Cabin Air Quality On Board *Mir* and the *International Space Station*—A Comparison

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Abstract

The maintenance of the cabin atmosphere aboard spacecraft is critical not only to its habitability but also to its function. Ideally, air quality can be maintained by striking a proper balance between the generation and removal of contaminants. Both very dynamic processes, the balance between generation and removal can be difficult to maintain and control because the state of the cabin atmosphere is in constant evolution responding to different perturbations. Typically, maintaining a clean cabin environment on board crewed spacecraft and space habitats is the central function of the environmental control and life support (ECLS) system. While active air quality control equipment is deployed on board every vehicle to remove carbon dioxide, water vapor, and trace chemical components from the cabin atmosphere, perturbations associated with logistics, vehicle construction and maintenance, and ECLS system configuration influence the resulting cabin atmospheric quality. The air-quality data obtained from the *International Space Station (ISS)* and NASA-*Mir* programs provides a wealth of information regarding the maintenance of the cabin atmosphere aboard long-lived space habitats. A comparison of the composition of the trace chemical contaminant load is presented. Correlations between ground-based and in-flight operations that influence cabin atmospheric quality are identified and discussed, and observations on cabin atmospheric quality during the NASA-*Mir* expeditions and the *International Space Station* are explored.

Introduction

The air-quality data obtained from the *International Space Station* (*ISS*) and NASA-*Mir* programs provides much information regarding the maintenance of the cabin atmosphere aboard long-lived space habitats. Cabin air quality information reflects not only chemicals introduced into the cabin atmosphere, but also the day-to-day functions and performance of the systems on the spacecraft and the crew tasks on-board. These factors combine in a synergistic manner to ultimately determine cabin air quality.

In terms of sealed atmospheres, submarines and tightly-built buildings are the closest analogs to manned spacecraft. All three are designed to protect occupants from external environments and the interior atmosphere of all three is subject to chemical infiltration. Chemical contaminants can be introduced by material off-gassing, system-related chemicals, human or animal metabolism, and by different human activities. The management of the quality of the interior atmosphere is paramount to the health and well-being of those who live and work in all three structures. One, simple way to deal with such contaminants is to vent the interior atmosphere to fresh air. However, the ability to vent the cabin atmosphere and exchange the interior atmosphere with clean, fresh air is one significant option not necessarily possible for manned spacecraft. Limited in-flight resources to perform an atmospheric purge in manned spacecraft precludes this option. Typically, cabin air quality in manned spacecraft can only be managed with integrated hardware in conjunction with design specifications and both ground-based and flight-

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based operational rules and procedures. These are essentially designed to minimize the release of chemical contaminants into the cabin atmosphere and to provide a means to remove contaminants that do get into the cabin atmosphere via numerous mechanisms.

Mir and the NASA-*Mir* Program

The MIR space station began with the launch of the "core module" *Mir*, also referred to as the "base block" or by its production designation, 17KS, in February 1986, with the first crew to occupy the station arriving in March 1986. Although physically resembling its two predecessors, the second generation space stations *Salyut-6* and *Salyut-7*, one relatively minor change radically differentiated the third generation core module. In the core module, the conical transfer compartment was replaced with a five-port docking and berthing node. A sixth docking port was still located at the aft end of the core module similar to *Salyut-6* and *Salyut-7*. The five-port node allowed for the creation of a multimodular space station originally proposed in 1962 by the Special Design Bureau of the Soviet space program, OKB-1 (an ancestor to NPO Energia), in a prospectus titled, "Complex for the Assembly of Space Vehicles in Artificial Satellite Orbit (the Soyuz)".[1] Docking different modules onto the core module involved a two step process. Modules were first docked to the centerline docking port of the five-port docking port and berthing node. With the aid of a manipulator arm, the module was then moved to one of the side docking ports to begin it operational life as part of the orbiting complex. If needed, the same manipulator arm can be used to move the module at a later time to other docking ports. The *Kvant-1* astrophysics module followed the core module approximately one year later, occupying the "sixth" docking port of the core module. Docking of the *Kvant-1* module was marked by an unscheduled spacewalk to remove debris apparently blocking the docking mechanism preventing the module from achieving a hard dock. Once removed the hard dock of the *Kvant-1* module was achieved. Modules that were subsequently attached are the following:

- *Kvant-2*, the airlock and scientific module, in December 1989
- *Kristall*, the biological and technology development module containing the shuttle docking port in June 1990
- *Spektr*, the atmospheric and surface research module in June 1995
- *Priroda*, the international ecology research module in April 1996.

At completion, the *Mir* space station was comprised of six modules, weighed approximately 125 tons, and contained approximately 350 m^3 of habitable volume. During the 15 years *Mir* orbited Earth, the crew complement ranged from a minimum of two to a maximum of nine.[2]

The NASA-*Mir* program, also referred to as ISS Phase I, began in February 1995 when the U.S. shuttle *Discovery*, STS-63, performed the first rendezvous between U.S. and Russian crewed spacecraft since Apollo-Soyuz roughly twenty years earlier. This was followed with the first docking of a U.S. shuttle to the *Mir* space station several months later in June 1995 with the docking of the shuttle *Atlantis* during STS-71. Throughout the program, U.S. shuttles docked to *Mir* a total of nine times to ferry crew, equipment,

and supplies. Three different U.S. shuttles docked to *Mir*—*Discovery*, *Atlantis*, and *Endeavor*—logging over 42 days of docked operations. STS-91 and the shuttle that started *ISS* Phase I, *Discovery*, marked the end of the NASA-*Mir* program in June 1998 with a final docking mission to *Mir*. In the 3½ years of the NASA-*Mir* program, U.S. shuttles carried 44 U.S. astronauts, seven of which accumulated over 900 hours on-board *Mir*, 7 Russian cosmonauts, 2 French astronauts and 1 Canadian astronaut.[3, 4]

Trace Contaminant Control

Trace contaminant control was handled by relatively rudimentary, yet effective, trace contaminant bed in the core module. The design of this system was the same basic design used on *Salyut-6* and *Salyut-7* space stations. Contaminant removal was made possible with a bed comprised of three layers: activated charcoal, a chemical absorber, and a catalyst bed. Carbon dioxide was scrubbed from the core module atmosphere using lithium hydroxide beds.[5] Trace contaminant control capabilities were significantly upgraded with the addition of the *Kvant-1* module. The upgraded trace contaminant control system in the *Kvant-1* module consisted of four separate beds: a non-regenerable, activated charcoal pre-filter, two regenerable, activated charcoal filters, and an ambient temperature catalyst canister. Cabin air was initially scrubbed with the non-regenerable, activated charcoal pre-filter designed to remove high molecular weight contaminants. Lower molecular weight contaminants were then removed by splitting the air flow into two equal streams and passing each stream through a regenerable, activated charcoal bed. Just prior to reintroduction into the cabin, the cabin air was passed through an ambient temperature catalyst canister to remove residual carbon monoxide and hydrogen. The nominal flow rate through the *Mir* trace contaminant control system was 20 m^3/hr. The regenerable, activated charcoal beds underwent thermal-vacuum regeneration approximately every twenty days. System level testing of the *Mir* trace contaminant control system has shown the system capable of maintaining the concentrations of the 17 compounds in a normal Russian contaminant load below the Russian limiting permissible concentrations (LPCs).[6]

The active trace contaminant control systems on-board the *ISS* can certainly trace its roots to the trace contaminant control assembly of *Mir*. Many of the lessons learned during the NASA-*Mir* program (*ISS* Phase I) regarding the maintenance of cabin atmosphere were applied to the design of the ISS systems. There are two, separate trace contaminant control systems on-board the *ISS*, one in the U.S. Lab, *Destiny,* and another in the Russian Service Module (SM), *Zvezda*. Both systems are designed to handle *ISS* cabin atmospheric scrubbing independently and are, therefore, redundant. However, if maximum scrubbing capabilities are required, e.g., during an off-nominal situation, both can be operated simultaneously.

