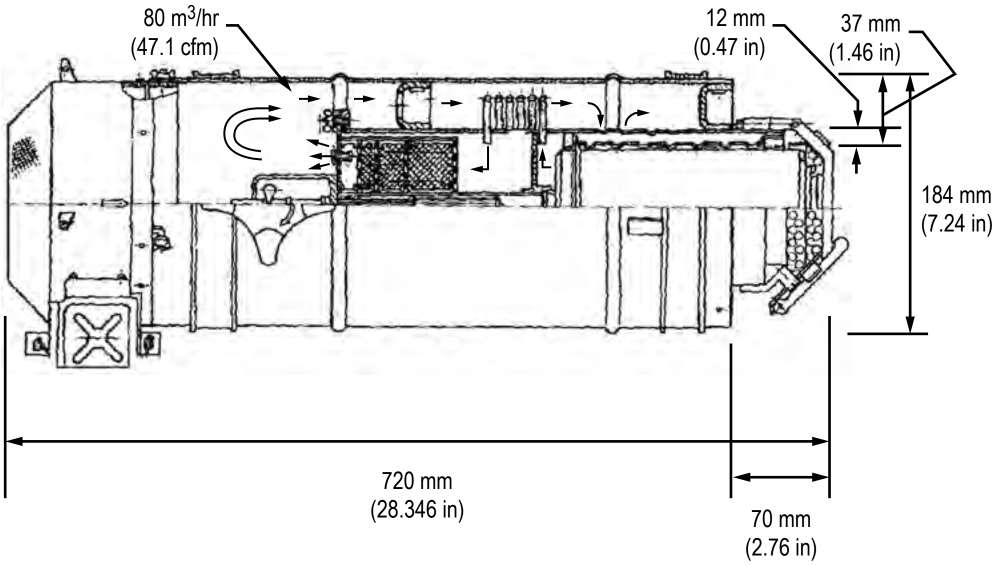


Figure 48. TGK SFOG equipment schematic.

GOX is released as the $LiClO_4$ reacts and flows out of the briquette into a coiled tubular heat exchanger. The external surface of the tubular heat exchanger is the only heated surface in direct contact with the cabin air that flows through the unit. Although the residence time within the SFOG unit itself is 0.76 s, the contact with the tubular heat exchanger surface is even shorter, likely on the order of 0.1 s or less. After flowing through the tubular heat exchanger, the oxygen flows through a purifier bed before it is entrained in an 80 m^3/hr air flow. The temperature condition encountered at the tubular heat exchanger surfaces is described as being much lower than the briquette's internal reaction temperature. Cabin air exiting the TGK unit is <90 °C. Given the operating temperature range, it is most likely that the surfaces in direct contact with the cabin air flowing through the TGK unit are >90 °C. A roughly estimated energy balance assessment for the TGK unit accounting for radiative and convective heat transfer indicates that surface temperatures surrounding the reaction chamber may exceed 500 °C. Conservatively, using a 10 °C approach to the maximum internal briquette temperature of 560 °C, or 550 °C, for the surface temperature is appropriate.

6.3.6.6.2.2 GKS Solid Fuel Oxygen Generation Unit. The GKS unit was transported to the ISS on board the Progress vehicle during logistics flight 24P. This unit employs a sodium perchlorate ($NaClO_4$) briquette and different reaction ignition method. While the TGK unit briquettes have an integral striker pin, the GKS briquettes have no integral igniter to increase the overall safety during transportation and storage. As shown in figure 49, the GKS briquettes are ignited using a heater element rather than a striker pin. The total minimum air flow through the GKS unit is 250 m^3/hr, >3 times that of the TGK unit. Given that both the TGK and GKS units occupy similar volumes, the implication is that the contact time between the cabin air and the heated surfaces within the GKS unit is likely ~3 times lower than that of the TGK unit. The $NaClO_4$ briquette is contained in a sealed tubular reactor and the oxygen flows through a heat exchanger before mixing with the 250 m^3/hr of air. The external briquette temperature is stated to be 310 °C maximum. The exiting air temperature is reported to be 50 °C maximum. Based on the available information, the heated surfaces within the GKS oxygen generator are expected to be <310 °C.

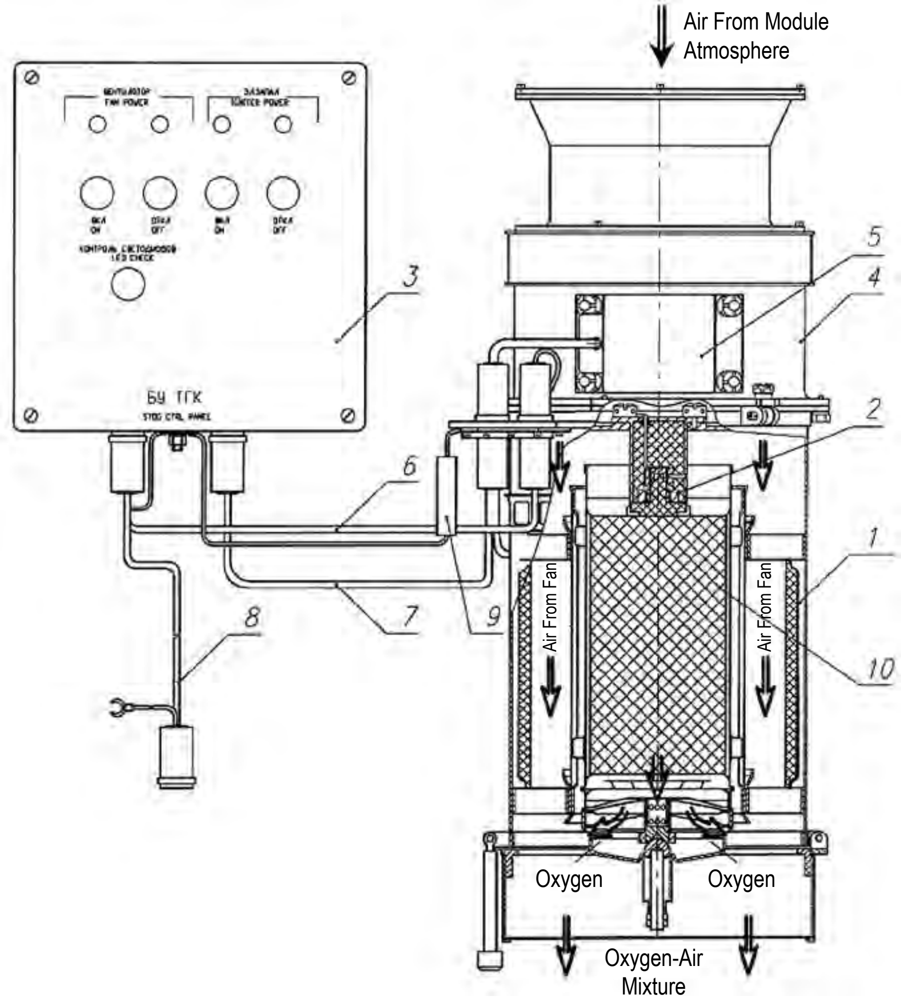


Figure 49. GKS SFOG equipment schematic.

6.3.6.7 Predicted Potential for Thermal Oxidation and Worst-Case Evaluation. Past evaluation of perfluorocarbon oxidation under ISS ECLSS process conditions, particularly for the TCCS and SFOG processes, has included all but the perfluoro-2-methylbutane compound. In all instances, the compounds were not found to oxidize to hazardous products under the temperature and contact time conditions that exist in the TCCS and GKS oxygen generator processes. It is predicted that perfluoro-2-methylbutane will not oxidize under the TCCS and GKS oxygen generator process conditions given its structural similarity to perfluoro-2-methylpentane which was observed to not oxidize. Given that perfluoro-2,5-dimethylheptane, a compound with structural similarities to perfluoro-2-methylpentane, was not found to thermally decompose at 400 °C after a soak period ranging between 8 to 15 hr, it is not anticipated that perfluoro-2-methylpentane will decompose under any ISS ECLS process conditions, including those of the TGK oxygen generator.[43]

It must be noted again that the TCCS activated carbon bed has a predicted capacity to remove ~3,400 g of perfluorodimethylbutane isomers, the compounds of most interest because of their potential to thermally decompose to form perfluoroisobutene. By comparison, the amount of perfluoro-2,3-dimethylbutane contained in 1.15 L of Flutec PP1 is 6.98 g. Therefore, at the most, only 0.2% of the TCCS activated carbon capacity is exhausted and under such conditions, no Flutec PP1 fluid components will break through the bed. Even with this being the case, a worst-case assessment of the primary impurity of interest, perfluoro-2,3-dimethylbutane, that assumes that no removal by the activated carbon was conducted for completeness even though it is very unlikely that this compound will break through the upstream activated carbon bed. Figure 50 shows the predicted perfluoroisobutene concentration that might result if the perfluorodimethylbutane isomers enter the TCCS catalytic oxidizer. As shown in figure 50, the highest possible concentration is <0.00012 mg/m^3.

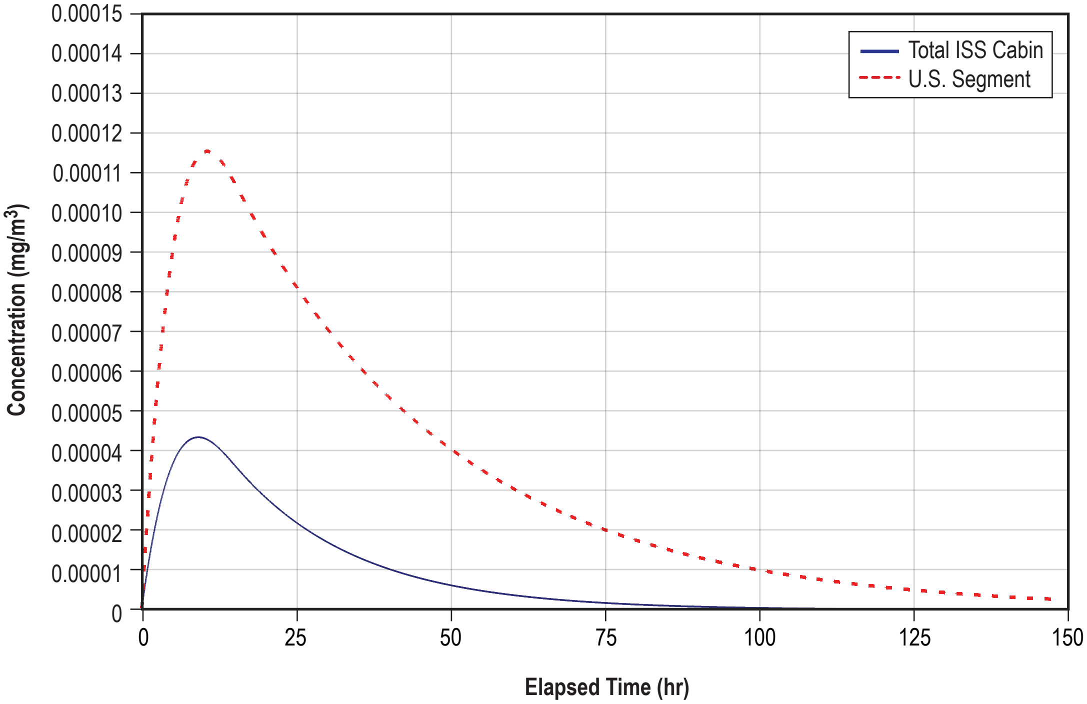


Figure 50. Calculated worst-case perfluoroisobutene concentration transient.

6.3.6.7.1 Thermal Oxidation Product Stability. PFIB's stability in an oxidizing environment must be considered. PFIB is reported to decompose rapidly when dissolved in water to form CO_2 and HF.[52] Also, work conducted by Oak Ridge National Laboratories and elsewhere has found that production of PFIB is suppressed in the presence of oxygen and that it undergoes hydrolysis on exposure to humidity. Oxygen and humidity are both present in the TCCS and SFOG process air streams. It must also be noted that the oxygen percentage of the gases in the SFOG unit are higher, leading to a potentially greater inhibition of PSIB production. Finally, even in the highly unlikely event that PSIB forms, it is readily removed by activated carbon and will be decomposed as it contacts the wetted surfaces in the Station's temperature and humidity control (THC) system condensing heat exchangers. As shown in figure 50, under the worst possible condition, PFIB's production rate is far lower than its removal rate, resulting in a very low maximum cabin concentration.

6.3.7 Summary

According to the assessment results and the ECLSS and cabin environmental impact definitions provided in tables 1 and 2, the rating for Flutec PP1 as planned for use in the Dragon vehicle is category E2-Minor (>10%, <25% ECLS resource consumption) and category D (>72 hr, <168 hr to recover from an event). Specific findings of the engineering assessment are the following:

- A rapid 1.15-L bulk fluid release is predicted to require ~15 hr to evaporate affording the opportunity to isolate and dispose of the leaked material before it fully evaporates.

- The 85,000 mg/m^3 SMAC is not exceeded in the ISS cabin for the Flutec PP1 fluid leakage scenario defined.

- The 85,000 mg/m^3 SMAC is exceeded in the Dragon vehicle's cabin in the event the Flutec PP1 fluid leaks during transit to the ISS.

- The maximum predicted ISS cabin environmental recovery duration is 120 hr (~5 days).

- The maximum predicted ISS ECLS resource consumption is ~21%.

- Flutec PP1 fluid components have no adverse effect on ISS ECLSS water processing equipment performance.

- Flutec PP1 fluid components exhibit no significant thermal stability concerns when in contact with heated ECLSS equipment or other heated equipment on board the ISS.

6.3.8 Conclusion

The ISS ECLSS engineering assessment finds the Flutec PP1 fluid planned for use in the Dragon vehicle TCS to be acceptable with respect to its ISS ECLSS equipment compatibility. The ISS ECLSS TCC processes are expected to recover from a worst-case perfluoropentane release event within 120 hr (~5 days) with ~21% ECLS resource consumption for the maximum 1.15-L leaked amount.

6.4 Perfluoropentane-Based Fluids

The following assessment was conducted in 2008 to evaluate a fluid to be used by the Zero Boil-off Tank (ZBOT) experiment to be conducted aboard the ISS. The assessment was documented under NASA memorandum ES22 08 058, "Compatibility of Perfluoropentane with The International Space Station's Environmental Control and Life Support System," dated July 2, 2008.

6.4.1 Background

The ZBOT experiment to be conducted on board the ISS in the microgravity science glovebox (MSG) employs a liquid fluorocarbon to experimentally verify a tank pressurization and pressure control computational model in microgravity. ZBOT builds on previous tank pressurization control experiments conducted in 1992 on board STS-43 and STS-52.

The fluid chosen for the ZBOT experiment is dodecafluoropentane (C_5F_{12}). Table 21 summarizes C_5F_{12}'s relevant physical properties. Commonly known as perfluoropentane, it replaces the fluid originally selected, HFE-7000 (1-methoxyheptafluoropropane), which was found to thermally decompose under some life support system cabin air purification process conditions. Assessment of the HFE-7000 series materials presented in section 6.6 for ISS ECLSS compatibility found it to be one of the most difficult commercial perfluoro-compounds to remove via activated carbon adsorption. The combination of thermal stability and clean-up difficulty contributed to significant cabin environmental impact to the ISS for the HFE-7000 series materials. Perfluoropentane was selected as a replacement for HFE-7000 to meet both experimental and flight safety objectives. The ZBOT equipment contains approximately 2 L of perfluoropentane containing 50 mg of 3-µm-diameter carboxylate-coated melamine resin beads.

Table 21. Dodecafluoropentane properties.

Property	Value
CAS number	678-26-2
Molecular weight (g/mole)	288.04
Melting point (°C)	–10
Boiling point (°C)	29.4
Liquid density (g/ml)	1.63
Solubility in water (mole fraction)	7.43×10^{-8}
Henry's Law constant (atm/mole fraction)	1.64×10^{8}
Vapor pressure (mm Hg @ 21 °C)	550
Oxygen solubility (mL O_2/100 mL)	80
Critical volume (cm^3/mole)	473
Critical pressure (mm Hg)	15,339
Critical temperature (°C)	147.6
Acentric factor	0.432

6.4.1.1 Commercial Applications. Perfluoroalkanes are used for medical applications due to their inert properties and ease of excretion from the body. Two applications are as ultrasound contrast agents and blood substitutes.[53,54] Perflouropentane has been studied as a blood substitute because a large amount of oxygen can dissolve in it. Sources report oxygen solubility of 80 mL oxygen/100 mL perfluoropentane. Dissolved gases can present difficulties for some experimental objectives, particularly those involving the fluid's thermal properties. It has been reported that perfluoropentane can be purified by purging it with a dry, inert gas such as nitrogen or argon.[55]

6.4.2 Purpose

The engineering assessment summarized by the following discussion addresses the compatibility of perfluoropentane with ISS ECLSS equipment and the potential environmental impact within the bounds of TCC design practice described in section 1.2.

6.4.3 Objective

The approach to maintaining acceptable cabin air quality in the ISS cabin in the event of a perfluoropentane release is assessed by engineering analysis. The primary objective of the assessment is to address interactions with ECLSS equipment and process conditions and to recommend appropriate actions, if any, necessary to ensure ISS cabin environmental conditions comply with relevant specifications and guidelines in the event of a perfluoropentane release into the cabin.

6.4.4 Assumptions

To conduct the perfluoropentane compatibility assessment, assumptions must be made concerning the cabin atmospheric conditions, payload hardware configuration, and TCC hardware configuration.

6.4.4.1 Cabin and Payload Conditions. Basic assumptions pertaining to the ISS cabin and ZBOT payload conditions are the following:

- Cabin conditions are on average 21 °C, 50% relative humidity, and 1 atm.
- The ISS habitable volume is the 1J assembly stage with ATV cargo carrier docked.
- The ZBOT total wetted volume is approximately 2 L.
- The ZBOT operational wetted volume is approximately 1.3 L (80 in^3).
- The ZBOT test fluid maximum operating pressurize is 276 kPa (40 psia).
- The ZBOT payload is operated in a contained glovebox facility in the Columbus module.
- The 85,000 mg/m^3 perfluoroalkane compound SMAC defined by JSC 20584 applies.

6.4.4.2 On-Orbit Configuration. During the ZBOT payload operations, it is assumed that the ISS will have achieved the 1J assembly stage configuration. The 1J stage assembly habitable on-orbit configuration consists of PMA-1, Unity (Node 1), Destiny (U.S. Laboratory), Quest (U.S. airlock), Harmony (Node 2), Columbus APM, Kibo ELM-PS, Kibo PM, Zarya (FGB), Zvezda (SM), a Soyuz spacecraft, a Program cargo vehicle, and the Jules Verne ATV. The ISS's total habitable volume is approximately 732 m^3.

The ZBOT payload is transported to the ISS via the multipurpose logistics module (MPLM) which has a 45-m^3 cabin volume. The ZBOT payload consists of a reservoir, fluids box, test tank assembly, and electronics box. The test tank assembly consists of an inner tank housed in an outer containment vessel outfitted with viewing ports. When deployed on board the ISS, the ZBOT payload components, with the exception of the electronics box, will be placed inside the MSG. The ZBOT payload equipment provides up to two physical containment levels while the MSG provides an additional physical containment level. The MSG also provides operational containment when operated at slight negative pressure relative to the cabin.

6.4.5 Approach

The ECLSS engineering assessment addresses the evaporation rate from a bulk release, the fugitive emission rate that may be accommodated by the ECLSS.

6.4.5.1 Governing Equations. The equations in section 2.3 serve as the calculation basis for evaporation rate, cabin mass balance, and removal route performance.

6.4.5.2 Assessment Cases Considered. Cases considered by the ECLSS engineering assessment address sudden bulk releases and slow, fugitive emissions. The following discussion provides summary details for each case. The 3-µm beads are not considered because they will be very effectively entrained in the ISS cabin ventilation flow and removed at ~100% efficiency by the high-efficiency particulate air- (HEPA-) rated filter elements in the U.S. Segment.

6.4.5.2.1 Maximum Leaked Amount. The maximum leaked amount considers the maximum operating pressure of 276 kPa and the wetted operating volume of 1.3 L. The mass of perfluoropentane that remains in the wetted operating volume is determined and subtracted from the beginning fluid mass. The mass differential is used to calculate the maximum expected ISS cabin concentration. The calculation of the ISS cabin concentration assumes that all of the ZBOT payload's containment levels fail as well as the MSG physical and operational containment, resulting in all of the leaked perfluoropentane entering the ISS cabin.

6.4.5.2.2 Evaporation Rate From a Sudden Bulk Release. Evaporation rate from a sudden bulk release builds on the calculation of the maximum leaked amount. Again, it is assumed that all of the ZBOT payload's and MSG's containment levels fail, allowing the bulk fluid released to be exposed directly to the ISS cabin atmosphere. The leaked fluid is assumed to take a spherical shape upon leaking due to surface tension forces becoming dominant in the free-fall environment. Equation (9) serves as the basis for the calculation. A stepwise calculation approach is used with the leaked amount adjusted for 1-min increments. The time for 95% of the initially leaked material to evaporate is determined. The rate of ISS cabin concentration rise is calculated using equation (2).

6.4.5.2.3 Control of Bulk and Fugitive Emissions. The time to reduce the starting concentration produced from a sudden bulk release is calculated using equation (4). The leakage rate corresponding to the 85,000 mg/m^3 perfluoroalkane SMAC is derived from equation (2), assuming steady state conditions apply.

6.4.5.2.4 Absorption by Humidity Condensate as a Removal Device. Perfluoropropane's solubility in water is considered to address its potential for partitioning into humidity condensate. Excessive humidity condensate loading may contribute to excessive water processing equipment resource consumption leading to more frequent maintenance and higher logistics costs. Available data on perfluoropropane's solubility in water serve as the basis for this aspect of the assessment.

6.4.5.2.5 Purity and Thermal Stability. Perfluoropropane's thermal stability is assessed based on available literature and testing results. Some ECLSS equipment process conditions reach 400 °C with contact times of ~0.5 s. The potential for perfluoropropane to thermally decompose to HF and lower molecular weight fluoroalkanes or fluoroalkenes that may be more hazardous than the starting material is explored. Ease of removal of any thermal decomposition products, if any, is addressed.

Impurities found in perfluoroalkane fluids must be considered. Trace, branched carbon chain impurities may thermally decompose more readily than the straight carbon chain primary component. Fluid purity testing results are reviewed for the presence of branched carbon chain impurities.

6.4.6 Results and Discussion

The following discussion presents and discusses results for estimated evaporation rates from stock solutions, basic control of cabin atmospheric quality under varying ITCS fluid leakage conditions, and effects upon humidity condensate loading. Guidelines are presented for maintaining single failure tolerance with respect to ECLS atmospheric quality and water quality control functions.

6.4.6.1 Maximum Leaked Amount. Theoretically, the maximum amount that may leak is 2 L or 3,260 g. However, if only the 1.3-L working volume is considered, the total amount of perfluoropentane that may leak is 7.42 moles (2,137 g). Allowing for pressure equalization between the working volume and the prevailing ~1 atm pressure of the ISS cabin finds that ~0.054 moles (16 g) of perfluoropentane would remain in the working volume at 1 atm. At this condition, approximately 7.36 moles (2,121 g) of perfluoropentane is likely to leak. Given that the ZBOT payload experimental volume is contained in a vacuum jacket, which is in turn inside the MSG, the likelihood that any leaked perfluoropentane may get into the ISS cabin is very low.

6.4.6.2 Evaporation From a Sudden Bulk Release. The evaporation rate assessment considers a full 2-L fluid release which is highly conservative given the levels of physical and operational containment employed. Assuming the fluid will coalesce into a spherical shape, a 15.6-cm-diameter sphere having a 771-cm^3 (0.83-ft^2) surface area. Understanding that the sphere shrinks as the liquid evaporates, a 1-min time increment calculation for evaporation rate over time was employed. Figure 51 shows the evaporation rate decay beginning with a 2-L sized fluid sphere. The initial evaporation rate as calculated from equation (9) is ~8.9 g/min. The calculation predicts that the entire 2-L fluid release will evaporate over 18 hr.

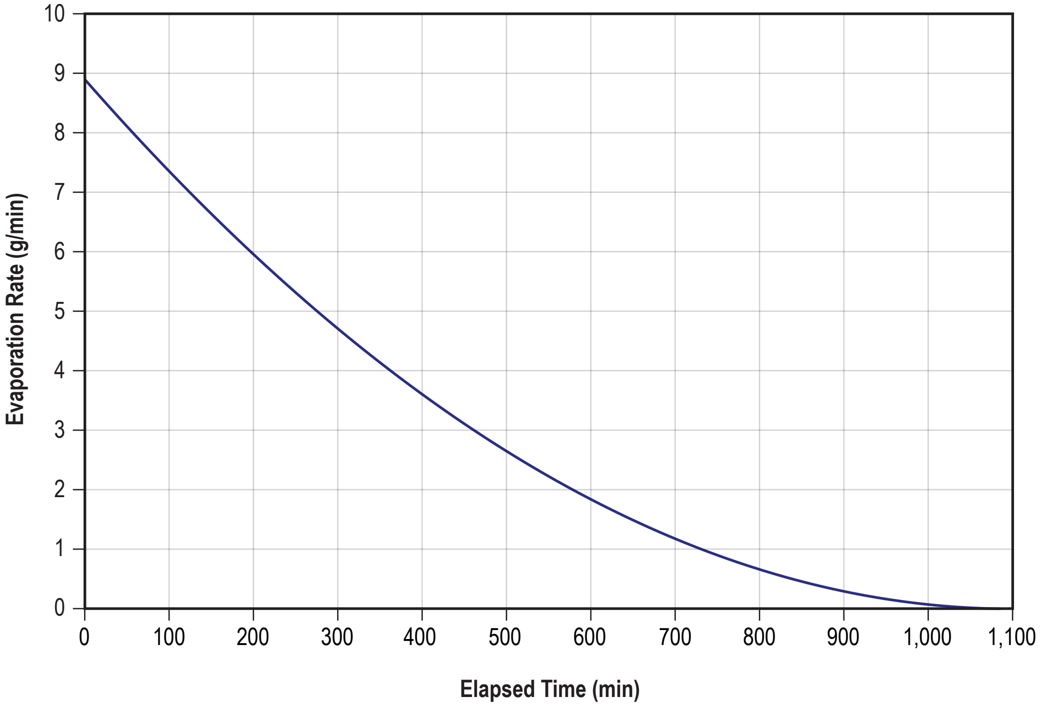


Figure 51. Evaporation rate over time from a 2-L perfluoropentane release.

6.4.6.3 Control of Fugitive Emissions. Activated carbon is predicted to possess a ~1.3 g perfluoropentane/g carbon equilibrium capacity. The 2 L of perfluoropentane contained in the ZBOT payload equipment represents ~11% of the total U.S. Segment's TCCS activated carbon saturation capacity. The calculated activated carbon equilibrium capacity indicates that perfluoropentane will be effectively removed by the activated carbon-based contamination control process equipment on board the ISS. Given the atmospheric scrubbing capabilities on board the ISS and the 85,000 mg/m^3 SMAC, the steady state perfluoropentane vapor-phase generation rate that may be accommodated is nearly 3.6 kg/hr (60 g/min). This rate is nearly 7 times greater than the absolute maximum vapor-phase generation rate expected from a 2-L perfluoropentane bulk fluid release.

In the event of the 2-L bulk fluid release, the expected maximum concentration ranges from 2,850 to 5,480 mg/m^3 for the total ISS and U.S. Segment cabins, respectively. Figure 52 shows the peak concentration is reached after ~9.6 hr (576 min) in the total ISS cabin. If the U.S. Segment is isolated after a perfluoropentane leak, the peak concentration is reached after 12.4 hr (744 min). It should be noted, however, that if the perfluoropropane escapes from its containment during transportation to orbit while in the MPLM, the maximum concentration can reach 72,444 mg/m^3 or 85% of the SMAC. In all cases, the 85,000 mg/m^3 SMAC is not exceeded.

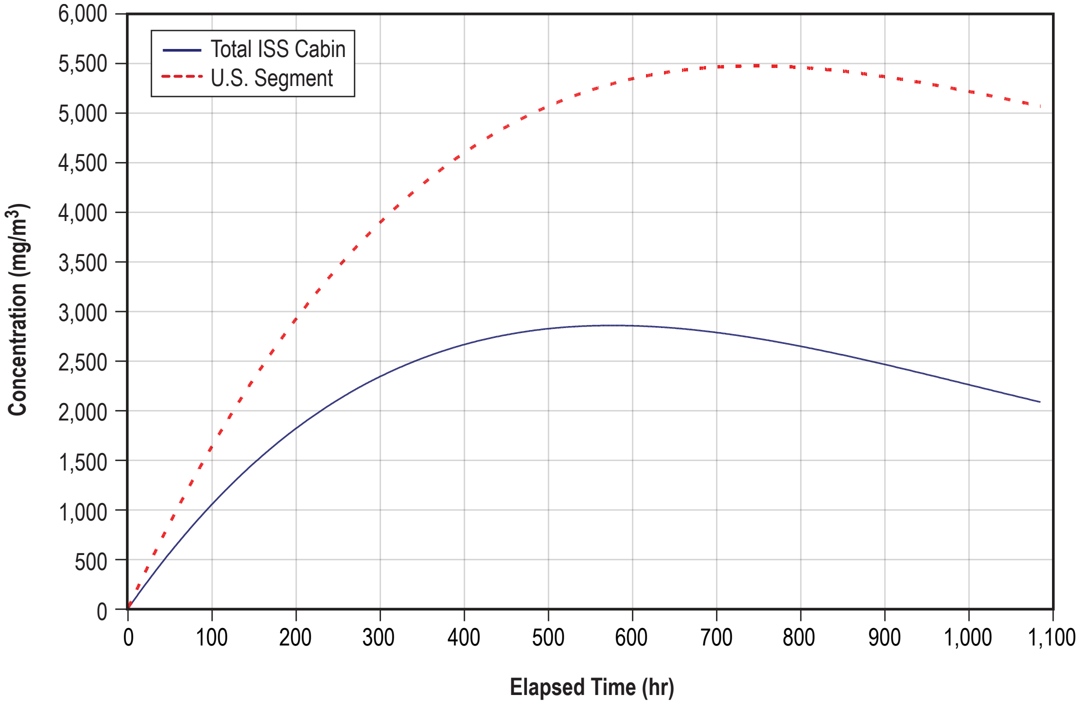


Figure 52. U.S. Segment and total ISS cabin concentration transient.

Continued scrubbing is required to return the cabin concentration condition to as close to its original state as possible. Removing 95% of the total mass of released perfluoropentane is considered a reasonable goal to define a successful cleanup operation. Using this definition, the final target concentration is 223 mg/m^3 in the total ISS cabin and 335 mg/m^3 for the U.S. Segment cabin. Once the 2-L fluid release has completely evaporated, the concentration in the total ISS cabin is predicted to be 2,087 mg/m^3. If the U.S. Segment volume is isolated after the release, the concentration is predicted to be 5,072 mg/m^3 at the time the fluid has completely evaporated. This represents ~89% further concentration reduction for the total ISS cabin and 93% concentration reduction for the U.S. Segment cabin. Figure 53 shows the concentration reduction dynamics for the total ISS cabin and the U.S. Segment. It is estimated to take approximately 40 to 85 hr beyond the initial 18 hr after a 2-L fluid release, depending on the cabin volume size and contamination control resources used, to achieve the success criteria defined for perfluoropentane cleanup. In total, the cleanup duration is estimated to require 58 to 103 hr if 2 L of perfluoropentane is released and allowed to completely evaporate.

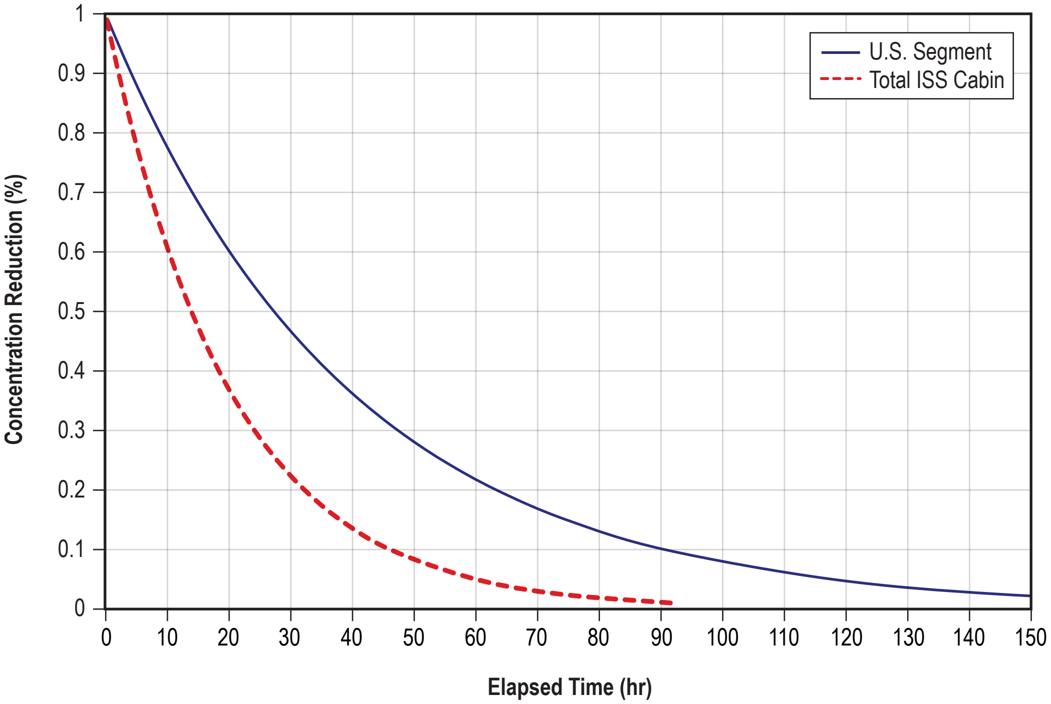


Figure 53. Cabin concentration reduction dynamics.

Other cabin air purification systems on board the ISS, such as the CDRA, have been shown to assist the TCC process equipment.[19] For conservatism, this added removal assist is not included in the calculations because the CDRA does not normally operate. Depending on the compound, the CDRA may provide up to ~50% single-pass removal efficiency if used to assist the TCCS equipment for cleanup operations.

6.4.6.4 Absorption Via Humidity Condensate and Impacts to Water Processing Equipment. According to table 1, perfluoropentane possesses a Henry's Law constant of ~10^{-8} atm/mole fraction. The calculated single-pass efficiency for absorption into humidity condensate is ~10^{-9}%. Therefore, it is predicted that perfluoropentane will have no effect on ISS water purification processes. This aspect of the assessment was conducted using calculation techniques documented by references 1 and 3.

6.4.6.5 Purity and Thermal Stability. Evaluation of a sample of perfluoropropane acquired from Exfluor Research Corporation, Round Rock, Texas, found the fluid to contain 98.87% perfluoropentane and 1.13% perfluoro-2-methylbutane (perfluoroisopentane). These compounds are not expected to undergo thermal decomposition under the maximum temperature conditions. Contact times exceeding 2 s at >1,200 °C are found to be required to thermally decompose the Exfluor Research Corporation product.

