

Analysis of Process Gases and Trace Contaminants in Membrane-Aerated Gaseous Effluent Streams

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In membrane-aerated biofilm reactors (MABRs), hollow fibers are used to supply oxygen to the biofilms and bulk fluid. A pressure and concentration gradient between the inner volume of the fibers and the reactor reservoir drives oxygen mass transport across the fibers toward the bulk solution, providing the fiber-adhered biofilm with oxygen. Conversely, bacterial metabolic gases from the bulk liquid, as well as from the biofilm, move opposite to the flow of oxygen, entering the hollow fiber and out of the reactor. Metabolic gases are excellent indicators of biofilm vitality, and can aid in microbial identification. Certain gases can be indicative of system perturbations and control anomalies, or potentially unwanted biological processes occurring within the reactor. In confined environments, such as those found during spaceflight, it is important to understand what compounds are being stripped from the reactor and potentially released into the crew cabin to determine the appropriateness or the requirement for additional mitigation factors. Reactor effluent gas analysis focused on samples provided from Kennedy Space Center's sub-scale MABRs, as well as Johnson Space Center's full-scale MABRs, using infrared spectroscopy and gas chromatography techniques. Process gases, such as carbon dioxide, oxygen, nitrogen, nitrogen dioxide, and nitrous oxide, were quantified to monitor reactor operations. Solid Phase Microextraction (SPME) GC-MS analysis was used to identify trace volatile compounds. Compounds of interest were subsequently quantified. Reactor supply air was examined to establish target compound baseline concentrations. Concentration levels were compared to average ISS concentration values and/or Spacecraft Maximum Allowable Concentration (SMAC) levels where appropriate. Based on a review of to-date results, current trace contaminant control systems (TCCS) currently on board the ISS should be able to handle the added load from bioreactor systems without the need for secondary mitigation.

Nomenclature

<i>AWP</i>	=	Alternative Water Processor
<i>BDL</i>	=	Below Detection Limit
<i>BQL</i>	=	Below Quantification Limit
<i>CoMANDR</i>	=	Counter-diffusion Membrane Aerated Nitrifying Denitrifying Reactor
<i>DMSD</i>	=	Dimethylsilanediol
<i>DO</i>	=	Dissolved Oxygen
<i>ECD</i>	=	Electron Capture Detector
<i>EtOH</i>	=	Ethanol
<i>FID</i>	=	Flame Ionization Detector
<i>FTIR</i>	=	Fourier Transform Infrared Spectrometer
<i>GC</i>	=	Gas Chromatograph

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<i>IPA</i>	= Isopropanol
<i>ISS</i>	= International Space Station
<i>JSC</i>	= Johnson Space Center
<i>KSC</i>	= Kennedy Space Center
<i>MABR</i>	= Membrane-aerated biofilm reactor
<i>MEK</i>	= Methyl Ethyl Ketone (aka 2-Butanone)
<i>MeOH</i>	= Methanol
<i>MS</i>	= Mass Spectrometer
<i>PDMS</i>	= Polydimethylsiloxane
<i>ppb</i>	= Parts-per-billion
<i>ppm</i>	= Parts-per-million
<i>SMAC</i>	= Spacecraft Maximum Allowable Concentration
<i>SPME</i>	= Solid Phase Microextraction
<i>ssMABR</i>	= Sub-scale Membrane-Aerated Biofilm Reactor
<i>TCCS</i>	= Trace Contaminant Control System
<i>TCD</i>	= Thermal Conductivity Detector
<i>VOC</i>	= Volatile Organic Compound

I. Introduction

IN membrane-aerated biofilm reactor (MABR) systems, microbial communities form biofilms on the outside of an oxygen-permeable fiber or membrane. The oxygen (or other desired feed gas) flows through the lumen of the fiber and diffuses through the membrane and into the biofilm, allowing for oxidation of contaminants residing at the biofilm-liquid interface within the bioreactor (Figure 1). The amount of oxygen supplied to the biofilm can be controlled via intramembrane oxygen partial pressure regulation, and membrane surface area¹⁻². Under this arrangement of gas gradients, a unique biofilm profile is formed: for nitrification bioreactors, the biofilm attached closest to the membrane serves as the aerobic region where oxidation on contaminants takes place; if the biofilm is thick enough, oxygen will be unable to fully penetrate the biofilm creating an oxygen-depleted anaerobic zone that is advantageous for denitrification¹.

Figure 1, by Syron and Casey¹, depicts this overall biofilm structure and the various fluxes that can occur in nitrification/denitrification systems. Just as oxygen diffuses across the membrane toward the biofilm, metabolic and process gases can diffuse across the membrane into the lumen, a process known as gas stripping¹⁻³. In MABR systems, heterotrophs will utilize organic carbon in the wastewater as a carbon food source, effectively degrading the entrained contaminants. Degradation of volatile organic compounds (VOCs) has been demonstrated in membrane-aerated reactor systems and is cited as an advantage of the system in diminishing gas stripping of these possibly harmful compounds⁴; however, it does not necessarily eliminate the release of these compounds. Aside from the release of VOCs (from the wastewater itself or microbial metabolic byproducts) via gas stripping, there is also the release of process gases from the system, such as carbon dioxide from heterotrophic metabolism, and nitrogenous species (i.e., nitrous oxide, nitric oxide, nitrogen dioxide, etc.) intermediates formed during the denitrification process.