The Russian trace contaminant control system, the БМП, is virtually identical to the system in the *Kavant-2* module of the *Mir* space station. The БМП in the SM also consists of four separate beds—a non-regenerable activated charcoal pre-filter, 2 regenerable activated charcoal filters, and an ambient temperature catalyst canister. Each

bed has the same function in the SM as they did on-board *Mir*. The nominal flow rate through the БМП is 27 m^3/hr.

The trace contaminant control system in the U.S. Lab is comprised of three beds. Cabin atmosphere is drawn into the trace contaminant control system and initially passed through an activated charcoal bed (treated with 10% phosphoric acid by weight) to remove high molecular weight compounds and ammonia. Approximately 30% of the cabin air exiting the activated charcoal bed is then passed through a catalytic oxidizer assembly at a temperature of 400°C to remove contaminants that absorb poorly on the activated charcoal bed. Immediately downstream of the catalytic oxidizer assembly is a lithium hydroxide bed to neutralize any acid gases that may form in the catalytic oxidizer assembly. Prior to reintroduction into the cabin, the 30% catalytically oxidized process air is recombined with the 70% that bypassed the catalytic oxidizer stream. The amount bypassed is a function of the chemicals that served as the design drivers for the catalytic oxidizer bed and the residence time required for complete oxidation. The nominal flow rate through the ISS trace contaminant control system is 15.3 m^3/hr. Although none of the beds are regenerable, orbital replacements for each bed can be launched. The recommended service intervals are estimated to be 4.5 years for the activated charcoal bed, 5 years for the catalytic oxidizer bed, and 3.5 years for the lithium hydroxide bed, depending on cabin atmosphere contaminant concentrations and any off-nominal events that may occur during the lifetime of the beds.[7]

Controlling contaminant concentrations in spacecraft cabin atmosphere can be assisted by other systems on-board whose primary function is not necessarily associated with cabin atmosphere scrubbing. Polar, water-soluble atmospheric contaminants can be readily removed with the humidity condensate by a spacecraft's air handling system. In certain cases, such as ammonia, scrubbing of the atmosphere via humidity condensate is more efficient that scrubbing via the trace contaminant control system. In the Russian SM, the БМП can scrub ammonia from cabin air at 58% efficiency under a normal regeneration cycle, resulting in an effective removal flow of 15.7 m^3/hr. Assuming a 50% bypass, the Russian humidity control unit, SKV, can scrub ammonia at 23.9% efficiency with a two-person latent load and at 32.1% efficiency with a three-person latent load. This results in an effective removal flow of 34.4 m^3/hr and 46.2 m^3/hr, respectively. Once collected, the water-soluble contaminants are removed from the water using the water revitalization equipment. Intermodular ventilation (IMV) fans can lower the cabin concentration for non-lethal contaminants simply by diluting the contaminant across the habitable volume of the spacecraft. Though certainly not ideal, it can, however, bring down a contaminant's cabin concentration to below its NASA Spacecraft Maximum Allowed Concentration (SMAC) until it can be properly scrubbed from the cabin atmosphere. Carbon dioxide removal in the U.S. Lab of ISS is handled by the Carbon Dioxide Removal Assembly (CDRA) that has flow rate of ~34 m^3/hr. The active removal components in the CDRA are four packed beds—2 containing zeolite 13X to dry the process air stream and 2 containing zeolite 5A molecular sieve to remove carbon dioxide. Zeolites are aluminosilicates noted for the acidity of their surfaces and their highly consistent pore size resulting from their highly symmetric structure. System level testing has shown that CDRA was effective in the removal of acetone at 33% efficiency,

methylene chloride at 50%, methanol at 33% efficiency, m-xylene at 53% efficiency, and ammonia at 43% efficiency.[8]

Archival Samples and Trending

Many lessons learned during the NASA-Mir program have driven many aspects of the ISS program. The need for archival sampling of spacecraft atmosphere is one such lesson that has certainly benefited the ISS program. Archival sampling provides a "snapshot" of the constituents that make up the cabin atmosphere. Obtained at regular intervals, these "snapshots" can be combined to provide insight into contaminant concentration trends over a period of time. This information is invaluable not only to systems engineering, but also to toxicologists who limit risks to crew health by setting exposure limits to chemicals. Trends in contaminant concentration provide direct feedback regarding the performance of life support systems on-board spacecraft.

Archival samples of spacecraft cabin atmosphere can be obtained by several methods. During the NASA-Mir program, samples were obtained using sorbent tubes and grab sample containers. Sorbent tubes were simply metal tubes, typically packed with Tenax GC beads, a polymer based on 2, 6-diphenyl-p-phenylene oxide. As a volume of the cabin atmosphere was drawn into the tube either by a battery-operated pump, e.g. the Solid Sorbent Air Sampler, or by a hand-operated bellow, contaminants in the atmosphere were absorbed onto the Tenax beads. When returned from orbit, contaminants adsorbed onto the Tenax beads were thermally desorbed off of the Tenax, concentrated, and analyzed by standard U.S. Environmental Protection Agency (EPA) method TO-14. Grab-sample containers were 500-ml evacuated stainless steel vessels with passivated interior walls. Passivation of the interior walls was accomplished by electropolishing and then coated with a proprietary inert coating. Each grab-sample container was dosed before launch with trace amounts of surrogate compounds to account for any bias introduced by handling, storage, and return of the sample container. Once in flight, a sample of the cabin atmosphere was obtained simply by opening the container to the cabin atmosphere and allowing the pressure inside the grab-sample container to equilibrate with the spacecraft cabin. As with the sorbent tubes, samples obtained with grab-sample containers were concentrated and analyzed by EPA method TO-14 when returned from orbit. The preparation of sorbent tubes and grab-sample containers and the analysis of their contents were rigorously documented and constantly inspected. The processes followed were governed by standard operating procedures and by safety, reliability, and quality assurance policies.[9]

Complimentary information can be obtained by using both sorbent tubes and grab-sample containers and together provide a broad coverage of a very wide range of chemical contaminants. Highly volatile contaminants not readily trapped by sorbent tubes such as hydrogen, carbon monoxide, C1-C4 hydrocarbons, and halocarbons are more reliably sampled with grab-sample containers. Likewise, sorbent tubes are best suited for polar and relatively heavy, non-polar organic contaminants. Also, sorbent tubes and grab-sample containers are relatively simple methods for "recording" transient events such as an unplanned release of chemicals into the cabin or any other off-nominal event. Time-

integrated samples during these times are of particular value in understanding contaminant dynamics aboard spacecraft.

The efficacy of sorbent tubes and grab-sample containers for sampling spacecraft cabin atmosphere has been thoroughly proven.[10, 11] Both were adopted for use in the *ISS* program to satisfy program requirements to monitor cabin atmosphere contaminants. Consistent sampling and analysis have allowed for trending of the concentrations of chemicals present in the *ISS* atmosphere. Although the sorbent tubes were slightly modified to include a second absorbent material to broaden the range of compounds captured, the logistics associated with the sorbent tubes and the grab-sample containers are essentially unchanged in the *ISS* program.