6.4.7 Summary

According to the assessment results and the ECLSS and cabin environmental impact definitions provided in tables 1 and 2, the rating for perfluoropentane as planned for use in the ZBOT payload equipment is E2 (>10%, <25% ECLS resource consumption) and D (>72 hr, <168 hr to recover from an event). Specific findings of the engineering assessment are the following:

- The credible maximum amount of perfluoropentane that may be released is 2,121 g (7.36 moles).
- The maximum ISS cabin concentration of ~5,500 mg/m^3 occurs for a 2-L release with the U.S. Segment isolated.
- The 85,000 mg/m^3 SMAC is not exceeded for any credible perfluoropentane leakage scenario during transportation to orbit and on-orbit operations.
- The maximum predicted cabin environmental recovery duration is 103 hr (~4 days).
- The maximum ECLS resource consumption is ~11%.
- Perfluoropentane has no adverse effect on ISS ECLSS water processing equipment performance.
- Perfluoropentane exhibits no thermal stability concerns when in contact with heated ECLSS equipment or other heated equipment on board the ISS.

6.4.8 Conclusion

The ECLSS engineering assessment finds the perfluoropentane fluid planned for use in the ZBOT payload equipment to be acceptable with respect to its ECLSS equipment compatibility. ECLSS TCC processes are expected to recover from a worst-case perfluoropentane release event within 103 hr (~4 days) with ~11% ECLS resource consumption.

6.5 Evaluation of Tetrafluoroethane-Based Fluids

The following assessment was conducted in April 2015 to evaluate the compatibility of 1,1,1,2-tetrafluoroethane, a candidate thermal working fluid under evaluation by Space Exploration Technologies Corporation (SpaceX).

6.5.1 Background

Space Exploration Technologies Corporation (SpaceX) is developing a spacecraft capable of transporting crew to the ISS. The spacecraft's designers are planning to use 1,1,1,2-tetrafluoroethane or hydrofluorocarbon 134a (HFC-134a) for the vehicle's TCS. The fluid selected to be used is a mixture of 85.6% by weight HFC-134a and 14.4% by weight polyolester (POE) oil. The total fluid quantity consists of approximately 796 g of HFC-134a and 134 g of POE oil. The two components are completely miscible. The following evaluation assesses the ECLSS equipment impact and cabin environmental impact of POE oil and HFC-134a.

The POE oil, manufactured by Nu-Calgon, St. Louis, Missouri, serves as a lubricating component in the fluid and is fully miscible with the HFC-134a. POE oil has a vapor pressure <0.1 mm Hg at 20 °C and its solubility in water is negligible. Due to its very low vapor pressure and insolubility in water, POE oil has no impact to the ECLSS or cabin environment. The HFC-134a component of the fluid mixture will evaporate rapidly leaving a nearly pure POE oil residue. POE oil is hygroscopic and saturates with water at 1,500 mg/L. Excess moisture can also cause POE oil to decompose to its organic acid- and alcohol-based compounds. Care must be taken, therefore, to protect the POE oil from exposure to humidity via direct or indirect contact with the spacecraft cabin or ground processing facility atmosphere. Direct contact may occur during TCS maintenance while indirect contact may occur via water permeation through flexible hoses. If fluoropolymer flexible hoses such as Teflon are used in the TCS, it is recommended that a vapor barrier be used in the external hose wrap to prevent moisture permeation into the POE oil component over time. A desiccant component may also be considered as part of the TCS to further address potential moisture accumulation.

The selected refrigerant fluid is marketed by DuPont™ under the Suva® trade name. An analysis of Dupont Suva HFC-134a reports an average composition summarized in table 22.

Table 22. Average Dupont Suva composition.

Compound	CAS No.	Composition (%)	Mass (g)
1,1,1,2-tetrafluoroethane	811-97-2	99.98	795.84
1,1,2,2-tetrafluoroethane	359-35-3	0.02	0.16

As shown in table 22, HFC-134a fluid is ~99.88% 1,1,1,2-tetrafluoroethane with ~0.0 2% 1,1,2,2-tetrafluoroethane as an impurity. For the purposes of evaluation, the fluid can be treated as pure 1,1,1,2-tetrafluoroethane. Table 23 provides relevant physical and chemical properties for 1,1,1,2-tetrafluoroethane relevant to ECLSS compatibility and cabin environmental impact evaluation.

Table 23. Tetrafluoroethane chemical and physical properties.

Property	Value
CAS number	811-97-2
Molecular weight (g/mole)	102.03
Boiling point (°C)	–26.1
Freezing point (°C)	–103.3
Liquid density (g/ml @ 25 °C)	1.206
Vapor pressure (kPa @ 25 °C)	666.1
Solubility in H_2O (wt.% @ 25 °C)	0.15
Solubility of H_2O in HFC-134a (wt.% @ 25 °C)	0.11
Henry's Law constant (atm/mole fraction)	2,767
Molar volume (cm^3/mole)	84.1
Critical volume (cm^3/mole)	197.9
Critical pressure (mm Hg)	4,060 kPa
Critical temperature (°C)	101.1
Global warming potential (CO_2 = 1)	1,200

6.5.1.1 Spacecraft Trace Contaminant Control Design Practice. The evaluation was conducted within the TCC design practice described in section 1.2.

6.5.1.2 International Space Station Trace Contaminant Control Equipment. Active TCC equipment is located in both the USOS and ROS. The USOS TCCS is located in the U.S. laboratory and the ROS BMP is located in the service module. Brief details for the TCCS and BMP are provided in section 6.3.1.2.

6.5.2 Purpose

The engineering assessment summarized by the following discussion addresses the compatibility of HFC-134a with ISS ECLSS equipment and the potential environmental impact.

6.5.3 Objective

The approach to maintaining acceptable cabin air quality in the ISS cabin in the event of an HFC-134a release is assessed by engineering analysis. The primary objective of the assessment is to address interactions with ECLSS equipment and process conditions and to recommend appropriate actions, if any, necessary to ensure ISS cabin environmental conditions comply with relevant specifications and guidelines in the event of an HFC-134a release into the cabin.

6.5.4 Assumptions

To conduct the HFC-134a compatibility assessment, assumptions must be made concerning the cabin atmospheric conditions, payload hardware configuration, and TCC hardware configuration.

6.5.4.1 International Space Station Cabin and Docked Vehicle Conditions. Basic assumptions pertaining to the ISS cabin and SpaceX crew transport vehicle conditions are the following:

- Cabin conditions are on average 21 °C, 50% relative humidity, and 1 atm.
- The ISS habitable volume is ~810 m^3.
- The SpaceX crew transport vehicle volume is ~10 m^3.
- The maximum leaked quantity of HFC-134a is 796 g.
- The maximum leaked quantity of POE oil is 134 g.
- The 85,000 mg/m^3 perfluoroalkane compound SMAC defined by JSC 20584 applies.

6.5.5 Approach

The ECLSS engineering assessment addresses the impacts from a bulk, simultaneous release of 796 g of HFC-134a and 134 g of POE oil into the cabin environment. The generation rate into the cabin is governed by the evaporation rate of the bulk fluid. ECLSS impacts are determined by predicting the resource consumption required to remove the contamination from the cabin atmosphere. Impacts on the atmosphere revitalization and water processing equipment and processes are assessed as is the potential for producing hazardous reaction products on exposure to ECLSS process conditions.

6.5.5.1 Governing Equations. The equations in section 2.3 serve as the calculation basis for evaporation rate, cabin mass balance, and removal route performance.

6.5.5.2 Assessment Cases Considered. The case considered by the ECLSS engineering assessment addresses a sudden bulk release of 796 g of HFC-134a and 134 g of POE oil. The following discussion provides summary details of the assessment.

6.5.5.2.1 Evaporation Rate From a Sudden Bulk Release. Evaporation rate from a sudden bulk release builds on the calculation of the maximum leaked amount. The leaked fluid is assumed to take a spherical shape upon leaking due to surface tension forces becoming dominant in the free-fall environment. In the case of binary liquids, equation (9) is applied using a method described by reference 14. A stepwise calculation approach at time steps ranging from 0.05- to 1-min increments is used with the mass of fluid remaining in the liquid phase adjusted for each increment. The time for 100% of the initially leaked material to evaporate is determined from this technique. The rate of ISS cabin concentration rise is calculated using equation (2).

6.5.5.2.2 Control of Bulk and Fugitive Emissions. The time to reduce the starting concentration produced from a sudden bulk release is calculated using equation (4). The leakage rate corresponding to the 85,000 mg/m^3 perfluoroalkane SMAC is derived from equation (5) which assumes steady state conditions apply.

6.5.5.2.3 Absorption by Humidity Condensate as a Removal Device. The solubility of the HFC-134a constituents in water is considered to address the potential for partitioning into humidity condensate. Excessive humidity condensate loading may contribute to excessive water processing equipment resource consumption leading to more frequent maintenance and higher logistics costs. Available data on solubility in water and Henry's Law constants serve as the basis for this aspect of the assessment.

6.5.5.2.4 Thermal Stability. Thermal stability is assessed based on available literature and testing results. Some ECLSS equipment process conditions reach 560 °C with contact times ranging between ~0.7 and ~0.8 s. The potential for HFC-134a to thermally decompose to HF and lower molecular weight fluoroalkanes or fluoroalkenes that may be more hazardous than the starting material is explored. Ease of removal of any thermal decomposition products, if any, is addressed.

6.5.6 Results and Discussion

The following discussion presents results for estimated evaporation rates from a simultaneous release of 796 g of HFC-134a and 134 g of POE oil into the ISS cabin atmosphere, basic control of cabin atmospheric quality under varying ITCS fluid leakage conditions and ECLSS resource impacts, effects upon humidity condensate loading, and aspects of thermal decomposition risk.

6.5.6.1 Evaporation From a Bulk Fluid Release. The evaporation rate assessment considers a total 800 mL fluid release. Conservatively, assuming the fluid will coalesce into a spherical shape before any evaporation occurs, an 11.5-cm-diameter sphere having a 418-cm^3 (0.45-ft^2) surface area results. Understanding that the sphere shrinks as the liquid evaporates, an incremental calculation for evaporation rate over time was employed. Figure 54 shows the evaporation rate decay beginning with an 800-mL-sized fluid sphere. The initial evaporation rate as calculated from equation (9) is ~4,260 g/min. The calculation predicts that the entire quantity of HFC-134a will evaporate within 42 s, leaving nearly pure POE oil. The remaining POE oil requires ~5 hr to fully evaporate as shown in figure 55. Evaluating the evaporation rates finds that the HFC-134a component will more likely evaporate nearly immediately upon release leaving the POE oil as the main liquid requiring cleanup. Therefore, the HFC-134a must be removed from the cabin atmosphere by the contamination control system. The POE oil evaporation rate is sufficiently slow to allow for it to be isolated and cleaned up by the crew, thus minimizing vapor phase contamination in the cabin.

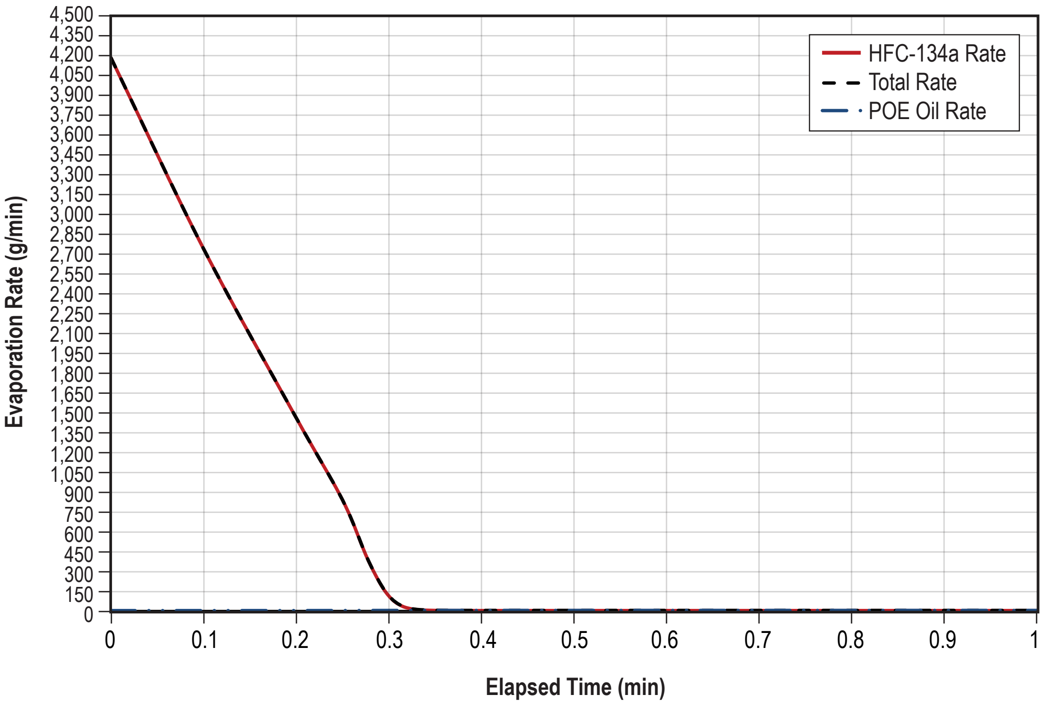


Figure 54. Evaporation rate over time from a combined 796-g release of HFC-134a and 134-g release of POE oil.

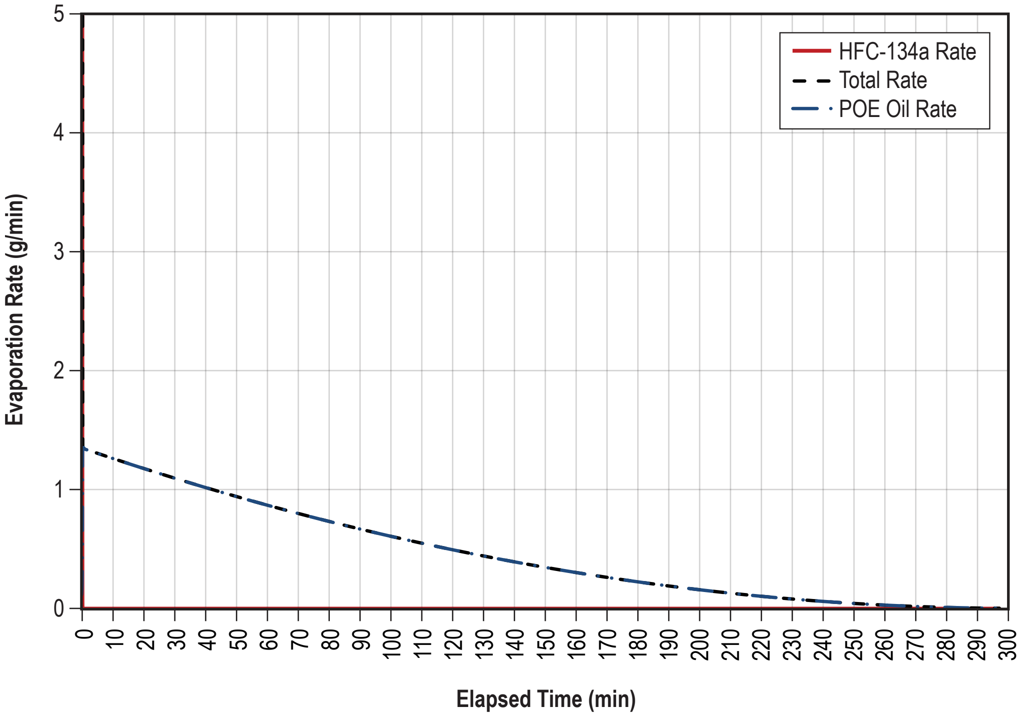


Figure 55. Evaporation rate over time from a 134-g release of POE oil.

6.5.6.2 Control of a Bulk Fluid Release. Activated carbon is predicted to possess a ~0.0152 g HFC-134a/g carbon saturation capacity. The 796 g of HFC-134a predicted to be released in the event of a vehicle thermal control system leak exceeds the ISS's total TCCS activated carbon saturation capacity which is estimated to be 437 g. Even incorporating a second USOS TCCS unit to remove an additional 276 g, the total leaked quantity of HFC-134a still exceeds the scrubbing capacity. At this level of resource consumption, it is possible that HFC-134a will break through the TCCS activated carbon bed and enter the catalytic oxidizer assembly. The Russian BMP may remove ~94 g for each ZPL-1M bed regeneration cycle. At such a rate, the complete removal is estimated to require ~76 days if a 20-day regeneration cycle is used. Using a 10-day regeneration cycle reduces the time to ~38 days. Containing only 160 g of activated carbon, the SpaceX crew transportation vehicle has insufficient contamination control capability to remove HFC-134a from the cabin. An untreated activated carbon is estimated to have a 0.042 g HFC-134a/g carbon saturation capacity. At this capacity, the SpaceX vehicle's contamination control unit can remove only ~5 g of HFC-134a.

The predicted HFC-134a maximum concentration in the ISS cabin is 1,358 mg/m^3 which is 1.6% of the SMAC. A leak isolated to the SpaceX crew transportation vehicle results in a peak concentration of 79,600 mg/m^3 which is 94% of the SMAC. Figure 56 shows the peak concentration in the ISS cabin is reached rapidly. After 9.5 hr, the Russian BMP becomes saturated and requires regeneration. The USOS TCCS becomes saturated after 31 hr. After this time, the Russian BMP is the sole removal device for the HFC-134a. The estimated time to reduce the concentration by over 95% is ~127 hr without accounting for periodic BMP regeneration cycles. The total time will be expected to increase by 24 hr for each BMP regeneration cycle required.

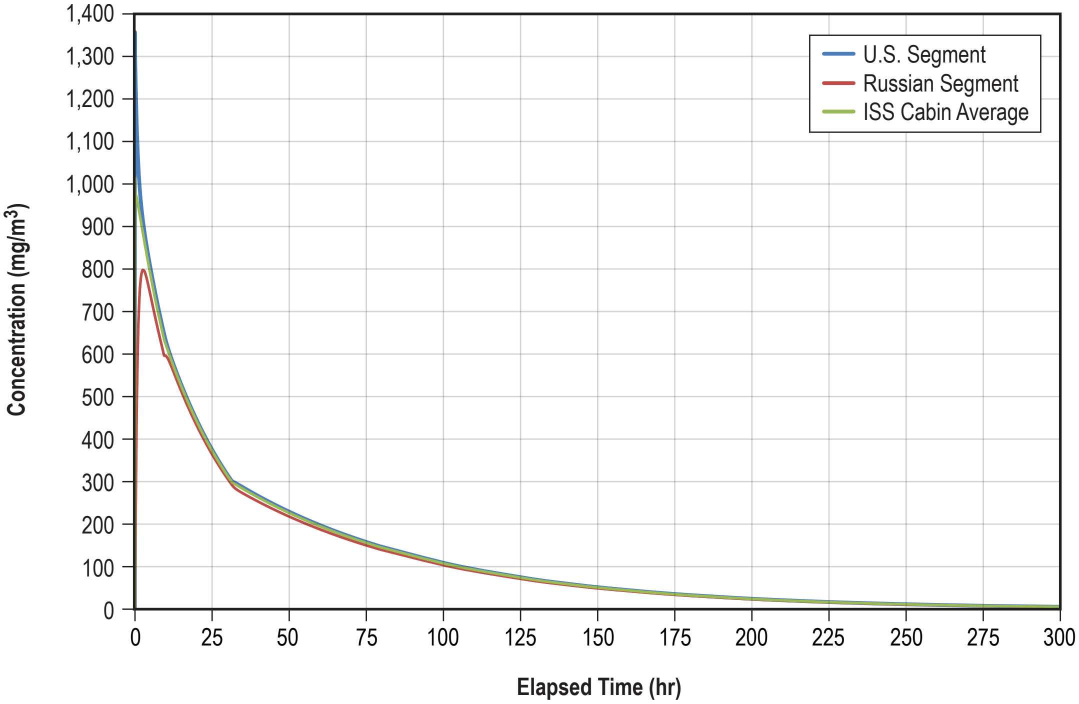


Figure 56. ISS cabin concentration transient resulting from an HFC-134a leak.

6.5.6.3 Absorption Via Humidity Condensate and Impacts to Water Processing Equipment. According to table 22, HFC-134a a Henry's Law constant of 2,767 atm/mole fraction. The calculated single-pass efficiency for absorption into humidity condensate is ~10^{-5}%. The Henry's Law constants for the impurity listed in table 22 is similar in magnitude to HFC-134a. Therefore, it is predicted that all compounds found in Suva HFC-134a will have no effect on ISS water purification processes. This aspect of the assessment was conducted using calculation techniques documented by references 1 and 3.

6.5.6.4 Thermal Stability. The thermal stability of HFC-134a was investigated and a correlation relating thermal decomposition rate constant to temperature was developed.[56] Using this correlation, the calculated rate constant at 560 °C is 8.97×10^{-3} s^{-1}. For a first order rate law, the thermal decay of HFC-134a under ECLSS thermal conditions up to 560 °C and contact times up to 0.76 s is ~0.7% for a single pass.

6.5.6.5 Regulatory Considerations. Although HFC-134a is an excellent choice for a coolant fluid that has insignificant ozone depletion potential, its global warming potential is significantly higher than CO_2. As a result, HFC-134a is receiving additional regulatory scrutiny and many markets for HFC-134a, particularly the automotive market, are beginning to replace HFC-134a with alternative fluids such as 2,3,3,3-tetrafluoropropene (HFO-1234yf). Consideration should be given to selecting a coolant fluid with excellent performance relative to both ozone depletion and global warming potential. Such a selection may reduce future risk associated with regulatory actions and possible fluid obsolescence.

6.5.7 Summary

According to the assessment results and the ECLSS and cabin environmental impact definitions provided in tables 1 and 2, the rating for Suva HFC-134a is category E4 (>50% ECLS resource consumption) and category D (>72 hr, <168 hr to recover from an event). Specific findings of the engineering assessment are the following:

- A 930-g bulk fluid release consisting of 14.4% POE oil and 85.6% HFC-134a is predicted to result in rapid, nearly instantaneous HFC-134a evaporation followed by slow POE oil evaporation.

- The 85,000 mg/m^3 SMAC is not exceeded in the ISS cabin for the HFC-134a fluid leakage scenario defined.

- The 85,000 mg/m^3 SMAC is not exceeded in the SpaceX crew vehicle's cabin in the event the HFC-134a fluid leaks during transit to the ISS; however, the resulting concentration approaches 94% of the SMAC.

- The predicted ISS cabin environmental recovery duration is >127 hr and will be extended by the need to regenerate the Russian BMP to continue recovery operations.

- The SpaceX crew vehicle's TCC capacity for HFC-134a is ~5 g; therefore, it is not possible to adequately scrub the cabin atmosphere before docking with the ISS or landing and places the crew at risk for high concentration exposure with no adequate remediation method other than purging the cabin.

- The maximum predicted ISS ECLS resource consumption is >50% based on TCC capacity utilization.

- Suva HFC-134a fluid components have no adverse effect on ISS ECLSS water processing equipment performance.

- Suva HFC-134a fluid components exhibit no significant thermal stability concerns when in contact with heated ECLSS equipment or other heated equipment on board the ISS.

6.5.8 Conclusion

The ISS ECLSS engineering assessment finds the Suva HFC-134a fluid planned for use in SpaceX crew transport vehicle TCS to present challenges to the ISS ECLSS with respect to ease of removal from the cabin atmosphere. Although the ISS ECLSS TCC processes are expected to recover from a worst-case HFC134a release event, rapid regeneration of the Russian BMP and consideration to U.S. Segment TCCS activated carbon beds may need to be considered. Leakage of >5 g of HFC-134a will overwhelm the SpaceX crew transport vehicle's contamination control system and place the crew at risk for high concentration exposure.

6.6 Thermal Working Fluid Candidates for Crew Transport Vehicles

The following assessment was conducted in 2006 to evaluate several candidate thermal working fluids for the CEV program. The assessment was documented under NASA memorandum EI12(06-004), "Compatibility Assessment of Thermal Working Fluid Candidates for the Crew Exploration Vehicle," dated May 11, 2006.

6.6.1 Introduction

The design and operation of crewed spacecraft requires identifying and evaluating chemical compounds that may present reactivity and compatibility risks with the ECLSS. Such risks must be understood so that appropriate design and operational controls, including specifying containment levels, can be instituted or an appropriate substitute material selected. Operational experience acquired during the ISS program has found that understanding ECLSS and environmental impact presented by TCS working fluids is imperative to safely operating any crewed space exploration vehicle. This experience provides the opportunity to address ECLSS and cabin environmental impacts for the CEV early in the conceptual design phase.

Perfluorocarbon fluids are used as working fluids in thermal control fluid loops on board the ISS. Also, payload hardware developers have identified perfluorocarbon fluids as preferred thermal control working fluids. Interest in using perfluorocarbon fluids as TCS working fluids for future crewed space vehicles and outposts is high.

In addition to perfluorocarbon fluids, aqueous mixtures of dihydric alcohols, commonly known as glycols, are of interest. Experience has been gained from using aqueous ethylene glycol on board early NASA spacecraft and the Space Station Mir. Leaks of this fluid and its low maximum allowable concentration in the cabin atmosphere (13 mg/m^3 NASA SMAC) lead to Russian designers using aqueous glycerol, a trihydric alcohol, on board their contribution to the ISS. Glycerol is much less toxic than ethylene glycol. Recent evaluations by NASA have promoted aqueous propylene glycol as a candidate working fluid for exploration vehicles.

Considerations for perfluorocarbon and aqueous propylene glycol thermal working fluid use on crewed spacecraft and outposts are summarized. Potential hazards associated with perfluorocarbon and aqueous propylene glycol fluids are discussed with specific attention given to engineering assessment of ECLSS compatibility, compatibility testing results, and spacecraft environmental impact. ECLS compatibility considers the ISS as the worst-case basis because the CEV's early mission objectives include transportation to and from the ISS and compatibility with the ISS's cabin environment and life support systems is necessary.

6.6.2 Background

The selection of a TCS working fluid for a spacecraft is a critical trade for developing future vehicles that will enable future crewed space exploration initiatives. NASA traditionally uses single-phase ATCSs comprised of separate internal and external circulating fluid loops. Vehicles presently operated by NASA use water for the internal working fluid. The ISS uses ammonia for the U.S. Segment's external ATCS working fluid while the Shuttle uses dichlorofluoromethane (Freon 21).

While effective, opportunity exists to reduce overall TCS mass by using a single fluid ATCS. This opportunity resides in using fluorocarbon fluids to reduce heat transfer systems based on two fluids, such as water and ammonia, thermally connected via a heat exchanger to a single-fluid loop with no heat exchangers. In addition, a multicomponent fluorocarbon fluid mixture might be able to take the place of current flash evaporators and ammonia boilers since each component has a unique boiling point. The result could be a drastic reduction of system size, weight, complexity, and power consumption while maximizing efficiency.

In addition to fluorocarbon fluids, NASA is also considering 60% aqueous propylene glycol. Experience has been gained from using ethylene glycol on board Mir and glycerol on board the ISS's Russian Segment. While ethylene glycol is considered a poor choice because of its toxicity, both glycerol and propylene glycol are commonly used in consumer products such as foodstuffs and cosmetics among many others.

A challenge for single-fluid ATCSs exists with selecting a working fluid that possesses the desired performance characteristics is demonstrated to present a minimal health risk to the crew, and is compatible with on-board life support systems. Several candidate working fluids have been identified that possess promising performance characteristics. To determine whether these fluids present minimal impact to the cabin environment and the ECLSS equipment, evaluation must be conducted with respect to the following:

- Chemical composition of the fluid.
- Water solubility and impacts to ECLS water processing systems.
- Volatility, relative ease of removal, and impacts to ECLS air processing systems.
- Thermal stability and decomposition products.
- Reactivity.
- Relative toxicity.

Water solubility, volatility, and ease of removal address—at a cursory level—the potential impacts to ECLS equipment performance, including their ability to maintain a cabin environment suitable to support the crew in the presence of leaked ATCS working fluid. Such ATCS leaks may be gross leaks or fugitive emissions resulting from slow leaks from fluid couplings, valves, pumps, or other potential leak paths. Likewise, thermal stability and decomposition products along with reactivity are evaluated based on cursory data to recommend whether a particular class of fluids is compatible with ECLS equipment process conditions. Some ECLS equipment may operate at high temperature and the potential for leaked ATCS fluid to thermally decompose to hazardous products must be understood. Reactivity addresses compatibility with ECLS equipment employing reactive adsorbents such as LiOH. Relative toxicity is evaluated by NASA toxicologists who set SMACs. The toxicologists' evaluation is important for engineers to determine the magnitude of the TCC challenge that the fluid may present to a future spacecraft or space habitat TCCS design. However, for early evaluation, recommended exposure data from vendor literature is considered sufficient for early screening purposes.

6.6.3 Compatibility Assessment of Candidate Active Thermal Control System Fluids

Candidate fluorocarbon-based and aqueous propylene glycol ATCS fluids are listed in table 24. These fluids are evaluated for ECLSS compatibility using the ISS as the reference system because the early products include the Novec™ engineered fluid HFE series and Fluorinert™ fluids manufactured by 3M Company and several Galden® heat transfer (HT) fluids manufactured by Solvay Solexis, Inc. Data obtained from material safety data sheets (MSDS) and technical literature provide basic information for use in the assessment. Journals were also consulted with respect to conditions of thermal decomposition. Table 24 also provides a summary of the chemical composition and chemical abstracts (CAS) reference number of the major constituents of each fluid.

Table 24. Candidate ATCS working fluids.

Trade Name	Constituent	Composition (%)	CAS Number
HFE-7000*	1-methoxyheptafluoropropane	>99.5	375-03-1
HFE-7100*	Methyl nonafluoroisobutyl ether Methyl nonafluorobutyl ether	20–80 20–80	163702-08-7 163702-07-6
HFE-7200*	Ethyl nonafluoroisobutyl ether Ethyl nonafluorobutyl ether	20–80 20–80	163702-06-5 163702-05-4
FC-72 Fluorinert*	C_6 perfluoro compounds	100	86508-42-1
FC-87 Fluorinert*	C_5 to C_{18} perfluoro compounds	100	86508-42-1
Galden HT 55**	Hexafluoropropene polyether	100	69991-67-9
Galden HT 135**			
Galden HT 170**			
Propylene glycol	Propylene glycol Water	60 40	57-55-6 7732-18-5

* 3M Company
** Solvay Solexis, Inc.

6.6.3.1 Fluid Major Components. The candidate HFE-7000 series fluids can be characterized as a whole as alkyl perfluoroalkyl ethers. HFE-7100 and HFE-7200 are a combination of two compounds while HFE-7000 is >99% pure 1-methoxyheptafluoropropane. Independent evaluation of HFE-7000 samples at Rutgers University by capillary GC-MS in electron ionization and negative ion chemical ionization modes of operation found the neat liquid to be >99.7% 1-methoxyheptafluoropropane with chemically similar perfluorocarbons, perfluorocarbon hydrides, and perfluoroalkyl ethers detected as impurities. As well, trace amounts of sulfur-containing and a chloride compound were observed.

Similar to the HFE-7000 series, the Galden HT product line is composed of perfluoroalkene ethers; however, the compounds are arranged in polymer chains. Purity of the candidate ATCS fluids from the Galden HT product line has not yet been independently tested.

The Fluorinert products are comprised of a mixture of perfluorinated compounds. FC-72 contains C6 perfluoro compounds while FC-87 contains C5-C18 perflouro compounds. The Flourinert products range widely in purity. Of these two products, FC-72's purity has been evaluated independently by Rutgers University. This evaluation found FC-72 to contain the major constituents summarized in table 25.

Table 25. FC-72 Fluorinert major components.

Compound	Percentage
n-perfluorohexane	73.2
Perfluoro-2-methylpentane	17.89
Perfluoro-3-methylpentane	5.95
Perfluorocyclohexane	1.1
Perfluorodimethylbutane*	1.72
Perfluoromethylcyclopentane	0.13

The aqueous propylene glycol is assumed to consist of only two components—propylene glycol and water. In practice, stabilizing, corrosion inhibiting, and antimicrobial additives may be necessary. Because the additives that may be used in the aqueous propylene glycol active thermal control (ATC) fluid candidate are unknown, their assessment is beyond the present evaluation's scope.

6.6.3.1.1 Importance of Considering Impurities and Additives. Impurities and additives in an ATCS working fluid must be considered as part of the overall environmental impact assessment. As can be seen, FC-72 is not a highly pure fluid although its technical literature states that it is composed of 100% C6 fluorocarbon compounds. While technically correct, the MSDS omits key information that is important for thoroughly evaluating the fluid's suitability. This highlights the unfortunate situation whereby the MSDS and technical literature typically do not provide details about impurities or additives. In addition, many stabilizing, corrosion inhibiting, and antimicrobial additives are considered proprietary.

It is important to understand the nature of impurities and additives for various reasons. Chief among these is chemical stability. For example, straight carbon chain perfluorinated compounds are typically chemically inert. However, if oxygen or hydrogen atoms replace any of the fluorine atoms in the molecule, they become more reactive and susceptible to thermal decomposition.[43,44] Testing to determine neat fluid purity as well as testing under anticipated ECLSS process conditions is necessary to fully understand the hazards presented by thermal decomposition. In general, the more pure fluids are considered to be better choices as overall chemical complexity is lower, leading to a simpler ECLS compatibility assessment.

6.6.3.2 Solubility in Water and Impacts to Environmental Control and Life System Water Processing Systems. Solubility in water is an important consideration for any fluid that may be used in bulk on board a crewed spacecraft. Experience has found that highly water-soluble compounds can present significant challenges to on-board water purification processes.[3]

Solubility in water for the candidate perfluorocarbon fluids ranges from ‘insoluble’ to as high as ~20 ppm by weight (ppm_w). Table 26 summarizes the solubility in water of the candidate fluids reported in technical literature. The HFE-7200 product has the highest solubility in water at ~20 ppm_w. The HFE-7100 fluid follows at 12 ppm_w. Solubility in water of the FC-72 and FC-87 Fluorinert fluids are both <5 ppm_w. All of the Galden HT fluids are described as ‘insoluble.’ Specific information on the HFE-7000 fluid is not provided in technical literature but it can be assumed that the solubility in water will be similar in magnitude as the other HFE fluids or less due to its higher vapor pressure.

Table 26. Solubility in water of candidate ATCS working fluids.

Fluid	Solubility in Water
HFE-7000	N/A
HFE-7100	12 ppm_w
HFE-7200	<20 ppm_w
FC-72 Fluorinert	<5 ppm_w
FC-87 Fluorinert	<5 ppm_w
Galden HT 55	Insoluble
Galden HT 135	Insoluble
Galden HT 170	Insoluble
Propylene glycol	Miscible

In comparison, the solubility of oxygen in water at 25 °C is 39.45 ppm_w.[57] Therefore, the potential impacts presented by the candidate perfluorinated compound ATCS fluids to the water processing systems on board the ISS or any similar water purification system on board future space vehicles can be projected to be negligible.