In terrestrial applications, the release of trace VOCs and reactor product gases is of little interest to the bioreactor and wastewater treatment communities as release into enclosed spaces is not an issue due to atmospheric venting. Extensive and ongoing studies at Johnson Space Center, Kennedy Space Center, Ames Research Center, and Texas Tech University are aimed at utilizing MABRs as a possible pre-treatment technology for the Alternative Water Processor (AWP). In this application the potential for possible harmful contaminant release into cabin air must be thoroughly examined to determine if any post-processor air remediation technology is required. Due to the niche

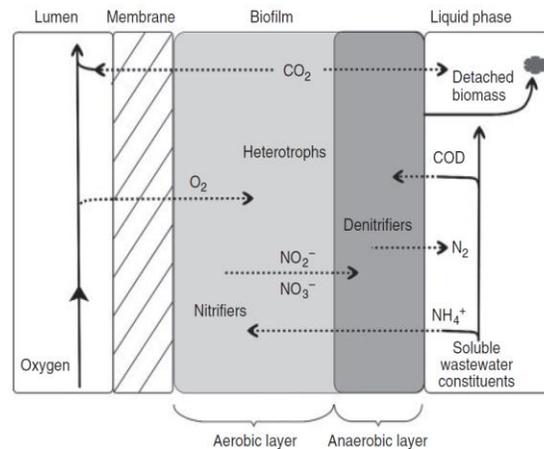


Figure 1: Transport fluxes of soluble constituents and microbial stratification within biofilms developed on membranes within nitrification-denitrification MABRs according to Syron and Casey¹.

application for bioreactors being studied here, there are few, if any, resources available on the various gas exchange phenomena present in such reactor systems. Rothmund et al.⁴ studied the rate of oxygen diffusion across reactor membranes, through biofilms, and into the bulk liquid to compare differences in the use of pure oxygen and air as oxygen sources; however, the main focus of this paper was to show biofilm respiration rate/metabolic rate changes with changes in dissolved oxygen (DO) flux rather than gas stripping events. Other studies involving gas flux trends were completed by Christensen et al.⁵ During operation of their CoMANDR (Counter-diffusion Membrane Aerated Nitrifying Denitrifying Reactor) system, lowering of pure oxygen flow in an attempt to limit bulk fluid DO resulted in an inhibition of nitrification. This inhibition could not be explained by the high bulk DO. It was hypothesized that the low gas flow rate caused an accumulation of CO₂ due to insufficient gas phase removal of the compound. The high concentration of CO₂ likely led to an excess of carbonic acid, lowering the pH of the system below optimal levels for nitrification. Thus, it was determined that CO₂ stripping, and presumably the stripping of other gas phase constituents as well, was dependent on influent gas flow, but little other work has been conducted to identify various trace constituents and monitoring process gases.

This paper focuses on the methodology developed for identifying trace contaminants and process gases present in MABR effluent gas streams, limited quantification of such constituents, and initial analysis of the ability for current air revitalization technologies onboard the International Space Station (ISS) to handle an added load from an MABR should one be implemented as part of a water processing system.

II. Methods

A. Gas Sample Collection & Solid Phase Microextraction Sampling

Approximately 1.5 L of a designated reactor effluent gas was collected in a 3-L FlexFoil® PLUS sample bag; if the sample was taken from a JSC MABR, it was sent overnight to KSC for analysis. To determine organic species present in the sample, Solid Phase Microextraction (SPME) analysis was conducted. A 75- μ m carboxen/polydimethylsiloxane SPME Field Sampler (Supleco) was allowed to adsorb the sample for 20 min. A one-minute desorb period at 200°C (within the GC-inlet) prior to injection. The sample was analyzed via GC-Mass Spectrometer (MS) using an HP-1 column (60 m x 0.320 mm x 1.00 μ m df) initially held at 35°C for 5 minutes, ramped to 200°C at a rate of 5°C/min, then held at the final temperature for 12 minutes. Once compounds were identified by this method, if desired, quantification via a follow-on GC method was completed.

B. Carbon Dioxide Quantification by GC

A GC-Thermal Conductivity Detector (TCD) was used with a HP Plot Q column (30 m x 0.53 mm x 40 μ m df), initially held at 45°C for 1 minute, ramped to 95°C at a rate of 10°C/min, then held at the final temperature for 3 minutes. Splitless injection at 150°C was utilized and the detector temperature set to 200°C with a reference flow of 15 mL/min and makeup flow of 5 mL/min.

C. Nitrogen & Oxygen Quantification by GC

A TCD was used with a Restek MSieve 5A column (30 m x 0.53 mm), initially held at 80°C for 1 minute, ramped to 100°C at a rate of 15°C/min, then held at the final temperature for 2 minutes. Split injection at 200°C was utilized and the detector temperature set to 200°C with a reference flow of 25 mL/min and makeup flow of 22 mL/min.