Care must be exercised so as not to impart a spatial or temporal bias to the samples. Samples obtained should be as representative of the spacecraft cabin atmosphere as possible. Temporal bias can occur because of the dynamic nature of cabin atmosphere contaminants, i.e., contaminants are generated and removed simultaneously. Spatial bias can occur due to the lack of natural convection in a microgravity environment on-board spacecraft. Contaminant concentrations may be artificially higher as sampling nears the contaminant source. Malfunctioning hardware can also contribute to spatial sampling bias. This can be seen in the trend data of formaldehyde on-board the *ISS* (Figure 1).
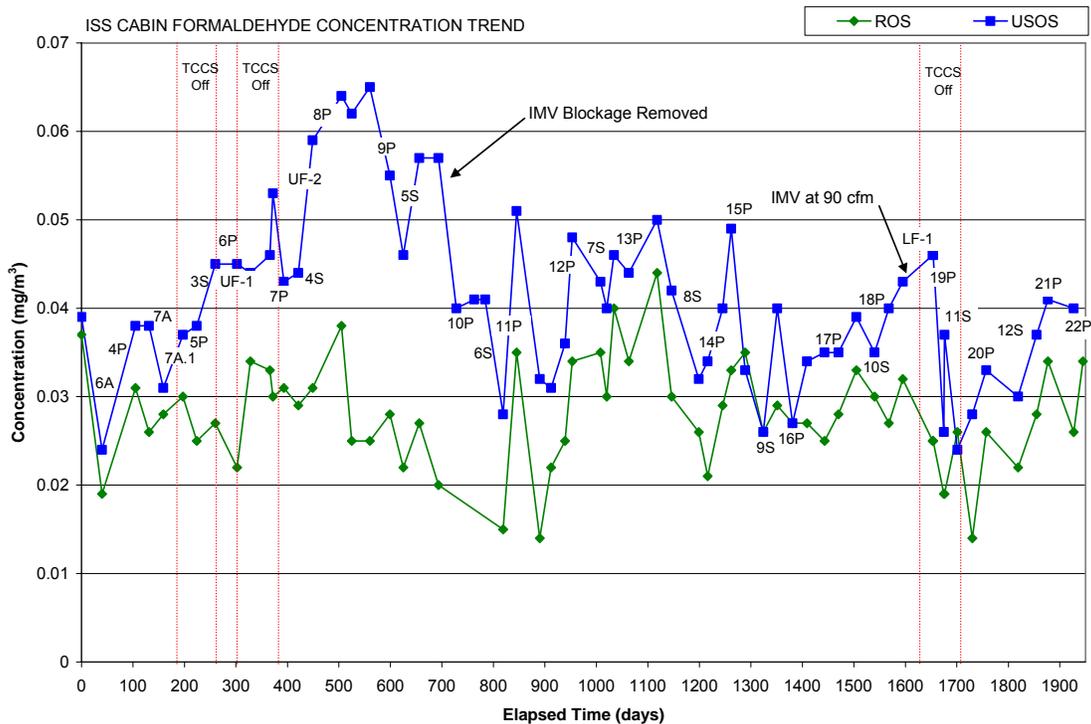
Figure 1. *ISS* Formaldehyde concentration trend.

In the first 200 days of *ISS* operations, the measured formaldehyde concentrations in the Russian On-Orbit Segment (ROS) tracked the measured formaldehyde concentrations in

the U.S. On-Orbit Segment (USOS). Between 200 and 700 days, a significant deviation between the measurements occurred which was attributed to blockage of IMV between the two segments. The lack of IMV essentially created an artificial spatial bias to the measured formaldehyde concentration. During this time, the measured formaldehyde concentration in the ROS was considerably lower than that measured in the USOS. Once removed, the measured formaldehyde concentrations in both segments tracked one another.

Chemicals in Spacecraft Cabin Atmosphere

Chemical contaminants in the cabin atmosphere of spacecraft can be attributed to two basic sources—hardware and crew. Within the context of this discussion, hardware includes equipment and payload. Chemicals from hardware may come from system chemicals or offgassing from materials used in the construction of the systems. Payloads can be further broken down to include equipment and experiments. Payload equipment, similar to systems, may have chemicals associated with their functionality, or may experience offgassing. Systems on-board spacecraft and payload equipment can be characterized as continuous sources of atmospheric contaminants. Continuous sources have long term emissions of chemical contaminants with constant source strength. Many experiments brought on-board spacecraft have chemicals associated with them. Experiments on spacecraft can be characterized as discontinuous sources of atmosphere contaminants. Discontinuous sources have short term emission of chemical contaminants with varying source strength. By and large, spacecraft systems and payload equipment are a greater source of cabin atmosphere contaminants than payload experiments. System chemicals such as coolants may be present in quanties to hundreds of kilograms on-board spacecraft. Comparatively, chemicals associated with payload experiments are typically present in very small quantities and are subject to multiple containment levels to prevent accidental release.

Although not necessarily considered a source of atmosphere contaminants when discussing indoor air quality on ground, the crew is a source of a diverse number of chemical contaminants. Human metabolism is the main source of ammonia, carbon monoxide, methane, hydrogen, several short chain carbonyl compounds, and alcohols on-board spacecraft and can be considered to be a continuous source of contaminant generation into the cabin atmosphere.[12] Contaminants from crew metabolism differ from contaminants generated by hardware in the sense that they cannot be regulated by ordinary means.

To a great extent, cabin atmospheric contaminants from hardware can be regulated by proper material selection and control, multiple containment levels, or design for minimum risk. Rules governing the amount of a contaminant that can be used on-board spacecraft can also limit contaminant concentration. Because of their potential negative impact on the Russian water processing system, SRV-K, the use on board *ISS* of water soluble volatile organic compounds such as alcohols, acetone, and glycols have been limited through a volatile usage agreement requirement. Items containing water soluble volatile organic compounds that can be introduced into the *ISS* cabin atmosphere in

excess of a 1 g/day limit are subject to this agreement. Justification by the payload organization and rationale as to why a substitute cannot be used must be provided. This requirement impacts not only items brought to the *ISS*, but also the on-ground procedures used to prepare hardware for flight. Alcohol wipes (medical, maintenance, and housekeeping), contact lens cleaning fluid, and other crew hygiene products previously allowed on-board were now replaced with water-based, benzalkonium wipes or something similar. On the ground, alcohol-containing wipes used to remove fingerprints or any oils just prior to stowage for launch were also replaced with water-based, benzalkonium wipes within 5 days of final hatch closure to reduce introduction of residual alcohol into the cabin atmosphere. Unfortunately, this type of requirement, or any other type, cannot be levied against crew metabolism. There are no measures to limit the byproducts of crew metabolism and as such, crew metabolism will be a constant source of cabin atmosphere contaminants on-board spacecraft.

Cabin atmospheric contaminant concentration on-board spacecraft is very dynamic responding to nominal fluctuations in temperature, humidity, pressure, and ventilation flow. Other perturbations which can have rather profound effects on the makeup of cabin atmosphere contaminants are docked operations, number of crew, and accidental releases. Docked operations on-board spacecraft can markedly change the contaminant profile. New contaminants not observed prior to docking can be introduced or contaminants observed prior to docking can be enhanced.

Cole et al. characterized the impact of docking and integrating the *Priroda* module to *Mir on its* cabin atmosphere.[10] The *Mir* atmosphere was sampled several days before docking, several hours before docking, after docking and opening the hatch, and several hours after hatch opening and the start of IMV. From the analysis of samples obtained prior to and after docking of the *Priroda* module, several trends were observed. Chlorinated hydrocarbons, which may have used as a solvent/degreaser during on-ground preparation of the module and not previously detected on *Mir*, were in significant concentrations in *Priroda*. Generally, *Priroda* contained significantly more aromatics and hydrocarbons than *Mir*. Concentrations of aromatics in *Mir* increased after docking and hatch opening and remained significantly high in *Mir* two months after docked operations. The high aromatics concentration suggested the offgassing of materials, paints, adhesives, or cleaners. Water soluble, volatile compounds such as alcohols, aldehydes, and ketones, normally found in the *Mir* atmosphere, were found not to significantly increase after docking operations. Crew metabolism is the major source of such contaminants and was expected to be low for an unmanned module. Vinyl chloride concentrations in *Mir* increased after docking and start of IMV. Ethanol was the only alcohol present in *Mir* prior to docking that subsequently increased after docking and start of IMV. Siloxanes were observed to increase several months after docking and IMV start. Vinyl chloride, ethanol, and siloxanes suggest a significant degree of offgassing occurred between hatch closing prior to launch to hatch opening after docking. From the work of Cole, et al., it is clear that significant offgassing occurs from the time the modules are launched to the time of docking and hatch opening.