Propylene glycol’s solubility in water is a particular issue. A previous engineering assessment of the impacts that polar organic compounds can have on the ISS’s water purification systems found that a propylene glycol concentration in the cabin atmosphere above 0.92 mg/m^3. To maintain the cabin concentration below this level, the introduction of propylene glycol into the cabin atmosphere must not exceed 44 mg/hr according to the study.[3] An assessment of volatility and its effect on evaporation rate is necessary to determine the maximum leaked amount that contributes to a water purification system incompatibility. For the sake of margin, it is most desirable to keep the introduction of propylene glycol under 20 mg/hr.

6.6.3.3 Volatility and Impacts to Environmental Control and Life Support Systems. Volatility must be considered because the rate that a leaked fluid evaporates and disperses in the cabin atmosphere is important in maintaining the cabin environment. Beyond a leak itself, evaporation of volatile components is the primary mechanism of impact to the cabin environment and for promoting contact with ECLSS processes. Volatility also plays a role in the ease that a dispersed fluid leak can be cleaned from the cabin atmosphere. Components possessing higher volatility typically are more difficult to remove from the cabin atmosphere by adsorption.

6.6.3.3.1 Impacts to Atmospheric Purification Systems. The vapor pressures of candidate ATCS fluids range from <0.13 to 81.1 kPa. Table 27 compares the vapor pressure for the candidate fluids. FC-87 Fluorinert possesses the highest vapor pressure at 81.1 kPa followed by HFE-7000 at 64.6 kPa. The other HFE-7000 series fluids have decreasing vapor pressures reflecting the shift from a methyl-substituted molecule to an ethyl-substituted molecule. Galden HT series fluids possess vapor pressures ranging from <0.13 to 29.9 kPa. This range is probably due to the extent of polymerization in the specific fluid with longer polymer chains possessing the lowest vapor pressure. Pure propylene glycol possesses the lowest vapor pressure, 0.017 kPa. For an ideal aqueous solution, however, the vapor pressure is ~1 kPa because water's pure vapor pressure is 2.5 kPa. Propylene glycol will, assuming ideality, make up 1.7% of the vapor from the aqueous solution.

Table 27. Vapor pressure of candidate ATCS working fluids.

Fluid	Vapor Pressure (kPa)
HFE-7000	64.6
HFE-7100	26.9
HFE-7200	14.5
FC-72 Fluorinert	30.9
FC-87 Fluorinert	81.1
Galden HT 55	29.9
Galden HT 135	1.1
Galden HT 170	<0.13
Propylene glycol*	0.017

* Aqueous vapor pressure = ~1 kPa with 1.7% of vapor being propylene glycol.

With respect to environmental impact, the fluids possessing the lowest vapor pressures are the most desirable. The combination of high molecular weight and low vapor pressure make compounds amenable to easy removal from the cabin atmosphere by activated carbon. Therefore, it is anticipated that the vapors of all candidate fluids can be removed with relative ease from the cabin atmosphere in the event of a leak by atmosphere revitalization and purification equipment typically used on board crewed spacecraft. For example, the TCC equipment—the U.S. Segment's TCCS and the Russian Segment's microimpurity removal assembly or BMP—both contain fixed beds of activated carbon designed specifically to remove trace components from the cabin atmosphere. In particular, the TCCS's activated carbon bed is designed to remove dichloromethane, a much lighter, more volatile halocarbon compared to the candidate fluids. Given this more challenging design point, it is expected that the TCCS will be capable of removing vapors of any of the candidate ATCS fluids from the cabin atmosphere.

Also, the compounds contained in the candidate fluids may be removed in the U.S. Segment's CDRA desiccant and CO_2 adsorbent beds. The desiccant bed contains layers of silica gel and 13X zeolite, and the CO_2 adsorbent bed contains 5A zeolite. Testing conducted by Lockheed in 1991 indicated that 1,1,2-trifluoro-1,2,2-trifluoroethane (Freon 113) is removed by the CDRA at a net 39% efficiency. Thirty-one percent of the Freon 113 entering the CDRA was removed in the desiccating stage while the CO_2 adsorption stage removed 25%. Net removal indicates some desorption back to the CDRA's exhaust when the desiccating stage is regenerated. Because the compounds under evaluation are larger molecules than Freon 113, it is possible that they may not be removed by the CDRA or a similar cabin atmosphere purification process due to their larger molecular size. The type of zeolite, its pore size, and the molecular size affect the removal performance.

Lockheed's testing did not indicate any degradation in the CDRA's ability to remove CO_2; however, the testing was not designed to evaluate life-related issues pertaining to CO_2 and contaminant co-adsorption. Due to their low volatility and the fact that the sorbent beds are heated to 200 °C during regeneration, it is not certain that either an undesirable buildup on the beds of the candidate ATCS fluids producing degraded performance or undesirable thermal degradation products could be produced during regeneration. Testing is necessary to fully characterize the potential for and extent of such impacts.

If bed materials similar to the CDRA are used in the CEV's CO_2 removal process, similar trace contaminant removal is likely. However, the use of vacuum-swing regeneration only may reduce the effective working capacity. Testing conducted on SA9T bed materials indicate it is less effective for removing trace contaminants such as dichloromethane with thorough regeneration. Using very short regeneration cycle times will contribute to further reduction of trace contaminant removal working capacity. Therefore, a significant assist to trace contaminant removal by the CEV's CO_2 removal process cannot be relied upon.

For a spacecraft employing vacuum-swing or combined vacuum/thermal swing adsorption processes for cabin atmosphere purification, care must be taken to ensure that compounds possessing high molecular weight, low vapor pressure do not enter the regenerable adsorbent beds. Such compounds may foul the beds over time, reducing their useful life. To this end, all efforts should be made to ensure persistent fugitive emissions into the cabin do not occur or appropriate guard beds are included as part of the atmosphere revitalization process design if long service life is a design criterion.

6.6.3.3.2 Impacts to Water Purification Systems. Impacts to water purification systems are minimal for all candidate fluids except propylene glycol. The earlier analysis documented by reference 3 determined that 0.92 mg propylene glycol/m^3 in the cabin atmosphere exceeds the allowable humidity condensate loading for efficient water purification function. This cabin concentration contributes to >35 mg/L loading of humidity condensate. While the CEV may not possess a concern in this area, compatibility with the systems on board the ISS must be considered.

Assessment of the ideal solution saturation vapor pressure indicates that the greatest concentration of propylene glycol that can exist is ~0.53 mg/m^3. This allows for a 42% margin with respect to ISS water processing system impacts for any size active thermal control ATC fluid leak.

6.6.3.3.3 Comparative Leak Size to Reach Default Spacecraft Maximum Allowable Concentration. The volatility of a fluid and the size of a leak determine how rapidly the cabin concentration may reach an unacceptable level. None of the candidate ATCS working fluids have an officially recognized SMAC. In the absence of an official SMAC, a default of 0.1 mg/m^3 is used for engineering evaluation purposes. First, estimating evaporation rate from leaked fluid is accomplished using a calculation technique recommended by the U.S. EPA for assessing environmental impacts of chemical spills. Equation (9) estimates evaporation rate, QR, in lb/min.[13]

When considering only the active contamination control removal provided on board the ISS as a basis, the maximum generation rate allowed is 4.2 mg/hr (1.54×10^{-7} lb/min). Rearranging equation (9) and solving for the surface area, A, the leaked amount can be determined from equation (21):

$$A = \frac{82.05 QR(T)}{0.284 u^{0.78} M^{2/3} P_V} . \tag{21}$$

A typical 0.0762 m/s cabin air flow velocity across the leaked fluid and temperature at 20 °C is assumed. The leaked volume can be found by applying equation (22), a relationship between volume and surface area for a sphere:

$$V = \frac{\pi}{6}\left(\frac{A}{\pi}\right)^{1.5} . \tag{22}$$

A spherically shaped leaked volume is the typical shape observed in microgravity conditions.

To maintain cabin concentration below the 0.1 mg/m^3 default SMAC leaked volumes average 8.75×10^{-4} mL for all but Galden 170 and aqueous propylene glycol. The leaked volumes for Galden 170 and aqueous propylene glycol are 0.1 and 0.04 cm^3, respectively.

With further guidance from toxicology experts, a higher SMAC guideline may be likely. For instance, earlier toxicology evaluation of Galden 135 and Galden 170 proposed saturation conditions assigned as toxic hazard levels 1 critical and zero, respectively. Galden 135's saturation condition is ~1% volume and Galden 170's saturation condition is ~0.1% volume. These concentrations are equivalent to ~250,000 mg/m^3 for Galden 135 and ~31,000 mg/m^3 for Galden 170. Limiting Galden concentration as a class to one-tenth the saturation condition of Galden 170, the allowable leaked volume grows to >600 L (160 gal).

If impacts to water processing systems are not considered, then aqueous propylene glycol may also enjoy a higher allowable concentration guideline but not until the CEV's mission goes beyond visiting the ISS. As long as the CEV visits the ISS water processing system, impacts will be the primary driver for limiting leaked quantities to <0.5 cm^3.

6.6.3.4 Thermal Stability and Decomposition. Understanding thermal stability and decomposition of candidate ATC fluids is necessary to ensure safety. LEL and thermal decomposition products are of most concern.

Because propylene glycol will readily decompose to CO_2 under typical high-temperature ECLS process conditions, emphasis is placed on the perfluorcarbon fluids in this discussion. However, it must be noted that propylene glycol vapors are flammable and the LEL is 2.6% by volume in air. This is equivalent to ~82,000 mg/m^3 in the cabin atmosphere. Higher oxygen partial pressure will lower the LEL evaluation of volatility, indicating that the greatest cabin atmospheric concentration that can be expected is <0.001% of the LEL. In this regard, thermal stability and decomposition is not a significant issue for aqueous propylene glycol.

Thermal stability of perfluorinated compounds is highly important in assessing compatibility with spacecraft ECLSS processes because some process conditions operate at temperatures of 400 °C or higher. According to MSDS literature, perfluorinated compounds may decompose to HF, COF_2, PFIB, CO, and CO_2 when exposed to high temperatures over a prolonged period. All of these are undesirable thermal degradation products. Early assessment of FC-72 Fluorinert, a product similar to FC-87 and HFE-7100 series fluids by NASA toxicology experts, recommended that the 'amount of volatile material used on board the ISS should be kept to a minimum' because of the limitations of atmosphere purification resources on board.

While means exist to remove CO and CO_2 from the cabin atmosphere, the other compounds—HF, COF_2, and PFIB—are highly toxic and much more difficult to remove. In all cases, vendor MSDS literature cautions against exposing the fluids to elevated temperatures for prolonged periods. MSDS temperature limit recommendations for the fluids range from 200 to 300 °C. Specifically, FC-87 must not be heated above 200 °C while HFE-7100 and HFE-7200 must not be heated above 300 °C to avoid thermal decomposition. Galden HT fluids must not be heated above 290 °C. No specific temperature is provided for HFE-7000 so it must be assumed that its limit is similar to HFE-7100 and HFE-7200.

The predominant thermal decomposition product is HF with PFIB typically produced at a 1,000 times lower rate. However, the HF exposure limit is 3 ppm_v while that for PFIB is 0.01 ppm_v. This still makes PFIB production a significant concern that must be addressed in more detail.

Due to the recommendations from MSDS literature and concerns for toxic hazard risks associated with some impurities found in the fluids, more rigorous evaluation and testing of thermal stability must be considered a requirement for any perfluorocarbon used as an ATCS working fluid.

6.6.3.4.1 Perfluorocarbon Thermal Stability Literature Review. A literature review found that the conditions necessary to form PFIB require a perfluorocarbon-rich environment coupled with a very long exposure time in the presence of halogen gases. In the studies documented by references 43 and 44, the experimental conditions involved sealing the perfluorocarbon under study in a tube by itself or with chlorine (Cl_2) or Br_2 gas followed by exposure to a high temperature for at least 1 hr. These conditions are not representative of those typically found on board the crewed spacecraft or within their cabin air purification systems.

On board a crewed spacecraft such as the ISS, the perfluoro compound will be in the presence of excess oxygen in the cabin air and the residence time within the cabin air purification systems is relatively short. For example, the exposure time to high temperature surfaces within both the ISS TCCS COA and solid-fuel oxygen generation system (Russian acronym TGK) is less than 1 s. The maximum estimated TCCS COA residence time is 0.67 s with a process temperature of 400 °C. Residence time for the TGK is 0.76 s with exposed surface temperature no greater than 90 °C for the TIK solid oxygen source cartridge. Typically, the TIK cartridge external surface temperature is 50 °C. The TIK cartridge is designed to withstand a maximum 450 °C external surface temperature. Both units currently are built from 300 series stainless steel alloys; however, a change to the TGK may change its construction to a titanium alloy. Neither alloy possesses catalytic properties under normal equipment operating conditions.

The literature survey findings indicate that oxygen plays a role by suppressing PFIB formation. Oxygen presence may result in other products such as HF, CO, COF_2, CH_4, and CO_2.

Residence time is also important. For instance, an experiment that flowed perfluoropropene through a tube held at 510 °C and 1 atm to provide a 10-s contact time found no PFIB was formed. In contrast, a 7-hr exposure in a sealed tube at the same temperature condition found reaction products. PFIB was not found below 700 °C in this experiment.

6.6.3.4.2 Perfluorocarbon Thermal Stability Testing. Overall, the literature survey indicated that PFIB production is not expected in detectable quantities under normal ISS or future crewed spacecraft cabin air purification process operating conditions. To test this hypothesis and also investigate the potential for producing other harmful oxidation products, two testing activities were defined and executed. The first, conducted by MSFC, subjected FC-72 and 99% perfluoro-n-hexane to a sustained temperature condition of 250 °C in a flowing gas stream in both oxidizing and non-oxidizing environments. The second testing was conducted at Rutgers University to investigate the thermal stability of FC-72, 99% perfluoro-n-hexane, and HFE-7000 under dynamic flow conditions representative of typical cabin air purification processes such as the ISS TCCS COA and the Russian TGK. In this testing, the composition of 3M Company FC-72, two samples of 99% perfluoro-n-hexane from different suppliers, and HFE-7000 were evaluated for impurities and for decomposition products when exposed to contact time and temperature conditions representative of the TCCS COA and Russian TGK.

6.6.3.4.2.1 Thermogravimetric-Infrared Testing of Perfluorohexane. Fluids qualitative screening tests were conducted at MSFC using a coupled TG-IR analysis technique. The test specifically targeted the appearance of carbon double bonds that would qualitatively indicate the presence of PFIB. Samples of 3M Company FC-72 Fluorinert and 99% perfluoro-n-hexane from Aldrich Chemical Co. were exposed to a sustained temperature of 250 °C. Exposure times exceeded 8 min. Results showed no evolution of functional groups containing carbon double bonds for all runs. Also, no signatures indicating other decomposition products were observed.

6.6.3.4.2.2 Dynamic Thermal Stability Testing of Perfluorohexane Fluids. This testing conducted at Rutgers University involved two steps: (1) An evaluation of the purity of 3M Company FC-72 and samples of 99% perfluoro-n-hexane from Aldrich Chemical Co. and F2 Chemicals Ltd., and (2) a series of five flow tests representative of TCCS and TGK process conditions in both oxidizing and nonoxidizing environments. Analytical methods were GC/MS and GC with FID.

The purity of 3M Company FC-72 observed is summarized in table 25. In addition to the compounds reported in table 25, trace and ultratrace quantities of other compounds were noted. The sample from Aldrich Chemical Company contained 99.4% perfluoro-n-hexane with some C_6, C_8, and C_{10} perfluorocarbons. The F2 Chemicals Ltd. sample contained 99.7% perfluoro-n-hexane, 0.1% perfluorocyclopentane, and 0.2% perfluoro-2-methylpentane.

Contact time and the temperature conditions exceeded the process conditions within the TCCS COA and Russian TGK. The TCCS COA operates at 400 °C while exposed surfaces within the Russian TGK do not exceed 90 °C. For the experimental runs, the contact time was >1.2 s with catalyst material packed in the reactor. This contact time accounts for catalyst interstitial volume only and is ~79% greater than the actual 0.67-s contact time in the TCCS COA. When empty, the reactor provided >8.7-s contact time which far exceeds the Russian TGK contact time of 0.76 s.

Testing under simulated TCCS and TGK process conditions found that the perfluorohexane samples were not degraded under any conditions and no trace PFIB was detected above the method detection limit of ~10 ppb_v. No changes in inlet composition were observed from analyses of the outlet condition. No other oxidation products of concern were noted.

6.6.3.4.2.3 Dynamic Thermal Stability Testing of HFE-7000. Samples of HFE-7000 were also evaluated for thermal stability under the same dynamic conditions. Observed results indicate 57%–59% of the HFE-7000 are converted to nonvolatile thermal decomposition products, leaving 41%–43% of the initial HFE-7000 mass as volatile products. Carbon monoxide, CO_2, and water vapor were also observed in the pyrolysis gas.

Under the experimental conditions, 100% of the primary component, 1-methoxyheptafluoropropane, as well as the sulfur-containing and chlorocarbon impurities decomposed. Several impurities, including perfluoroethane, perfluoropropane, and a perfluorocarbon hydride were unchanged. Methane was observed in the pyrolysis gas. This is likely due to the release of the methyoxy group from HFE-7000's primary component. Since fluorine is a known strong oxidation catalyst poison, it is likely that perfluorocarbon radicals may also act as poisons. Combined with the very short contact time in the reactor, further decomposition of the methoxy group beyond its most stable form—methane—did not occur. No harmful products, such as PFIB, were observed.

6.6.3.4.3 Summary of Perfluorocarbon Thermal Stability Tests. In summary, testing was conducted on FC-72 using two separate methods. In both sets of tests, no evidence of PFIB production was observed after exposure to a 250 °C condition for 8 min or 450 °C in the presence of the TCCS catalyst in an oxidizing environment. HFE-7000 was also subjected to testing under simulated TCCS process conditions and decomposed completely. For all tests involving multiple analytical methods and two candidate ATCS fluids, no hazardous pyrolysis products were observed. Based on these results, the hypothesis that PFIB is not produced in measurable quantities under short exposure times and in the presence of excess oxygen as advanced by the literature survey is supported. Also, no other oxidation products of concern were observed.

6.6.4 Predicted FC-72 Impurity Stability Under Environmental Control and Life Support System Process Conditions

The experimental conditions used for assessing the decomposition of the components comprising FC-72 have been established to be conservative relative to the ISS and likely for most future spacecraft ECLSS process conditions with respect to temperature and contact time. Further, the ECLSS process temperature conditions within the ISS TCCS and Russian TGK exceed the temperature where some branched carbon chain perfluorocarbon compounds may decompose to produce hazardous products such as PFIB according to references 43 and 44. To understand the theoretical extent of PFIB production during contact with heated ECLSS process equipment and to better understand the ECLS testing results, reaction rate data and conditions favorable to PFIB formation must be considered. Therefore, literature sources documenting the potential for hazardous thermal decomposition product formation were evaluated with respect to the relevance of experimental conditions to ISS and future spacecraft ECLSS process conditions. Other literature sources were also reviewed to understand contributing and inhibiting factors associated with PFIB formation under high temperature conditions.

6.6.4.1 Comparison of Literature Experimental and Environmental Control and Life Support Process Conditions. Review of references 43 and 44 that indicates the potential for hazardous thermal decomposition product formation found that the experimental conditions were specifically tailored to form pyrolysis products so that reaction mechanisms could be studied. Specifically, each 10-mmole experimental sample under evaluation was sealed in a 10-mL glass tube and held at high temperature for 8 to 15 hr. During this time, pressure in the reaction volume could rise to ~34 atm. To promote reaction, other compounds such as halogens or toluene were injected in some instances. All experiments were conducted in the absence of air or oxygen. This is a key point of departure from actual crewed spacecraft air quality control system process conditions. It is also important because studies conducted at Oak Ridge National Laboratories found that PFIB formation is suppressed in the presence of oxygen.[45,46] As well, references 45 and 46 as well as reference 47 indicate PFIB hydrolysis by moisture in the air will occur with HF, CO, COF_2, and CO_2 as the resulting products. Overall, the literature sources that indicate the potential for a hazard are meaningful only to the extent that reaction rate data are provided for perfluorocarbon compounds similar in structure to perfluoro-2,2-dimethylbutane, an impurity found in FC-72.

Because the experimental conditions with respect to residence time, pressure, and nonoxidizing conditions are not representative of those typically found within crewed spacecraft cabin air quality control system processes, references 43 and 44 are useful for information only. At most, these reference materials demonstrate that hazardous thermal decomposition products are produced under static conditions over a long contact time. Such conditions are extraordinary compared to those that exist within cabin air quality control process equipment on board the ISS or envisioned for future crewed spacecraft.

Even so, the potential for thermal decomposition should not be taken lightly and efforts to best understand the situation presented by ATCS fluid leakage scenarios must be undertaken. Therefore, to achieve a complete, conservative assessment, reaction rate data from references 43 and 44 are considered for predictive purposes with appropriate adjustment to eliminate the effects of radical traps. It must be noted that, although highly likely under ECLSS process conditions, further reaction of PFIB with oxygen and moisture to form other products is not considered and, as such, the predictions that follow are considered to be conservative. The degree of conservatism, unfortunately, cannot be fully quantified except to apply the predictive technique as a check of the observed ECLS compatibility testing results.

6.6.4.2 Predicted Extent of Reaction. While review of the available literature on the subject of hazardous thermal decomposition products demonstrates that the documented experimental conditions are not representative of typical ECLSS process conditions, it is prudent to consider the reaction rate data contained in these sources as a potentially conservative means to estimate PFIB formation. Of the perfluorohexane isomers present in FC-72, the most likely to thermally decompose to PFIB is perfluoro-2,2-dimethylbutane. Perfluoro-2,2-dimethylbutane, combined with perfluoro-2,3-dimethylbutane, comprise approximately 1.7% of FC-72. Of all the isomers, however, only perfluoro-2,2-dimethylbutane has the potential to thermally decompose at some ECLSS process conditions, such as those found in the ISS TCCS COA, to produce PFIB. All other isomers are not expected to decompose according to the cited literature.[48]

By using as a basis a rate constant at 181 °C (0.77×10^{-5} s^{-1}) from data acquired by Rutgers University for a similar compound that may produce PFIB among its three decomposition products, a reasonable rate constant estimate at 400 °C is made using the Arrhenius equation.[49] The result is 0.78 s^{-1}. This is a first order rate constant and does not reflect the enhancement of the rate constant in the presence of radical traps. Pressure effects on the rate constant are not considered because rate constant decrease is typically not observed until pressure falls below 26.7 kPa.[49]

6.6.4.2.1 Theoretical Perfluoroisobutene Production in the Trace Contaminant Control System Catalytic Oxidizer Assembly. For a case based on a planned ISS application in the JEM where 75 mL (0.37 moles) of FC-72 leaks, the predicted cabin concentration of perfluoro-2,2-dimethylbutane is 1.74×10^{-5} moles/m^3. For the purpose of this assessment, it is conservatively assumed that the TCCS activated carbon capacity is completely consumed and all the FC-72 and its impurities enter the COA. In the TCCS COA, the maximum residence time is 0.67 s. Using a solved form of a first order plug flow reactor mass balance equation, the single-pass extent of reaction is 41%.[50,57] Keeping in mind that three or more different decomposition products result, the extent of reaction to PFIB is 13.5%. If it is assumed that the perfluoro-2,2-dimethylbutane isomer conservatively accounts for all of the 1.7% perfluorodimethylbutane impurity in FC-72, then the maximum PFIB concentration in the TCCS exhaust gases in the event of a 75-mL release is 0.14 mg/m^3 (0.02 ppm_v).

PFIB is easily removed by activated carbon so the absolute maximum cabin concentration that may result from sustained FC-72 processing via the TCCS COA at an inlet concentration representative of a 75-mL FC-72 leak is 0.05 mg/m^3 (6 ppb$_v$). Production, of course, is transient from a static leak as the FC-72 concentration in the cabin is reduced.

6.6.4.2.2 Comparison to the Observed Environmental Control and Life System Compatibility Testing Results. Applying the rate constant data to the ISS TCCS COA testing conducted by Rutgers University, the highest calculated extent of reaction predicts ~0.01 mg PFIB/m^3 (~1.3 ppb$_v$) in the test gas effluent. This is far lower than the analytical method's ~10 ppb$_v$ detection limit. Therefore, the ECLS process experimental results are indeed expected because, even under the most conservative conditions, the maximum amount of PFIB formed is predicted to be far below the analytical method detection limit.

6.6.4.2.3 Considerations for Perfluoroisobutene Reaction in Humid Air. It must be kept in mind that in the presence of oxygen and humidity and under higher temperature conditions encountered in some crewed spacecraft ECLSS processes, PFIB will very likely react further or its formation may be depressed. Other reaction products expected in humid air include CO, HF, COF_2, and CO_2. These effects are not quantified by available literature sources or ECLS compatibility testing data so cannot be accounted for in any risk assessment. Further testing using analytical methods that target these compounds is necessary to fully understand the role that oxygen and humidity play in PFIB's persistence under high temperature conditions. Also, the perfluoro-2,2-dimethylbutane isomer is present in lower quantities than assumed for this assessment. For example, an assay provided by the 3M Company indicates it is present at 0.74%. Therefore, the calculated results are conservative by approximately a factor of 2.

6.6.4.2.4 Considerations for Removal by Activated Carbon. Previous ECLS assessment presented in section 6.1 found the equilibrium GAC loading for perfluoro-n-hexane is 0.2 g/g GAC. At this capacity, >4,500 g or 2.7 L of perfluorohexane is required to saturate the 22.7 kg of GAC in the ISS TCCS CBA. Allowing for 20% operational margin, the total leakage required to saturate the CBA is 2.1 L.

Similarly, the BMP in the ROS contains an expendable packed bed (FOA unit) containing 2 kg GAC and two regenerable packed beds (ZPL-1M units) containing 2.8 kg GAC combined. In total, the BMP may accommodate ~960 g or 570 mL of perfluorohexane. Its expendable GAC bed, however, can accommodate only 400 g or ~240 mL of perfluorohexane.

In total, the maximum quantity of FC-72 that may be leaked into the ISS cabin leading to complete saturation of the TCCS and BMP is 2.6 L. This amount includes 20% operational margin to account for the effects of co-adsorption on activated carbon saturation. From a maintenance perspective, however, any leak exceeding 120 mL will require maintenance on the BMP to replace its expendable GAC bed and any leak exceeding 1 L will require maintenance on the TCCS to replace the CBA. These amounts represent one-half the equilibrium capacity of the expendable activated carbon beds in the TCCS and BMP. Given that perfluorohexane is not water soluble, it is expected to have minimal impact on elution of previously adsorbed contaminants from GAC beds.

Comparatively, the FC-72 is one of the more difficult of the candidate ATCS fluids to remove using activated carbon adsorption. Ease of removal by activated carbon can be projected by examining the relative magnitude of the vapor pressure. Using this comparison, FC-87 and HFE-7000 are expected to be more difficult than FC-72 to remove from the cabin atmosphere. Galden HT 55 and HFE-7100 are projected to be removed with comparable ease to FC-72. The HFE-7200, Galden HT 135, and Galden HT 170 fluid components are expected to be removed much more easily than FC-72. The latter fluids, especially Galden HT 135 and Galden HT 170, however, must be evaluated for their compatibility with regenerable cabin air quality control processes. Their very low vapor pressures may cause them to act as fouling agents for regenerable adsorbent media, especially for adsorbent media regenerated solely by vacuum swing processes.

6.6.5 Reactivity

Reactivity hazards noted for the candidate perfluorocarbon-based compounds are consistent for all. Essentially, they must not be exposed to strong or nonaqueous alkali. Most spacecraft ECLSSs use granular LiOH either as the primary or backup means to remove CO_2 from the cabin atmosphere. Based on vendor recommendations, it is not recommended to allow the candidate compounds to enter an LiOH bed unless specific testing indicates no reactivity issues exist for the expected range of cabin temperature and relative humidity conditions.

Typically, reaction of halocarbons over an alkali material requires elevated temperature for the reaction hazard to exist. However, only the Galden HT series literature notes a temperature threshold of >100 °C where the reactivity hazard may be present. The literature for the other fluids only states that contact with strong bases should be avoided and provide no guidance with respect to temperature. Given that there are potential incompatibilities with LiOH, further investigation in this area is required if one of the candidate fluids is selected for use on board crewed spacecraft that use LiOH to remove CO_2 from the cabin atmosphere.

No significant reactive hazards are noted for aqueous propylene glycol.

6.6.6 Relative Toxicity

Recommended industrial 8-hr exposure limits for the candidate fluids range from 75 to 750 ppm_v. The HFE-7000 fluid has the lowest industrial 8-hr exposure limit at 75 ppm_v. HFE-7100 has an industrial 8-hr exposure limit of 750 ppm_v, while HFE-7200 has a limit of 200 ppm_v. No exposure limit is available for FC-87 Fluorinert and no inhalation hazards are noted; however, it is noted that ‘significant irritation’ may occur in the event of skin or eye contact. Likewise, no exposure limit is established for the Galden HT series fluids but it is noted that they are potential eye, skin, and respiratory irritants. Previous study of Galden HT 135 and HT 170 fluids classified their saturation conditions as toxic hazard level 1 and level zero, respectively. Propylene glycol safety data sheets do not note any significant inhalation hazards. Some eye irritation may occur on contact.

Some of the supplier literature compares the fluids to acetone. The 8-hr exposure limit for acetone is 500 ppm_v. Note also that acetone has a vapor pressure comparable to HFE-7100 and the high end of the Galden HT series fluids. The official 180-day SMAC for acetone is 22 ppm_v.[58] While it is beyond the expertise of ECLS engineering to set exposure limits by mere comparison, it can be anticipated that a potential SMAC for these compounds may be a factor of 23 lower than their 8-hr exposure limits. This could result in HFE-7000 being classified as more toxic than ammonia, one of the thermal working fluids presently in use by NASA, which has a 180-day SMAC of 10 $\mathrm{ppm_V}$.[59] The HFE-7100 and HFE-7200 fluids may be less toxic than ammonia while it is not possible to speculate about FC-87 Fluorinert and the Galden HT series fluids.

In summary, if selected for further study, any of the candidate fluids must be evaluated by toxicology experts to establish SMAC guidelines. Upon establishing specific cabin air quality guidelines for each fluid, a further detailed analysis of the spacecraft ECLSS's ability to control specific leakage scenarios to within the toxicologist's guidelines will be necessary. Until that time, allowable leaked amounts are limited to <1 $\mathrm{cm^3}$.

6.6.7 Summary

A variety of candidate ATCS working fluids have been described and evaluated by testing and analysis to determine their potential environmental impact if used on board the ISS or future crewed spacecraft. All of the candidate fluids, with the exception of propylene glycol, are minimally soluble in water. All except Galden HT 135, Galden HT 170, and aqueous propylene glycol possess moderate to high low vapor pressures. Thermal stability testing of FC-72 and HFE-7000 was conducted under conditions representative of some ISS ECLSS processes and no harmful decomposition products were observed. The FC-72 fluid was found to be more thermally stable than the HFE-7000, which was completely decomposed. Impurities in the fluids must be considered for their potential to contribute to hazardous thermal decomposition products. Worst-case assessment of impurities contained in FC-72 found the absolute worst-case PFIB production under simulated ECLSS conditions to be well below air quality monitoring method detection limits. All candidate perfluorocarbon-based fluids note reactivity hazards with strong or nonaqueous alkali. For this reason, compatibility studies with LiOH should be considered.

6.6.8 Conclusions and Recommendations

Based on data acquired from vendor and scientific literature supplemented with data from tests of two candidate fluids, conclusions and recommendations regarding the candidate ATCS fluids are the following:

- The candidate perfluorocarbon-based fluids are no more soluble in water than oxygen and, therefore, are considered a negligible risk to ISS and future space vehicle and outpost water purification systems.

- Aqueous propylene glycol presents a potential risk to ISS water purification systems in leaked amounts >0.5 $\mathrm{cm^3}$.

- The vapors from the candidate fluids should be removed from the cabin atmosphere by activated carboncontained in typical spacecraft cabin atmosphere purification systems. Testing is prudent for high molecular weight components to address the potential for long-term fouling of regenerable bed processes.

- Thermal stability issues of perfluorocarbon-based fluids must be addressed on a case-wise basis. Processconditions in high temperature ECLSS equipment are typically greater than the recommended ‘not to exceed’ temperatures leading to the risk that HF and PFIB may be produced and liberated into the cabin upon contact with the heated surfaces. Specific testing of fluorocarbon fluids under representative ECLSS process conditions is required.

- Attention should be given to selecting fluids possessing high purity to minimize compatibility and reactivity risks. For instance, selecting a highly pure form of n-perfluorohexane over FC-72 Fluorinert significantly reduces risks presented by possible hazardous thermal decomposition products associated with impurities.

- A significant reactivity hazard exists for all the candidate perfluorocarbon-based fluids with strong, nonaqueous alkali materials. If any of the candidate fluids are selected for use on board future crewed spacecraft or space outposts, a full evaluation of compatibility with LiOH over a range of temperature is necessary.

- All candidate ATC fluids require evaluation by toxicology experts to establish SMAC guidelines. Maximum leaked quantities are presently constrained by using the 0.1 mg/m^3 default SMAC.

7. LEAKAGE FROM BATTERY FAILURE

The following assessment considers the ECLS compatibility and cabin environmental impact of chemicals released upon a battery failure.

7.1 Remedial Response for Lithium Thionyl Chloride Battery Failure

The following assessment was conducted in 2004 and documented by NASA memorandum FD21(04-100), "Environmental Control and Life Support System Compatibility and Remedial Response for Granada/Japanese Crystallization Facility Lithium Thionyl Chloride Battery Failure," dated August 5, 2004.

7.1.1 Background

An assessment of ECLSS compatibility and remedial response in the event of lithium thionyl chloride ($LiSOCl_2$) battery failure has been conducted to address risks associated with delivering the Granada Crystallization Facility (GCF)/Japanese Crystallization Facility (JCF) to the ISS on board logistics flight 15P. The primary hazard presented by batteries containing $LiSOCl_2$ is rupture followed by containment loss that allows the electrolyte to contact the cabin atmosphere. A variety of batteries used in equipment on board the ISS contain $LiSOCl_2$. A listing is provided in table 28 for reference. The batteries of interest for logistics flight 15P are the Sonnenschein SL-550 ½ AA type contained in data logging equipment used in the GCF/JCF payload. Other payloads or equipment may use other battery types not listed in table 28.

Table 28. $LiSOCl_2$ battery types.

Manufacturer and Model	Size	Amount of $LiSOCl_2$ (g/battery)
Sonnenschein SL-550	1/2 AA	3.42
Tadiran TL2186	ER22G75 (Wafer)	1.2
Tadiran TL2134	1/10 D, ER32L65	5.13
WGL	D	36

Of particular concern is the thionyl chloride ($SOCl_2$) component of the battery electrolyte. $SOCl_2$ is a pale yellow to red fuming liquid possessing properties summarized in table 29.[35] On contact with water, thionyl chloride decomposes to sulfur dioxide (SO_2) and HCl. The worst-case assumption is that decomposition occurs in condensing heat exchangers and may also occur upon interaction with humid air. Whether $SOCl_2$ decomposes on contact with water adsorbed on activated carbon beds is unknown but considered possible.