D. Nitrogen Dioxide & Nitrous Oxide Quantification by GC

A GC-Electron Capture Detector (ECD) was used with a Plot Q column (30 m x 0.32 mm x 10 μ m df), initially at 28°C, was ramped to 75°C at a rate of 10°C/min, then held at the final temperature for 1 minute. Split injection at 200°C was utilized and the detector base temperature was set to 250°C, with a reference current of 1.0 nA, pulse amplitude of 50V, pulse width of 50 μ sec, and makeup flow of 20 mL/min (Argon/5% Methane).

E. Volatile Organics Quantification by GC

A GC-Flame Ionization Detector (FID) was used with a HP Plot Q column (30 m x 0.32 mm) initially held at 60°C for 2 minutes, ramped to 150°C at a rate of 15°C/min, then held at the final temperature for 3 minutes. Splitless injection at 200°C was utilized and the detector base temperature was set to 250°C with an air flow of 350 mL/min, hydrogen flow of 35 mL/min, and makeup flow of 30 mL/min.

III. Results & Discussion

A. Fourier Transform Infrared (FTIR) Spectroscopy for Effluent Composition Identification

Fourier Transform Infrared (FTIR) analysis is a powerful tool for identifying constituents in unknown gas mixtures, monitoring gas streams in-line with processes, and in many cases, quantifying those components as has been demonstrated by several researchers⁶⁻⁸. Even so, of most documented FTIR monitoring systems are highly dependent on the analysis software for parsing out complicated, overlapping spectra^{7,9}; many are not capable of identifying large numbers (5-8 unknown constituents are generally the limit for these types of software systems) due to complications arising from spectral overlaps in complex mixtures. Furthermore, IR spectroscopy is an energy-limited technique; situations often occur where there is not enough energy to accurately measure very weak or very strong bands necessary for analysis⁹. Drawbacks aside, initial attempts were made to utilize a KSC in-house portable FTIR system for the identification of effluent constituents. Based on software limitations, the system was only capable of monitoring for compounds chosen by the user rather than analyzing the mixed spectra to extract the identity of compounds present. A procedure was devised whereby 12 gases were chosen based on probability of presence and monitored using a five-second averaging scheme. Other system limitations disallowed for optimal analysis of small volumes of effluent gases. While the FTIR system claims to allow for monitoring of up to 30 gases simultaneously, common spectral peaks from multiple components greatly confounds the results. Detection of some compounds such as carbon monoxide was also determined to be due to residual peaks from other components as it was not present when the effluent was analyzed via gas chromatography. Based on the inability for these limitations to be overcome, analysis exclusively through gas chromatographic techniques was employed for future samples.

B. SPME-GC-MS Analysis for Effluent Composition Identification

Solid Phase Microextraction techniques were used to concentrate volatile organic compounds from various reactor types in order to qualitatively identify constituents in different effluent streams. A sub-scale MABR (ssMABR) at KSC was sampled just prior to entering a hibernation event, during which it did not have a gas feed and was unable to be further sampled. A second empty (i.e., not containing any microbes) ssMABR was also sampled to compare profiles of supply air and material off-gassing and biological metabolic products. Similarly, four of JSC's full-scale MABR systems and supply air were profiled for effluent composition.

1. KSC Supply Gas and ssMABR1 system

Kennedy Space Center bioreactor system gas samples were used to determine the best methodology for VOC identification within reactor systems prior to analysis of JSC's full-scale reactor system. Gas samples were collected from three reactor systems at KSC: 1.8-L ssMABRs 1 and 2 and a two-stage reactor system with dedicated carbon oxidation and nitrification reactors. These systems were used to develop a methodology for analysis via FTIR as discussed previously; due to the inconsistency in concentrations between FTIR and GC results, as well as the physical limitations of the FTIR system available for this analysis, these studies served to down-select the techniques used in future analyses. As such, SPME analysis was not completed for the systems while biological activity was present in the reactor systems.

Within the timing of bioreactor project goals at KSC, a SPME profile was completed for ssMABR1 (Figure 2) during a reactor header change-out phase to determine what constituents may be present from reactor construction materials and supply gas. During this testing, KSC utilized pure oxygen as the reactor supply gas, differing from JSC, which utilized house compressed air for their reactor gas supply. As seen in Figure 2, there is a lack of long-chain alkanes compared to JSC supply gas profiles (Figure 3 and Figure 4) due to the use of bottled oxygen. Of the constituents found in the KSC ssMABR1 reactor system, none were unexpected; methylene chloride and other solvents were used during the construction of the reactor header system and the siloxanes present are likely off-gassing products from the polydimethylsiloxane (PDMS) fibers utilized. This data was able to confirm the ability of the SPME procedure to identify VOCs within the effluent gas stream of a bioreactor and complements other GC methods delineated above for quantification of such compounds. Further quantified analysis of process gases for these KSC reactor systems for process gases will be discussed later.