Trends in Cabin Atmosphere Contaminants

Typical air quality data obtained from spacecraft cabin atmosphere reports the identity of the contaminant and its concentrations at the time of sampling in mg/m^3 or ppm. Trending data is usually presented in these terms as well. One major advantage of this approach is to easily identify contaminants that that have exceeded the SMACs or the Russian LPCs. The toxic hazard index or total relative toxicity (T-value) of the cabin atmosphere can be determined and used as a measure of the quality of the cabin atmosphere.[13] By plotting contaminant concentration over a period of time, the behavior of the contaminant can be observed. These plots, however, show a great deal of scatter making the extraction of correlations from these plots difficult. However, if contaminants were grouped into classes and the contribution of these classes to the overall picture of cabin atmosphere contaminants, it may be possible to extract correlations from air quality archival data. We have categorized contaminants based on the functional group of the contaminant. Using the concentrations of all the contaminants in each functional group, a percentage contribution of each functional group to the overall cabin atmosphere contamination was determined. By plotting the percent contribution to the overall cabin atmosphere contamination versus time, we hope to clarify how different perturbations may have in cabin air quality.

Typical samples from the ISS atmosphere and Mir atmosphere during the NASA-Mir program were analyzed for compounds listed in Table 1. The atmospheric samples were taken either by grab-samples or by sorbent tubes previously discussed. Table 1 categorizes the compounds in terms of their functional groups.

| Halocarbons	Ketones
Dichlorodifluoromethane (Freon 12)	Acetone
Chloromethane (Methyl Chloride)	2-Butanone (Methyl Ethyl Ketone)
Dichloromethane (Methylene Chloride)	Cyclohexanone
1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113)	**Esters**
Octafluoropropane (Perfluoropropane, (Freon 218)	Ethyl acetate
Bromotrifluoromethane (Halon 1301)	Butyl acetate
Aldehydes	**Aromatic**
Acetaldehyde	Benzene
Propanal	Toluene
Propenal (Acrolein)	m-Xylene/p-Xylene/
Butanal (Butyraldehyde)	o-Xylene
Pentanal	**Siloxanes**
Hexanal	Octamethylcyclotetrasiloxane
Heptanal	Decamethylcyclopentasiloxane
Alcohols	Hexamethylcyclotrisoloxane
Methanol	
Ethanol	**Methane**
Isopropanol	**Hydrogen**
n-Butanol	**Carbon Monoxide**

Table 1. Cabin atmosphere contaminants and functional group classes.

The contaminants listed were categorized into seven different classes based on the functional groups of each compound. Concentration data for each contaminant was obtained during the NASA-Mir program from March 1995 to June 1998. Concentration data for the same contaminants on the ISS has been collected from December 1998 to August 2006.

The compounds categorized in Table 1 can be linked to crew metabolism, hardware or equipment offgassing, or system chemicals. Most of the alcohols, aldehydes and ketones can be attributed to crew metabolism. Virtually, all the halocarbons are system chemicals. Bromotrifluoromethane (Halon 1301) is the fire suppressant agent used in the U.S. Shuttle. Octafluoropropane (Freon 218) is the coolant in the Russian SM and aboard *Mir*. Siloxanes and aromatics can be linked to offgassing of lubricants, seals, adhesives, paints, and coating used in hardware. Esters can be linked to either crew metabolism or hardware offgassing. However, since esters are common solvents, the greater source is most likely the latter of the two.

Figure 2 shows the percent contribution of each function group to the total non-methane volatile organic compound (NMVOC) concentrations measured during NASA-*Mir* Program and the *ISS* Program.
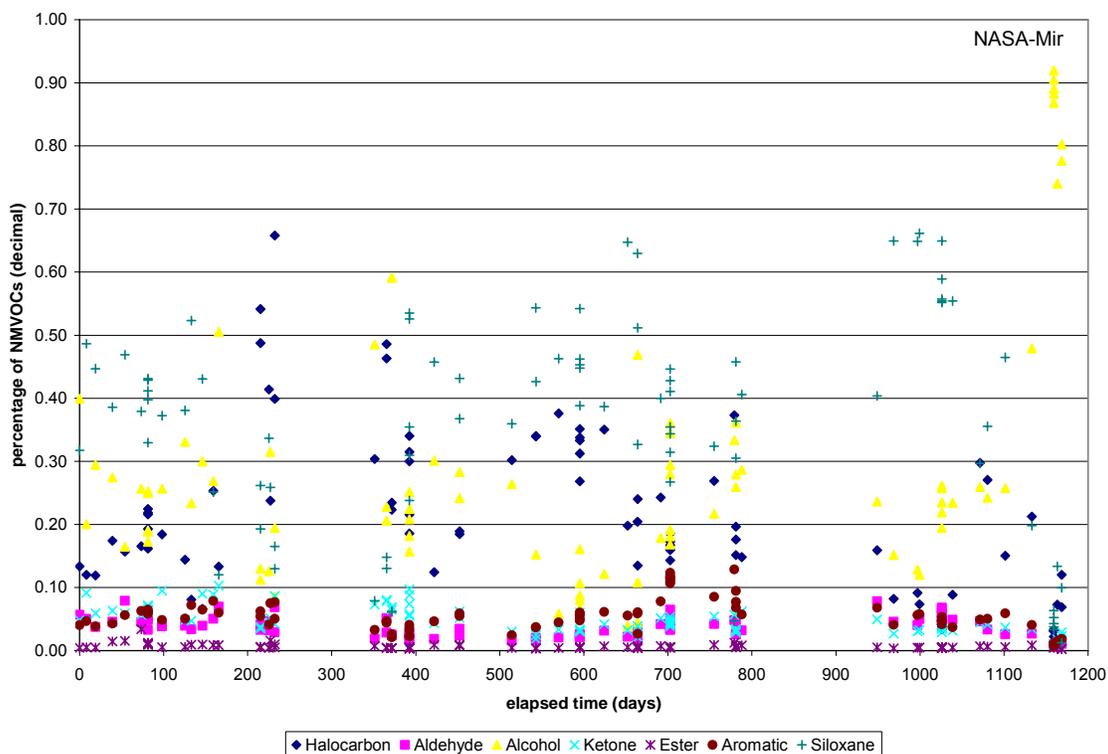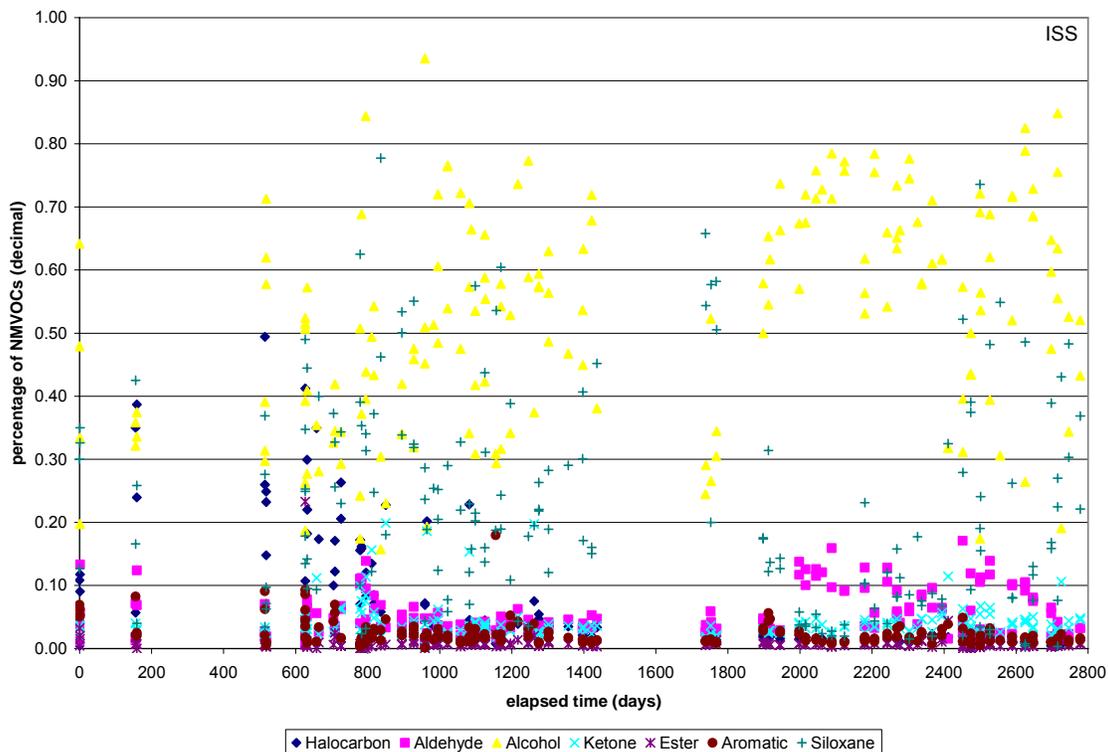
Figure 2. The percent contribution of each function group to the total non-methane volatile organic compound (NMVOC) concentrations during NASA-*Mir* and *ISS* programs.