Table 29. $SOCl_2$ properties.

Property	Value
Color	Pale yellow to red
Phase	Liquid
Odor	"Suffocating"
Molecular weight (g/mole)	118.96
Specific gravity	1.638
Boiling point (°C)	79
Thermal stability	Decomposes at 140 °C
Solubility	Soluble in benzene and carbon tetrachloride
Interaction with water	Decomposes (fumes)
Vapor pressure (mm Hg @ 20 °C)	92
Liquid molar volume (cm^3/g-mole)*	77

* Estimated using Schroeder method, Reid et al.: *The Properties of Gases and Liquids*. 3rd Ed. pp. 59–60, 1977.

To simplify the assessment's complexity and address the range of potential conditions contributing to $SOCl_2$ decomposition, it is assumed that a minimum of 96% of any released $SOCl_2$ exposed to the cabin atmosphere decomposes. This is considered to be a conservative assumption because a documented decomposition half-life for $SOCl_2$ is on the order of 8 to 9 hr (32,000 s) at 320 °C. Therefore, decomposition at room temperature is anticipated to be much slower because the natural logarithm of the reaction rate constant is inversely proportional to temperature ($\log k \approx -1/T$).

Given the information on decomposition half-life, it is anticipated that immediate attention to containment and cleanup of exposed liquid, therefore, can serve to lessen the hazard associated with decomposition products evolving from released electrolyte. Appropriate personal protective equipment must be worn by crewmembers participating in any remedial activities involving released electrolyte. Sodium bicarbonate (baking soda – $NaHCO_3$) may be used to neutralize the electrolyte.

7.1.2 Payload Containment

The GCF/JCF payload includes both the Granada Crystallization Facility (GCF) and the Japanese Crystallization Facility (JCF). The GCF and JCF equipment both include a 'sugar-cube' temperature data logging device that contains the $LiSOCl_2$ battery. The battery is enclosed in a hermetically sealed polycarbonate housing that includes a single O-ring seal. Both the GCF and JCF payloads house the experiment equipment, including the data logging device, inside an outer container. The GCF outer container is made from aluminum and is sealed by dual Viton O-rings. The JCF outer container is made from 304 stainless steel and also sealed by dual Viton O-rings. Absorbent material is provided in the design to neutralize leaked battery electrolyte. Overall, the GCF/JCF payload design provides three levels of containment for the battery electrolyte.

7.1.3 Environmental Impact

Compatibility with the ECLSS equipment on board the ISS is based upon the worst-case scenario during which an $LiSOCl_2$ battery fails and both the data logger seals and outer containment dual Viton O-ring seals fail. It is further assumed in this worst case that 100% of the electrolyte released during the battery failure is exposed to the cabin atmosphere. Two cases are considered. The first case involves a battery failure where the leak is contained to the U.S. Laboratory alone. The second case involves contamination dispersal throughout the ISS volume. In both cases, it is assumed that decomposition of $SOCl_2$ to SO_2 and HCl has occurred.

7.1.3.1 Evaporation Rate and Dispersal in the Cabin. In the event 100% of the electrolyte is released, the estimated evaporation rate for $SOCl_2$ is 748 mg/hr. This calculation is based upon U.S. EPA guidelines for estimating evaporation from liquid spills.[11,13] Complete $SOCl_2$ evaporation of 1 g of spilled electrolyte is estimated to take 1.3 hr when using this evaporation rate. For 3 g, as is the case for Sonnenschein SL-550 ½ AA batteries, complete evaporation is estimated to take 4 hr. At prevailing cabin intermodule ventilation flows, mixing throughout the entire ISS cabin is estimated to take less than 2 hr. Therefore, in the case where all containment levels fail and the leaked electrolyte is not found within 4 hr, complete mixing throughout the ISS cabin is assumed.

Under this condition it is also assumed that all $SOCl_2$ will ultimately decompose to SO_2 and HCl as it is exposed to water in condensing heat exchangers. Presently, humidity condensate is removed in the Russian Segment. At the typical 144 m^3/hr air flow through the SKV unit, a complete ISS volume exchange is expected within 2.6 hr. Assuming 100% decomposition of $SOCl_2$ in the SKV and further assuming the crew does not find the leaked material before complete evaporation occurs, it is estimated that complete decomposition and dispersion of SO_2 and HCl throughout the ISS cabin can occur within 7 hr.

7.1.3.2 Estimated Cabin Concentration. Isolated to the U.S. Laboratory volume, the maximum amount of SO_2 and HCl produced from decomposition of $SOCl_2$ from a single battery failure result in 15.5 mg/m^3 and 17.7 mg/m^3 concentrations, respectively. Allowing dispersion throughout the ISS cabin, concentrations are 4.2 mg SO_2/m^3 and 4.8 mg HCl/m^3.

Note that the odor threshold for SO_2 is 2.9 mg/m^3 (1.1 ppm_v), while for HCl, it is 1.5 mg/m^3 (0.77 ppm_v).[28] Predicted peak concentrations for both cases exceed the odor threshold; therefore, it is possible that the crew may detect the problem by a sharp, pungent odor.

Interestingly, the 7-day/30-day/180-day SMAC for HCl is 1.5 mg/m^3—equal to the odor threshold. There is no documented SMAC for SO_2; however, the National Institute for Occupational Safety and Health has recommended a short-term exposure limit of 1.3 mg/m^3 and OSHA has recommended an 8-hr, time-weighted average of 5.2 mg/m^3. For the purposes of spaceflight, however, the 0.1 mg/m^3 default SMAC applies when no interim or formally documented SMAC is available.

Comparing the predicted concentrations for both isolation within the U.S. Laboratory volume and dispersal throughout the entire ISS cabin does indicate potential for both odor and health risk to the crew because maximum predicted concentrations exceed documented SMACs and odor thresholds. Therefore, quick remedial action is required.

7.1.3.3 Environmental Control and Life Support System Compatibility. If $SOCl_2$ does not decompose, the TCCS located in the U.S. Laboratory and the BMP located in the SM can be considered as a primary means for remediation in the event of a battery failure. In this case, the TCCS activated CBA and the BMP's regenerable charcoal beds can remove it. The estimated saturation capacity for the TCCS's activated charcoal is 14.5 mg/g charcoal. The BMP's charcoal capacity typically is similar to the TCCS. For 3 g of $SOCl_2$ released in a worst-case single battery failure from the GCF/JCF payload, approximately 207 g of charcoal, or 0.9% of the TCCS's charcoal capacity, will be consumed. This is considered a negligible impact to TCCS operational and logistics performance.

If $SOCl_2$ decomposes, the TCCS and BMP are not suitable for removing the SO_2 and HCl. Testing has shown that LiOH—both in its initial form and after its conversion to lithium carbonate (Li_2CO_3)—will remove both SO_2 and HCl.[30] Therefore, any $SOCl_2$ decomposition products entering the TCCS will be removed in the TCCS's SBA. For a single ½ AA cell battery failure, 1.55 g SO_2 (0.024 moles) and 1.77 g HCl (0.049 moles) can be produced. The total SBA capacity is 3.92 moles of acid gas.[21] Reaction of the SBA adsorbent material with acid gases is on a 1:1 molar basis so the total estimated consumption is 0.073 moles or about 2% of the SBA's total capacity. The SBA maintains an operational performance margin of at least 20%. Therefore, the impact upon the TCCS for up to two failed batteries is considered acceptable. However, in the case of larger batteries such as the D-cell manufactured by WGL, 12 times the amount of $SOCl_2$ can be released, resulting in complete consumption of the SBA's operational margin. It is not recommended that the TCCS be used during remedial activities for D-cell $LiSOCl_2$ batteries.

Although there is potential for using the TCCS as a tool for remedial action, specific attention must be given to compatibility with the its COA. The COA contains a platinum group metal catalyst that can be poisoned by both sulfur-containing and halogenated compounds. In the case of sulfur-containing compounds, the effect is irreversible. Based upon testing, the concentration of sulfur dioxide (SO_2) is important in maintaining the TCCS COA function. The maximum free sulfur concentration that could enter the TCCS is 7.8 mg S/m^3. At this concentration, the COA can be expected to lose 70% of its activity for removing methane. Recovery to normal operations requires removal and replacement of the COA. Evaluation of the CBA's capacity for SO_2 indicates that only 315 mg can be removed. This is only 20% of the SO_2 that can be evolved if all $SOCl_2$ decomposes. Without the ability to monitor $SOCl_2$ or SO_2, it is not recommended to use the TCCS during remedial activities for any battery failure. It is anticipated that effects upon the TCCS can occur within 7 to 9 hr after a battery failure if the electrolyte escapes from all the containment levels.

Because LiOH has been demonstrated to be effective in removing both SO_2 and HCl, deploying a portable fan assembly (PFA) with the CDRK in the U.S. Segment as well as activating the LiOH-based backup CO_2 removal equipment in the Russian Segment is recommended. Either fresh or used LiOH canisters can be used. To preserve functional backup, using spent LiOH canisters is recommended. Neither SO_2 nor HCl are highly water soluble, leading to minimal effects on water processing systems. For a two-person latent load being removed by the SKV in the Russian Segment, the single-pass removal efficiencies are 0.12% and 0.0079% for HCl and SO_2, respectively.

With respect to normally functioning ECLSS equipment, the TCCS should be shut down. Consideration should be given to placing the BMP into its rapid regeneration mode to assist with removing SO_2. However, using the BMP in this manner must be coordinated with the appropriate Russian technical specialists. Like the TCCS, the BMP also contains platinum group metal catalyst materials that can also be susceptible to irreversible poisoning. If it is determined that SO_2 presents an excessive risk to the BMP's catalyst materials, then it too should be shut down.

7.1.3.4 Estimated Remediation Time. Because the TCCS COA can be damaged under worst-case conditions, remediation equipment in the U.S. Segment is limited to the PFA with the CDRK. This equipment provides approximately 15 m^3/hr flow. Because no testing specific for LiOH's efficiency for removing SO_2 and HCl in this configuration has been accomplished, a single-pass efficiency of 75% is assumed. This same efficiency is assumed for Russian LiOH. The SKV removes contaminants via absorption. The calculated single-pass efficiency is 0.12% for HCl and 0.0079% for SO_2 for a two-person latent load. Air flow through the SKV heat exchanger core is 144 m^3/hr. Predicted removal time for SO_2 and HCl are provided in figures 57 and 58. The cases where the contamination is isolated to the U.S. Laboratory and dispersed throughout the ISS cabin are considered. Overall remediation time is estimated to take 40 hr from PFA/CDRK deployment if the contamination is isolated to the U.S. Laboratory only. This time applies to reducing both SO_2 and HCl concentration by 99%. Remediation takes much longer if the contamination is dispersed. Total elapsed time for 99% concentration reduction is nearly 65 hr. As seen in figure 58, HCl removal drives the elapsed time. In theory, $SOCl_2$ by itself can be removed much more quickly because it is effectively removed by activated charcoal; however, it is extremely difficult to estimate how rapidly it decomposes and it is not known whether it will react with water adsorbed on the carbon.

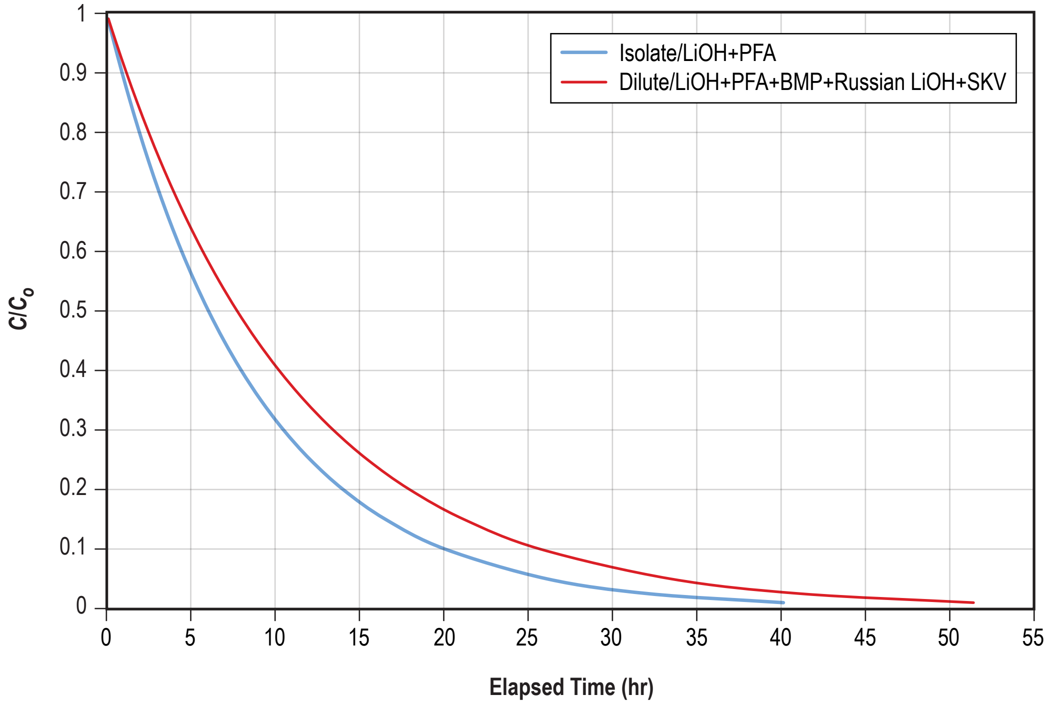


Figure 57. Estimated SO_2 remediation time.

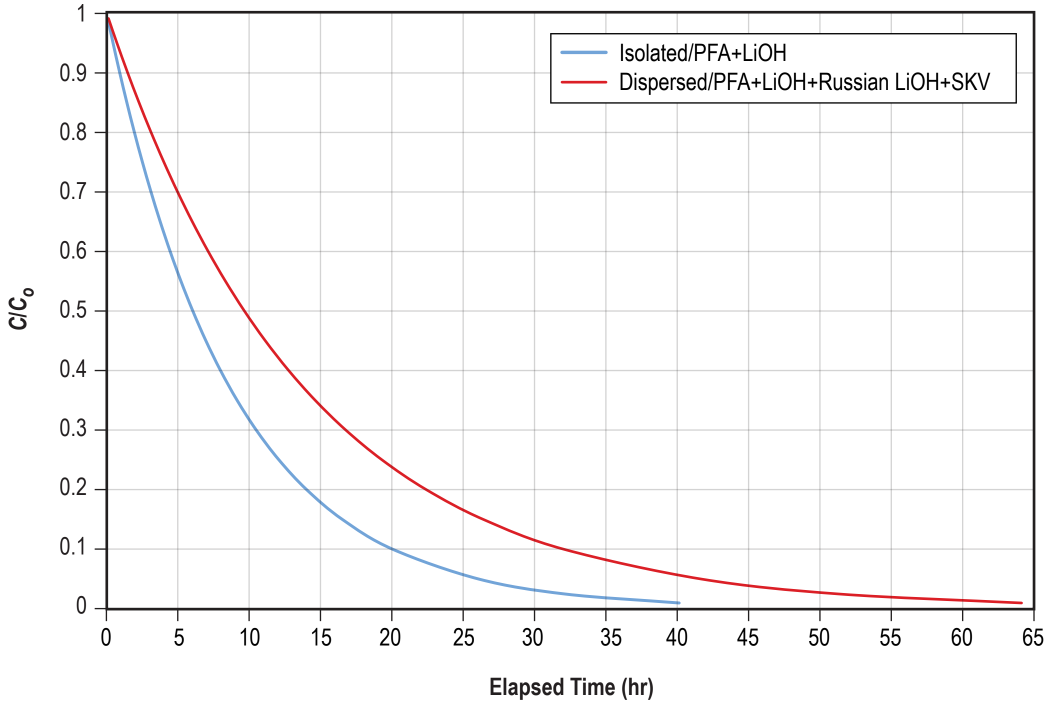


Figure 58. Estimated HCl remediation time.

7.1.3.5 Summary Observations. The chemical contaminants associated with a worst-case $LiSOCl_2$ battery failure and complete containment breech have been evaluated with respect to their compatibility with ECLSS equipment. Evaporation and dispersion rate estimates indicate that contamination can be expected to spread throughout the entire Station cabin within 7 to 9 hr. Dispersal may be accompanied by a sharp pungent or suffocating odor. The primary component, $SOCl_2$, is removed by activated charcoal; however, it also decomposes in the presence of water to form SO_2 and HCl. It is not known whether this decomposition can result from interaction with water adsorbed by activated charcoal contained in the TCCS and BMP. Both SO_2 and HCl can be removed by reaction with LiOH or Li_2CO_3. While the TCCS contains a sufficient quantity of LiOH in its SBA to accommodate contamination from most battery failures, the SO_2 is deleterious to the upstream COA's function. Therefore, the TCCS must not be used during remediation activities. Remediation duration can last as long as 65 hr, depending upon the level of contaminant isolation.

7.1.3.6 Environmental Control and Life Support System Compatibility Rating and Remediation Rating. Based upon the worst-case situation, the ECLSS compatibility rating is category E3/E4 if all containment levels are breeched because the TCCS COA can be damaged by SO_2, a $SOCl_2$ decomposition product. Damage to the COA is a critical impact to ECLSS operational performance maintenance and logistics because no spare equipment is on board the ISS. Environmental impact is category C or D, depending upon how quickly the leak is found and the degree of isolation achieved. If the contamination can be isolated to a single module, the rating is C. However, if the contamination spreads throughout the ISS cabin, the recovery time is significantly longer and the impact is category D. These environmental impact levels are based upon reducing the contamination to 1% of the starting concentration. If medical operations and toxicology specialists determine that >10% of the starting concentration defines a safe condition for the crew, then the impact category for contamination dispersed throughout the ISS cabin could be reduced to category C. This does not, however, change the ECLSS compatibility rating.

7.1.4 Recommendation

Remediation must be accomplished by containing and neutralizing any electrolyte that escapes all the containment levels. If all containment levels are breeched, the TCCS in the U.S. Segment must be turned off and the PFA with CDMK deployed. If it is determined that more than 7 hr have elapsed before the leak is discovered then, in addition to shutting down the TCCS and deploying the PFA with CDMK, the supplementary CO_2 removal system in the Russian Segment must be started. In this case, consideration should be given to operating the BMP in its rapid regeneration mode if Russian specialists determine that there is negligible risk for functional damage. In all cases, it is not necessary for fresh LiOH canisters to be used for the remediation because Li_2CO_3 has the same capacity to remove $SOCl_2$ decomposition products.

8. CONTAMINANT EMISSIONS FROM PROCESS VENTS

The following assessments document a Programion from preliminary evaluation through detailed assessment of the vent gases produced by the ISS vapor compression distillation (VCD) urine processor assembly (UPA) conducted between 2000 and 2001.

8.1 Odor Potential of Vapor Compression Distillation Purge Gases

Two separate VCD UPA purge gas analyses conducted separately by Life Systems, Inc. and Boeing Analytical Services have been evaluated for their odor potential. These analyses isolated several organic sulfides, hydrocarbons, and halocarbons. The concentrations of these compounds have been compared to documented odor and olfactory threshold concentrations documented in the literature.[60–62] This comparison is summarized in table 30.

As can be seen in table 30, several sulfide compounds—dimethyldisulfide, dimethyltrisulfide, and carbonyl sulfide—along with phenol, 4-methylphenol, menthol, and 4-heptanone would contribute to any composite odor that the purge gas may have. Taken as a whole, the remaining compounds would not most contribute to a composite odor. The composite odor could be described as combination solvent/rotten egg which would be consistent with recent anecdotal accounts of a 'chemical' odor.

Since it appears likely that the purge gases may have an odor, it is necessary to assess its potential to cause a persistent odor in the cabin. The VCD flight experiment vented approximately 200 mL/day of purge gas. According to VCD operation protocol, this is a conservative estimate for actual daily purge gas production when deployed on board the ISS. This small amount of gas is significantly diluted in the cabin, which at the time of node 3 activation, is approximately 500 m^3. Thus, if the VCD vents 200 mL/day of purge gas into the cabin, the chemical contaminant concentrations will be diluted by a factor of 4×10^{-7}. This would effectively reduce any chemical contaminant load well below odor thresholds. Further, the types of compounds isolated in the purge gas would be readily removed by the onboard TCCSs as well as by absorption into humidity condensate.

According to the assessment, it is anticipated that the VCD purge gas will have some chemical odor. However, the amount of gas produced relative to the cabin volume is so small that the risk of a cabin-wide odor is negligible. Further, onboard contamination control equipment is capable of removing purge gas constituents. Therefore, it can be concluded that the purge gas may be vented directly to the ISS cabin with no special treatment or filtration.

Table 30. Odor threshold concentrations versus UPA purge composition.

Compound	Odor Threshold (mg/m^3)	Concentration (mg/m^3)	
		Boeing Lab	Life Systems
Benzene	180	–	0.12
Carbon disulfide	23	–	3.7
Carbon tetrachloride	1,260	–	0.23
Chloroform	~500 – 1,000	–	6.3
Chloromethane	~500	–	3.6
Chloropentane	~500	–	8.2
Furan	~90	–	7.4
Hexane	~900	–	1.2
Dichloromethane	520 – 550	9.8	1.5
2-methylfuran	~90	4.6	1.2
1,1,1-trichloroethane	2,100	–	3.0
Trimethylpentane	~500	–	1.9
Toluene	140	–	0.34
Unknown amine*	96	–	5.6
Phenol	12	105	–
2-butanone	80	5.8	–
4-methylphenol	~12	760	–
4-methyl-2-pentanone	32	3.5	–
2-propanone	770	22	–
Trichlorofluoromethane	300 – 500	4.2	–
Dimethyldisulfide	~0.0011**	71	–
Menthol	10	44	–
2-pentanone	27	10.4	–
4-heptanone	~30 – 80	116	–
Dimethyltrisulfide	~0.0011**	2.4	–
Carbonyl sulfide	~0.0011**	20	–

* As trimethylamine.

** Assumed odor threshold similar to mercaptans.

8.2 Effects of Vapor Compression Distillation Purge Gas Load on Cabin Atmospheric Quality

The following assessment was conducted in July 2000 to refine the preliminary VCD UPA vent gas evaluation and revised in December 2000. The updated December 2000 assessment is presented. This assessment was documented by NASA memorandum FD21(01-039), “Urine Processor Assembly Vent Gas Evaluation,” dated January 17, 2001.

8.2.1 Background

The VCD UPA will be deployed on board node 3 to reclaim water from urine. In the course of processing urine, noncondensable gases are removed from the UPA's still and purged into the cabin atmosphere. Chemical analysis of the purge gases has been conducted by the Boeing Analytical Services Laboratory in Huntsville, Alabama, and by Life Systems, Inc. (LSI) of Cleveland, Ohio. Evaluation of the purge gas composition with respect to odor thresholds and onboard contamination control system capacity has been conducted to determine the potential effects that the various purge constituents may have on the cabin atmospheric quality. These effects are considered with respect to the potential need for point source purge gas treatment.

8.2.2 Purge Gas Composition

According to analyses conducted by LSI, the VCD purge gas composition is 58.9% nitrogen, 21.5% oxygen, and 17.8% CO_2 with some trace contaminants. It is the purge gas trace contaminant load, summarized in table 30, that may contribute to odors in the cabin and add to the base cabin atmospheric load resulting from equipment offgassing and human metabolism. The trace contaminant load is handled by the TCCS. It is important to avoid overloading the TCCS; therefore, the VCD purge gas trace contaminant load must be evaluated relative to the percentage of the base load as well as its potential to cause odors in the cabin.

8.2.3 Effects on Cabin Atmospheric Quality

The most prominent trace contaminant load reported from purge gas analyses conducted by Boeing and LSI are summarized in table 31. As can be seen by inspecting these data, several compounds in the purge gas are above their respective odor thresholds before dilution with the cabin atmosphere.[28,62,63] The VCD purge gas production rate averages 33.3 mL/hr during a typical 4.5-hr operational period. Therefore, the typical total daily purge gas production is approximately 150 mL. As a worst case, dispersing this volume of purge gas uniformly into the node 3 cabin, which is approximately 71 m^3, reduces the concentration by a factor of 2.1×10^{-6}. Cabin concentrations will be in the range of 10^{-7} to 10^{-4} mg/m^3, assuming no removal. The highest concentration is a factor of 10 lower than the lowest odor threshold of approximately 10^{-3} mg/m^3. Thus, after complete dilution, any odor potential is considered negligible. Further dilution by a total factor of 2.3×10^{-7} is achieved by dispersing the purge gas throughout the entire 644-m^3 U.S. Segment cabin.

Table 31. VCD purge gas trace contaminant loading and diluted concentrations versus odor threshold.

Compound	Concentration (mg/m^3)		Diluted Concentration* (mg/m^3)	Odor Threshold (mg/m^3)
	Boeing	LSI		
Phenol	105.3	–	2.2×10^{-4}	0.15 ×/÷ 1.5**
Menthol	44	–	9.2×10^{-5}	10
Benzyl alcohol	42.5	–	8.9×10^{-5}	None available
2-ethyl-1-hexanol	155	–	3.3×10^{-4}	None available
4-methylphenol	536.7	–	1.1×10^{-3}	~12
α-terpineol	71.5	–	1.5×10^{-4}	None available
Benzaldehyde	46	–	9.7×10^{-5}	None available
Benzene	–	0.12	2.5×10^{-7}	38.3 ×/÷ 1.6
Toluene	–	0.34	7.1×10^{-7}	10.9 ×/÷ 6
Furan	–	7.4	1.6×10^{-5}	~90
2-methylfuran	4.6	1.2	9.7×10^{-6}	11 ×/÷ 2.2
4-ethylmorpholine	320	–	6.7×10^{-4}	1.4 ×/÷ 18
Dichloromethane	9.8	1.5	2.1×10^{-5}	868.4 ×/÷ 1.2
Carbon tetrachloride	–	0.23	4.8×10^{-7}	604 ×/÷ 1.8
Chloroform	–	6.3	1.3×10^{-5}	415 ×/÷ 1.7
Chloromethane	–	3.6	7.6×10^{-6}	~800
Chloropentene	–	8.2	1.7×10^{-5}	~800
Tetrachloroethane	–	3	6.3×10^{-6}	10.3 ×/÷ 5.4
Trichlorofluoromethane	4.2	–	8.8×10^{-6}	5
Hexane	–	1.2	2.5×10^{-6}	458.2 ×/÷ 2
Trimethylpentene	–	1.9	4×10^{-6}	~400
2-butanone	5.8	–	1.2×10^{-5}	15.9 ×/÷ 1.9
4-methyl-2-pentanone	3.5	–	7.4×10^{-6}	2.8 ×/÷ 2.3
2-propanone	22	–	4.6×10^{-5}	30.9 ×/÷ 1.6
2-pentanone	10.4	–	2.2×10^{-5}	38.7 ×/÷ 2.2
4-heptanone	116	–	2.4×10^{-4}	~30
Carbon disulfide	–	3.7	7.8×10^{-6}	~0.0011
Dimethyldisulfide	71	–	1.5×10^{-4}	~0.0011
Dimethyltrisulfide	2.4	–	5×10^{-6}	~0.0011
Carbonyl sulfide	20	–	4.2×10^{-5}	~0.0011
Cyanogen chloride	–	7.8	1.6×10^{-5}	None available

* Highest reported concentration multiplied by Node 3 dilution factor.

** Standard error is used to determine upper and lower confidence range. For example, the 99% confidence interval for phenol's odor threshold is $(((0.15/1.5)/1.5)/1.5) = 0.04$ and $(((0.15\times1.5)\times1.5)\times1.5) = 0.51$.

Results of the analysis comparing the generation of trace contaminants from the VCD purge gas compared to the TCCS design load documented by the node 3 Prime Item Development Specification (SSP 50318) are summarized in table 32. From this assessment, it can be seen that the VCD purge gas increases the overall trace contaminant load by a fraction of 1%. This increase is negligible compared to the load that the TCCS can handle. Therefore, the TCCS capacity is more than sufficient to control contaminants contained in the VCD purge. Further, the TCCS is designed to handle 3.36 mg sulfide compounds/day. The VCD purge gas production for these compounds is 0.0149 mg/day. This represents a 0.4% increase in the load that the TCCS must accommodate. Again, this is a negligible increase in the overall trace contaminant load which will not compromise the TCCS's performance in any way.

Table 32. Purge gas contaminant load compared to the TCCS design load.

	Generation Rate (mg/day)		**Generation Ratio[*] (%)**
Compound	**Node 3 PIDS**	**Purge Gas**	
Phenol	36.2	1.6×10^{-2}	0.044
Menthol	–	6.6×10^{-3}	–
Benzyl alcohol	–	6.4×10^{-3}	–
2-ethyl-1-hexanol	–	2.3×10^{-2}	–
4-methylphenol	–	8×10^{-2}	–
α-terpineol	–	1.1×10^{-2}	–
Benzaldehyde	1.5	6.9×10^{-3}	0.46
Benzene	1.6	1.8×10^{-5}	0.0011
Toluene	148.5	5.1×10^{-5}	0.000034
Furan	0.14	1.1×10^{-3}	0.79
2-methylfuran	0.26	6.9×10^{-4}	0.27
4-ethylmorpholine	9.2	4.8×10^{-2}	0.52
Dichloromethane	161.2	1.5×10^{-3}	0.00093
Carbon tetrachloride	0.72	3.4×10^{-5}	0.0047
Chloroform	1.32	9.4×10^{-4}	0.071
Chloromethane	0.51	5.4×10^{-4}	0.11
Chloropentene	–	1.2×10^{-3}	–
Tetrachloroethane	–	4.5×10^{-4}	–
Trichlorofluoromethane	105.8	6.3×10^{-4}	0.00060
Hexane	5.2	1.8×10^{-4}	0.0035
Trimethylpentene	–	2.8×10^{-4}	–
2-butanone	450.8	1.2×10^{-5}	0.0000027
4-methyl-2-pentanone	105.8	8.7×10^{-4}	0.00082
2-propanone	272.6	3.3×10^{-3}	0.0012
2-pentanone	0.3	1.6×10^{-3}	0.53
4-heptanone	–	1.7×10^{-2}	–
Carbon disulfide	2.4	5.6×10^{-4}	0.023
Dimethyldisulfide	–	1.1×10^{-2}	–
Dimethyltrisulfide	–	3.6×10^{-4}	–
Carbonyl sulfide	0.45	3×10^{-3}	0.67
Cyanogen chloride	–	1.2×10^{-3}	–

[*] (Purge gas rate ÷ Node 3 PIDS rate) × 100.

8.2.4 Vent Plume Size Approximation

Methods for controlling the contamination emanating from the VCD purge include dilution with the cabin atmosphere and treatment with an adsorbent bed. Some aspects of dilution have been discussed in section 8.2.3. It was assumed that the purge gas is dispersed evenly throughout the cabin instantaneously. However, in practice, a plume from the purge outlet down the rack face can be expected. The dilution occurs as the purge gas is entrained in the circulating cabin atmosphere and moved toward the THC supply intakes. Diffusion of contaminants from the purge gas plume into the cabin will occur during the time necessary for the purge plume to reach the THC supply intake where it will be diluted by a large volumetric air flow.

First, the time required for the purge gases to travel from the vent to a point approximately 1 m away is considered. This distance is approximately the distance between the purge vent and the THC supply intake. The cabin atmosphere is circulated at 304.8 to 457.2 cm/min (10 to 15 ft/min) and the VCD purge gas velocity at 33.3 mL/hr through a 0.634-cm-diameter (0.25-in-diameter) tube is 1.75 cm/min. According to vector analysis, it will take nearly 40 s for the plume to travel 100 cm. During that time, the plume will travel 1.15 cm away from the rack face.

Also key is the rate of diffusion of contaminants out of the plume into the surrounding cabin atmosphere. In effect, diffusion will cause a broadening of the plume from its original 0.634-cm diameter, neglecting any nozzle effects. Using carbon disulfide (CS_2), which has a diffusion coefficient of 0.102 cm^2/s as the key contaminant, the average distance traveled away from the plume can be determined. Using the Einstein-Smoluchowski equation, $\langle(\Delta x)^2\rangle = 2Dt$, the root mean square distance that the diffusing molecule travels can be determined.[49] In the equation, D is the diffusion coefficient in cm^2/s and t is the time in seconds. Using the 40 s time to travel 100 cm and the diffusion coefficient for CS_2, a distance of 2.86 cm is obtained. Therefore, the plume can be expected, based upon one of its more odiferous compounds, to be approximately 6.35 cm in diameter after traveling 100 cm.

Dilution of the plume will also occur during the time it travels from the vent to the THC supply intake. Effectively, the cabin atmospheric flow contained in approximately 56 cm^2, obtained from the plume diameter plus the distance traveled from the rack face $(6.35\text{ cm} + 1.15\text{ cm})^2$, will dilute the plume. This is equivalent to 17,163 cm^3/min. The plume volumetric flow is 0.55 cm^3/min. The cabin atmospheric flow through this cross-sectional area provides a dilution factor of 3.2×10^{-5}. Even though this factor is 15 times higher than that obtained by diluting the purge gas concentrations by the total cabin volume, it still reduces all the concentrations in the purge gas, with the exception of dimethyldisulfide, to less than odor thresholds before further mixing with the larger volumetric flow within the THC ducts. This indicates a very small risk for odor in the vicinity of the rack face.

8.2.5 Odor Control Cartridge Sizing

Given that sulfur-containing compounds present a very small odor risk, it is reasonable to investigate the size of a granular activated carbon bed necessary to remove a 1-yr load. The calculation approach used is that documented by reference 1. Again, using CS_2 to represent the sulfide compounds, the loading is 5.2 mg/yr. At a total sulfide concentration of 95 mg/m^3 in the purge gas, the adsorption potential is 18.56. Assuming 100% relative humidity, a worst case, the charcoal loading is 7.81×10^{-6} g sulfide/g charcoal. At 5.2 mg sulfide/yr, a total of 665.97 g charcoal is required. Adding a 20% margin increases that to 800 g. Typical coconut shell-based activated charcoals have bulk densities of 0.576 g/cm^3. Therefore, the bed packing volume can be expected to be approximately 1,389 cm^3 (84.76 in^3). The external casing and fitting necessary can easily increase the total volume associated with a charcoal bed by 50%. Using a standard bed depth that is twice the diameter, the resulting charcoal bed dimensions (packing only) is approximately 10 cm diameter × 20 cm long. Given the vent flow, the pressure drop for such a 20-cm bed depth, calculated from the Ergun equation, is 0.163 Pa (6.55×10^{-4} in water (H_2O)).[64] If it is necessary to have a different bed geometry to meet rack packaging constraints, the material has a pressure drop of 0.00815 Pa/cm of bed (0.00253 inch H_2O/inch of bed).

8.2.6 Conclusions

Based upon the evaluation of VCD purge gas trace constituents relative to documented odor thresholds and TCCS contamination removal capability as well as diffusion considerations, conclusions are the following:

- Exhausting the purge gas into the node 3 cabin dilutes the purge gas to trace constituent concentrations far below individual compound odor thresholds with the exception of dimethyldisulfide.