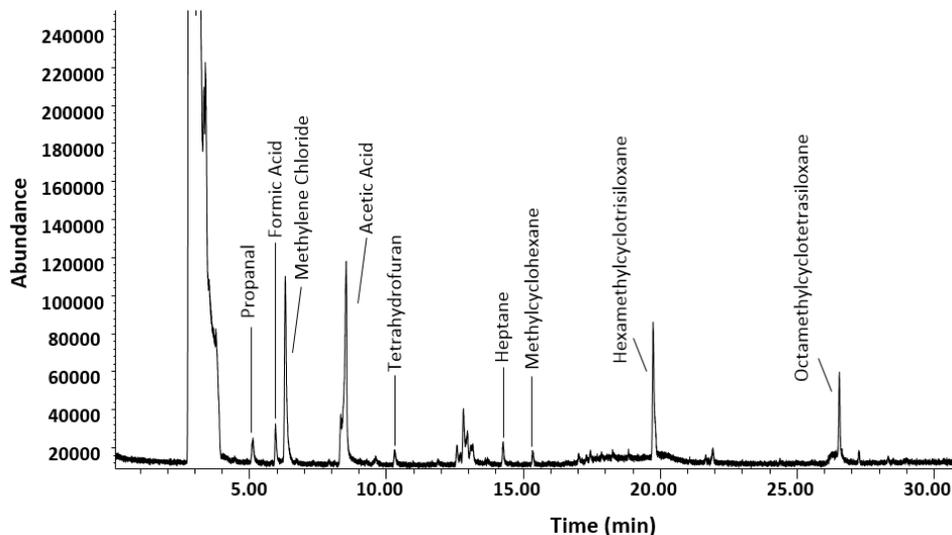


Figure 2: SPME Profile from KSC ssMABR1 with no biological activity present.

2. JSC Supply Gas and MABRs

Several samples of the supply gas used for JSC's MABR system were analyzed via SPME-GC-MS (Figure 3 and Figure 4). The supply gas used by the JSC team is house-supplied compressed air; it is not surprising to see the composition of this stream change slightly over time. In general for the two analyses shown in Figure 3 and Figure 4, distinct classes of compounds are noted: common VOCs such as acetone, toluene, and isopropanol; alkanes and alkenes; and siloxanes. The source for most of these compounds is likely from greases and oils used in the house air compressor system. Since it is highly unlikely that long-chain hydrocarbons would be produced by any microbial activity or off-gas from any of the reactor construction materials, the presence of these compounds in SPME profiles from the MABRs was discounted. The concentration of the VOCs, as well as the siloxane derivatives, in the influent gas are important to note in order to determine if any evolution of these gases are from the microbial activity within the MABRs or from the construction of the MABRs (e.g., the silastic tubing used throughout the system). Quantification of these compounds is discussed later along with the implications of the results in relation to the need for any environmental controls.

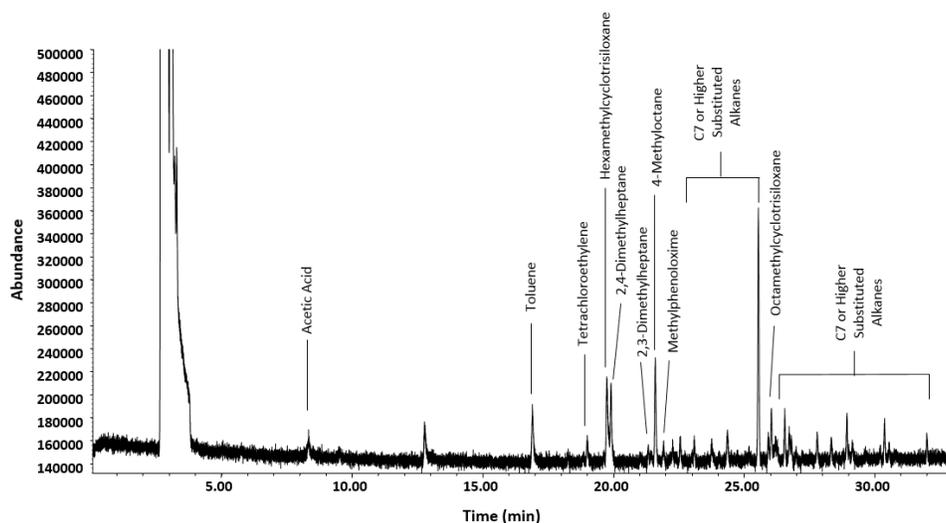


Figure 3: SPME Profiles from JSC Supply Gas on 2/24/14.

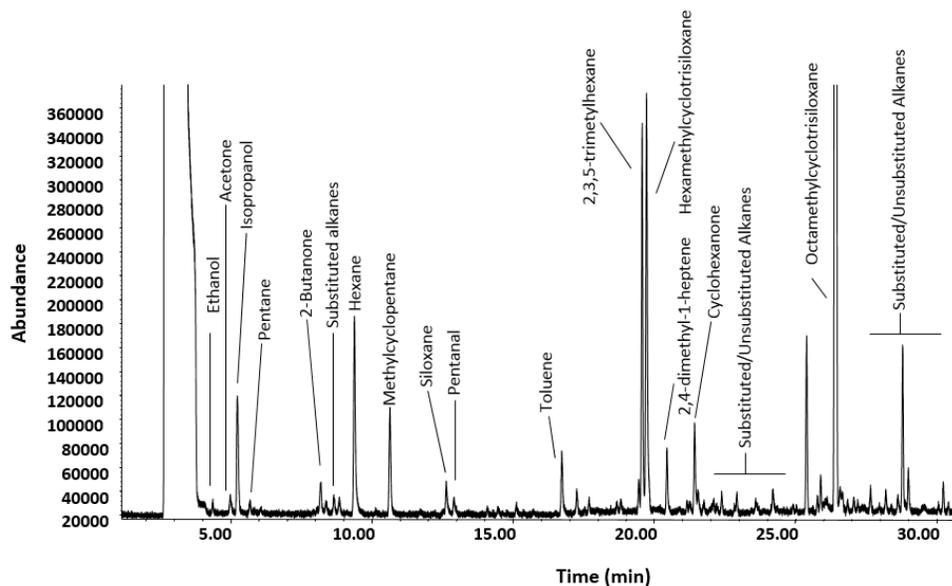


Figure 4: SPME Profiles from JSC Supply Gas on 7/24/14.