As can be seen in Figure 2, the predominant NMVOCs contributing to the total NMVOC concentration on-board are alcohols and siloxanes. Interestingly, this is true for both programs. Halocarbons appear to have also dominated the *Mir* atmosphere during the NASA-*Mir* program to a greater extent than the *ISS* atmosphere. From Figure 2, approximately 80% of the total NMVOCs aboard *Mir* were comprised of alcohols, siloxanes, and halocarbons during the NASA-Mir program; whereas, approximately 80% of the total NMVOCs on the *ISS* were comprised primarily of alcohols and siloxanes. In the first 1200 days of the *ISS*, significant percentage contributions from halocarbons were observed. It should be noted despite the percentage contributions of each functional group class, the concentrations of all these contaminants were well below their SMACs and LPCs.

Previously, it was noted that Cole, et al. observed an increase in the concentrations of chlorinated hydrocarbons, aromatics, ethanol, and siloxanes in the *Mir* atmosphere after docking and hatch opening of the *Priroda* module. This observation can be seen in the functional group plots for siloxanes, halocarbons, aromatics, and alcohols, seen in Figure 3. When plotted as percentages of NMVOCs, each functional group shows an increase in their percentage contribution to the total NMVOC concentration aboard *Mir* during the *Priroda* docking and hatch opening. In addition, the percentage contribution of siloxanes and aromatics remained relatively high even after the initial docking and hatch opening. A dramatic decrease in the ethanol percentage contribution after docking and hatch

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opening can be attributed to the synergistic scubbing from the trace contaminant control system and the humidity condensate.

3a.

Priroda docking and hatch opening

Siloxanes (NASA/Mir)

3b.

Priroda docking and hatch opening

Halocarbons (NASA/Mir)
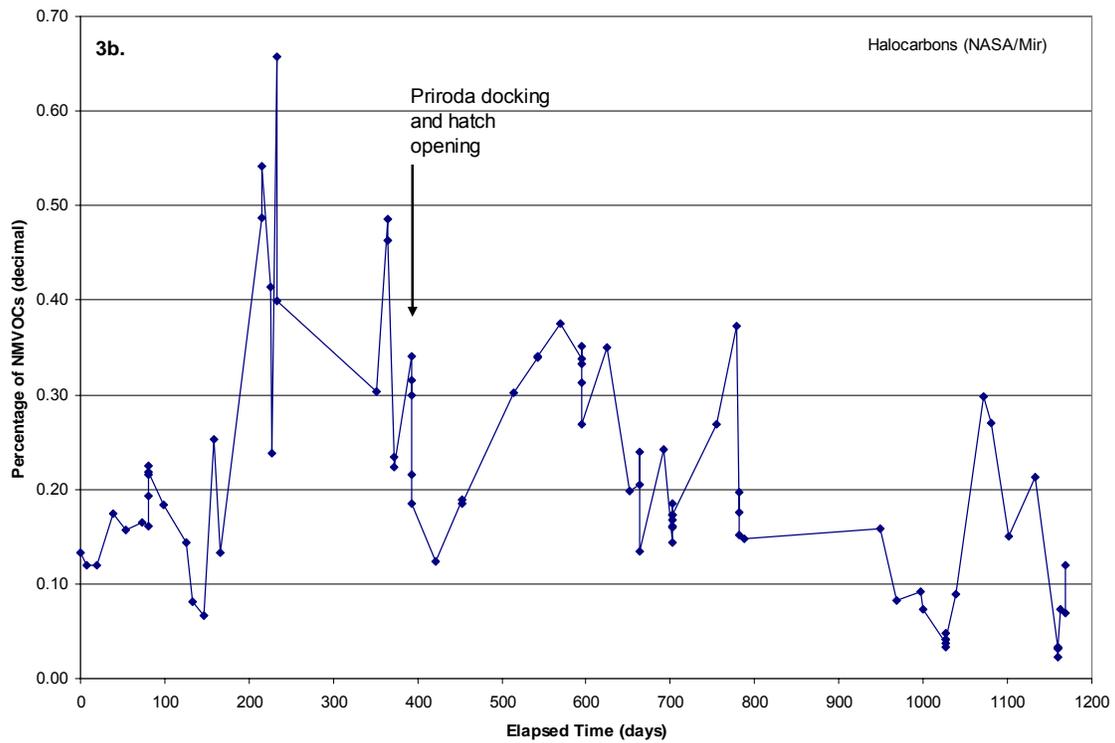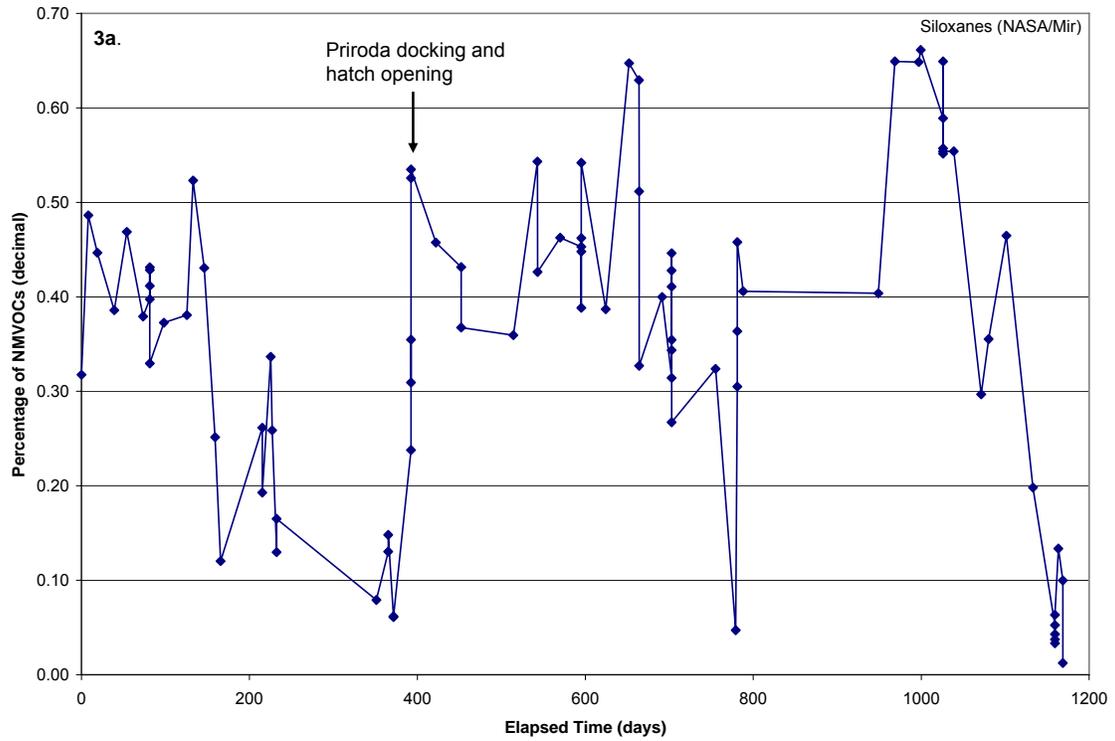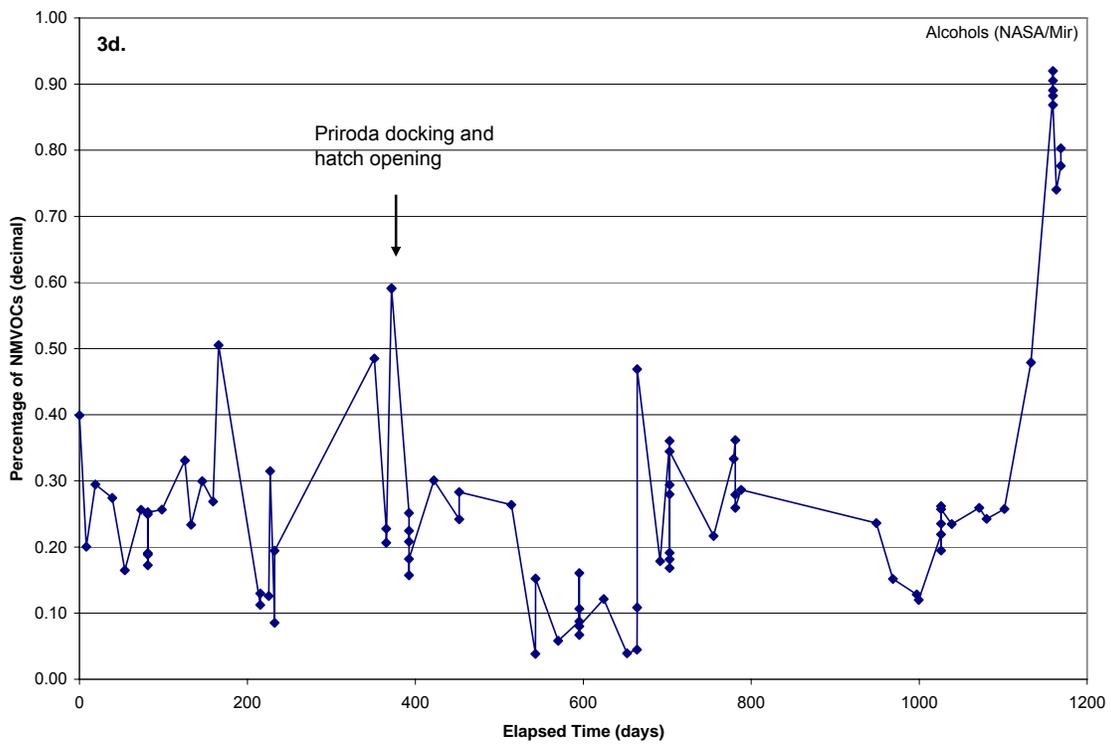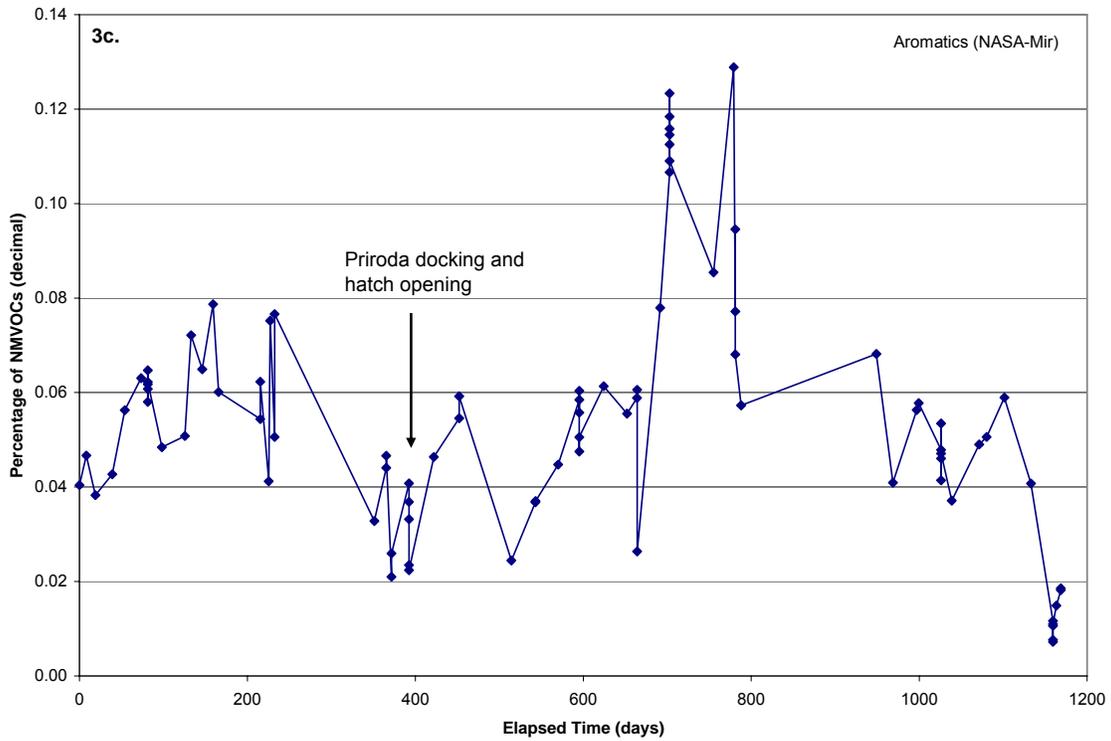
Figure 3. Siloxanes (a), halocarbons (b), aromatics (c), and alcohols (d) plotted as percentages of NMVOCs during NASA-*Mir* Program.