- Trace constituent generation from daily purge gas production increases the load that the TCCS must control by a fraction of 1%.

- The potential for pervasive odors in the cabin is very small; however, there is potential for odors within 7.5 cm of the vent opening and in the plume emanating from the vent.

- Approximately 800 g of activated charcoal would be necessary for source treatment of the purge gas. The pressure drop introduced into the purge line is estimated to be 0.00815 Pa/cm of bed (0.00253 inch H_2O/inch of bed).

8.2.7 Recommendation

Based upon the VCD purge gas evaluation, it is recommended that the purge gases be directed through the rack face directly into the cabin close to the THC supply intakes in the node 3 floor to promote rapid dilution. No point-source treatment of the purge gas is required.

8.3 Urine Processing Assembly Purge Gas Impacts on Cabin Atmospheric Quality

The following assessment updates the December 2000 evaluation. This version of the evaluation was documented by NASA memorandum EV50(05-003), “Effects of Urine Processing Assembly Purge Gas Trace Components on Cabin Air Quality,” dated July 19, 2000.

8.3.1 Background

The VCD UPA will be deployed on board Node 3 to reclaim water from urine. In the course of processing urine, noncondensable gases are removed from the UPA's still and purged into the cabin atmosphere. Chemical analysis of the purge gases collected while processing urine pretreated with OXONE® and sulfuric acid have been conducted by the Boeing Analytical Services Laboratory and Life Sciences, Inc. (Cleveland, OH). Because there is potential for using the Russian-provided hexavalent chromium pretreatment formulation, additional purge gas composition data were acquired by MSFC's chemistry laboratory from purge gas samples collected while processing urine pretreated with this formulation. As required by the Prime Item Development Specification for Node 3 (SSP 50318) and the Urine Processor Assembly Specification (MSFC-SPEC-3036D), evaluation of the purge gas composition for both pretreatment formulations with respect to odor thresholds and onboard contamination control system capacity has been conducted to determine the potential effects that the trace purge gas components may have on cabin atmospheric quality. These effects are considered with respect to the potential need for point source purge gas treatment.

8.3.2 Purge Gas Composition

Data were acquired from laboratory analysis of UPA purge gases for two urine pretreatment formulations. Specifics relating to purge gas composition are provided by the following summary.

8.3.2.1 OXONE and Sulfuric Acid Pretreatment. According to laboratory analyses conducted by Boeing and LSI of the UPA, purge gases collected while processing urine pretreated with OXONE and sulfuric acid had a composition of 58.9% nitrogen, 21.5% oxygen, and 17.8% CO_2 with some trace components. Table 33 summarizes the overall composition for this pretreatment option. In total, 30 different chemical compounds contribute to the trace component composition of purge gases produced when using OXONE and sulfuric acid to pretreat urine.

Table 33. UPA purge gas composition when using OXONE and sulfuric acid pretreatment.

COMPOUND	MOLECULAR WEIGHT	PURGE COMPOSITION (mg/m³)		GENERATION		DILUTION		ODOR THRESHOLD						
	(g/mole)	Boeing	LSI	RATE (mg/h)	DAILY MASS (mg)	NODE 3 (mg/m³)	USOS (mg/m³)	1 (mg/m³)	2 (mg/m³)	3 (mg/m³)	4 (mg/m³)	5 (mg/m³)	6 (mg/m³)	7 (mg/m³)
2-ethyl-1-hexanol (octyl acohol)	130.23	155.00	0.00	5.16E-03	2.32E-02	3.27E-04	6.26E-05	*	*	*	*	*	0.4	0.4
4-methylphenol (p-cresol)	120.15	536.70	0.00	1.79E-02	8.04E-02	1.13E-03	2.17E-04	0.0014	*	*	*	0.0044	0.0049	0.02
Benzyl alcohol	108.14	42.50	0.00	1.42E-03	6.37E-03	8.97E-05	1.72E-05	*	*	*	*	*	*	*
Menthol	156.27	44.00	0.00	1.47E-03	6.59E-03	9.29E-05	1.78E-05	*	*	10	*	*	*	0.9
Phenol	94.11	105.30	0.00	3.51E-03	1.58E-02	2.22E-04	4.25E-05	0.15	0.18	2	12	0.23	3.8	0.18
Terpineol	154.25	71.50	0.00	2.38E-03	1.07E-02	1.51E-04	2.89E-05	*	*	*	*	*	2.2	0.2
Benzaldehyde	106.12	46.00	0.00	1.53E-03	6.89E-03	9.71E-05	1.86E-05	*	*	0.03	*	*	0.13	0.5
Benzene	78.11	0.00	0.12	4.00E-06	1.80E-05	2.53E-07	4.85E-08	38.3	15	960	180	108	8.8	3
Toluene	92.15	0.00	0.34	1.13E-05	5.09E-05	7.18E-07	1.37E-07	10.9	8.1	*	140	10.6	0.64	80
2-Methylfuran	82.10	4.60	1.20	1.53E-04	6.89E-04	9.71E-06	1.86E-06	*	*	*	*	*	90.7	*
4-ethylmorpholine	115.18	320.00	0.00	1.07E-02	4.80E-02	6.75E-04	1.29E-04	6.6	*	*	*	*	*	0.4
Furan	68.07	0.00	7.40	2.46E-04	1.11E-03	1.56E-05	2.99E-06	*	*	*	*	*	*	*
Carbon tetrachloride	153.82	0.00	0.23	7.66E-06	3.45E-05	4.85E-07	9.29E-08	604	134.6	*	1260	884	132.1	800
Chloroform	119.38	0.00	6.30	2.10E-04	9.44E-04	1.33E-05	2.54E-06	415	*	*	*	650	3300	700
Chloromethane	50.49	0.00	3.60	1.20E-04	5.39E-04	7.60E-06	1.45E-06	*	*	*	*	*	*	21
Chloropentene	104.58	0.00	8.20	2.73E-04	1.23E-03	1.73E-05	3.31E-06	*	*	*	*	*	*	*
Dichloromethane	84.93	9.80	1.50	3.26E-04	1.47E-03	2.07E-05	3.96E-06	868.4	743.4	*	550	500	729.5	200
Tetrachloroethane	167.78	0.00	3.00	9.99E-05	4.50E-04	6.33E-06	1.21E-06	10.3	*	*	*	50	*	20
Trichlorofluoromethane	137.40	4.20	23.60	1.40E-04	6.29E-04	8.86E-06	1.70E-06	28.1	*	*	*	*	28.1	28
Hexane	86.18	0.00	1.20	4.00E-05	1.80E-04	2.53E-06	4.85E-07	458.2	*	*	*	*	*	230
Trimethylpentene	112.21	0.00	1.90	6.33E-05	2.85E-04	4.01E-06	7.67E-07	*	*	*	*	*	*	*
4-heptanone	114.18	116.00	0.00	3.86E-03	1.74E-02	2.45E-04	4.69E-05	*	*	*	*	*	0.0042	*
Acetone	58.08	22.00	0.00	7.33E-04	3.30E-03	4.64E-05	8.89E-06	30.9	237.5	1100	770	*	47.5	50
Methyl ethyl ketone (MEK)	72.11	5.80	0.00	1.93E-04	8.69E-04	1.22E-05	2.34E-06	15.9	29.5	*	80	5.8	5.9	32
Methyl isobutyl ketone	100.16	3.50	0.00	1.17E-04	5.24E-04	7.39E-06	1.41E-06	2.8	1.9	*	32	0.4	0.4	20
Methyl propyl ketone	86.13	10.40	0.00	3.46E-04	1.56E-03	2.19E-05	4.20E-06	38.7	*	*	27	*	155.4	20
Carbon disulfide	76.14	0.00	3.70	1.23E-04	5.54E-04	7.81E-06	1.49E-06	0.34	0.65	2.6	23	0.07	2.6	0.05
Carbonyl sulfide	60.07	20.00	0.00	6.66E-04	3.00E-03	4.22E-05	8.08E-06	*	*	*	*	0.25	*	*
Dimethyl sulfide	94.20	71.00	0.00	2.36E-03	1.06E-02	1.50E-04	2.87E-05	*	0.0039	0.004	0.051	*	0.0013	0.009
Dimethyl trisulfide (as dimethyl sulfide)	126.25	2.40	0.00	7.99E-05	3.60E-04	5.07E-06	9.69E-07	*	0.0039	0.004	0.051	*	0.0013	0.009
Cyanogen chloride	61.45	0.00	7.80	2.60E-04	1.17E-03	1.65E-05	3.15E-06	*	*	*	*	*	2.5	2.5
				5.44E-02	2.45E-01	3.45E-03	6.60E-04							

Balance Gas Analysis

Carbon dioxide	44.00	*	17.80%
Oxygen	32.00	*	21.50%
Nitrogen	28.00	*	58.90%

Odor Threshold Data Sources:

1. Amoore and Hautala. Journal of Applied Toxicology, Vol. 3, No. 6, 1983.
2. Leonardos, Kendall, and Barnard. Journal of the Air Pollution Control Association, Vol. 19, No. 2, 1969.
3. Human Response to Environmental Odors, Edited by Turk, Johnston, and Moulton, 1974.
4. Summer. Odour Pollution of Air - Causes and Control, 1971.
5. Reference Guide to Odor Thresholds for Hazardous Air Pollutants Listed in the Clean Air Act Amendments of 1990. EPA/600/R-92/047. 1992.
6. Fazzalari, editor. Compilation of Odor and Taste Threshold Values Data. ASTM DS 48A. 1978.
7. Verscheuren, editor. Handbook of Environmental Data on Organic Chemicals. 3rd Ed. 1996.

8.3.2.2 Hexavalent Chromium Pretreatment. Laboratory analyses conducted by NASA of purge gases collected while processing urine pretreated with the hexavalent chromium formulation indicate the composition is 72.4% nitrogen, 20.4% oxygen, and 7% CO_2 with some trace components. Table 34 summarizes the overall purge gas composition for this pretreatment option. Twenty-nine chemical compounds comprise the greatest portion of the trace component loading. An additional 11 compounds are reported at trace concentrations. Compared to purge gases produced when processing urine pretreated with OXONE and sulfuric acid, the number and functional class of the trace components are similar. The purge gas produced when processing urine pretreated with the hexavalent chromium formulation contains significantly less CO_2.

Table 34. UPA purge gas composition when using Russian hexavalent chromium pretreatment.

COMPOUND	MOLECULAR WEIGHT	PURGE COMPOSITION		GENERATION		DILUTION		ODOR THRESHOLD						
				RATE	DAILY MASS	NODE 3	USOS	1	2	3	4	5	6	7
	(g/mole)	(ppm)	(mg/m^3)	(mg/h)	(mg)	(mg/m^3)	(mg/m^3)	(mg/m^3)	(mg/m^3)	(mg/m^3)	(mg/m^3)	(mg/m^3)	(mg/m^3)	(mg/m^3)
Methanol	32.04	9.1	11.92	3.97E-04	1.79E-03	2.52E-05	4.82E-06	131	131	10	7800	5.5	5.6	4.3
Phenol	94.11	178	685.14	2.28E-02	1.03E-01	1.45E-03	2.77E-04	0.15	0.18	2	12	0.23	3.8	0.18
3-Methylbutanal	86.14	0.31	1.09	3.64E-05	1.64E-04	2.31E-06	4.41E-07	*	*	*	*	*	0.046	*
Butanal	72.10	0.35	1.03	3.44E-05	1.55E-04	2.18E-06	4.17E-07	*	*	*	*	*	0.014	0.014
Ethanal	44.05	104.26	187.84	6.26E-03	2.81E-02	3.96E-04	7.59E-05	0.09	0.38	*	*	0.12	0.12	0.05
Pentanal	86.13	0.79	2.78	9.27E-05	4.17E-04	5.87E-06	1.12E-06	0.099	*	*	*	*	0.042	0.072
2-Methylfuran	82.10	0.55	1.85	6.15E-05	2.77E-04	3.90E-06	7.46E-07	*	*	*	*	*	90.7	*
Furan	68.07	24.7	68.77	2.29E-03	1.03E-02	1.45E-04	2.78E-05	*	*	*	*	*	*	*
Chloroform	119.38	1.78	8.69	2.89E-04	1.30E-03	1.83E-05	3.51E-06	415	*	*	*	650	3300	700
Chloromethane	50.49	0.17	0.35	1.17E-05	5.26E-05	7.41E-07	1.42E-07	*	*	*	*	*	*	21
Tetrachloroethene	165.83	2.07	14.04	4.68E-04	2.10E-03	2.96E-05	5.67E-06	183.1	6.8	*	320	*	31.7	35
Trichloroethene	131.39	9.58	51.48	1.71E-03	7.71E-03	1.09E-04	2.08E-05	150.5	115	*	1350	440	112.8	100
Trichlorotrifluoroethane (Freon 113)	187.40	0.39	2.99	9.95E-05	4.48E-04	6.31E-06	1.21E-06	*	*	*	*	*	344.9	344.9
2-Methyl-1-propene	57.10	0.47	1.10	3.66E-05	1.64E-04	2.32E-06	4.43E-07	*	*	*	*	*	*	1.3
Butane	58.12	1.37	3.26	1.08E-04	4.88E-04	6.87E-06	1.32E-06	6418.2	*	*	*	*	*	11885
C5 Unsaturated Hydrocarbon (as pentene)	70.14	0.54	1.55	5.16E-05	2.32E-04	3.27E-06	6.26E-07	*	*	*	*	*	0.54	0.0062
C8 Saturated Aliphatic Hydrocarbon (as octane)	114.23	0.18	0.84	2.80E-05	1.26E-04	1.77E-06	3.40E-07	224.3	*	*	710	*	*	700
Di-isobutylene (as octene)	112.21	0.29	1.33	4.43E-05	1.99E-04	2.81E-06	5.38E-07	*	*	*	*	*	*	5
Isobutane (as butane) 2-methylpropane	58.12	0.11	0.26	8.71E-06	3.92E-05	5.52E-07	1.06E-07	*	*	*	*	*	*	2.9
Isopentene (as pentane)	71.15	1.2	3.49	1.16E-04	5.23E-04	7.37E-06	1.41E-06	*	*	*	*	*	*	0.73
Pentane	72.15	0.09	0.27	8.84E-06	3.98E-05	5.61E-07	1.07E-07	1180.4	*	*	*	*	*	300
Acetone	58.08	92.17	218.95	7.29E-03	3.28E-02	4.62E-04	8.84E-05	30.9	237.5	1100	770	*	47.5	50
Methyl ethyl ketone (MEK)	72.11	3.38	9.97	3.32E-04	1.49E-03	2.10E-05	4.03E-06	15.9	29.5	*	80	5.8	5.9	32
Methyl propyl ketone	86.13	0.44	1.55	5.16E-05	2.32E-04	3.27E-06	6.26E-07	38.7	*	*	27	*	155.4	20
Carbon disulfide	76.14	4.73	14.73	4.91E-04	2.21E-03	3.11E-05	5.95E-06	0.34	0.65	2.6	23	0.07	2.6	0.05
Carbonyl sulfide	60.07	147.5	362.39	1.21E-02	5.43E-02	7.65E-04	1.46E-04	*	*	*	*	0.25	*	*
Dimethyl sulfide	94.20	0.94	3.62	1.21E-04	5.43E-04	7.64E-06	1.46E-06	*	0.0039	0.004	0.051	*	0.0013	0.009
N,N-Dimethylacetamide	69.10	0.43	1.22	4.05E-05	1.82E-04	2.56E-06	4.91E-07	132.8	132.3	*	*	*	132.8	165
Unidentified Fluoroaliphatic Hydrocarbon (total)		1.64						*	*	*	*	*	*	*
TRACES														
2-Methylpropanal	69.09	0.002	5.65E-03	1.88E-07	8.47E-07	1.19E-08	2.28E-09	*	*	*	*	*	*	0.13
Benzene	78.11	0.002	6.39E-03	2.13E-07	9.57E-07	1.35E-08	2.58E-09	38.3	15	960	180	108	8.8	3
Toluene	92.15	0.001	3.77E-03	1.26E-07	5.65E-07	7.95E-09	1.52E-09	10.9	8.1	*	140	10.6	0.64	80
1,1-Dichloro-1-fluoroethane (as dichloroethane)	114.93	0.001	4.70E-03	1.57E-07	7.04E-07	9.92E-09	1.90E-09	*	*	*	*	*	*	564
Chloropropenes (as allylchloride)	76.53	0.002	6.26E-03	2.08E-07	9.38E-07	1.32E-08	2.53E-09	*	*	*	*	*	1.5	0.66
Fluoroethers (as fluoro dimethyl ether)	64.06	0.001	2.62E-03	8.72E-08	3.93E-07	5.53E-09	1.06E-09	*	*	*	*	*	*	*
C8-C9 Saturated Aliphatic Hydrocarbon (as nonane)	142.28	0.001	5.82E-03	1.94E-07	8.72E-07	1.23E-08	2.35E-09	273.5	*	*	*	*	3782.5	2.3
Propene	42.08	0.003	5.16E-03	1.72E-07	7.74E-07	1.09E-08	2.09E-09	130.8	*	*	*	*	39.6	30
Methyl isopropyl ketone	86.13	0.001	3.52E-03	1.17E-07	5.28E-07	7.43E-09	1.42E-09	6.7	*	*	*	*	5.9	*
Methanethiol	48.10	0.003	5.90E-03	1.97E-07	8.84E-07	1.25E-08	2.38E-09	0.003	0.004	0.0002	0.0022	*	0.081	0.0022
Unidentified components (total)	*	0.005	*	*	*	*	*	*	*	*	*	*	*	*
				5.54E-02	2.49E-01	3.51E-03	6.72E-04							
Balance Gas Analysis		(ppm or %)												
Carbon monoxide	28.00	534.7	612.34	2.04E-02	9.18E-02	1.29E-03	2.47E-04							
Hydrogen	2.00	1302.3	106.53	3.55E-03	1.60E-02	2.25E-04	4.30E-05							
Carbon dioxide	44.00	7.00%												
Oxygen	32.00	20.40%												
Nitrogen	28.00	72.40%												

Odor Threshold Data Sources:

1. Amoore and Hautala. Journal of Applied Toxicology, Vol. 3, No. 6, 1983.
2. Leonardos, Kendall, and Barnard. Journal of the Air Pollution Control Association, Vol. 19, No. 2, 1969.
3. Human Response to Environmental Odors, Edited by Turk, Johnston, and Moulton, 1974.
4. Summer. Odour Pollution of Air - Causes and Control, 1971.
5. Reference Guide to Odor Thresholds for Hazardous Air Pollutants Listed in the Clean Air Act Amendments of 1990. EPA/600/R-92/047. 1992.
6. Fazzalari, editor. Compilation of Odor and Taste Threshold Values Data. ASTM DS 48A. 1978.
7. Verscheuren, editor. Handbook of Environmental Data on Organic Chemicals. 3rd Ed. 1996.

8.3.3 Effects on Cabin Atmospheric Quality

While nitrogen, oxygen, and CO_2 account for the major purge gas constituents when processing urine pretreated with either formulation, the trace components must be considered with respect to their potential to contribute to odors in the cabin and add to the base cabin atmospheric load resulting from equipment offgassing and human metabolism. The trace contaminant load is handled by the TCCS. It is important to avoid overloading the TCCS; therefore, the UPA purge gas trace contaminant load must be evaluated relative to the percentage of the base load as well as its potential to cause odors in the cabin.

On inspection of data for trace component concentrations found in the UPA purge gas while processing urine pretreated wit OXONE and sulfuric acid, several compounds are found to be above their respective odor thresholds before dilution with the cabin atmosphere.[28,62–68] Therefore, the vent plume can be expected to have a characteristic odor. The UPA purge gas production rate averages 33.3 mL/hr during a typical 4.5-hr operational period. Therefore, the typical total daily purge gas production is approximately 150 mL. During this time, the purge gas introduces 0.054 mg trace contaminants/hr into the cabin. For a single run per day, the total mass of trace contaminants introduced into the cabin is 0.24 mg.

As a worst case, dispersing this volume of purge gas and its trace components uniformly into the Node 3 cabin, which is approximately 71 m^3, reduces the concentration by a factor of 2.1×10^{-6}. Cabin concentrations will be in the range of 10^{-7} to 10^{-3} mg/m^3, assuming no removal. The highest concentration after dilution is for 4-methylphenol. That concentration is just under its lowest documented odor threshold. Thus, after complete dilution, any odor potential is considered negligible. Further dilution by a total factor of 2.3×10^{-7} is achieved by dispersing the purge gas throughout the entire 644-m^3 U.S. Segment cabin.

Similarly, trace components are introduced into the cabin at 0.055 mg/hr when urine pretreated with the Russian hexavalent chromium formulation is processed by the UPA. The total mass of trace contaminants introduced into the cabin during a single batch run is 0.25 mg. As with the OXONE and sulfuric acid pretreatment formulation, several trace component concentrations found in the purge gas exceed their lowest documented odor threshold. Therefore, the vent plume can be expected to have a characteristic odor. After dilution within the cabin atmosphere, the highest concentration is a factor of 100 lower than the lowest documented odor threshold.

The TCCS is designed to remove 230 mg trace contaminants/hr. The additional trace contaminant load contained in the UPA purge gas represents 0.024% increase in the total load the TCCS must remove from the cabin atmosphere. Therefore, the impact of the trace components contained in the UPA purge gas present an insignificant impact to the TCCS's capability to maintain acceptable cabin air quality. Further, the TCCS is designed to handle 3.36 mg sulfide compounds/day. The maximum UPA purge gas production for these compounds is 0.3 mg/day. This represents a 9% increase in the load that the TCCS must accommodate. This increase is within the TCCS's capabilities and is not expected to adversely affect its functional maintenance.

8.3.4 Vent Plume Size Approximation

Methods for controlling the contamination emanating from the UPA purge include dilution with the cabin atmosphere and treatment with an adsorbent bed. Some aspects of dilution have been discussed in the previous section. It was assumed that the purge gas is dispersed evenly throughout the cabin instantaneously. However, in practice, a plume from the purge outlet down the rack face can be expected. The dilution occurs as the purge gas is entrained in the circulating cabin atmosphere and moved toward the THC supply intakes. Diffusion of contaminants from the purge gas plume into the cabin will occur during the time necessary for the purge plume to reach the THC supply intake where it will be diluted by a large volumetric air flow.

First, the time required for the purge gases to travel from the vent to a point approximately 1 m away is considered. This distance is approximately the distance between the purge vent and the THC supply intake. The cabin atmosphere is circulated at 304.8 to 457.2 cm/min (10–15 ft/min) and the UPA purge gas velocity at 33.3 mL/hr through a 0.634-cm- (0.25-in-) diameter tube is 1.75 cm/min. According to vector analysis, it will take nearly 40 s for the plume to travel 100 cm. During that time, the plume will travel 1.15 cm away from the rack face.

Also key is the rate of diffusion of contaminants out of the plume into the surrounding cabin atmosphere. In effect, diffusion will cause a broadening of the plume from its original 0.634-cm diameter, neglecting any nozzle effects. Using CS_2, which has a diffusion coefficient of 0.102 cm^2/s as the key contaminant, the average distance traveled away from the plume can be determined. Using the Einstein-Smoluchowski equation, $\langle(\Delta x)^2\rangle = 2Dt$, the root mean square distance that the diffusing molecule travels can be determined.[49] In the equation, D is the diffusion coefficient in cm^2/s and t is the time in seconds. Using the 40-s time to travel 100 cm and the diffusion coefficient for CS_2, a distance of 2.86 cm is obtained. Therefore, the plume can be expected, based upon one of its more odiferous compounds, to be approximately 6.35 cm in diameter after traveling 100 cm.

Dilution of the plume will also occur during the time it travels from the vent to the THC supply intake. Effectively, the cabin atmospheric flow contained in approximately 56 cm^2, obtained from the plume diameter plus the distance traveled from the rack face, $(6.35\ \text{cm} + 1.15\ \text{cm})^2$, will dilute the plume. This is equivalent to 17,163 cm^3/min. The plume volumetric flow is 0.55 cm^3/min. The cabin atmospheric flow through this cross-sectional area provides a dilution factor of 3.2×10^{-5}. Applying this factor, all concentrations in the purge gas, regardless of pretreatment option used, are reduced to less than odor thresholds before further mixing with the larger volumetric flow within the THC ducts. This indicates a very small risk for odor in the vicinity of the rack face and essentially no risk for odor in the cabin as a whole.

8.3.5 Odor Control Cartridge Sizing

Given that sulfur-containing compounds present the most significant odor risk in the purge gas plume, it is reasonable to investigate the size of a granular activated carbon bed necessary to remove a 1-yr load. The calculation approach used is that documented by reference 1. Using carbonyl sulfide (COS), the most difficult sulfur-containing compound to remove, to represent the sulfide compounds and the maximum loading of 0.0208 g/yr found when using the Russian hexavalent chromium pretreatment, a conservative total adsorbent amount is calculated. Further, by conservatively using the lowest observed total sulfide concentration of 95 mg/m^3 in the purge gas found when using the OXONE and sulfuric acid pretreatment, the adsorption potential is 32.9. Assuming 100% relative humidity, a worst case, the charcoal loading is 7.81×10^{-6} g sulfide/g charcoal. At 0.0208 g sulfide/yr, a total of 2,663 g charcoal is required. Adding a 20% margin increases the total charcoal mass to 3,200 g. Coconut shell-based activated charcoals typically have bulk densities of 0.576 g/cm^3. Therefore, the total bed packing volume can be expected to be approximately 5,550 cm^3 (339 in^3) if a single bed with a 1-yr service life is used. The external casing and fitting necessary can easily increase the total volume associated with a charcoal bed by 50%.

To manage the overall pressure drop and size, conveniently using four beds containing 800 g charcoal each over the course of a year is reasonable. In this configuration and using a standard bed depth that is twice the diameter, the resulting charcoal bed dimensions (packing only) is approximately 10 cm diameter × 20 cm long. Given the vent flow, the pressure drop for a 20-cm bed depth, calculated from the Ergun equation, is 0.163 Pa (6.55×10^{-4} in H_2O).[64] If it is necessary to have a different bed geometry to meet rack packaging constraints, the material has a pressure drop of 0.00815 Pa/cm of bed (0.00253 inch H_2O/inch of bed). Other configurations using radial flow may also be considered to manage pressure drop.

8.3.6 Conclusions

Based upon the evaluation of UPA purge gas trace constituents relative to documented odor thresholds and TCCS contamination removal capability as well as diffusion considerations, conclusions are the following:

- Exhausting the purge gas into the Node 3 cabin dilutes the trace constituent concentrations below individual compound odor thresholds.

- Trace constituent generation from daily purge gas production increases the load that the TCCS must control by <1%.

- The potential for pervasive odors in the cabin is very small; however, there is potential for odors within 7.5 cm of the vent opening and in the plume emanating from the vent.

- Approximately 3,200 g of activated charcoal would be necessary for source treatment of the purge gas. Four 800-g beds of activated charcoal limits pressure drop.

- An estimated pressure drop of 0.00815 Pa/cm of bed packing depth (0.00253 inch H_2O/inch of bed packing depth) is estimated for an axial flow purge gas treatment device. This pressure drop does not include bed material containment or other bed structural components.

8.3.7 Recommendation

Based upon the UPA purge gas evaluation, purge gases may be introduced directly into the cabin through the rack face. It is recommended that the purge vent be located close to the THC supply intakes in the Node 3 floor to promote rapid dilution. No point-source treatment of the purge gas is required as long as the vent location promotes rapid dilution.

9. PAYLOAD SYSTEM COMPATIBILITY ASSESSMENT

Compatibility assessment can involve the reactive hazards presented by cabin environmental contamination interaction with experiment payload equipment as well as the ECLSS. Such evaluations determine the production rate of reaction products and their interaction with the ECLSS.

9.1 Octafluoropropane Compatibility With Experiment Payload Heated Surfaces

The following assessment was conducted in September 2008 to evaluate the compatibility of octafluoropropane with the Smoke Point in Co-Flow Experiment (SPICE) payload operations.

9.1.1 Background

The SPICE payload planned for delivery to the ISS on board STS-126/ULF-2 is designed to produce a smoky fire that will allow for smoke particulate matter behavior to be studied. The SPICE experimental equipment will be operated in the MSG located in the Columbus laboratory module. Experimental operations will liberate CO_2, H_2O vapor, and trace products, which may include oxides of nitrogen (NO_x), CO, and hydrocarbons, in addition to particulate matter. The MSG working volume ventilation system is outfitted with filters that include HEPA media, activated carbon, and an ambient temperature CO oxidation catalyst. Most of the byproducts from the SPICE payload operations are anticipated to be removed by the MSG filters. Flame temperatures encountered during SPICE operations are predicted to exceed 1,000 °C.

The MSG, however, does not contain filtration media to remove acid gases. This is a concern because of the persistent concentration of octafluoropropane (OFP) in the cabin atmosphere. OFP is the thermal working fluid in the two ROS condensing heat exchanger units (Russian acronym CKB) units located in the Service Module. Each CKB unit contains ~750 g of octafluoropropane (OFP). In late April 2008, ~600 g of OFP coolant spilled into the ISS cabin producing a concentration >900 mg/m^3 (117 ppm_v). After the leak in April 2008, subsequent volume dilution provided by adding the Japanese and European laboratory modules combined with action of the USOS TCCS and ROS ΦBΠ units have reduced the concentration to ~500 mg/m^3 (65 ppm_v). Unfortunately, additional OFP spilled into the cabin during a CKB refill operation leading to a concentration of ~600 mg/m^3 (78 ppm_v). Figure 59 shows the OFP concentration profile between late April and early August 2008. It is assumed that no additional OFP has spilled into the cabin since August 8, 2008.

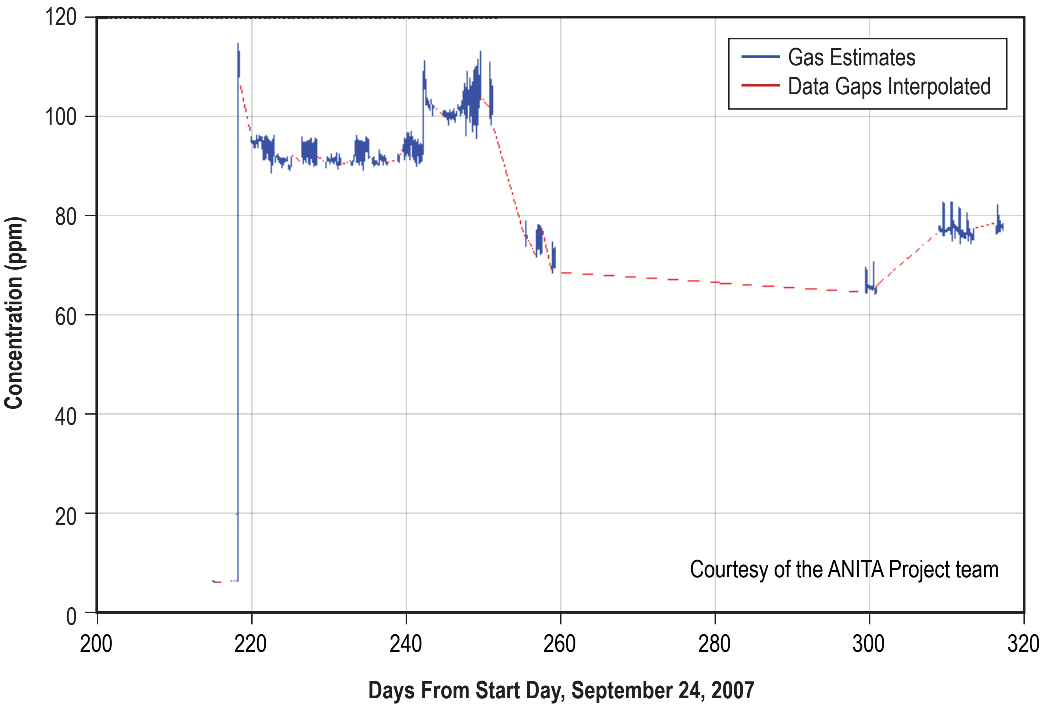


Figure 59. Octafluoropropane concentration in the ISS cabin—April 30 through August 8, 2008.

When exposed to temperatures >600° C in the presence of air and humidity, OFP may decompose to form HF according to the following reaction: $C_3F_8 + O_2 + 5H_2O \rightarrow 3CO_2 + H_2O + 8HF$.

OFP is very stable thermally; however, if it is exposed to high temperatures for a long time, on the order of minutes or 10's of minutes, concern for thermal decomposition exists. Because the MSG ingests unfiltered cabin atmosphere into its working volume, there is concern that repeated experimental runs may produce conditions that may promote OFP decomposition. While the extent of decomposition is likely low, it is unknown. For this reason, it must be assumed, conservatively, that all of the OFP within a 0.471-L volume envelope surrounding the flame in the SPICE experiment will decompose to form HF. Approximately 12 experimental runs may be accomplished during a typical 8-hr work day on board the ISS, leading to a 0.706-L/hr atmospheric gas contact with the highest temperatures. Hydrogen fluoride has a SMAC of 2 mg/m^3 (1 hr), 1 mg/m^3 (24 hr), and 0.1 mg/m^3 (7-/30-/180-day). Safe operations dictate that SMAC concentrations be met.

9.1.2 Environmental Control and Life Support System Engineering Assessment

The ISS ECLSS engineering organization has assessed the following four scenarios:

(1) Cabin OFP concentration >2,000 mg/m^3 (263 ppm$_v$) representing a spill of the entire 1,500 g contained in the 2 CKB units.

(2) Cabin OFP concentration >1,000 mg/m^3 (132 ppm$_v$) representing a spill of the entire 750 g contained in a single CKV unit.

(3) Cabin OFP concentration >800 mg/m^3 (105 ppm$_v$) representing the magnitude of a spill that occurred between August and December 2000.

(4) Cabin OFP concentration of 600 mg/m^3 (78 ppm$_v$) representing the cabin atmospheric condition as of August 8, 2008.

Of these cases considered, (1), (3), and (4) are discussed in more detail. Cases (2) and (3) are very similar to each other and well represented by case (3) alone. Dispersion through the entire ISS cabin and dispersion between the Columbus module and the rest of the USOS cabin are considered.

In addition to these cases, the buildup of HF in the 250-L (0.25 m^3) MSG working volume is considered for each OFP concentration case and for a range of runs between working volume purges. Dilution into the 460-L (0.46 m^3) rack volume is evaluated. In all cases, 100% OFP conversion to HF is assumed.

Hydrogen fluoride removal is assumed to occur only very minimally via absorption into humidity condensate and via reaction with LiOH contained in the USOS TCCS unit.

9.1.3 Results

The following presents the assessment results on the dispersion of HF, interaction with the ECLSS, and time to recover the cabin environment to normal conditions.