SPME profiling was completed for all four of JSC’s MABR systems over a two-and-a-half-month period to determine the common VOCs present within each system. Figure 5 and Figure 6 show selected profiles for JSC MABRs 1 and 2, respectively. Throughout the SPME sampling period, the profiles for each reactor did not change significantly; furthermore, there was little variation in the species found between the different reactors. Many of the identified constituents were also present in the supply gas profiles. As discussed earlier, it is not likely that the systems would produce long-chain alkane/alkene compounds and such were eliminated from further investigations. Based on the SPME findings, VOCs including ethanol, methanol, isopropanol, and 2-butanone were the major constituents focused on for quantification. Limited siloxane analysis was also a focus for further investigations, focusing on hexamethylcyclotrisiloxane and octamethylcyclotrisiloxane. It is important to note that the SPME technology does not allow for the detection of most process gases within the bioreactor systems (i.e., O₂, N₂, NO, NO₂, N₂O, CO₂) but only organic compounds. Many of these process gases were also examined based on the possibly harm they could cause crew members via other GC methods described earlier. No sulfur-containing organics such as mercaptans that could be produced by microbes in anoxic sections of a bioreactor were present according to the SPME analysis; however, further determination to ensure these types of compounds are not being stripped should be completed in future analyses.

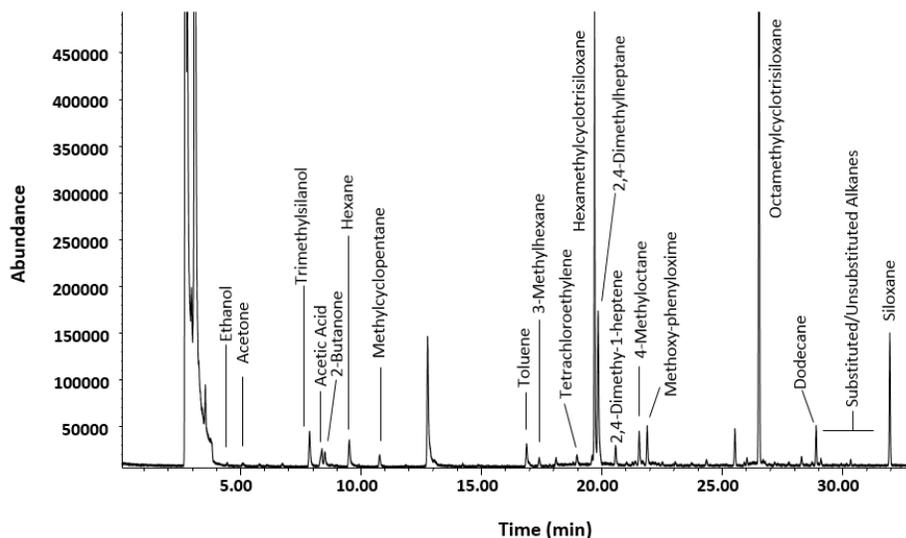


Figure 5: SPME Profiles from JSC MABR 1 on 1/31/14.

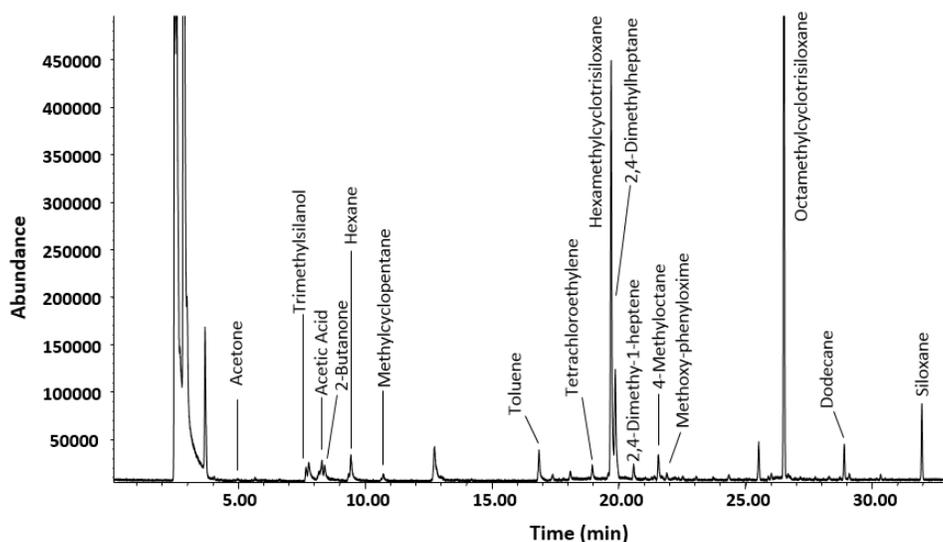


Figure 6: SPME Profiles from JSC MABR 2 on 1/31/14.