Today, modules to be docked to the *ISS* are thoroughly tested for offgassing so as not to overwhelm the *ISS* atmosphere with chemical contaminants. Through a careful materials selection and control process and testing, the impact of docking modules to spacecraft atmosphere can be minimized.

A closer look at the percentage contribution of halocarbons to the total concentration of NMVOCs can also show the effects of U.S. Shuttle dockings throughout the NASA-*Mir* Program (Figure 4). This observation was driven by the presence of Halon 1301 which, prior to U.S. Shuttle dockings, was not observed as a contaminant in the *Mir* atmosphere. U.S. Shuttle fire extinguishers containing Halon 1301 were known to leak, and upon docking with *Mir*, inadvertently introduced Halon 1301 in the *Mir* atmosphere. The introduction of Halon 1301 can be attributed directly to the docking of U.S. Shuttles to *Mir* because no other source of the halocarbon existed on board Mir. This operation manifested itself in the halocarbon percentage contribution data during the NASA-*Mir* Program that is not necessarily observed in the halocarbon concentration trend plot (Figure 5).
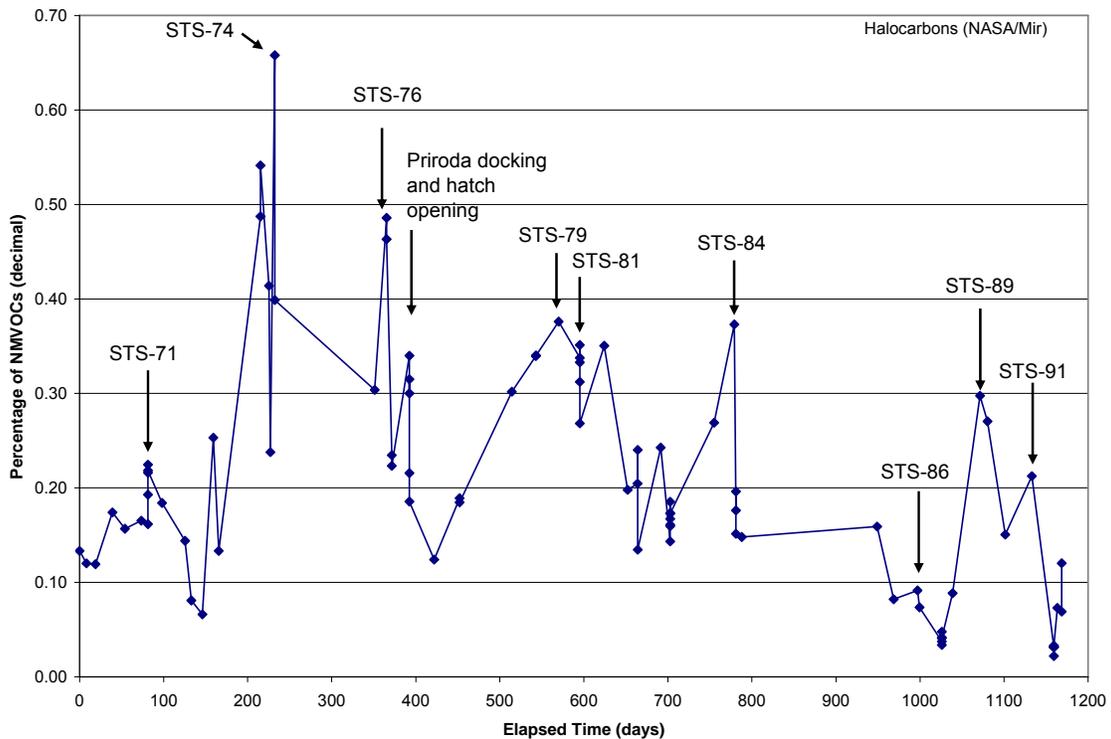