9.1.3.1 Dispersion of Hydrogen Fluoride Into the Total International Space Station Cabin. The cases considered for dispersion into the total ISS cabin yield results shown in figures 60–62. Figure 60 shows the HF concentration profile resulting from 100% conversion of OFP to HF for the condition that might be expected if both ROS CKB units leak all of their OFP into the cabin. The predicted peak HF concentration during a typical set of daily runs with MSG working volume venting to the cabin is ~0.0013 mg/m^3 (0.0017 ppm$_v$ or 1.7 ppb$_v$). This is far below the HF 7-/30-/180-day SMAC of 0.1 mg/m^3. Similarly, the cabin conditions resulting from lesser OFP leaked quantities do not result in cabin HF concentrations exceeding the long-duration SMAC. Maximum predicted HF concentrations are ~0.0053 mg/m^3 (0.00069 ppm$_v$ or 0.69 ppb$_v$) and ~0.0039 mg/m^3 (0.00051 ppm$_v$ or 0.51 ppb$_v$) in the event of OFP concentrations resulting from a 600-g OFP leak, indicative of a single CKB containment failure, and for the prevailing OFP concentration presently on board the ISS, respectively.

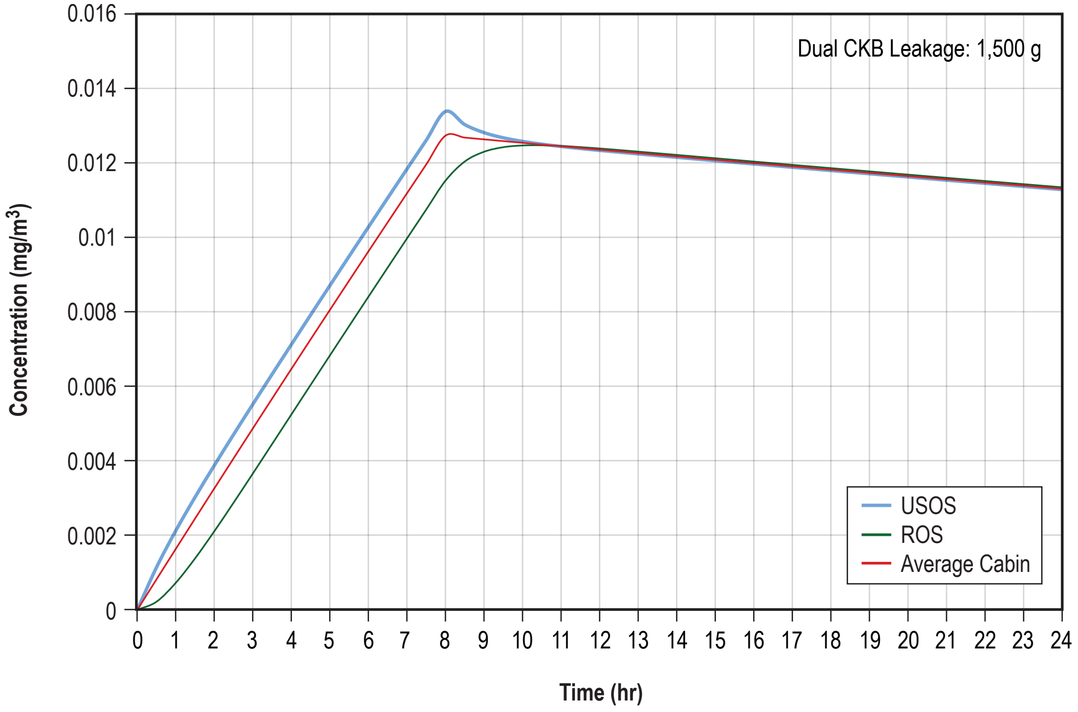


Figure 60. Hydrogen fluoride concentration in the ISS cabin for SPICE operations after a 1,500-g OFP leak.

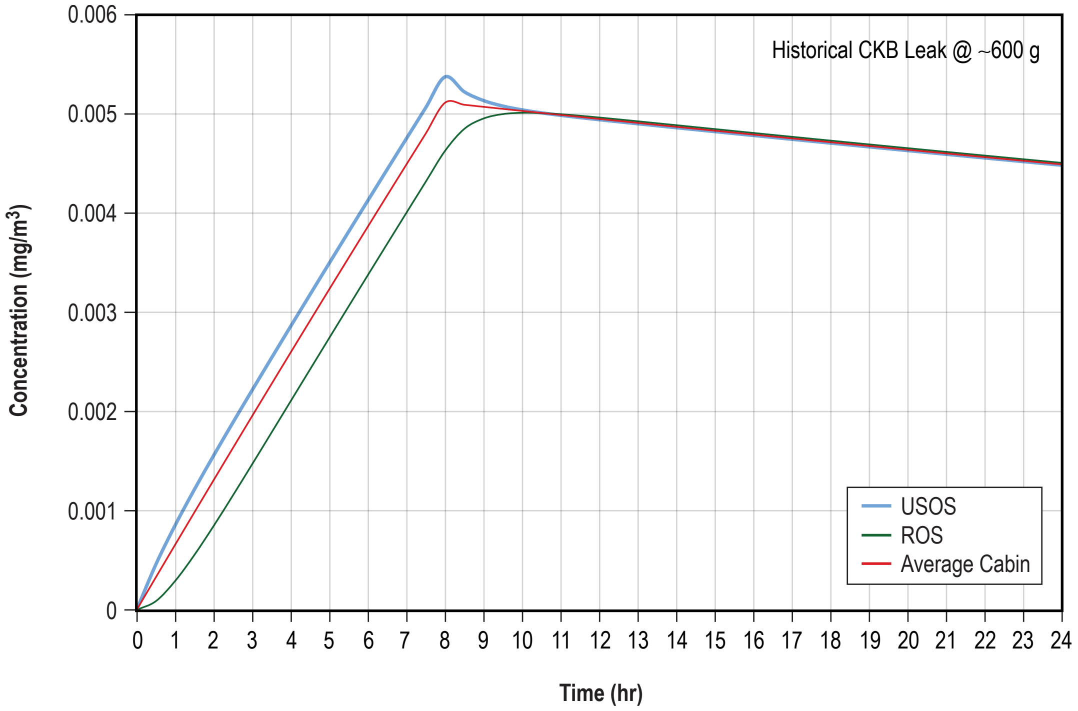


Figure 61. Hydrogen fluoride concentration in the ISS cabin for SPICE operations after a 600-g OFP leak.

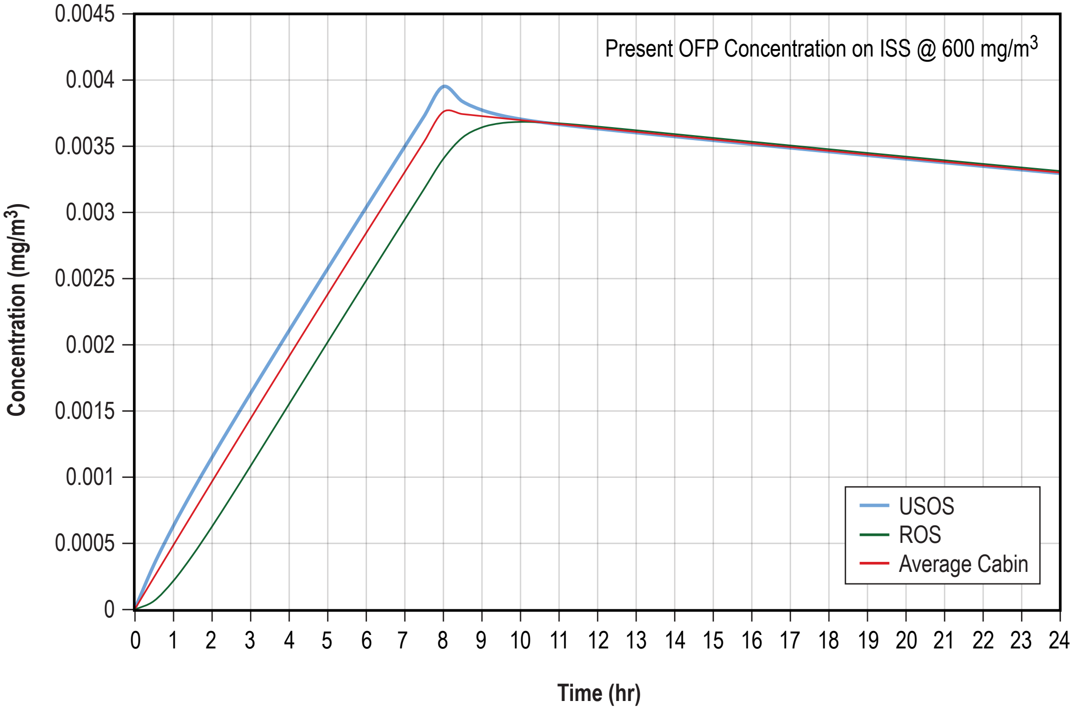


Figure 62. Hydrogen fluoride concentration in the ISS cabin for SPICE operations at present cabin OFP levels.

9.1.3.2 Dispersion of Hydrogen Fluoride Into the U.S. On-Orbit Segment Only. Evaluating the same cases—a 1,500-g OFP leak, a 600-g OFP leak, and presently prevailing OFP cabin concentration—with dispersion into the USOS only is appropriate because isolating the USOS from the ROS is one method for maintaining a 'safe haven' in the event of a cabin atmosphere contamination event. In this case, the HF generation occurs in the Columbus module and disperses into the rest of the USOS. The results, shown in figures 63–65, indicate that the 7-/30-/180-day SMAC is not exceeded for any case. The peak concentration in the Columbus module for the three cases is ~0.024 mg/m^3 (0.029 ppm$_v$), ~0.0095 mg/m^3 (0.012 ppm$_v$), and ~0.007 mg/m^3 (0.0086 ppm$_v$) for the conditions resulting from a 1,500-g OFP leak, a 600-g OFP leak, and the presently prevailing OFP concentration condition on board the ISS, respectively.

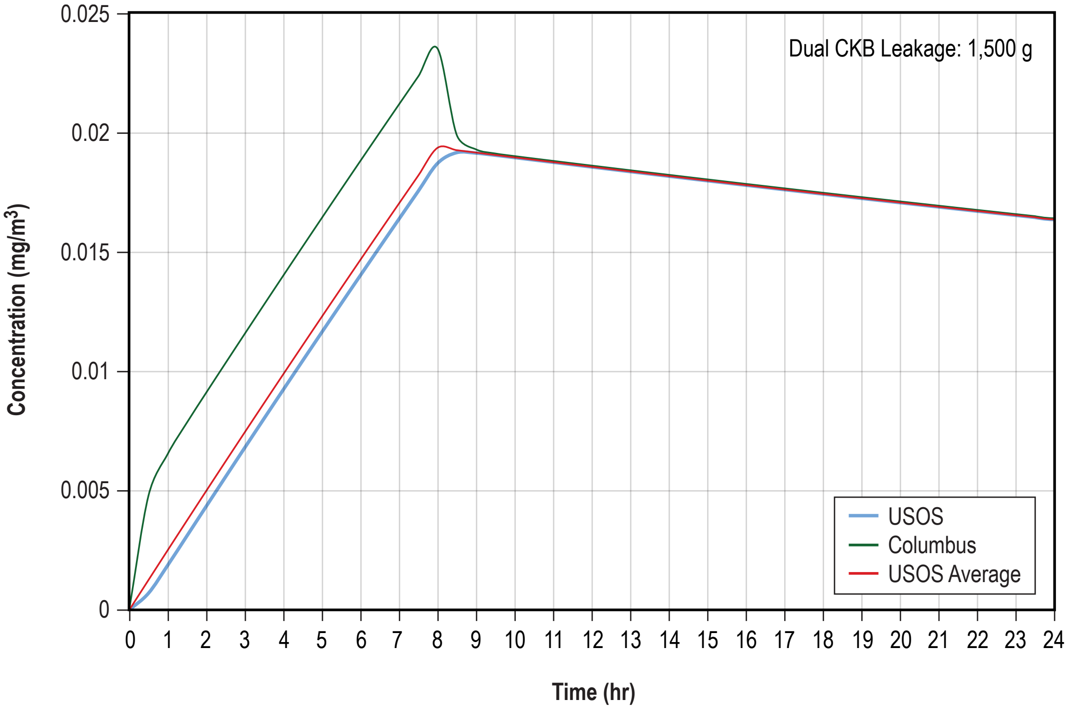


Figure 63. Hydrogen fluoride concentration in the ISS cabin for SPICE operations after a 1,500-g OFP leak.

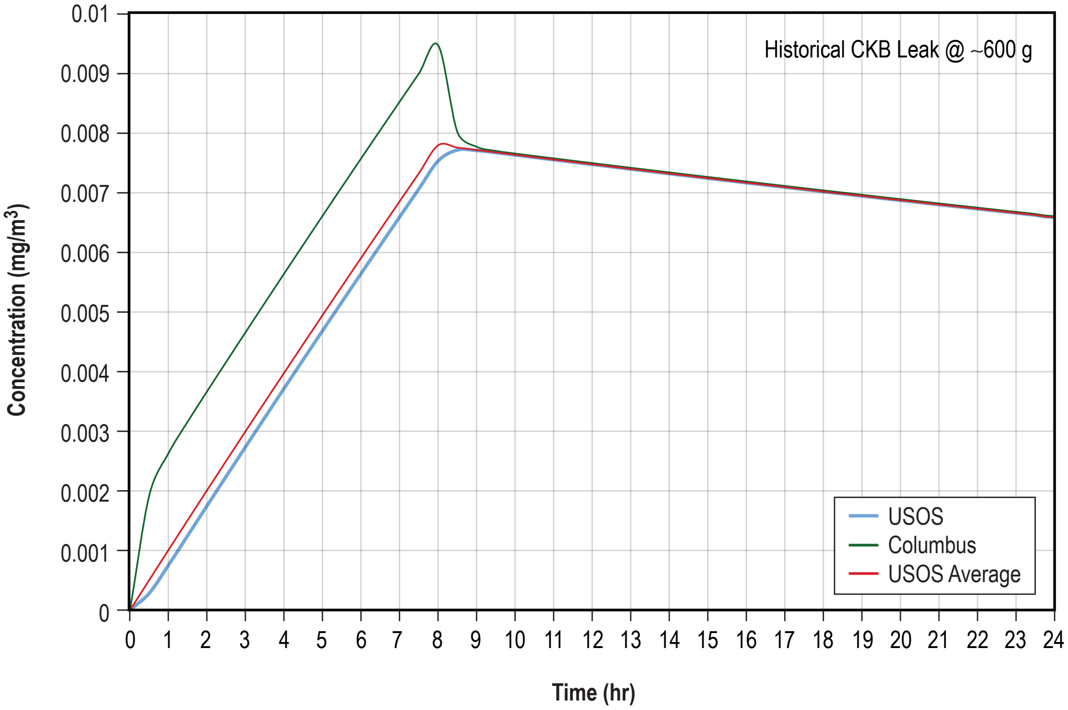


Figure 64. Hydrogen fluoride concentration in the USOS cabin for SPICE operations after a 600-g OFP leak.

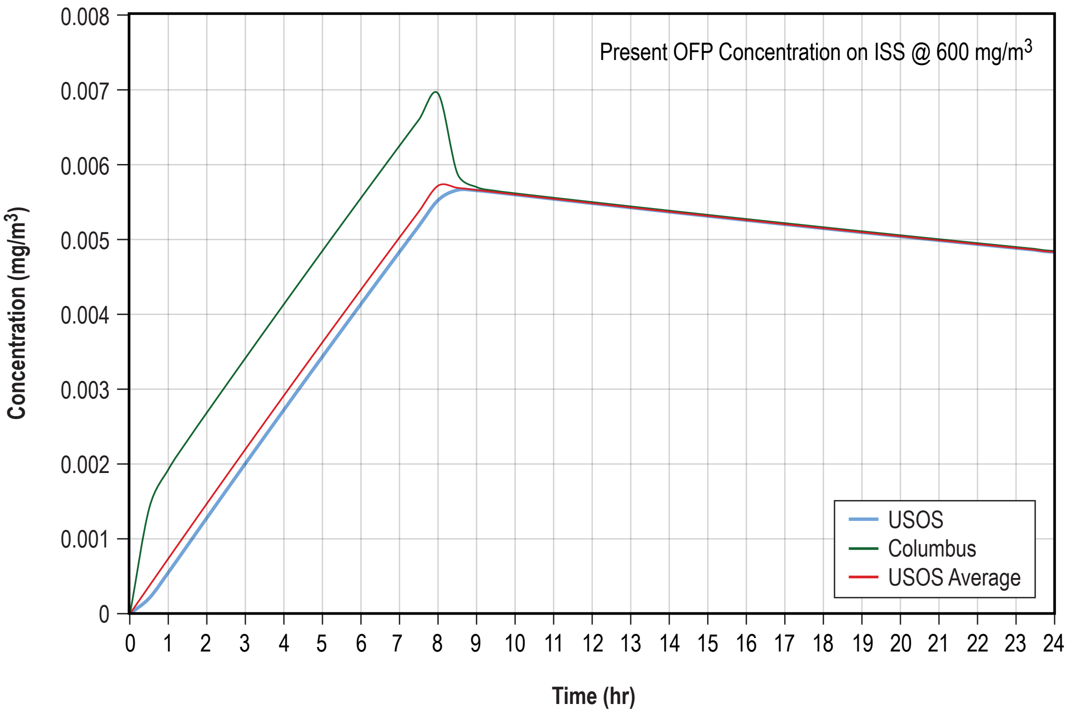


Figure 65. Hydrogen fluoride concentration in the USOS cabin for SPICE operations at present cabin OFP levels.

9.1.3.3 Internal Microgravity Science Glovebox Hydrogen Fluoride Concentration Buildup. During SPICE operations in the MSG, several working volume purge scenarios are possible. These include ventilating the MSG's working volume after twelve, six, three, or one SPICE runs. Figure 66 shows the buildup within the MSG's working volume for a range of OFP leak quantities. The MSG total working volume is ~250 L (~0.25 m^3). For the three cabin atmosphere OFP loading discussed, varying HF concentrations are predicted that exceed both the long- and short-term SMACs in the MSG working volume. For the case where the cabin atmosphere is loaded from a 1,500-g OFP leak, the predicted MSG working volume HF concentration is 38.9 mg/m^3 (48 ppm$_v$), 19.5 mg/m^3 (24 ppm$_v$), 9.7 mg/m^3 (12 ppm$_v$), and 3.2 mg/m^3 (0.4 ppm$_v$) for operational scenarios for venting after 12 runs, 6 runs, 3 runs, and a single run, respectively. Similarly, the MSG working volume HF concentration conditions predicted from cabin loading from a 600-g OFP leak are 15.6 mg/m^3 (19 ppm$_v$), 7.8 mg/m^3 (10 ppm$_v$), 3.9 mg/m^3 (5 ppm$_v$), and 1.3 mg/m^3 (0.17 ppm$_v$) for working volume ventilation after 12 runs, 6 runs, 3 runs, and a single run, respectively. For the presently prevailing ISS cabin OFP loading the predicted HF concentrations in the MSG working volume are 11.6 mg/m^3 (14 ppm$_v$), 5.8 mg/m^3 (7 ppm$_v$), 2.9 mg/m^3 (4 ppm$_v$), and 0.96 mg/m^3 (0.12) for ventilating the working volume after 12 runs, 6 runs, 3 runs, and a single run, respectively. Examining figure 66 shows that most purge scenarios result in accumulated HF concentrations within the MSG's working volume that exceed the 1- and 24-hr SMACs. Ventilating after no more than two runs provides the best result for the most likely range of OFP leaked quantities. Overall, ventilating after the fewest number of runs is most likely to present the lowest risk to the crewmembers while working with the SPICE apparatus and reduce the need for using personal protective equipment when working near the MSG during SPICE operations.

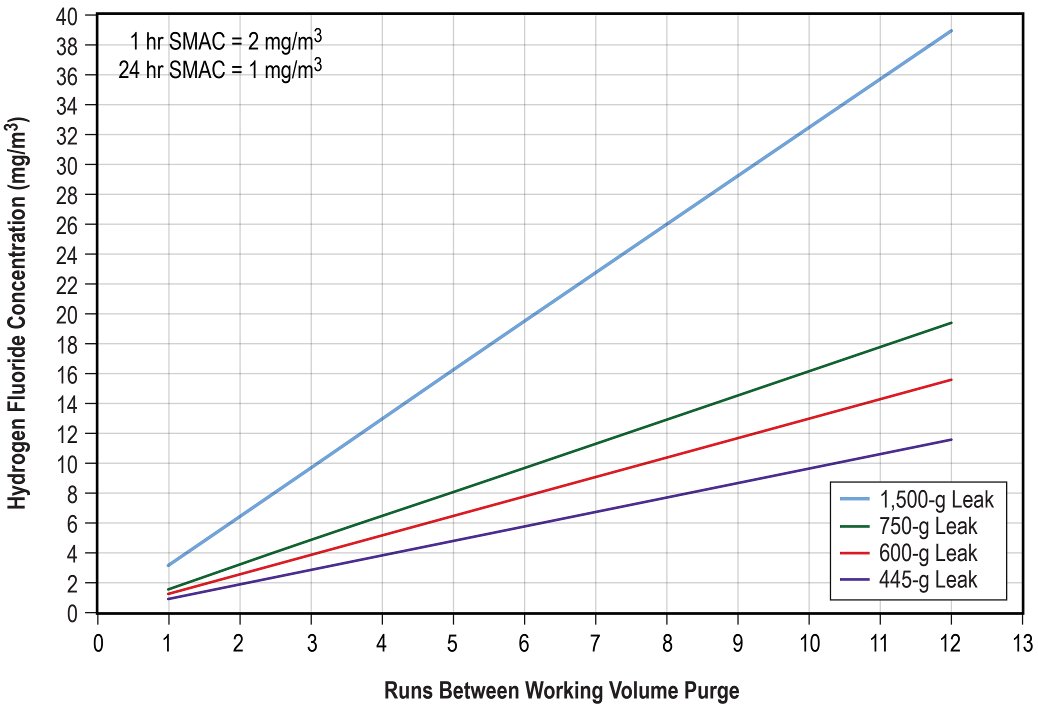


Figure 66. Hydrogen fluoride accumulation in the MSG working volume.

9.1.3.4 Microgravity Science Glovebox Working Volume Postrun Hydrogen Fluoride Concentration Dilution. After a selected number of runs, the MSG will be configured into 'open mode.' In this mode, the MSG's fans circulate 200 L of cabin atmosphere/minute through the working volume. The atmosphere originally in the MSG working volume is diluted with this ventilation flow and the combined atmosphere exhausts into the back of the MSG rack. The MSG rack volume adds an additional 460 L (0.46 m^3) of volume. In less than 3 min, a significant dilution is achieved with a peak concentration shown in figure 67. This is the peak concentration because the purge duration is assumed to be sufficient to fully dilute the HF concentration below the long-term SMAC. As with the HF concentration accumulation in the MSG working volume, purging the working volume after no more than two runs provides the most favorable result.

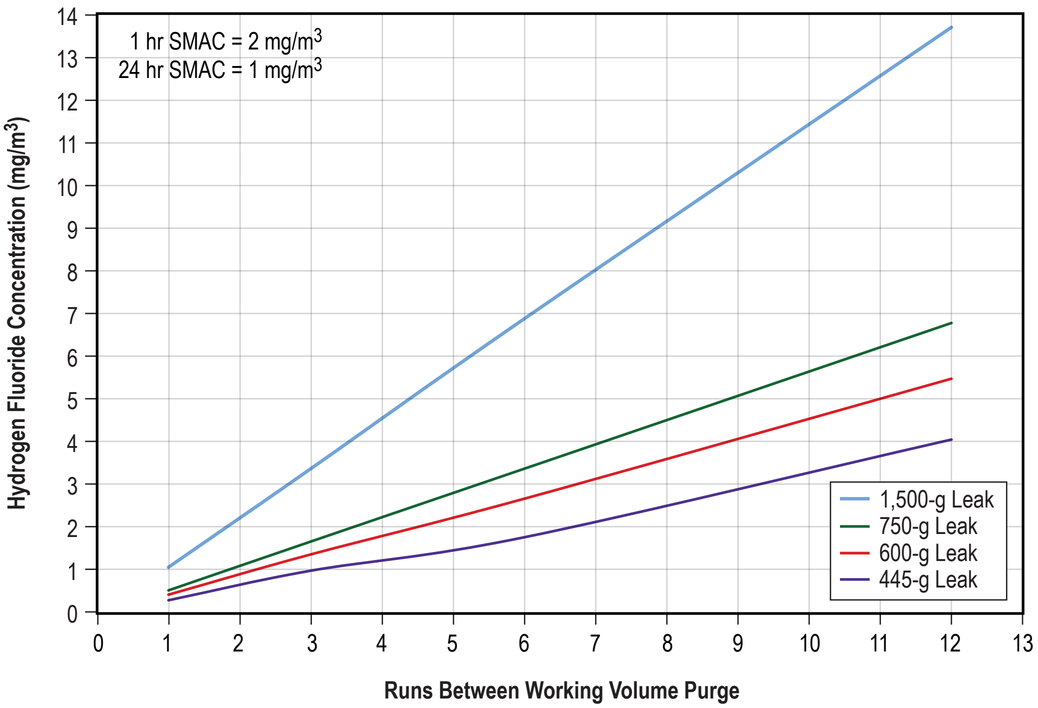


Figure 67. Postrun peak HF concentration after dilution in the MSG rack.

9.1.3.5 International Space Station Environmental Control and Life Support System Impact Potential. The impact to ISS ECLSS function and long-term logistics needs presented by the SPICE payload operations is minimal. The small amount of HF produced will not consume significant quantities of the USOS TCCS sorbent bed assembly LiOH and, therefore, will not result in added life cycle costs or functional degradation to maintaining the ISS cabin atmospheric quality. Absorption of HF into humidity condensate is very slight, leading to no perceptible increase in condensate pH.

9.1.4 Conservatism of Assessment

The ECLS engineering assessment is considered to be highly conservative for a number of reasons. First, the assessment assumes 100% conversion of OFP exposed to the temperatures produced by the SPICE experimental runs. This is conservative because most perfluorinated compounds require long-duration exposure at high temperatures to begin to undergo pyrolysis (i.e., thermal decomposition). Most perfluorinated compounds require high temperature exposures lasting 10's of minutes to hours before significant pyrolysis product yields are observed. Other factors that contribute to the pyrolysis in addition to the contact time include the flame surface area and the rate of transport of OFP across the flame boundary into the hottest temperature zone. Finally, the shorter the carbon chain of a perfluorocarbon, the more thermally stable it is. Literature shows that a much larger compound, perfluorononane (C_9F_{20}) has a $T_{1/2}$ of 756 °C.[69] The smaller OFP molecule can be expected to possess a much higher $T_{1/2}$ and indeed carbon bond cleavage is reported to be observed for temperatures >1,000 °C in the presence of platinum.[70] Without a catalyst present, the decomposition is likely to be all the more difficult.

9.1.5 Conclusion

The operation of the SPICE experimental apparatus is not predicted to result in exceeding the HF long- or short-term SMACs in either the total ISS or isolated USOS cabins even for the most conservative assessment assumptions of 100% OFP decomposition. Under these conservative assessment assumptions, it is predicted that HF concentration within the MSG working volume may exceed both the long- and short-term SMACs. Ventilating the MSG working volume after no more than two experimental runs is most likely to present the lowest risk to the crewmembers while working with the SPICE apparatus and to reduce or eliminate the need for using personal protective equipment when working near the MSG during SPICE operations. Neither functional nor logistics resupply impacts are anticipated for the ISS ECLSSs as a result of SPICE payload operations on board the ISS.

10. POLAR VOLATILE ORGANIC COMPOUND ASSESSMENT

The effect of polar VOCs present challenges to crewed spacecraft water processing systems. Evaluation must consider loading into humidity condensate to understand the impact to life cycle costs and logistics requirements to maintain the system.

10.1 Effects of Polar Organic Compounds on Water Processing Systems

The following assessment was conducted in 2002 and served as the basis for developing the ISS program's volatile usage agreement (VUA) process. The evaluation was documented by NASA memorandum FD21(03-012), Effects of Polar Volatile Organic Compound Use During Crew Activities on Humidity Condensate Loading and International Space Station Water Processor Performance," dated November 15, 2002.

10.1.1 Background

The planned U.S.- and present Russian-provided water processing systems on board the ISS have a limited capacity for removing polar VOCs which can carry over from the cabin atmosphere into humidity condensate. Though the water processing systems are designed to remove polar VOCs from wastewater streams, using large quantities of these compounds in the cabin during flight operations may load the ISS humidity condensate to levels beyond the water processors' capacity. Polar VOCs of primary concern include methanol; ethanol; 2-propanol (isopropanol); n-propanol; n-butanol; 2-propanone (acetone); 1,2-ethanediol (ethylene glycol); 1,2-propanediol (propylene glycol); and 1,2,3-propanetriol (glycerol). These compounds can originate from equipment offgassing, crew metabolism, and crew activities. Careful attention to materials selection and control as well as controlled solvent use during manufacturing and preflight ground processing can minimize the polar VOC load from offgassing. This is the goal of the materials selection and control process combined with a good ground processing contamination control plan. The crew metabolic load can fluctuate according to crew size, activity level, and from person to person. These fluctuations tend to be moderate; therefore, the metabolic polar VOC load is considered fairly static on average. In-flight polar VOC generation from crew activities can fluctuate widely unless strict controls on their use are in place.

Controls imposed during short duration flights, such as Shuttle and Spacelab missions, typically focus upon proper containment to prevent excessively large releases into the cabin. This approach minimizes the risk that a release could result in exceeding individual compound SMACs. While these controls address safety and acute health effects, the policy for using volatile solvents for cleaning and personal hygiene purposes on board the Shuttle and Spacelab has been liberal. This has not presented a significant problem to these programs because the humidity condensate is not recycled for the crew's use. The situation changes significantly when the condensate is recycled.

NASA's recent participation in the Shuttle-Mir program was the U.S. space program's first experience with the inherent sensitivities of onboard water processing systems to in-flight polar VOC use by the crew. Typically, products containing polar VOCs such as low molecular weight alcohols were not permitted on board Mir because they load humidity condensate significantly and are difficult to remove from water once in it. Essentially a duplicate of Mir's water processor is on board the ISS SM, Zvezda. This means that the sensitivities to alcohol use that were characteristic of Mir apply to the ISS. Therefore, the issue of polar VOC use by the crew is an immediate issue to be addressed.

Onboard TCCSs located in Zvezda and the U.S. Laboratory, Destiny, are designed to handle the basic cabin air loads produced by offgassing and crew metabolism. These systems include design margin that can handle the added load produced by crew activities such as housekeeping, maintenance, food preparation and consumption, personal hygiene, and experimental facility operations. The baseline TCCSs, however, are not the only processes that removed VOCs from the cabin atmosphere. System-level testing and analysis has demonstrated that absorption in humidity condensate is a significant removal route.[3,15,19] Because the ISS water processing equipment must remove the polar VOCs from humidity condensate as well as other waste water sources to provide the crew with a potable water supply, a design load has been defined.[71] As well, technical experts have attention must be placed upon further limiting their in-flight use by the crew. While the U.S. Segment water processor's (WP's) capability to handle the polar VOC design load has been demonstrated, several polar VOCs have been identified that their use by the crew may affect the WP's ability to meet the potable water quality standards.[72] The following analysis addresses the generation of several polar VOCs produced by typical crew activities and the effect of varying rates of production on their concentration in humidity condensate.

10.1.2 Relation of Cabin Atmospheric and Condensate Loading

Section 2.5 summarizes a mass balance on a typical condensing heat exchanger, assuming co-current condensate and process air flow, to provide a general equation relating bulk liquid (condensate) and gas (atmospheric) phase mole fraction in the form of equation (11). The Henry's Law constant in equation (11) must be adjusted for the condensing heat exchanger operating temperature according to equation (13) and converted into the appropriate units according to equation (14) as described in section 2.5.

The liquid phase mole fraction, x, in equation (11) can be expressed by equation (23) in which n_i is the number of moles of the dilute VOC and n_w is the number of moles of water. In equation (23), the total moles of water is 55.494 for a 1-L condensate basis. The contribution from the dilute VOC is considered negligible and does not significantly change the total moles of water. The number of moles is defined by the liquid phase concentration in mg/L, C_L, divided by molecular weight, M, in g/mole, and a unit conversion of 10^3 mg/g as shown by equation (24). Substituting equation (24) and total moles of water into the definition of mole fraction yields equation (25) for the dilute condition in which $n_i << n_w$:

$$x = \frac{n_i}{n_w + n_i} \ , \tag{23}$$

$$n_i = \frac{C_L}{10^3 M} \ , \tag{24}$$

and

$$x = \frac{C_L}{\left(55.454 \times 10^3 \times M\right)} \ . \tag{25}$$

Similarly, assuming that the ideal gas law applies to dilute contaminants, the gas phase mole fraction, y, can be defined by equation (26)—unit conversions of 10^3 mg/g and 10^6 cm^3/m^3 are applied in the denominator:

$$y = \frac{C_A \mathbf{R} T}{10^9 MP} \ , \tag{26}$$

where

C_A = atmospheric concentration (mg/m^3)
$\mathbf{R}$ = ideal gas constant (82.06 cm^3-atm/mole-K)
T = temperature is set at the condenser's operating temperature (Kelvin)
M = molecular weight (g/mole)
P = total pressure (1 atm).

Combining equations (11), (25), and (26) in addition to applying the appropriate constants and solving for C_A yields equation (27):

$$C_A = \frac{18{,}019.97 P C_L}{\mathbf{R} T} \left[\frac{L}{G} + \frac{k_H(T)}{P} \right] . \tag{27}$$

As described in section 2.5,

L = condensate molar flow rate
G = bulk gas molar flow rate
$k_H(T)$ = Henry's Law constant adjusted for the condensing heat exchanger's operating temperature.

Using equation (27) along with the physical constants in table 35, an estimate of the cabin air concentration that can produce a specific condensate loading can be made. Water processor design condensate loading for the four compounds of interest are listed in table 36 along with the associated cabin atmospheric concentration necessary to produce them. The WP condensate design load was developed to reflect the anticipated composition of the ISS condensate. The data are based upon analyses of condensate samples collected from the Shuttle, Spacelab, and developmental testing at MSFC.[19]

Table 35. Physical and experimental constants for selected compounds.

Compound	Molecular Weight (g/mole)	Henry's Constant (atm)	Shape Factor (α)
Methanol	32.04	0.39	0.38
Ethanol	46.07	0.45	0.4
Isopropanol	60.09	0.62	0.4
n-propanol	60.09	0.51	0.4
n-butanol	74.12	1.36	0.4
Acetone	58.08	2.38	0.54
Ethylene glycol	62.07	0.0001	0.4
Propylene glycol	76.1	0.0833	0.4
Glycerol	92.1	0.0007	0.4

Table 36. Condensate and atmospheric loading.