C. Quantification of Selected Process Gases and Trace Contaminants

Process gases including O₂, N₂, NO₂, N₂O and CO₂ were quantified on a near-weekly basis for all reactors. Quantification of oxygen and nitrogen is important for monitoring reactor conversion metrics such as oxygen consumption and denitrification rates. Utilizing air as the reactor supply gas easily complicates the ability to calculate nitrogen production rates as the small increase in nitrogen concentration in the reactor effluent is often within the error of the already high nitrogen readings of the supply gas itself. Calculation of oxygen consumption rates is not usually hampered by quantification limitations as seen with nitrogen, but are not a focus of this paper as a major or trace contaminant generated by the reactor systems. The remainder of the analysis, instead, focuses on carbon dioxide stripping and evolution of other nitrogenous compounds and the VOCs discussed above from SPME profiling.

1. KSC Systems

As previously mentioned, there was limited quantification of process gases and VOC trace contaminants for the KSC reactor systems, as they were used to develop analytical methodologies. Oxygen, nitrogen, carbon dioxide, and nitrous oxide were the only constituents assessed for KSC's ssMABR2 and two-stage reactor system. For the purposes of the intent of this report to discuss gaseous constituents which may require a treatment technology beyond current systems and not performance metrics of the reactor systems, only carbon dioxide and nitrous oxide will be examined.

KSC's ssMABR systems are a 1/30th direct scaled-down system to the JSC MABR systems and operate as combined-stage reactor where carbon oxidation and nitrification/denitrification processes

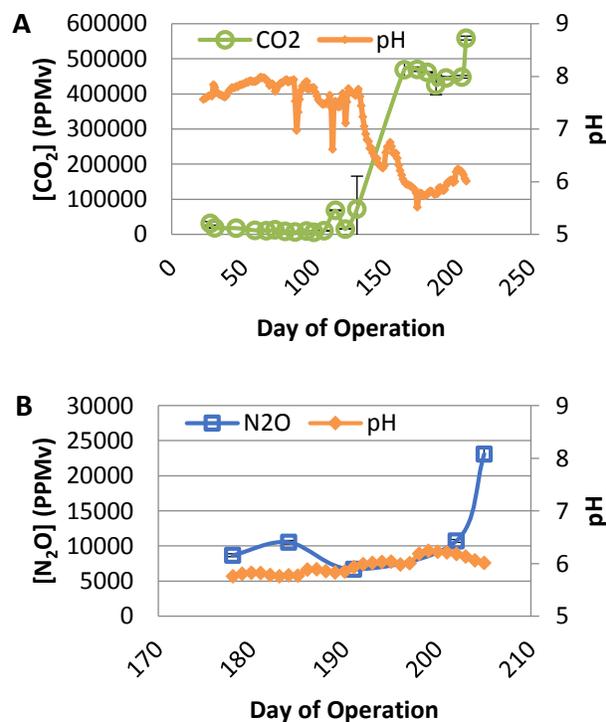


Figure 7: A) Carbon dioxide and B) Nitrous oxide trends in KSC ssMABR2.

are carried out in a single reactor. Figure 7 shows the CO₂ and N₂O trends in this ssMABR system. It can be seen that there are significant amounts of both species present in the effluent stream; carbon dioxide was seen to reach ~50% near the end of the analysis period during reactor steady state operation. There are many differences in the operational parameters between ssMABR2 and the JSC MABRs discussed below such as choice of gas supply matrix discussed above. As Christenson et al.⁵ discussed, CO₂ stripping is highly dependent on gas flow rate and gas stream makeup; this phenomenon is evident in the KSC CO₂ data. Nitrous oxide, a main intermediate in the denitrification process¹⁰⁻¹¹, levels were also seen to be very high in the effluent gas stream. A possibility is that with the flow rate of O₂ used in the system (1.00 mL/min during the period documented in Figure 7B) caused N₂O stripping at a higher rate that the denitrification process could handle or due to limitations based on low carbon to nitrogen ratios that limit denitrification. Based on the operational parameters of the KSC ssMABR2 system during this period, the set points utilized are not equivalent to what would be used in a full-scale systems, so the data presented should not be used solely to judge trace contaminant control mechanisms. The data does, however, demonstrate that a myriad of operational parameters must be considered to minimize the release of high concentrations of possibly harmful constituents.

A process gas trends were also collected for a second KSC reactor system – a two-stage reactor system where stage 1 served as a dedicated carbon oxidation reactor and stage 2 served as a dedicated nitrification reactor. In stage 1, urea hydrolysis and oxidation of other carbon species are the main reaction. In stage 2, nitrification to nitrate and nitrite species occurs, and with very limited organic carbon, denitrification is highly limited. While differing from the general combined-stage reactors currently under investigation for the AWP, the system demonstrates how different reactor setups can alter gaseous effluent streams.