Figure 4. Effect of U.S. Shuttle docking to *Mir* atmosphere as shown by the percentage contribution of halocarbons to the total NMVOC concentration on the *Mir* Space Station.
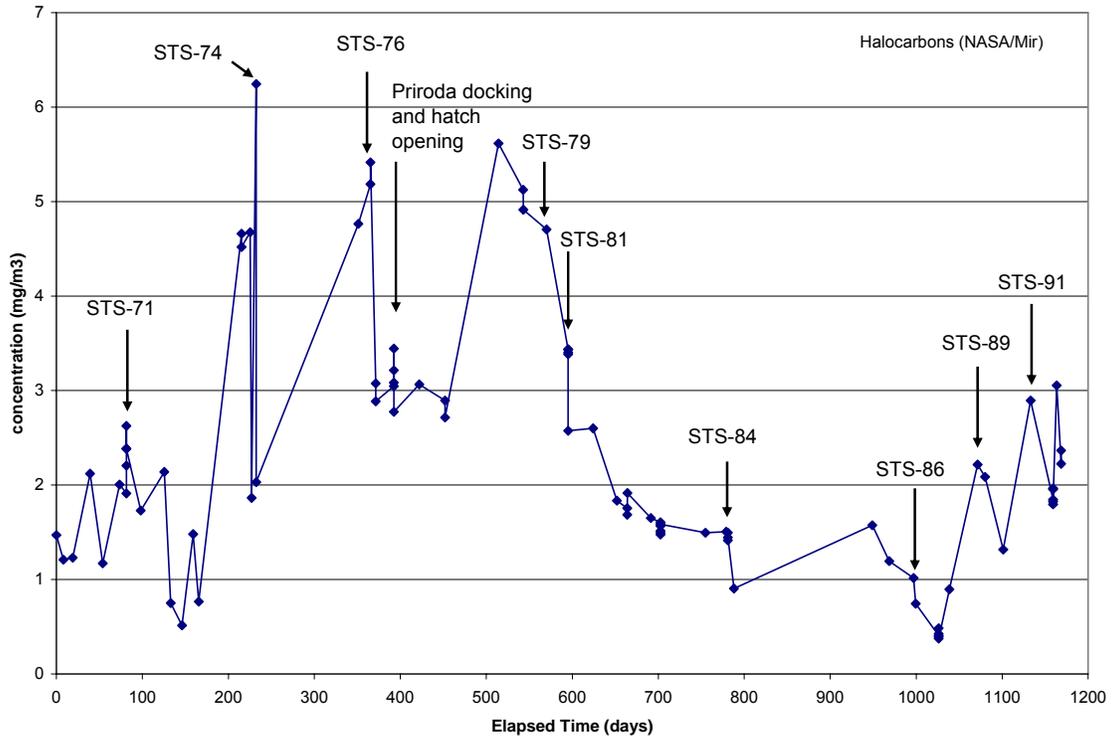
Figure 5. Halocarbon concentration (mg/m^3) on-board Mir during NASA-*Mir* Program.

Similar correlations can be made with data obtained from the *ISS* atmosphere. In Figure 2 for the *ISS*, significant percentage contributions from halocarbons were observed for the first 1200 days of the *ISS*. After that, the percentage contribution of halocarbons to the total NMVOCs concentration decrease to approximately <5%. The percentage contribution of halocarbons to the total NMVOC concentration on-board the *ISS* is shown in Figure 6.
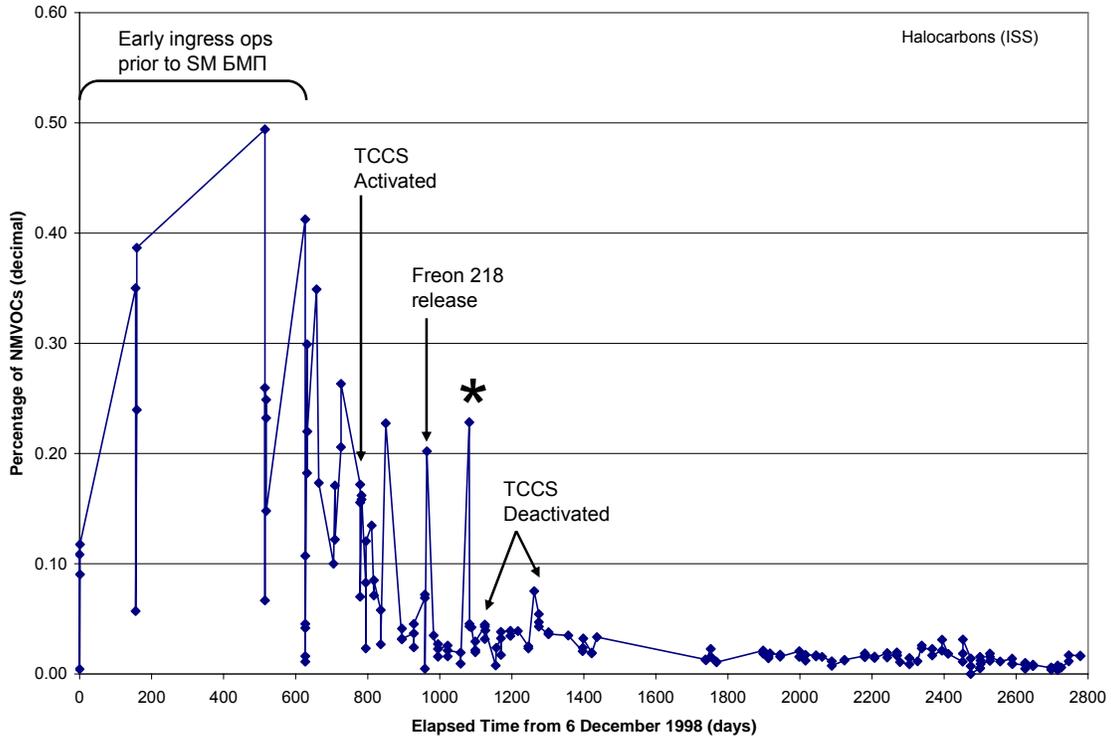
Figure 6. Halocarbons as percentage of total NMVOCs on-board *ISS*.

Early docking operations by U.S. Shuttles to the *ISS* prior to the activation of the БМП in the Russian SM resulted in relatively high concentration of Halon 1301 in the *ISS* atmosphere (Figure 7a) accounting for its high percentage contribution to the *ISS* total NMVOC concentration. Upon activation of the БМП, concentrations decreased. Activation of the U.S. Lab TCCS helped to further reduce the concentration levels of Halon 1301 in the ISS atmosphere and subsequently reduce its percentage contribution to the *ISS* NMVOC concentration. Two spikes appear at approximately 1100 days and 1300 days. These spikes can be attributed to U.S. Shuttle dockings, STS-113 and STS-111, and TCCS deactivation, both of which resulted in an increase in the concentrations of Halon 1301 in the *ISS* atmosphere. A spike in the Halon 1301 percentage contribution to total NMVOCs correlates with the release of Freon 218 from the Russian humidity condensate removal system, SKV. The spike marked with a star corresponds to the spike in Halon 1301 concentration marked in Figure 7b.