Compound	Condensate Design Load (mg/L)	Atmospheric Concentration (mg/m^3)	SMAC (mg/m^3)
Methanol	3.1102	0.35	9
Ethanol	6.1156	0.86	2,000
Isopropanol	38.3327	7.4	150
n-propanol	0.1986	0.031	98
n-butanol	0.9368	0.4	80
Acetone	3.9642	4	50
Ethylene glycol	8.6974	0.0027	13
Propylene glycol	35.0483	0.92	NA
Glycerol	2.832	0.0014	NA

Table 36 shows that the individual contaminant atmospheric concentrations that can result in condensate loading at the water processor's design level are well below their respective SMACs. The materials selection and control process passively limits trace contaminant generation via offgassing while the onboard TCCSs remove the crew metabolic, residual offgassing, and other miscellaneous loads from crew activities to low levels. The load of the primary generation sources—crew metabolism and equipment offgassing—versus the trace contaminant removal capability must be assessed to determine the margin that exists to accommodate generation from the various crew activities.

It should be noted that the atmospheric concentrations listed in table 36 for ethylene glycol and glycerol fall below the typical analytical method's detection limit in air of 0.05 mg/m^3. Therefore, it is possible for these compounds to be in the cabin atmosphere at concentrations that are deleterious to the WP's performance but not detected in archival grab samples.

10.1.3 Contaminant Generation Source Evaluation

Trace atmospheric contamination in a spacecraft cabin can originate from many sources.[1] Chief among these are materials offgassing and human metabolism. Other major sources are from crew activities such as housekeeping, food preparation and consumption, personal hygiene, and payload operations. Table 37 lists predicted hourly offgassing rates derived from element offgassing tests conducted through STS-100/6A and those predicted for the ISS at assembly complete. The assembly complete case applies offgassing rates derived from Node 1 flight element offgassing test data to 75,000 kg of internal hardware and metabolic loading reported by reference 72 applied to six people. Glycerol's rate is derived from its evaporation rate from a shallow pool having a 1-m^2 surface area.[73] The total rates for both cases were evaluated to determine the predicted cabin concentration in the ISS at its present assembly stage and at assembly complete. Predicted concentrations are compared with the atmospheric concentrations from table 36 that correspond to the WP's condensate load limits. To evaluate additional polar VOC use by the crew, the base rates were increased by 1,000 mg/day.

Table 37. Base contaminant generation rates.

	Conclusion of STS-100/6A			Assembly Complete		
Compound	Offgassing Rate (mg/hr)	Metabolic Rate (mg/hr)	Total Rate (mg/hr)	Offgassing Rate (mg/hr)	Metabolic Rate (mg/hr)	Total Rate
Methanol	1.6	0.11	1.71	0.73	0.22	0.95
Ethanol	10.9	0.55	11.4	16.4	1.1	17.5
Isopropanol	3.37	0.21	3.58	15.4	0.42	15.8
n-propanol	0.36	0.07	0.43	0.75	0.14	0.89
n-butanol	1.55	0.065	1.62	14.7	0.13	14.8
Acetone	3.15	2.35	5.5	4.0	4.7	8.7
Ethylene glycol	–	–	–	0.0188	–	0.0188
Propylene glycol	–	–	–	0.0008	–	0.0008
Glycerol	–	–	–	0.00146	–	0.00146

10.1.4 Station Trace Contaminant Removal Devices

The ISS cabin free volume is estimated to be approximately 300 m^3 as of STS-100/6A and will increase to approximately 644 m^3 once completed. Presently, the ISS trace contaminant removal capability consists of one TCCS unit in Destiny and one BMP unit in Zvezda. Normally, two condensing heat exchangers are operating to control cabin temperature and relative humidity.

At assembly complete, the ISS will contain two TCCS units, one BMP, and up to seven condensing heat exchangers. For the purpose of the assembly complete case of this analysis, it has been assumed that four condensing heat exchangers are the primary contributors to the latent heat removal and one TCCS unit will be operating at any given time in parallel with the BMP. These units will remove contamination generated at the rates listed in table 37 plus that generated by crew activities.

The TCCS removes trace contaminants via physical adsorption by activated charcoal and high temperature catalytic oxidation. Process air flow through the charcoal bed is 15.29 m^3/hr and through the oxidizer is 4.59 m^3/hr. The BMP also removes contaminants via physical adsorption, but instead of using a high temperature catalytic oxidizer, it uses an ambient temperature catalyst to oxidize CO. The flow through the BMP is 27 m^3/hr.

It has been assumed that the daily latent load of 1.6 L/day-person is divided between four condensing heat exchangers at assembly complete and two heat exchangers for the STS-100/6A case. Based on flight data, approximately 0.02 kg condensate/hr is being removed by the heat exchanger in Destiny while 0.27 kg condensate/hr is being removed by Zvezda's heat exchanger. A similar loading is used for assembly complete with two exchangers removing condensate at the higher rate to account for greater time spent by the crew in some parts of the Station. Process air flow is 680 m^3/hr through the U.S. Segment central ventilation system and 600 m^3/hr through the Russian Segment ventilation system. Up to 90% of the total air flow bypasses the heat exchanger core in the U.S. Segment unit in the configuration to maximize condensate collection in the Russian Segment. Similarly, approximately 76% of the total air flow in the Russian Segment ventilation system bypasses the heat exchanger. Therefore, the actual process air flow through the U.S. Segment and Russian Segment heat exchanger cores is approximately 68 m^3/hr and 144 m^3/hr, respectively.

10.1.5 Calculation Approach

Information on the ISS configuration, TCCS, BMP, and condensing heat exchangers along with physical properties of the contaminants of interest are used as input to a cabin mass balance model, the Trace Contaminant Control Simulation Computer Program (TCCS CP).[74] The TCCS CP solves the cabin mass balance, summarized by equation (2) in section 2.3, using a backwards differencing technique.

Two cases are investigated for the STS-100/6A and assembly complete configurations. The first case uses the base contaminant generation rates listed in table 37 while the second case uses rates that are increased by 1 g/day across the board. The difference between the concentrations are determined for the two configurations, then divided by the generation rate difference. This number is the slope of the curve relating contaminant generation rate to cabin concentration. For simplicity, this curve is assumed to be linear with a y-intercept at zero. Using the threshold cabin concentrations that correspond to the WP's design limit from table 36, the corresponding threshold generation rate is determined by either interpolation or extrapolation. The base rates are then subtracted to arrive at the additional generation above the base that is allowable for housekeeping and other crew activities. In addition, the same cases were run for the U.S. Segment only to bound the range of allowable daily VOC use.

10.1.6 Results

Results from the system-level analysis are summarized in tables 38 and 39. The calculated delta rate is the difference between the base rate and the rate that results in individual cabin concentrations equal to those listed in table 36. Table 38 shows that the ISS's full atmospheric scrubbing capability can accommodate approximately 13 g/day of additional polar VOC generation. This generation rate corresponds to a total polar VOC concentration of approximately 13.9 mg/m^3 as obtained by summing the atmospheric concentrations in table 36. Individually, no single contaminant has exceeded its maximum allowable rate.

Table 38. Station-level polar VOC usage rates.

Compound	Conclusion of STS-100/6A			Assembly Complete		
	Concentration Delta (mg/m^3)	Maximum Rate (mg/hr)	Delta Rate (mg/day)	Concentration Delta (mg/m^3)	Maximum Rate (mg/hr)	Delta Rate (mg/day)
Methanol	4.91	2.93	29.3	4	3.6	63.5
Ethanol	1.34	26.57	364	1.26	28.32	259.9
Isopropanol	0.96	320.2	7,598	0.93	329	7,517
n-propanol	0.98	1.34	21.9	0.98	1.34	10.8
n-butanol	0.98	16.74	363	0.98	16.79	47.7
Acetone	0.98	168.2	3,904	0.98	168.7	3,840
Ethylene glycol	0.17	0.65	15.7	0.12	0.98	23.1
Propylene glycol	0.92	41.35	992.4	0.87	44.06	1,057
Glycerol	0.2	0.3	7.1	0.13	0.44	10.6
	Total VOC Rate		13,295.4	Total VOC Rate		12,829.6

Table 39. U.S. Segment-level polar VOC usage rates.

Compound	Conclusion of STS-100/6A			Assembly Complete		
	Concentration Delta (mg/m^3)	Maximum Rate (mg/hr)	Delta Rate (mg/day)	Concentration Delta (mg/m^3)	Maximum Rate (mg/hr)	Delta Rate (mg/day)
Methanol	8.48	1.7	–0.28	5.6	2.57	38.9
Ethanol	7.04	5.1	–152.1	5.99	5.95	–277.3
Isopropanol	2.08	148.3	3,474	2.45	125.5	2,632
n-propanol	2.09	0.63	4.8	2.58	0.51	–9.2
n-butanol	2.09	7.9	150.3	2.67	6.17	–207.1
Acetone	4.54	36.3	739.4	6.34	25.96	414.3
Ethylene glycol	0.33	0.35	8.3	0.1	1.13	26.6
Propylene glycol	2.04	18.7	449.6	2.05	18.59	446.1
Glycerol	0.43	0.14	3.3	0.12	0.5	11.9
	Total VOC Rate		4,677.3	Total VOC Rate		3,076.2

The situation changes when considering the scrubbing capability of only the U.S. Segment. At the completion of phase II, the U.S. Segment can accommodate approximately 4.7 g/day above the base generation rates. This decreases, however, to as low as 3 g/day above the base generation rates at assembly complete. The decrease occurs because the U.S. Segment's scrubbing capacity remains static while the projected base alcohol loading from equipment offgassing and human metabolism increase due to additional equipment and a larger crew size. Projected increases in n-butanol and 2-propanol offgassing rates are the primary drivers. As well, during all ISS assembly phases, the low molecular weight alcohols will rapidly saturate the expendable charcoal bed leaving the catalytic oxidizer as the primary removal device in the TCCS. The oxidizer flow, at 4.6 m^3/hr, is only one-third of the flow through the charcoal bed; the result is a lower removal rate. The 13.9 mg/m^3 total polar VOC concentration also applies to this case.

10.1.7 Comparison to Flight Experience

The following compares the engineering analysis results for atmospheric loading and humidity condensate loading to loading reported from samples collected during flight from the Shuttle, Spacelab, Mir, and the ISS.

10.1.7.1 Atmospheric Loading. To understand how well the base predictions correlate to actual ISS operations, the past and present on-orbit experience regarding atmospheric trace contaminant loading must be examined. Concentration data collected during ISS missions 5A and 5A.1 that reflect the Station's total scrubbing capability are summarized in table 40. These data are consistent with the base offgassing and human metabolic loading used for the analysis because few logistics flights had yet occurred. In addition, all of the available TCC equipment was operating as of mission 5A, giving a good representation of joint U.S. and Russian equipment operation. As can be seen, the predicted concentrations are lower by an average factor of 2.7 relative to the measured in-flight atmospheric quality. This means that actual generation is higher than the available equipment offgassing data indicate.

Table 40. Predicted versus observed concentrations on board the ISS.

Compound	SMAC (mg/m^3)	Predicted (mg/m^3)	ISS (mg/m^3)
Methanol	9	0.058	0.09
Ethanol	2,000	0.28	1.43
Isopropanol	150	0.084	0.14
n-propanol	98	0.01	0.025
n-butanol	80	0.038	0.15
Acetone	50	0.13	0.16

Average observed concentrations from 100 grab samples for the Shuttle, from 43 grab samples for Spacelab, and from 87 grab samples for Mir are summarized in table 41.[1] Comparison of the average concentrations from table 41 to analysis results in table 40 indicate that the atmospheric concentrations on board the ISS are being controlled to similar levels or better than previous space programs.

Table 41. Average Shuttle, Spacelab, and Mir atmospheric concentrations.

Compound	SMAC (mg/m^3)		Shuttle (mg/m^3)	Spacelab (mg/m^3)	Mir (mg/m^3)
	NASA	Russian			
Methanol	9	0.2	0.04	0.05	0.21
Ethanol	2,000	10	2.8	2	1.6
Isopropanol	150	1.5	2	4.5	0.51
n-propanol	98	0.6	0.014	0.031	0.024
n-butanol	80	0.8	0.031	0.077	0.26
Acetone	50	2	0.83	0.46	0.48

Further comparison of the reported concentrations from Mir to the average concentrations observed to date on board the ISS indicate that some net increase in most steady state atmospheric concentrations should be expected. Methanol is an exception as its early offgassing rate has been quite high. Air quality data from the ISS do show that methanol's offgassing decayed significantly between the time that the ground-based offgassing test was conducted on Unity and the first early ingress during STS-88/2A approximately 2 months later.[75] It is expected that methanol's offgassing rate will continue to decay and cabin concentrations should not rise appreciably through the remainder of ISS assembly.

This typical offgassing rate behavior will be repeated with every new Station element deployed so that atmospheric concentration peaks are expected. Once Station operations become more routine and its habitable configuration more stable, it is anticipated that an average atmospheric trace contaminant load representative of that observed during Shuttle, Spacelab, and Mir missions will prevail. The concentration range observed in flight from these three programs indicate that the results of the analysis of polar VOC control capability can be used to reach a sound conclusion concerning constraints on their use during crew activities.

10.1.7.2 Condensate Loading. To complete the comparison between predicted atmospheric loading and humidity condensate loading, it is also necessary to consider results from humidity condensate analyses. Table 42 shows the condensate loading for a sample returned on STS-104/7A and two samples collected during Increment 3 and returned on STS-108/UF-1. The first sample was collected on July 19, 2001, the second on September 6, and the third on November 24. All three samples were collected in the U.S. Segment. Equation (27) was used to calculate the atmospheric loading that corresponds to the measured humidity condensate loading. Reported atmospheric concentrations from samples collected as close as possible to the time the condensate samples are used as a comparison to that calculated from the humidity condensate loading. This approach allows for a second basis for evaluating polar VOC use to be considered.

Table 42. Atmospheric loading indicated by the measured condensate load.

	STS-104/7A			Increment 3a			Increment 3b		
	C_L	C_A (mg/m^3)		C_L	C_A (mg/m^3)		C_L	C_A (mg/m^3)	
Compound	**(mg/L)**	**Predicted**	**Measured**	**(mg/L)**	**Predicted**	**Measured**	**(mg/L)**	**Predicted**	**Measured**
Methanol	6.87	0.76	0.22	6.32	0.7	0.54	6.9	0.77	0.64
Ethanol	50.4	7	2	47.7	6.67	2.28	71.3	9.98	6.2
Isopropanol	2.55	0.49	0.082	2.93	0.56	0.22	2.06	0.4	0.16
n-propanol	0.59	0.09	0.025	0.788	0.12	0.05	0.66	0.1	0.06
n-butanol	2.88	1.22	0.12	2.4	1.01	0.14	1.43	0.6	0.13
Acetone	0.39	0.39	0.14	0.525	0.52	0.26	0.349	0.35	0.22
Ethylene glycol	11	0.0034	–	6.5	0.002	–	7.08	0.0022	–
Propylene glycol	113	2.95	–	52	1.36	–	58.9	1.54	–
Glycerol	–	–	–	–	–	–	–	–	–

The sample collected on September 6 shows loading that is comparable to that collected on July 19. Exceptions are higher acetone and n-propanol loading as well as markedly lower ethylene glycol and propylene glycol loading. The sample collected on November 24 shows loading similar to the one collected on September 6 except that ethanol loading is nearly 50% higher.

Comparison shows that the measured humidity loading indicates a higher atmospheric loading than measurements indicate for all three data sets. Predicted atmospheric concentrations for methanol, ethanol, n-propanol, and acetone corresponding to the humidity condensate loading reported in the sample collected on July 19 are greater than those reported from flight grab samples by an average factor of 3.4. Isopropanol's predicted atmospheric concentration is 6 times higher than measured, while the predicted concentration for n-butanol is 10.3 times higher than measured. Weighted with respect to the total condensate loading, the predicted atmospheric loading is approximately 4 times higher than was measured in grab samples for the sample collected on July 19. Similarly, the predicted atmospheric concentrations corresponding to the condensate loading reported in the samples collected on September 6 and November 24 are approximately 3 and 1.6 times higher, respectively, than measured in the grab samples.

There may be many reasons why the condensate loading indicates a higher cabin atmosphere loading that what has been measured. Contributing factors may reside in the analytical techniques employed or with differences between the ground and flight gravity environments. Based upon evaluation, these sources are considered to be the most likely contributing factors.

Relative analytical errors as well as limitations associated with the grab sampling technique may contribute to the perceived higher condensate loading. The grab sampling technique provides only an indication of atmospheric loading at a single point in time. Sustained peaks in loading can be missed by the technique whereas the condensate loading indicates a time-integrated sample that includes the effects of peaks in atmospheric loading. To achieve better comparison, it is necessary to coordinate condensate and atmospheric sampling to be done within the same hour.

The effects of the free-fall environment in flight must also be considered. Liquid phase molecular interactions such as hydrogen bonding and bulk liquid characteristics such as surface tension may become enhanced in microgravity conditions. As the effect of gravity is reduced, surface tension can dominate, leading to a change in flow regime within the heat exchanger channels. In the free-fall environment, liquids will tend to adhere to pipe and container walls. In the case of the condensing heat exchanger, this can produce an annular flow phenomenon. This becomes highly likely given the high mass velocity of air and the small cross-sectional area of the channels. In such a situation, the shear stress in the channel begins to govern the condensation process leading to annular flow.[76] Therefore, there are two contributing factors that govern the development of annular flow. A comparison of the mass transfer rate expected for stratified versus annular flow indicates that a factor of $1/\pi$ is required in the basic condensate loading equation to account for this effect. Using this factor, the predicted and measured cabin atmospheric concentrations closely agree. It should be noted that the ground testing that investigated the mass transfer of contaminants into humidity condensate used a heat exchanger geometry that was not sensitive to the development of annular condensate flow. Therefore, this effect is neglected in the computer model.

These are some of the leading hypotheses that may be presented about the cause of the condensate and atmospheric loading differences. The available data indicate that development of annular condensate flow through the heat exchanger's channels may be the principle cause. Overall, the difference must be considered as an indicator of uncertainty when setting polar VOC use limits because the computer model as it presently exists does not include the adjustment for annular flow. This is accomplished by conservatively adjusting the concentration limits associated with total polar VOCs downward by a factor of 3. The same adjustment also applies to allowable daily generation rates reported in tables 38 and 39.

10.1.8 Contamination Dynamics and Distribution Aboard the International Space Station

The following presents the results from the spatial distribution analysis and the fate of polar VOCs between the U.S. and Russian active TCC devices.

10.1.8.1 Spatial Distribution. Figure 68 shows the total VOC loading in the ISS cabin throughout the Station's early assembly stages beginning with STS-88/2A in December 1998, continuing through STS-108/UF-1 in December 2001. As can be seen, higher concentrations were observed at the beginning of each ingress period. After the Station atmosphere dilutes with the Orbiter volume and continues to be scrubbed, lower concentrations comparable to those summarized in table 40 are achieved. For example, at the conclusion of 2A.1 ingress operations, average cabin concentrations were 0.36 mg/m^3, 2.35 mg/m^3, 0.62 mg/m^3, and 0.22 mg/m^3 for methanol, ethanol, isopropanol, and acetone, respectively. Propanol was not detected but the n-butanol concentration grew from trace levels to an average of 0.26 mg/m^3. Ethylene glycol, propylene glycol, and glycerol have not been reported above detection limits.

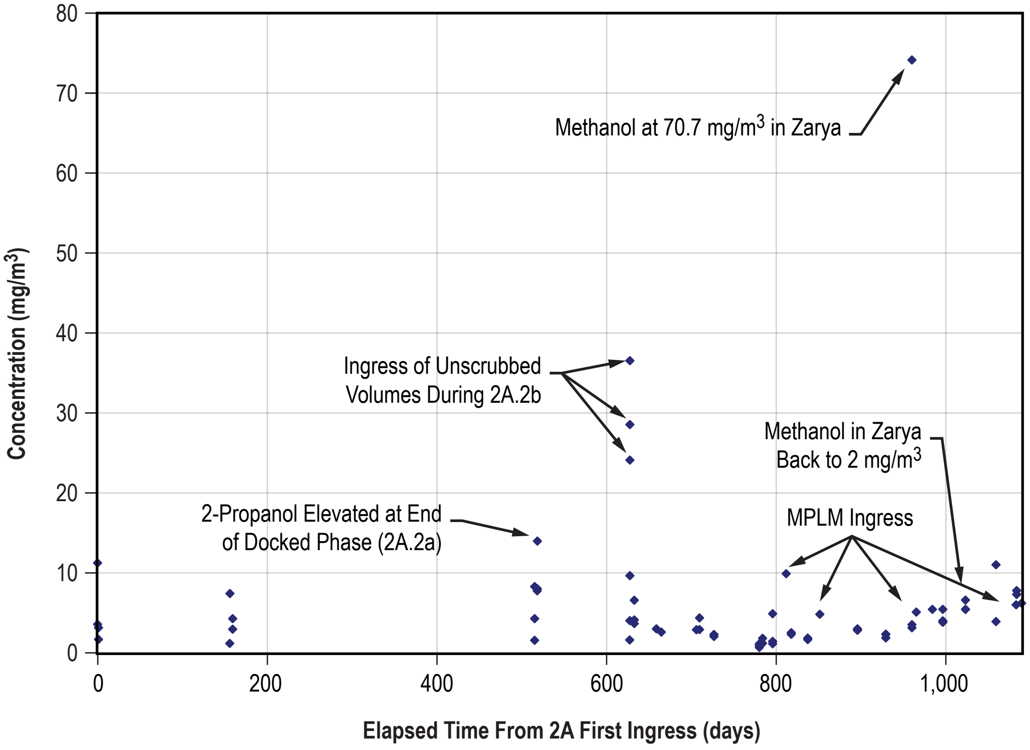


Figure 68. Total VOC loading in the ISS cabin.

With respect to total polar VOC concentration transients, three in-flight cases are noteworthy. The first is 2A.2a where the maximum isopropanol concentration reached 13 mg/m^3. This concentration was measured from a sample collected at the end of the docked phase. Concentrations in the Orbiter approached 10 mg/m^3 during the same time. This increase was indicative of in-flight isopropanol use by the crew. The second case, 2A.2b, saw ethanol as high as 25 mg/m^3 during ingress of unscrubbed volumes in the PMA-1, Zvezda, and the Program. The concentration across the ISS was reduced to 2.7 mg/m^3 by the end of the docked phase. The third case occurred just before STS-105 was launched. It involved a methanol concentration of approximately 70 mg/m^3 in a sample collected in the Zarya. Samples that were collected later and returned on a Soyuz vehicle showed the methanol had been reduced to nearly 2 mg/m^3. The methanol's source was not determined.

The high ethanol concentrations during the first ingress operations during 2A.2b demonstrate the contamination potential of new modules and equipment. For this reason, VOC use during ground processing should be restricted close to final element closeout. Employing such a restriction is attributed to reducing the total VOC concentration in the MPLM at first ingress by half. The first flight of an MPLM, STS-102/5A.1, saw total VOCs at nearly 10 mg/m^3 at first ingress. Subsequent MPLM flights, STS-100/6A, STS-105/7A.1, and STS-108/UF-1, reported total VOCs at approximately 5 to 6 mg/m^3 at first ingress.

Even with precautions taken, concentration peaks are expected as new modules and equipment are added to the vehicle. As the hardware ages, average concentrations will decrease. Therefore, it is expected that cabin concentrations will decrease to magnitudes similar to those experienced on average during Shuttle, Spacelab, and Mir missions as the Russian Segment BMP on board Zvezda and U.S. Segment TCCS on board Destiny continue to operate.

The elevated methanol concentration in Zarya demonstrates that local transients are possible. Even so, the entire ISS cabin remains nearly well mixed with some noted exceptions. Figure 69 shows the total polar VOC distribution by module beginning with Zvezda's activation during mission 2R. The peak of 70 mg/m^3 at approximately day 250 is not shown. Elapsed time begins at Zvezda activiation. As can be seen, the measured concentrations in Zvezda and Destiny follow each other closely indicating good ventilation exchange between them. An increasing trend is evident with significant peaks in Zvezda indicating local polar VOC use. As well, there are instances where the loading in Zarya is noticeably higher. This can be attributed to the fact that there is forced ventilation flow from Zvezda, forward to Unity and Destiny, but only plenum flow through the hatches into Zarya. Additionally, Zvezda and Destiny have local contamination and humidity control systems that remove the contaminants while Zarya has no active contamination control system normally operating. As a result, it is not surprising that periodic high concentrations occur in Zarya.

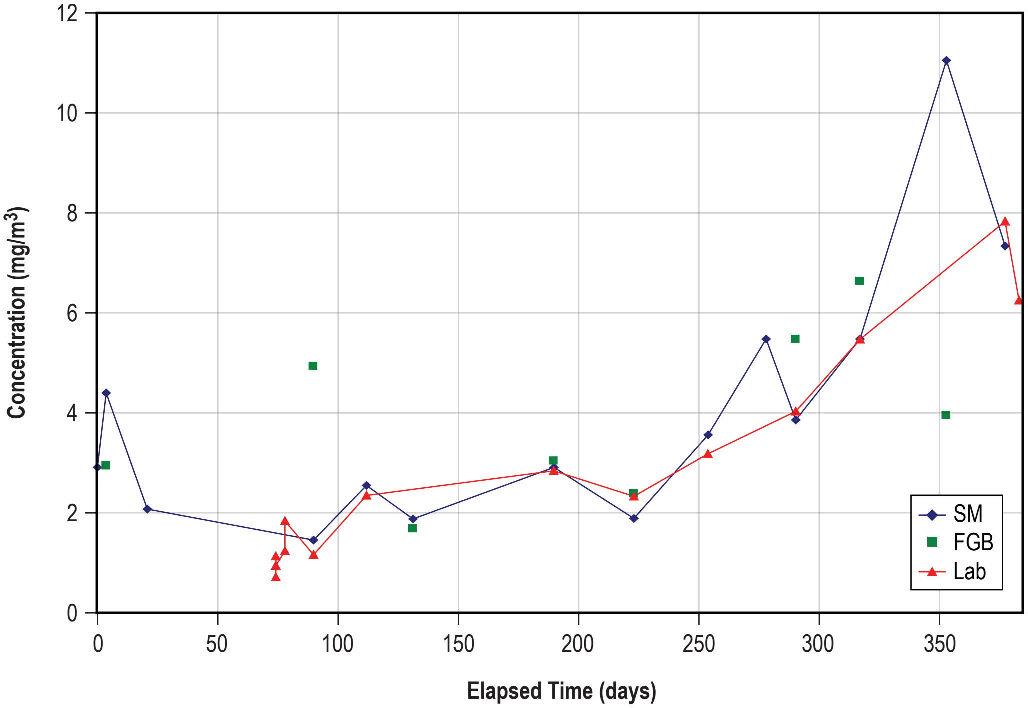


Figure 69. Spatial distribution of polar VOCs on board the ISS.

10.1.8.2 Distribution Between Removal Devices. Upon evaluating the engineering analysis results, it was found that the average removal of methanol, alcohols, acetone, and glycols under all loading conditions are summarized according to table 43 for a typical 20-day period representing fresh TCCS and BMP bed materials. This distribution reflects a large initial capacity of the TCCS charcoal bed compared to that of the BMP beds. The alcohols and acetone are especially noteworthy. As can be seen, during this initial period, even though the total process air flow through the TCCS is only 58% that of the BMP, the large axial flow charcoal bed initially maintains a higher overall removal efficiency. The glycols exhibit overall removal distribution between the TCCS and BMP that reflect the different flow capacities during this period.

Table 43. Average polar VOC removal fraction early in TCCS and BMP service life.

Compound	Removal Device		
	TCCS	BMP	Condensate
Methanol	0.46	0.18	0.36
Alcohols*	0.44	0.53	0.03
Acetone	0.52	0.47	0.01
Ethylene glycol and glycerol	0.05	0.13	0.82
Propylene glycol	0.33	0.56	0.11

* Average of ethanol, 2-propanol, n-propanol, and n-butanol.

As time passes, the TCCS charcoal bed becomes saturated and the total removal flow for the methanol is best represented by the 4.6 m^3/hr that flows through the thermal catalytic oxidizer. This situation is illustrated by methanol in table 44. As can be seen, the percentage of methanol removed by the TCCS begins to fall compared to table 43 while the BMP removal fraction remains fairly steady. The BMP does lose some capacity as its expendable bed also becomes saturated with alcohols and acetone within the first 90 days of its service life. As this happens, the humidity condensate removal systems begin to remove a larger share of the contaminants. Over a long period of time, the ratio of total contaminant removed by the TCCS compared to the BMP will approach 0.17, the ratio of catalytic oxidizer flow to BMP flow, as the charcoal bed becomes saturated and the catalytic oxidizer becomes the dominant removal device within the TCCS. Table 45 shows that the alcohols and acetone follow this trend. This will have to be accounted for as an extension of the TCCS charcoal bed assembly service life is considered. The TCCS continues to provide the major share of methanol removal because the catalytic oxidizer is more effective than the activated charcoal in the BMP.

Table 44. Average polar VOC removal fraction after 90 days of TCCS and BMP operation.

	Removal Device		
Compound	**TCCS**	**BMP**	**Condensate**
Methanol	0.3	0.15	0.55
Alcohols*	0.52	0.43	0.045
Acetone	0.67	0.32	0.02
Ethylene glycol and glycerol	0.05	0.09	0.86
Propylene glycol	0.35	0.54	0.12

* Average of ethanol, 2-propanol, n-propanol, and n-butanol.

Table 45. Average polar VOC removal fraction after 360 days of TCCS and BMP operation.

	Removal Device		
Compound	**TCCS**	**BMP**	**Condensate**
Methanol	0.41	0.24	0.34
Alcohols*	0.36	0.58	0.06
Acetone	0.25	0.73	0.02
Ethylene glycol and glycerol	0.05	0.07	0.88
Propylene glycol	0.36	0.5	0.14

* Average of ethanol, 2-propanol, n-propanol, and n-butanol.

10.1.9 Condensate Loading Limits

The limit for condensate loading specified for the Russian Segment water processor (Russian acronym SRV-K2M) is 100 mg total alcohols/L including 80 mg total ethanol and isopropanol/L. This compares to the total alcohol limit of 99.24 mg/L for the U.S. Segment water processor. The U.S. design specification has a more stringent limit for total ethanol and isopropanol of 44.45 mg/L. Compared to the U.S. WP's total polar VOC design specification of 13.9 mg/m^3, the SRV-K2M is capable of handling a slightly higher concentration—15.1 mg/m^3. Based upon this comparison, it is reasonable to apply the conclusions and recommendations of the polar VOC usage assessment to the entire ISS. Typically, the total polar VOC loading has been maintained below 10 mg/m^3 with the exception of the noted cases. Considering the observed difference between humidity condensate and atmospheric loading, the total polar VOC loading concentration limit is in the range of 4.6 and 5 mg/m^3. The lower limit of this range, 4.6 mg/m^3, is therefore a reasonable limit. For simplicity, rounding the limit to 5 mg/m^3 is recommended.

10.1.10 Polar Volitile Organic Compound Management On Board the International Space Station

To minimize the introduction of polar VOCs into the ISS cabin, controls must be implemented for their use. By thoroughly assessing in-flight operations, the primary uses on board the ISS, namely, maintenance, housekeeping, personal hygiene, and payloads, have been identified. Appropriate ISS program documents have been revised to implement a process to screen for and regulate polar VOC use on board the U.S. Segment. This process is designed to effectively control the daily load beyond the baseline. International partners must also embrace and participate in the regulatory process to achieve Station-wide success.

The regulation process defined by Space Station Requirements for Materials and Processes (SSP 30233, paragraph 3.1.5) requires submission of a volatile usage agreement (VUA) to JSC Materials Review Board for each use of a restricted compound. The VUA must specify the quantity of the compound to be released into the ISS atmosphere and provide rationale for its use, including an explanation of why no alternatives will suffice for the intended application. Based upon the information provided, the Materials Review Board may approve the compound's use if the expected daily release of the contaminant is <0.01 g. If greater than this quantity and below the recommended maximum allowable limit, the VUA will be approved as long as sufficient justification for the intended use has been provided. An ISS Alcohol Manager maintains the approved VUAs to ensure the daily VOC load on board the ISS does not exceed the WP's capacity.

Implementing the process in flight requires timelining maintenance, payload, and housekeeping activities as necessary to keep the daily VOC below acceptable limits. Though the process has been initiated, the daily limit is currently being exceeded because of ISS operations approved before the VOC management process was in place. Personnel representing ECLS, vehicle systems, mission operations, and materials and processes are identifying VOC sources on board the ISS that may be replaced with suitable alternatives. Two major polar VOC sources presently on board the ISS are premoistened wipes and no-rinse shampoo that contain propylene glycol. Both of these items will be replaced. A continual evaluation of other VOC sources on board the ISS will ensure the safe and reliable operation of ECLS hardware.

10.1.11 Conclusions

When using equipment offgassing data and atmospheric quality as the primary basis to evaluate the polar VOC removal capacity and considering the evaluation of past and present flight atmospheric trace contaminant loading data, the total allowable polar VOC usage rate for the ISS is 13 g/day with no more than 3 g/day of this within the U.S. Segment. The atmospheric concentration for total low molecular weight alcohols and acetone should not exceed 14 mg/m^3 to protect the onboard water processing systems. The conditions on board the ISS are presently well below this limit.

However, when using measured humidity condensate loading as the primary evaluation basis, the difference between measured condensate and atmospheric loading must be considered. Accounting for this difference, the total polar VOC usage rate for the entire ISS may be as low as 4 g/day with no more than 1 g/day of this generated within the U.S. Segment. The allowable cabin concentration decreases to 5 mg/m^3. The conditions on board the ISS are presently exceeding this allowable concentration.

Further, observations can be made concerning the distribution and dynamics of polar VOCS in the ISS cabin atmosphere. First, distribution of the polar VOCs in the ISS cabin has shown a fairly uniform concentration throughout. This finding supports the basic engineering analysis assumption that the cabin is well mixed. By providing good mixing, the various removal devices may best remove the contaminants from the atmosphere. Second, evaluation of the engineering analysis results indicates that there is a shift over time in the distribution of the contaminant load among the primary removal devices. This aspect of the evaluation shows that early in the TCCS's charcoal bed service life, it shares a dominant removal role with humidity condensate absorption. At the same time, both the TCCS and BMP are the dominant removal devices for most other polar VOCs during their early operating phases with the exception of ethylene glycol and glycerol. As time passes,the BMP becomes the dominant removal device. This results from the saturation of the TCCS charcoal bed, making its catalytic oxidizer the only effective removal device. The BMP's ability to maintain a high average removal efficiency through regeneration and its much higher process air flow rate relative to the TCCS's catalytic oxidizer contribute significantly to this shift. During all operational periods, a large percentage of the ethylene glycol and glycerol are removed by absorption into the humidity condensate. Overall, humidity condensate absorption is a highly significant removal route for methanol, ethylene glycol, propylene glycol, and glycerol.

Finally, the analysis indicates that the effect of the free-fall environment may have a significant effect on the removal of polar VOCs and other soluble trace contaminants via absorption in humidity condensate. The high potential for developing annular condensate flow in the heat exchanger channels exists and the difference in interfacial surface area accounts for observed differences between calculated and measured cabin atmospheric quality.