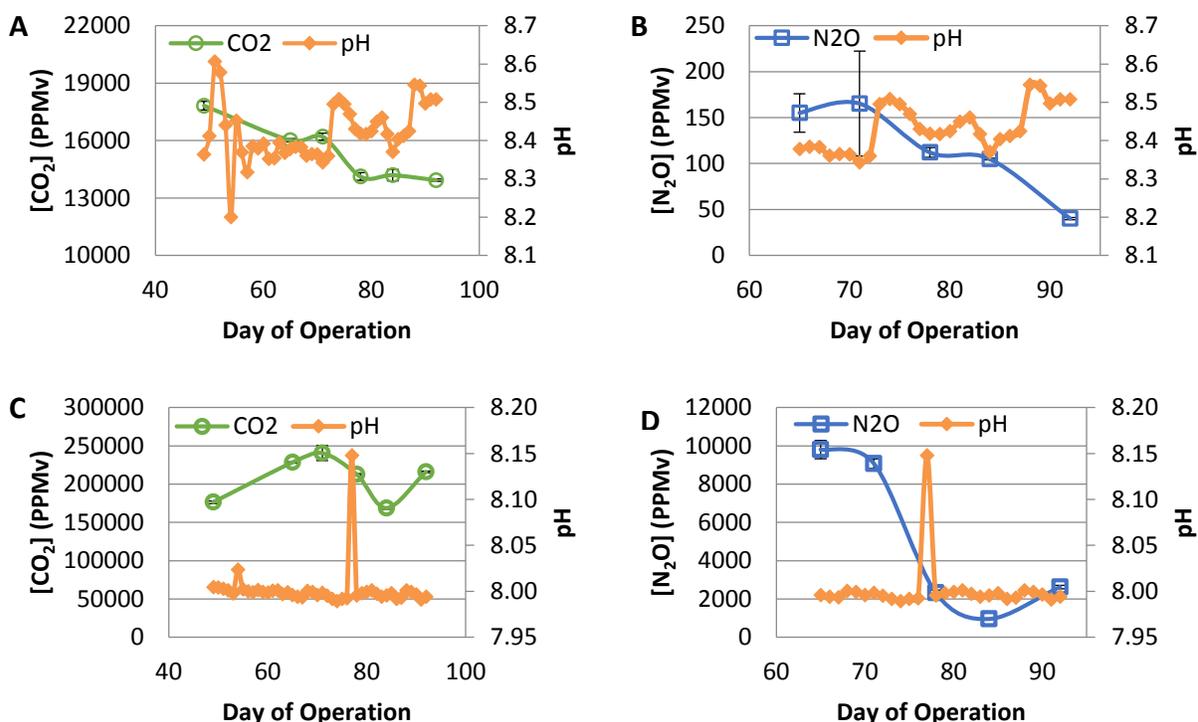


Figure 8: KSC Two-Stage Reactor Stage 1 A) carbon dioxide and B) nitrous oxide and Stage 2 C) carbon dioxide and D) nitrous oxide trends.

Figure 8 outlines how segregating the carbon oxidation and nitrification reactions can alter process gas evolution. The CO₂ stripping in the Stage 1 reactor (Figure 8A) was relatively low (~1-2%) because of the higher pH of the system and associated pKa-associated dynamics of carbonic acid. Nitrous oxide levels (Figure 8B) remained within baseline levels since no nitrification and subsequent denitrification occurred in Stage 1. Extreme differences in the effluent from Stage 2 are noted in comparison to Stage 1, as expected with completely different processes occurring. Throughout the experiment, the reactor pH for Stage 2 was controlled to 8.0 with the use of potassium carbonate to discourage denitrification. Carbon dioxide levels (Figure 8C) were seen to increase to the 15-25% range due to the

near 0.5-point drop in pH as well as due to the introduction of the carbonate for pH control. Figure 8D shows low, while widely varying, values of N₂O (0.1-1%) due to the lack of denitrification in the system. After the initial decrease of N₂O to ~0.1-0.2%, levels remained steady throughout the entirety of the experiment (data not presented). In terms of gaseous effluent trends, this experiment serves to demonstrate that splitting microbial processes into separated systems can directly alter the evolution rates of process gas constituents. This has several implications to be discussed in relation to JSC's effluent gas composition discussed below.

2. JSC MABRs

Since the reactors at JSC are full-scale systems tailored to handling the load of four crew members, the results from these reactors serve as the most realistic example of what would be expected in the gaseous effluent stream of a bioreactor system for ISS-type applications. Table 1 delineates approximated minimum and maximum concentrations of eight compounds present in the JSC MABR effluent streams. Depending on reactor operation metrics, carbon dioxide concentrations were seen to fluctuate between ~0.12 and 3.8%. The next most prevalent compound found in the effluent streams for all MABRs was nitrous oxide, a common intermediate seen during denitrification¹⁰⁻¹¹, at up to 0.95%. Nitrogen dioxide levels were never above the baseline supply gas levels for any reactor; thus little to no NO₂ evolution was encountered. Nitric oxide, NO, is difficult to detect via GC methodology due to the ease in which it oxidizes to NO₂ in the presence of oxygen. Based on the makeup of the reactor supply gas, it is suspected that any evolved NO would be easily converted to NO₂ and thus not a concern in this instance. Of the VOCs quantified, the only two showing concentrations higher than those seen in the supply gas were ethanol and acetone; both however, were seen in ppb levels and near the limit of detection for the GC-FID. Methanol was below the detection limit (~100 ppb) for the instrument and both 2-butanone (MEK) and isopropanol (IPA) were detected, but below the limit of quantification for the instrument (~50 ppb for both).

