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Towards a Universal Passive Dosimeter for Monitoring Submarine Air Quality

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READINESS THROUGH RESEARCH & DEVELOPMENT

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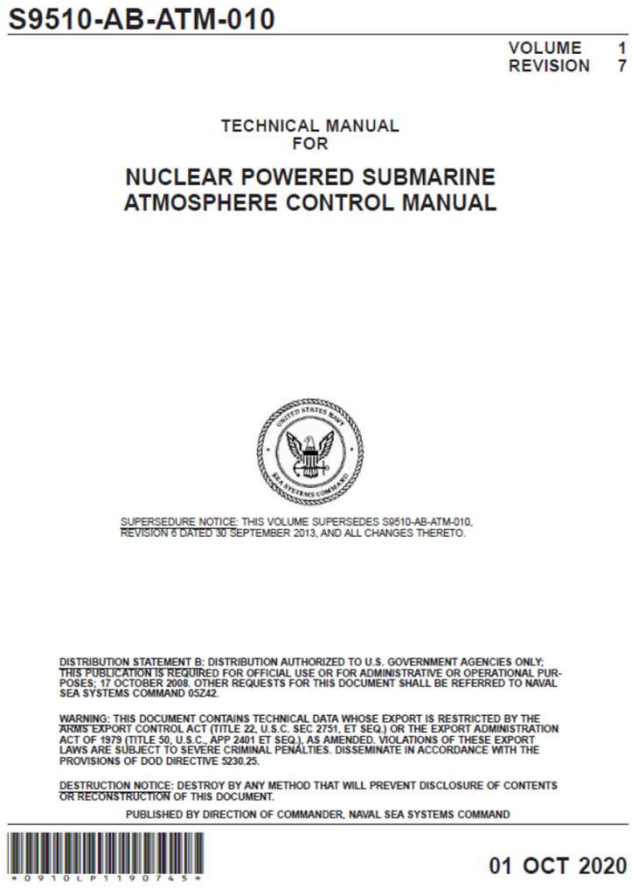
Submarine Atmosphere Monitoring

- **Enclosed environment;** limited venting could cause build-up of **airborne contaminants**.
- **Exposure** to potential contaminants **24h/day** for weeks-months could affect crew health.
- Monitored real-time by Central Atmosphere Monitoring System.
  - Mass spectrometry and near infrared technology for life gases (H_2O, CO_2, N_2, O_2), and common contaminants (H_2, CO, refrigerants)
- VOCs/semi-VOCs monitored retrospectively using passive dosimeters (SAHAP)

Submarine Atmosphere and Health Assessment Program (SAHAP)

SAHAP CNO mandated.

Since 1995 NSMRL tasked to identify & quantify constituents present in the submarine atmosphere and to employ technological advancements in constituent measurement and identification and maintain a long-term database of submarine atmosphere constituents.



S9510-AB-ATM-010

VOLUME 1
REVISION 7

TECHNICAL MANUAL
FOR

NUCLEAR POWERED SUBMARINE
ATMOSPHERE CONTROL MANUAL

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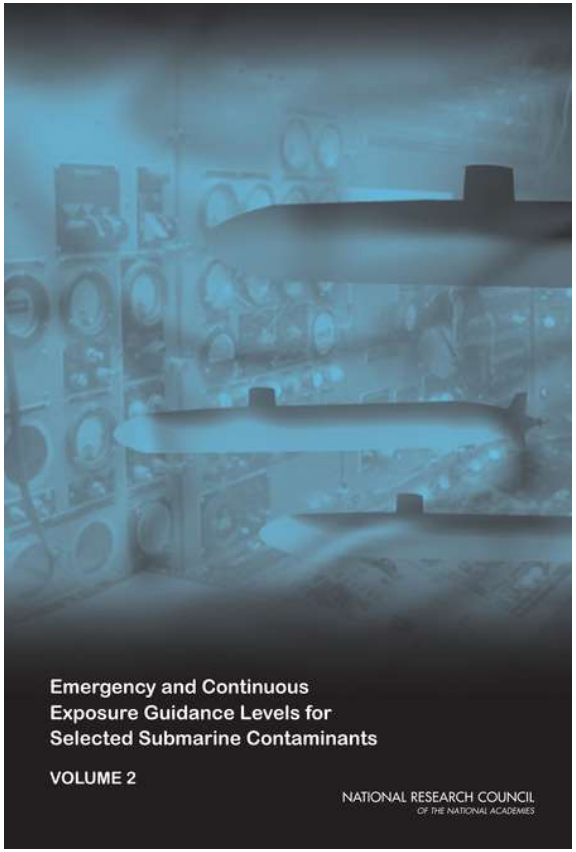


Current SAHAP Passive Dosimetry Technology

Multiple samplers capable of monitoring 29 different air born contaminants

Pros

- Gold-standard passive sampling device
- Broad spectrum (multiple chemistries)
- Commercial analysis pipeline (Assay Technology Inc)

Cons

- High per unit cost
- Cumbersome form factor – not for individual monitoring (11 cm x 8 cm x 2 cm)

Image taken by the Author (MR)