10.1.12 Recommendations

Because the humidity condensate loading directly affects water processor performance, it is recommended that the total daily in-flight polar VOC usage rate for crew activities be limited by appropriate ISS program controls to 4 g/day Station wide with no more than 1 g/day of this within the U.S. Segment. This limit accounts for observed differences between polar VOC loading in humidity condensate and the cabin atmosphere. Further, it considers that direct measurement of the humidity condensate loading is most reasonable when considering the onboard water processing equipment performance. Likewise, the total polar VOC atmospheric concentration, measured as low molecular weight alcohols and acetone, should be maintained below 5 mg/m^3. Steps should be taken to determine the present polar VOC usage on board the ISS as air quality data indicate that this limit may already be exceeded on a regular basis. Also, sampling of the humidity condensate and cabin atmosphere should be coordinated to happen within the same hour on the same day during increment operations so that the observed difference in contaminant loading between the two phases can be better understood. As well, it is recommended that modifications be made to the condensing heat exchanger subroutine in the TCCS CP to account for the development of annular flow in the heat exchanger channels.

11. SYNOPSIS

Contamination of a crewed spacecraft's cabin environment leading to ECLSS functional capability and operational margin degradation or loss can have an adverse effect on NASA's space exploration mission figures of merit—safety, mission success, effectiveness, and affordability. Therefore, as a key component of the overall system safety approach for crewed space exploration missions, careful evaluation and selection of materials and chemicals used in vehicle and crew systems as well as experiment hardware must be conducted to ensure that the ECLSS's capabilities and functional margins are preserved in the event that a substance is released into the cabin environment. In implementing NASA's safety and mission success objectives, ECLSS engineering must assume leadership in implementing NASA's safety and mission success objectives by thoroughly assessing the potential impacts on ECLSS hardware and processes as well as the vehicle cabin environment from contamination releases into the habitable environment either by design or by accident.

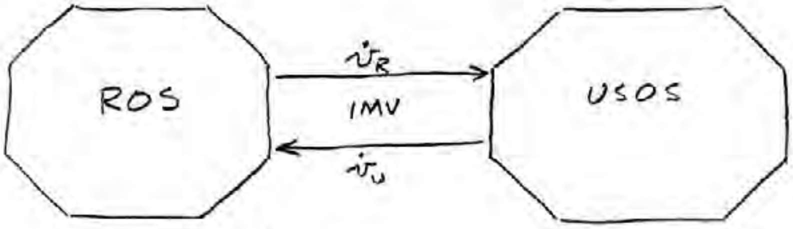
Evaluating ECLSS compatibility and cabin environmental impact is an integral part of TCC engineering. Its relation to TCC design practice as a key component of passive TCC that seeks to minimize the total trace contaminant load into the cabin environment was presented and discussed. The approach to conducting ECLSS and cabin environmental impact assessments was presented and the rating definitions were introduced. The approach is reinforced by examples of assessments conducted for a variety of chemicals used in vehicle systems and experiment equipment aboard the ISS.

The ECLSS compatibility and cabin environmental impact assessment can provide guidance to crewed spacecraft system and payload developers relative to design criteria assigned ECLSS compatibility and cabin environmental impact rating can be used by payload and system developers as criteria for ensuring adequate physical and operational containment. In additional to serving as an aid for guiding containment design, the assessments can guide flight rule and procedure development toward protecting the ECLSS as well as approaches for contamination event remediation.

APPENDIX A—MASS BALANCE EQUATION DERIVATION

CABIN MASS BALANCE – GENERALIZED

V.L. PERRY
MSFC/FD21
4-7-04



$V_R = 180.6\ m^3$	CABIN VOLUME	$V_U = 190.4\ m^3$
$C_R = 0.02\ mg/m^3$	CONCENTRATION @ $t=\infty$	$C_U = 0.04\ mg/m^3$
$\dot{v}_R = 252.7\ m^3/h$	IMV FLOW	$\dot{v}_U = 118.6\ m^3/h$
$g_R = ?$	GENERATION RATE	$g_U = ?$
	REMOVAL DEVICES	
	TCCS →	$\eta\dot{v} = (1.0)(4.6) = 4.6\ m^3/h$
$\eta\dot{v} = (0.9)(27)$	← BMP	
$\eta\dot{v} = (0.073)(144)$	← SKV	
$\Sigma\eta\dot{v}_R = 34.8\ m^3/h$	TOTAL REMOVAL	$\Sigma\eta\dot{v}_U = 4.6\ m^3/h$

USOS MASS BALANCE

$$\frac{dm_U}{dt} = \dot{v}_R C_R - \dot{v}_U C_U - \left(\Sigma\eta\dot{v}_U\right) C_U + g_U$$

$$= \left(\frac{\dot{v}_R}{V_R}\right) M_R - \left(\frac{\dot{v}_U}{V_U}\right) M_U - \left(\frac{\Sigma\eta\dot{v}_U}{V_U}\right) M_U + g_U \qquad \text{①}$$

ROS MASS BALANCE

$$\frac{dM_R}{dt} = \dot{v}_U C_U - \dot{v}_R C_R - \left(\Sigma\eta\dot{v}_R\right) C_R + g_R$$

$$= \left(\frac{\dot{v}_U}{V_U}\right) M_U - \left(\frac{\dot{v}_R}{V_R}\right) M_R - \left(\frac{\Sigma\eta\dot{v}_R}{V_R}\right) M_R + g_R \qquad \text{②}$$

DEFINE IN OPERATOR FORM

USDS

$$\frac{dM_U}{dt} = \frac{\dot{v}_R}{V_R} M_R - \frac{\dot{v}_U}{V_U} M_U - \left(\frac{r_u}{V_U}\right) M_U + g_U$$

$$\frac{dM_U}{dt} = \frac{\dot{v}_R}{V_R} M_R - \left(\frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right) M_U + g_U$$

so $$\left[D + \left(\frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right)\right] M_U - \left(\frac{\dot{v}_R}{V_R}\right) M_R = g_U \qquad ③$$

RDS

$$\frac{dM_R}{dt} = \frac{\dot{v}_U}{V_U} M_U - \frac{\dot{v}_R}{V_R} M_R - \left(\frac{r_R}{V_R}\right) M_R + g_R$$

$$\frac{dM_R}{dt} = \frac{\dot{v}_U}{V_U} M_U - \left(\frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R}\right) M_R + g_R$$

so $$\left[D + \left(\frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R}\right)\right] M_R - \frac{\dot{v}_U}{V_U} M_U = g_R \qquad ④$$

USING THE ANNIHILATOR METHOD

- TAKE DERIVATIVE OF BOTH SIDES OF ③ AND ④

$$D\left[D + \left(\frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right)\right] M_U - D\left(\frac{\dot{v}_R}{V_R}\right) M_R = 0 \qquad (3a)$$

$$D\left[D + \left(\frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R}\right)\right] M_R - D\left(\frac{\dot{v}_U}{V_U}\right) M_U = 0 \qquad (4a)$$

- ELIMINATE M_R

$$\left[D + \left(\frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R}\right)\right] D\left[D + \left(\frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right)\right] M_U - \cancel{\left[D + \left(\frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R}\right)\right]} D\left(\frac{\dot{v}_R}{V_R}\right) M_R = 0$$

$$+ \cancel{\left(\frac{\dot{v}_R}{V_R}\right) D\left[D + \left(\frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R}\right)\right]} M_R - \left(\frac{\dot{v}_R}{V_R}\right) D\left(\frac{\dot{v}_U}{V_U}\right) M_U = 0$$

$$\left[D + \left(\frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R}\right)\right] D\left[D + \left(\frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right)\right] M_U - \frac{\dot{v}_R \dot{v}_U}{V_R V_U} D M_U = 0$$

$$\cancel{D}\left[D + \left(\frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R}\right)\right]\left[D + \left(\frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right)\right] M_U - \cancel{D}\frac{\dot{v}_R \dot{v}_U}{V_R V_U} M_U = 0$$

$$\left[D^2 + D\left(\frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U} + \frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R}\right) + \cancel{\frac{\dot{v}_R \dot{v}_U}{V_R V_U}} + \frac{\dot{v}_R r_U}{V_R V_U} + \frac{r_R \dot{v}_U}{V_R V_U} + \frac{r_R r_U}{V_R V_U} - \cancel{\frac{\dot{v}_U \dot{v}_R}{V_R V_U}}\right] M_U = 0$$

$$\left[D^2 + D\left(\frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U} + \frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R}\right) + \frac{\dot{v}_R r_U}{V_R V_U} + \frac{r_R \dot{v}_U}{V_R V_U} + \frac{r_R r_U}{V_R V_U}\right] M_U = 0$$

⑦

$D = 0$

$a = 1$

$$b = \frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R} + \frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}$$

$$c = \frac{\dot{v}_R r_U + r_R \dot{v}_U + r_R r_U}{V_R V_U}$$

$$\therefore\ x_1 = 0\ ;\quad x_2 = \frac{-b + \sqrt{b^2 - 4ac}}{2a}\ ;\quad x_3 = \frac{-b - \sqrt{b^2 - 4ac}}{2a}$$

and

$$x_2 = \frac{-\left(\frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R} + \frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right) + \sqrt{\left(\frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R} + \frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right)^2 - 4(1)(C)}}{2(1)}$$

$$x_3 = \frac{-\left(\frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R} + \frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right) - \sqrt{\left(\frac{\dot{v}_R}{V_R} + \frac{r_R}{V_R} + \frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right)^2 - 4(1)(C)}}{2(1)}$$

so

$$m_U = a + b e^{x_2 t} + c e^{x_3 t}$$

$$D_{m_U} = b\, x_2 e^{x_2 t} + c\, x_3 e^{x_3 t}$$

SUBSTITUTE D_{MU} INTO ③

$$b e^{x_2 t} + c e^{x_3 t} + \left(\frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right)\left(a + b e^{x_2 t} + c e^{x_3 t}\right) - \frac{\dot{v}_R}{V_R} M_R = g_U$$

$$\left(\frac{\dot{v}_R}{V_R}\right) M_R = \left(\frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right) a + \left(x_2 + \frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right) b e^{x_2 t} + \left(x_3 + \frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right) c e^{x_3 t} - g_U$$

$$* \quad \boxed{M_R = \left(\frac{V_R}{\dot{v}_R}\right)\left[\left(\frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right) a + \left(x_2 + \frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right) b e^{x_2 t} + \left(x_3 + \frac{\dot{v}_U}{V_U} + \frac{r_U}{V_U}\right) c e^{x_3 t} - g_U\right]}$$

③

DETERMINE CONSTANTS – a, b, c

FOR TOTAL MASS BALANCE, $M_T = M_U + M_R$

AT $t \to \infty$, $C_i = \frac{g_i}{\Sigma \eta \dot{v}}$ OR $\frac{M_T}{V_U + V_R} = \frac{(g_U + g_R)}{(r_U + r_R)}$

SO $M_T = \frac{(g_U + g_R)(V_U + V_R)}{r_U + r_R}$

SUBSTITUTE M_U AND M_R INTO EQUATION FOR M_T

$$\frac{(g_U + g_R)(V_U + V_R)}{r_U + r_R} = a + b e^{\chi_2 t} + c e^{\chi_3 t} + \left(\frac{V_R}{\dot{v}_R}\right)\left(\frac{\dot{v}_U + r_U}{V_U}\right) a + \left(\frac{V_R}{\dot{v}_R}\right)\left(\chi_2 + \frac{\dot{v}_U + r_U}{V_U}\right) b e^{\chi_2 t} + \left(\frac{V_R}{\dot{v}_R}\right)\left(\chi_3 + \frac{\dot{v}_U + r_U}{V_U}\right) c e^{\chi_3 t} - \frac{V_R g_U}{\dot{v}_R}$$

$$\frac{(g_U + g_R)(V_U + V_R)}{r_U + r_R} = \left[\left(\frac{V_R}{\dot{v}_R}\right)\left(\frac{\dot{v}_U + r_U}{V_U}\right) + 1\right] a + \left[\left(\frac{V_R}{\dot{v}_R}\right)\left(\chi_2 + \frac{\dot{v}_U + r_U}{V_U}\right) + 1\right] b e^{\chi_2 t} + \left[\left(\frac{V_R}{\dot{v}_R}\right)\left(\chi_3 + \frac{\dot{v}_U + r_U}{V_U}\right) + 1\right] c e^{\chi_3 t} - \frac{V_R g_U}{\dot{v}_R}$$

FOR χ_2 AND $\chi_3 < 0$

$$\frac{(g_U + g_R)(V_U + V_R)}{r_U + r_R} = \left[\left(\frac{V_R}{\dot{v}_R}\right)\left(\frac{\dot{v}_U + r_U}{V_U}\right) + 1\right] a - \frac{V_R g_U}{\dot{v}_R}$$

$$\frac{(g_U + g_R)(V_U + V_R)}{r_U + r_R} = \left(\frac{V_R}{\dot{v}_R}\right)\left[\left(\frac{\dot{v}_U + r_U}{V_U} + \frac{\dot{v}_R}{V_R}\right) a - g_U\right]$$

$$\frac{(g_U + g_R)(V_U + V_R)\dot{v}_R}{(r_U + r_R) V_R} = \left(\frac{\dot{v}_U + r_U}{V_U} + \frac{\dot{v}_R}{V_R}\right) a - g_U$$

$$* \; a = \left[\frac{(g_U + g_R)(V_U + V_R)\dot{v}_R}{(r_U + r_R) V_R} + g_U\right] \Big/ \left(\frac{\dot{v}_U + r_U}{V_U} + \frac{\dot{v}_R}{V_R}\right)$$

DETERMINE CONSTANTS b AND C:

AT $t = 0$, $M_U = M_{U0}$, $M_R = M_{R0}$

SO, $M_{U0} = a + b + c$

$$M_{R0} = \left(\frac{V_R}{\dot{v}_R}\right)\left[\left(\frac{\dot{v}_U + r_U}{V_U}\right)a + \left(x_2 + \frac{\dot{v}_U + r_U}{V_U}\right)b + \left(x_3 + \frac{\dot{v}_U + r_U}{V_U}\right)c - g_U\right]$$

ELIMINATE b:

$$-\left[\left(\frac{V_R}{\dot{v}_R}\right)\left(x_2 + \frac{\dot{v}_U + r_U}{V_U}\right)\right]M_{0U} = -\left[\left(\frac{V_R}{\dot{v}_R}\right)\left(x_2 + \frac{\dot{v}_U + r_U}{V_U}\right)\right](a \cancel{+ b +} c)$$

$$+ \quad M_{R0} = \left(\frac{V_R}{\dot{v}_R}\right)\left[\left(\frac{\dot{v}_U + r_U}{V_U}\right)a + \cancel{\left(x_2 + \frac{\dot{v}_U + r_U}{V_U}\right)b} + \left(x_3 + \frac{\dot{v}_U + r_U}{V_U}\right)c - g_U\right]$$

$$M_{R0} - \left[\left(\frac{V_R}{\dot{v}_R}\right)\left(x_2 + \frac{\dot{v}_U + r_U}{V_U}\right)\right]M_{0U} = -\left[\left(\frac{V_R}{\dot{v}_R}\right)\left(x_2 + \frac{\dot{v}_U + r_U}{V_U}\right)\right]a$$

$$+ \left(\frac{V_R}{\dot{v}_R}\right)\left(\frac{\dot{v}_U + r_U}{V_U}\right)a - \left[\left(\frac{V_R}{\dot{v}_R}\right)\left(x_2 + \frac{\dot{v}_U + r_U}{V_U}\right)\right]c$$

$$+ \left[\left(\frac{V_R}{\dot{v}_R}\right)\left(x_3 + \frac{\dot{v}_U + r_U}{V_U}\right)\right]c - \frac{V_R g_U}{\dot{v}_R}$$

$$\frac{\dot{v}_R M_{R0}}{V_R} - \left(x_2 + \frac{\dot{v}_U + r_U}{V_U}\right)M_{0U} = -\left(x_2 + \cancel{\frac{\dot{v}_U + r_U}{V_U}}\right)a + \left(\cancel{\frac{\dot{v}_U + r_U}{V_U}}\right)a$$

$$- \left(x_2 + \cancel{\frac{\dot{v}_U + r_0}{V_U}}\right)c + \left(x_3 + \cancel{\frac{\dot{v}_U + r_0}{V_U}}\right)c - g_U$$

$$\frac{\dot{v}_R M_{R0}}{V_R} - \left(x_2 + \frac{\dot{v}_U + r_U}{V_U}\right)m_{00} = (x_3 - x_2)c - x_2 a - g_U$$

SOLVE FOR C:

$$* \quad c = \left(\frac{1}{x_3 - x_2}\right)\left[\frac{\dot{v}_R M_{R0}}{V_R} - \left(x_2 + \frac{\dot{v}_U + r_U}{V_U}\right)M_{0U} + x_2 a + g_U\right]$$

$$* \quad b = M_{0U} - a - c$$

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APPENDIX B—TABULAR RESULTS OF THE GLUTARALDEHYDE EVALUATION

100 ppm Loading/4R Configuration												
	Concentration											
	All Operating			TCCS Off			BMP Off			TCCS and BMP Off		
Leak Rate (mL/hr)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)
0.16	0.000134	5.66E-05	9.63E-05	0.000149	6.05E-05	0.000106	0.000152	7.6E-05	0.000115	0.000173	8.36E-05	0.000129
0.2	0.000168	7.07E-05	0.00012	0.000187	7.56E-05	0.000133	0.00019	9.5E-05	0.000144	0.000216	0.000105	0.000162
1.6	0.001341	0.000566	0.000963	0.001494	0.000605	0.001061	0.00152	0.00076	0.00115	0.001725	0.000836	0.001292
2.7	0.002262	0.000954	0.001626	0.002521	0.001021	0.00179	0.002565	0.001283	0.001941	0.002911	0.001411	0.002181
3.9	0.003267	0.001379	0.002348	0.003641	0.001474	0.002586	0.003705	0.001853	0.002804	0.004205	0.002038	0.00315
5.3	0.00444	0.001873	0.003191	0.004948	0.002003	0.003515	0.005035	0.002519	0.00381	0.005714	0.00277	0.004281

50 ppm Loading/4R Configuration												
	Concentration											
	All Operating			TCCS Off			BMP Off			TCCS and BMP Off		
Leak Rate (mL/hr)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)
0.16	6.7E-05	2.83E-05	4.82E-05	7.47E-05	3.02E-05	5.31E-05	7.6E-05	3.8E-05	5.75E-05	8.63E-05	4.18E-05	6.46E-05
0.2	8.38E-05	3.53E-05	6.02E-05	9.34E-05	3.78E-05	6.63E-05	9.5E-05	4.75E-05	7.19E-05	0.000108	5.23E-05	8.08E-05
1.6	0.00067	0.000283	0.000482	0.000747	0.000302	0.000531	0.00076	0.00038	0.000575	0.000863	0.000418	0.000646
2.7	0.001131	0.000477	0.000813	0.00126	0.00051	0.000895	0.001283	0.000642	0.000971	0.001456	0.000706	0.00109
3.9	0.001634	0.000689	0.001174	0.00182	0.000737	0.001293	0.001853	0.000927	0.001402	0.002102	0.001019	0.001575
5.3	0.00222	0.000937	0.001595	0.002474	0.001002	0.001757	0.002518	0.001259	0.001905	0.002857	0.001385	0.002141

100 ppm Loading/Assembly Complete												
	Concentration											
	All Operating			TCCS Off			BMP Off			TCCS and BMP Off		
Leak Rate (mL/hr)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)
1.6	0.000513	0.000201	0.000453	0.000537	0.000206	0.000474	0.000544	0.000266	0.000491	0.000572	0.000276	0.000515
2.7	0.000866	0.000339	0.000765	0.000907	0.000348	0.000799	0.000918	0.00045	0.000828	0.000964	0.000466	0.000869
5.3	0.0017	0.000666	0.001501	0.001779	0.000684	0.001569	0.001802	0.000883	0.001625	0.001893	0.000915	0.001705
14.7	0.004714	0.001846	0.004163	0.004936	0.001896	0.004352	0.004998	0.002448	0.004508	0.005251	0.002539	0.00473

50 ppm Loading/Assembly Complete												
	Concentration											
	All Operating			TCCS Off			BMP Off			TCCS and BMP Off		
Leak Rate (mL/hr)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)
1.6	0.000257	0.0001	0.000227	0.000269	0.000103	0.000237	0.000272	0.000133	0.000245	0.000286	0.000138	0.000257
2.7	0.000433	0.00017	0.000382	0.000453	0.000174	0.0004	0.000459	0.000225	0.000414	0.000482	0.000233	0.000434
5.3	0.00085	0.000333	0.00075	0.00089	0.000342	0.000784	0.000901	0.000441	0.000813	0.000947	0.000458	0.000853
14.7	0.002357	0.000923	0.002082	0.002468	0.000948	0.002176	0.002499	0.001224	0.002254	0.002625	0.001269	0.002365

APPENDIX C—TABULAR RESULTS OF THE METHYL ISOTHIAZOLONE EVALUATION

100 mg/L Loading/4R Configuration												
	Concentration											
	All Operating			TCCS Off			BMP Off			TCCS and BMP Off		
Leak Rate (mL/hr)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)
0.16	0.0001772	0.000103	0.000141	0.000207	0.000118	0.000163	0.00022	0.000149	0.000185	0.000269	0.00018	0.000225
0.2	0.0002215	0.000129	0.000177	0.000258	0.000147	0.000204	0.000275	0.000187	0.000232	0.000336	0.000225	0.000282
1.6	0.0017717	0.001033	0.001412	0.002066	0.001177	0.001633	0.002196	0.001494	0.001854	0.002687	0.001798	0.002254
2.7	0.0029897	0.001744	0.002383	0.003486	0.001986	0.002755	0.003706	0.002521	0.003129	0.004534	0.003034	0.003803
3.9	0.0043185	0.002519	0.003442	0.005035	0.002868	0.00398	0.005353	0.003641	0.00452	0.006548	0.004382	0.005494
5.3	0.0058688	0.003423	0.004678	0.006842	0.003898	0.005409	0.007274	0.004948	0.006142	0.008899	0.005955	0.007466

150 mg/L Loading/4R Configuration												
	Concentration											
	All Operating			TCCS Off			BMP Off			TCCS and BMP Off		
Leak Rate (mL/hr)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)
0.16	0.0002658	0.000155	0.000212	0.00031	0.000176	0.000245	0.000329	0.000224	0.000278	0.000403	0.00027	0.000338
0.2	0.0003322	0.000194	0.000265	0.000387	0.000221	0.000306	0.000412	0.00028	0.000348	0.000504	0.000337	0.000423
1.6	0.0026576	0.00155	0.002118	0.003098	0.001765	0.002449	0.003294	0.002241	0.002781	0.00403	0.002696	0.003381
2.7	0.00454	0.002648	0.003619	0.005293	0.003015	0.004184	0.005627	0.003828	0.004751	0.006884	0.004606	0.005775
3.9	0.0064224	0.003746	0.00512	0.007488	0.004265	0.005919	0.007961	0.005415	0.006722	0.009739	0.006516	0.00817
5.3	0.0088585	0.005167	0.007062	0.010328	0.005883	0.008164	0.01098	0.007469	0.009271	0.013433	0.008988	0.011269

200 mg/L Loading/4R Configuration												
	Concentration											
	All Operating			TCCS Off			BMP Off			TCCS and BMP Off		
Leak Rate (mL/hr)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)
0.16	0.0003543	0.000207	0.000282	0.000413	0.000235	0.000327	0.000439	0.000299	0.000371	0.000537	0.00036	0.000451
0.2	0.0004429	0.000258	0.000353	0.000516	0.000294	0.000408	0.000549	0.000373	0.000464	0.000672	0.000449	0.000563
1.6	0.0035434	0.002067	0.002825	0.004131	0.002353	0.003266	0.004392	0.002988	0.003708	0.005373	0.003595	0.004508
2.7	0.0059795	0.003488	0.004767	0.006971	0.003971	0.005511	0.007412	0.005042	0.006258	0.009067	0.006067	0.007607
3.9	0.008637	0.005038	0.006885	0.010069	0.005736	0.00796	0.010706	0.007282	0.009039	0.013097	0.008764	0.010987
5.3	0.0117375	0.006846	0.009357	0.013684	0.007795	0.010817	0.014549	0.009897	0.012284	0.017798	0.011909	0.014932

100 mg/L Loading/Assembly Complete												
	Concentration											
	All Operating			TCCS Off			BMP Off			TCCS and BMP Off		
Leak Rate (mL/hr)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)
1.6	0.0012824	0.000791	0.001149	0.001444	0.00088	0.001291	0.001542	0.001128	0.00143	0.001783	0.001295	0.001651
2.7	0.0021641	0.001334	0.00194	0.002437	0.001484	0.002179	0.002602	0.001903	0.002413	0.002675	0.001943	0.002477
5.3	0.004248	0.002619	0.003807	0.004783	0.002914	0.004277	0.005107	0.003736	0.004736	0.005907	0.00429	0.005469
14.7	0.0117821	0.007265	0.01056	0.013267	0.008082	0.011863	0.014165	0.010362	0.013136	0.016382	0.011898	0.015169

150 mg/L Loading/Assembly Complete												
	Concentration											
	All Operating			TCCS Off			BMP Off			TCCS and BMP Off		
Leak Rate (ml/hr)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)
1.6	0.0019236	0.001186	0.001724	0.002166	0.00132	0.001937	0.002313	0.001692	0.002145	0.002675	0.001943	0.002477
2.7	0.0032862	0.002026	0.002945	0.0037	0.002254	0.003309	0.003951	0.00289	0.003664	0.004569	0.003319	0.004231
5.3	0.006412	0.003954	0.005747	0.00722	0.004398	0.006456	0.007709	0.005639	0.007149	0.008916	0.006475	0.008255
14.7	0.0177133	0.010923	0.015875	0.019945	0.012151	0.017836	0.021295	0.015579	0.019748	0.024629	0.017888	0.022805

200 mg/L Loading/Assembly Complete												
	Concentration											
	All Operating			TCCS Off			BMP Off			TCCS and BMP Off		
Leak Rate (ml/hr)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)
1.6	0.0025648	0.001582	0.002299	0.002888	0.001759	0.002583	0.003083	0.002256	0.002859	0.003566	0.00259	0.003302
2.7	0.0043281	0.002669	0.003879	0.004873	0.002969	0.004358	0.005203	0.003807	0.004825	0.006018	0.004371	0.005572
5.3	0.008496	0.005239	0.007614	0.009566	0.005828	0.008555	0.010214	0.007472	0.009472	0.011813	0.00858	0.010938
14.7	0.0235643	0.014531	0.021119	0.026533	0.016164	0.023727	0.028329	0.020725	0.026271	0.032765	0.023796	0.030337

APPENDIX D—TABULAR RESULTS OF THE ORTHO-PHTHALDEHYDE EVALUATION

100 mg/L Loading/Assembly Complete												
	Concentration											
	All Operating			**TCCS Off**			**BMP Off**			**TCCS and BMP Off**		
Leak Rate (mL/hr)	**USOS (mg/m^3)**	**ROS (mg/m^3)**	**Total Cabin (mg/m^3)**	**USOS (mg/m^3)**	**ROS (mg/m^3)**	**Total Cabin (mg/m^3)**	**USOS (mg/m^3)**	**ROS (mg/m^3)**	**Total Cabin (mg/m^3)**	**USOS (mg/m^3)**	**ROS (mg/m^3)**	**Total Cabin (mg/m^3)**
0.16	0.0003045	0.000241	0.000274	0.000414	0.000325	0.000371	0.00053	0.000487	0.000509	0.001035	0.000946	0.000992
0.2	0.0003806	0.000302	0.000342	0.000518	0.000407	0.000464	0.000663	0.000608	0.000636	0.001294	0.001183	0.00124
1.6	0.003045	0.002415	0.002738	0.004142	0.003254	0.00371	0.005304	0.004866	0.005091	0.010352	0.009463	0.009919
2.7	0.0051385	0.004075	0.004621	0.00699	0.00549	0.00626	0.00895	0.008211	0.008591	0.017469	0.015969	0.016739
3.9	0.0074223	0.005886	0.006675	0.010097	0.00793	0.009042	0.012928	0.011861	0.012409	0.025233	0.023067	0.024178
5.3	0.0100867	0.008	0.009071	0.013722	0.010777	0.012288	0.017569	0.016118	0.016863	0.034291	0.031347	0.032858

150 mg/L Loading/Assembly Complete												
	Concentration											
	All Operating			**TCCS Off**			**BMP Off**			**TCCS and BMP Off**		
Leak Rate (mL/hr)	**USOS (mg/m^3)**	**ROS (mg/m^3)**	**Total Cabin (mg/m^3)**	**USOS (mg/m^3)**	**ROS (mg/m^3)**	**Total Cabin (mg/m^3)**	**USOS (mg/m^3)**	**ROS (mg/m^3)**	**Total Cabin (mg/m^3)**	**USOS (mg/m^3)**	**ROS (mg/m^3)**	**Total Cabin (mg/m^3)**
0.16	0.0004568	0.000362	0.000411	0.000621	0.000488	0.000556	0.000796	0.00073	0.000764	0.001553	0.001419	0.001488
0.2	0.0005709	0.000453	0.000513	0.000777	0.00061	0.000696	0.000994	0.000912	0.000955	0.001941	0.001774	0.00186
1.6	0.0045675	0.003622	0.004107	0.006214	0.00488	0.005565	0.007956	0.007299	0.007636	0.015528	0.014195	0.014879
2.7	0.0078029	0.006188	0.007017	0.010615	0.008337	0.009506	0.013591	0.012469	0.013045	0.026527	0.024249	0.025418
3.9	0.0110382	0.008754	0.009926	0.015016	0.011794	0.013448	0.019227	0.017639	0.018454	0.037526	0.034304	0.035958
5.3	0.0152251	0.012075	0.013692	0.020712	0.016268	0.018549	0.02652	0.024329	0.025453	0.05176	0.047316	0.049597

200 mg/L Loading/Assembly Complete												
	Concentration											
	All Operating			**TCCS Off**			**BMP Off**			**TCCS and BMP Off**		
Leak Rate (mL/hr)	**USOS (mg/m^3)**	**ROS (mg/m^3)**	**Total Cabin (mg/m^3)**	**USOS (mg/m^3)**	**ROS (mg/m^3)**	**Total Cabin (mg/m^3)**	**USOS (mg/m^3)**	**ROS (mg/m^3)**	**Total Cabin (mg/m^3)**	**USOS (mg/m^3)**	**ROS (mg/m^3)**	**Total Cabin (mg/m^3)**
0.16	0.000609	0.000483	0.000548	0.000828	0.000651	0.000742	0.001061	0.000973	0.001018	0.00207	0.001893	0.001984
0.2	0.0007613	0.000604	0.000685	0.001036	0.000813	0.000927	0.001326	0.001216	0.001273	0.002588	0.002366	0.00248
1.6	0.0060901	0.00483	0.005477	0.008285	0.006507	0.007419	0.010608	0.009732	0.010181	0.020704	0.018926	0.019839
2.7	0.010277	0.008151	0.009242	0.013981	0.010981	0.01252	0.017901	0.016422	0.017181	0.034938	0.031938	0.033478
3.9	0.0148445	0.011773	0.013349	0.020194	0.015861	0.018085	0.025857	0.023721	0.024817	0.050466	0.046133	0.048357
5.3	0.0201733	0.015999	0.018141	0.027444	0.021555	0.024577	0.035138	0.032236	0.033726	0.068583	0.062694	0.065716

100 mg/L Loading/Assembly Complete												
	Concentration											
	All Operating			TCCS Off			BMP Off			TCCS and BMP Off		
Leak Rate (mL/hr)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)
1.6	0.0028317	0.00228	0.002682	0.003813	0.003054	0.003608	0.004981	0.004684	0.0049	0.009372	0.008802	0.009218
2.7	0.0047785	0.003847	0.004526	0.006435	0.005154	0.006088	0.008405	0.007905	0.00827	0.015815	0.014853	0.015555
5.3	0.00938	0.007552	0.008885	0.012631	0.010116	0.01195	0.016498	0.015517	0.016233	0.031045	0.029157	0.030534
14.7	0.0260162	0.020946	0.024644	0.035033	0.028058	0.033145	0.04576	0.043038	0.045023	0.086105	0.080869	0.084688

150 mg/L Loading/Assembly Complete												
	Concentration											
	All Operating			TCCS Off			BMP Off			TCCS and BMP Off		
Leak Rate (mL/hr)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)
1.6	0.0042468	0.003419	0.004023	0.00572	0.004581	0.005411	0.007469	0.007025	0.007348	0.014058	0.013203	0.013827
2.7	0.007255	0.005841	0.006872	0.009771	0.007826	0.009245	0.012759	0.012	0.012554	0.024016	0.022555	0.02362
5.3	0.0141561	0.011397	0.013409	0.019066	0.01527	0.018038	0.024896	0.023415	0.024495	0.04686	0.04401	0.046089
14.7	0.0391063	0.031484	0.037043	0.052669	0.042182	0.049831	0.068774	0.064684	0.067667	0.12945	0.121578	0.12732

200 mg/L Loading/Assembly Complete												
	Concentration											
	All Operating			TCCS Off			BMP Off			TCCS and BMP Off		
Leak Rate (mL/hr)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)	USOS (mg/m^3)	ROS (mg/m^3)	Total Cabin (mg/m^3)
1.6	0.0056624	0.004559	0.005364	0.007626	0.006108	0.007215	0.009961	0.009369	0.009801	0.018744	0.017604	0.018435
2.7	0.0095554	0.007693	0.009051	0.012869	0.010307	0.012176	0.01681	0.01581	0.016539	0.03163	0.029707	0.03111
5.3	0.0187568	0.015101	0.017767	0.025262	0.020232	0.023901	0.032997	0.031034	0.032466	0.062089	0.058313	0.061067
14.7	0.0520237	0.041884	0.049279	0.070067	0.056116	0.066291	0.091519	0.086076	0.090046	0.17221	0.161737	0.169375

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14. ABSTRACT

Contamination of a crewed spacecraft's cabin environment leading to environmental control and life support system (ECLSS) functional capability and operational margin degradation or loss can have an adverse effect on NASA's space exploration mission figures of merit—safety, mission success, effectiveness, and affordability. The role of evaluating the ECLSS's compatibility and cabin environmental impact as a key component of pass trace contaminant control is presented and the technical approach is described in the context of implementing NASA's safety and mission success objectives. Assessment examples are presented for a variety of chemicals used in vehicle systems and experiment hardware for the International Space Station program. The ECLSS compatibility and cabin environmental impact assessment approach, which can be applied to any crewed spacecraft development and operational effort, can provide guidance to crewed spacecraft system and payload developers relative to design criteria assigned ECLSS compatibility and cabin environmental impact ratings can be used by payload and system developers as criteria for ensuring adequate physical and operational containment. In additional to serving as an aid for guiding containment design, the assessments can guide flight rule and procedure development toward protecting the ECLSS as well as approaches for contamination event remediation.

15. SUBJECT TERMS

system compatibility, environmental impact, environmental control and life support, contaminant control, air quality, water quality, activated carbon, catalyst, humidity condensate, maximum allowable concentration, material balance, fugitive emission, safety, mission success

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