Table 1: Approximate Concentrations (Minimum and Maximum) of Selected Gases Present in JSC MABRs.

Compound	Concentration (ppm)			
	MABR1	MABR2	MABR3	MABR4
CO ₂	4,350-38,250	1,175-28,150	4,000-27,500	4,265-27,325
N ₂ O	1,675-8,125	0-9,540	6,325-7,900	0-8,890
NO ₂	0	0	N/A	0
EtOH	0.003-0.013	0	0-0.054	BDL
MeOH	BDL	BDL	BDL	BDL
Acetone	0-0.08	0-0.06	0.007-0.08	0-0.06
MEK	BQL	BQL	BQL	BQL
IPA	BQL	BQL	BQL	BQL

Siloxane derivatives are of particular concern in closed habitat environments; recent testing of the ISS potable water has shown the presence of polydimethylsiloxane (PDMS) degradation products, namely, dimethylsilanediol (DMSD). The source of DMSD was identified as PDMS and other siloxanes present in the ISS cabin air being converted to DMSD and entering the water system through the heat exchange system¹². At the time of the above analysis, an octamethylcyclotrisiloxane standard was not available for quantification; thus, quantification was based on hexamethylcyclotrisiloxane to develop initial estimates for amounts present. In initial samples (February 2014), significant amounts of both compounds were present in all JSC reactors (2-3% hexa- and 3-9% octamethylcyclotrisiloxane). Samples analyzed later in the operational lifetime of the reactors (July 2014), showed that siloxane concentrations in the effluent stream were equivalent to those in the supply gas. This shows a possible initial off-gassing of siloxane derivatives from reactor hardware that decreases over time. Further studies are warranted that focus on the extent of off-gassing with amount of PDMS fibers used within the system, as well as examination of other siloxane derivative compound analysis such as trimethylsilanol which was present in all JSC reactor effluent streams, but not present in the supply gas profiles.

IV. Conclusions

Gaseous effluent monitoring is an essential analysis required for operation of MABR systems in an enclosed habitat environment. While KSC small scale systems were used to develop methodology for constituent analysis and demonstrated, on a reduced scale, that altering reactor conditions can alter process gas concentrations in the effluent stream, JSC's full-scale MABR system is of the most important focus for researching what possible harmful compounds may be evolving into the cabin space. Based on SPME results, JSC supply air contained many of the

same compounds as those identified in the reactor effluent samples. Of the trace volatile compounds quantified to date, none are produced in any detectable or appreciable amounts by the microbial community or a product of reactor component off-gassing. SPME analysis also determined that common siloxanes (octamethylcyclotrisiloxane and hexamethylcyclotrisiloxane) were present in both the supply gas and reactor effluent samples; these compounds are of particular concern onboard ISS; further confirmation of the concentrations and possible remediation technologies remain a requirement. After this initial investigation, trace volatile contaminants that have been quantified do not appear to pose a crew risk. The amounts detected during these studies are orders of magnitude lower than SMAC values¹³ and present concentrations on ISS. With such low amounts, it is believed that the current trace contaminant control system (TCCS) would be able to handle the small added load.

More concerning are levels of process gases, namely, nitrous oxide. Currently, no SMAC values exist for the nitrogen process gases mentioned. The reactors did not generate nitrogen dioxide; however, nitrous oxide levels were significant. Nitrous oxide time-weighted average (TWA) limits over an eight-hour period range from 25 to 50 ppm depending on the regulatory authority cited¹⁴; reactor effluent gas contained up to 7200 ppm N₂O. Carbon dioxide levels in the reactor effluent streams were also significant, and must be related to the added load per day that would enter the current ISS system or equivalent to ensure the added load could be handled.

There remains a lack of knowledge with respect to sulfur species in the effluent gas streams. Limitations at KSC did not allow for the development of a method capable of detecting this class of compounds during the current experiment. Further analysis on these compounds must be completed, as sulfur compounds are known to foul catalyst beds and can be quite harmful to crew.

Many of the potentially harmful (N₂O, NO_x, VOCs) metabolic gases produced are the result of incomplete mineralization of the feed stock. A possible solution for limiting emissions by bioreactors is to recycle the effluent gas stream internally or move to a multi-stage reactor system where the evolution of various process conditions could be different gases could be controlled. Gas recirculation allows for increased gas residence time, which in turn allows for a more complete mineralization of the metabolic compounds to N₂ and CO₂. Further, this could reduce the amount of oxygen required (currently, less than 50% of the supplied oxygen is utilized by the bioreactors). This would require more complex plumbing but the trade-offs of lower oxygen demand and less gas scrubbing is worth the implementation costs. No matter the configuration of reactors, either as a combined stage system, or as a multi-stage system, carbon dioxide evolution is significant. While CO₂ evolution can be controlled to an extent by tight control of reactor pH, active CO₂ management may be required to limit CO₂ build-up in the liquid (at the cost of alkalinity to make up for the CO₂ acidity/carbonic acid). As mentioned, initial data analysis shows a low need for further trace contaminant control beyond an equivalent ISS TCCS; further evidence must be compiled and reviewed to substantiate this determination for several classes of compounds.

Acknowledgments

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