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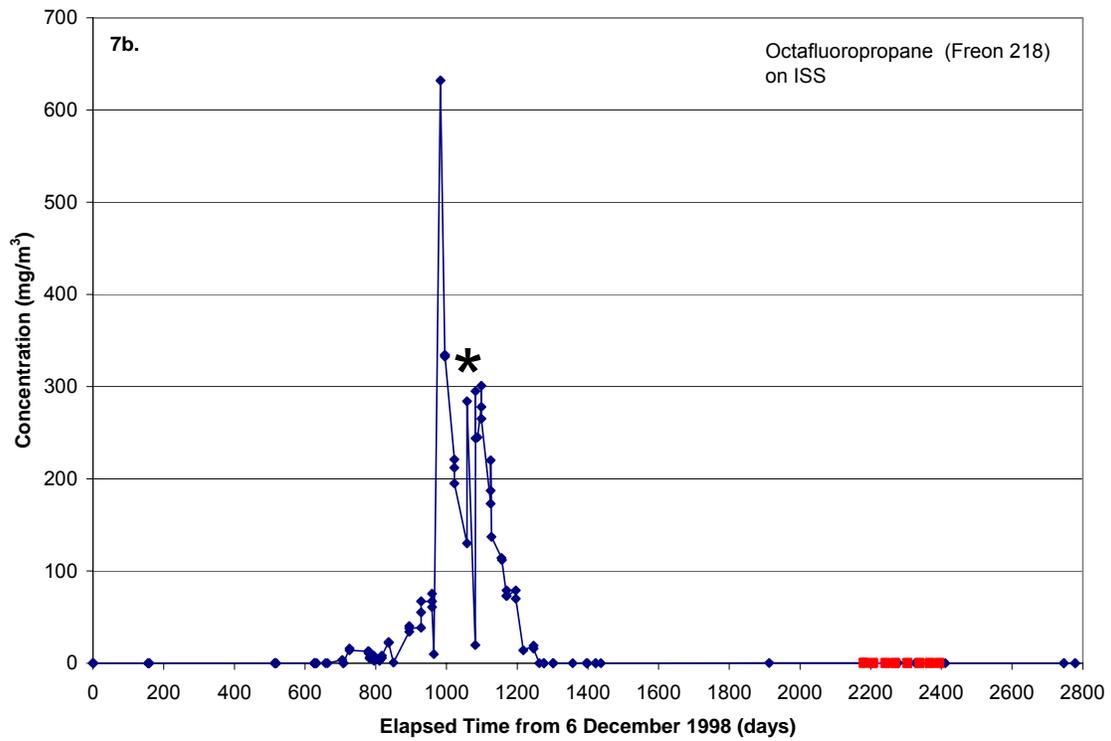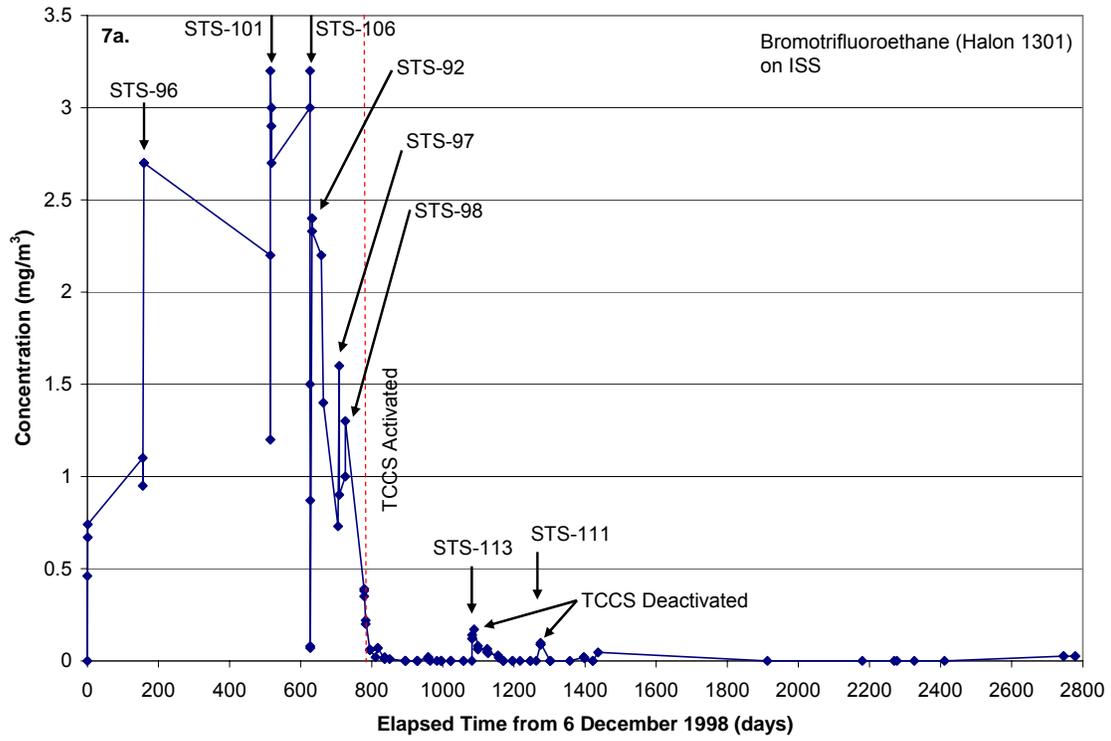
Figure 7. Concentration plots for Halon 1301 (a) and Freon 218 (b) on-board ISS.

Figure 2 clearly illustrates the effects different approaches to trace contaminant control may have in controlling cabin atmosphere contaminant concentrations. As mentioned above, trace contaminant control on-board *Mir* was accomplished with a four bed system comprised of a non-regenerable, activated charcoal pre-filter, two regenerable, activated charcoal filters, and an ambient temperature catalyst canister. On the *ISS*, trace contaminant control is accomplished with a three bed system comprised of an acid-impregnated, activated charcoal bed, high-temperature catalyst bed, and a lithium hydroxide sorbent bed. Additional trace contaminant capacity on the *ISS* is provided by the Russian БМП in the SM. Halocarbons are known to adsorb poorly onto activated charcoal.[11] As shown in Figure 2, halocarbons are a major percentage contributor to the total NMVOC concentration in the *Mir* during the NASA-*Mir* Program. Halocarbon percentage contributions to the *ISS* NMVOC concentration were high during its early assembly before continual active contamination control equipment became operational. Activation of the БМП reduced halocarbon concentrations considerably, and activation of the TCCS in the U.S. Lab further reduced halocarbon concentrations on-board the *ISS* to almost insignificant levels. With the added benefit of a thermal catalytic oxidation reactor in the TCCS, halocarbon percentage contributions can be effectively maintained to very low levels as shown in Figure 6.

Conclusions

The only means to maintain the quality of spacecraft cabin atmospheres is to effectively manage the balance between the generation and removal of volatile trace contaminants. This is accomplished only with a thorough understanding of the dynamics of atmospheric contaminants during various phases of a space mission. Archival air sampling has proven to be a powerful tool in understanding atmospheric contaminantion by providing insight into the time-evolution of contaminant concentrations. Contaminants can be categorized into classes based on their organic functional groups to gain a better understanding of which types of chemicals contribute most to cabin atmosphere contamination and which types of chemicals are most affected by perturbations to the cabin air quality. Perturbations to the cabin air quality can arise from on-ground operations and in-flight operations. By studying the changes in the percentage contribution of various contaminants relative to the total contaminant concentration, the direction and magnitude of the effects of on-ground and in-flight operations on the cabin atmosphere can be observed. This information will ultimately provide valuable guidance in the design of future spacecraft and their contamination control processes, procedures, and equipment.

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