Submarine Air Sampling Locations

Fwd Locations

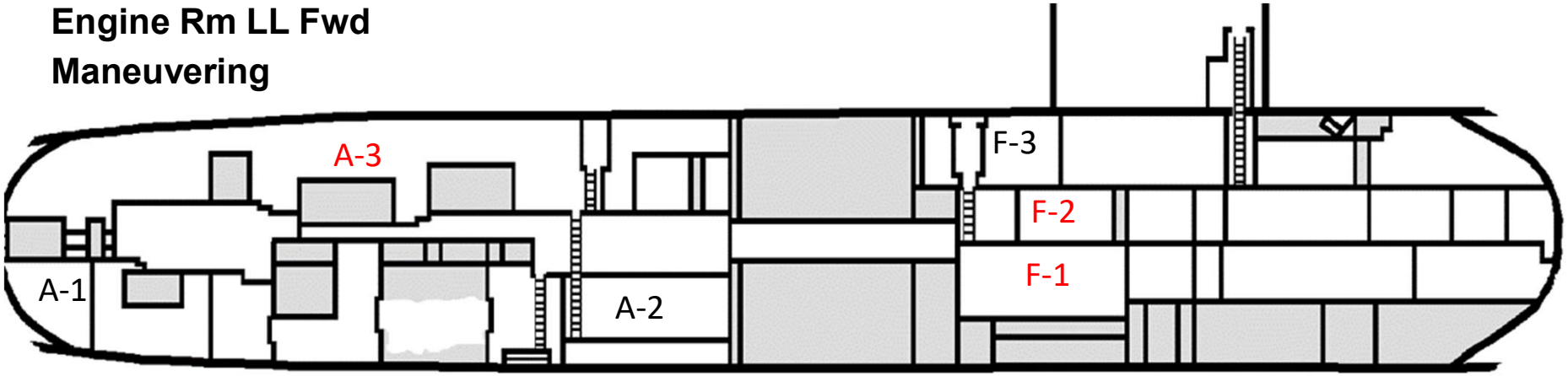
F-1 **Aux Mach Rm 1 (Near Workbench)**
F-2 **Crew's Mess**
F-3 **Fan Rm (Aft Bulkhead)**

Aft Location

A-1 **Engine Rm LL Aft (ASW bay)**
A-2 **Engine Rm LL Fwd**
A-3 **Maneuvering**

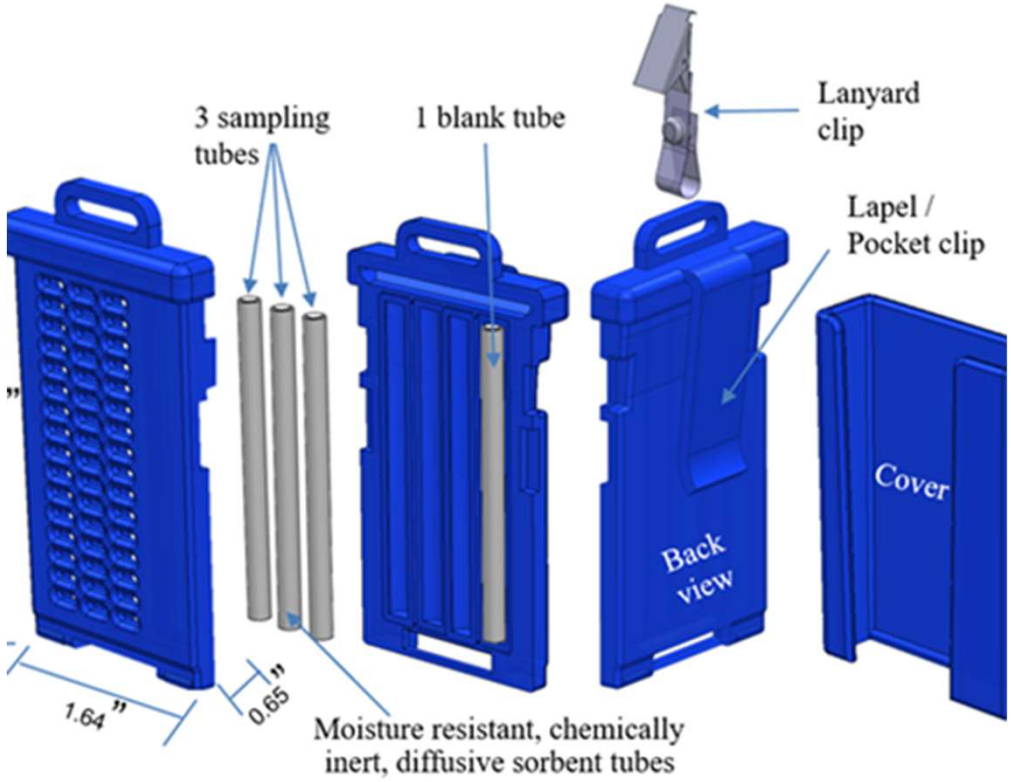
Sample Locations:

- 6 locations VA and OH class
- 3 locations LA class



Study Objective

Assess XCel+ Passive Dosimeter as a personalized passive sampling monitor of contaminates in the submarine atmosphere



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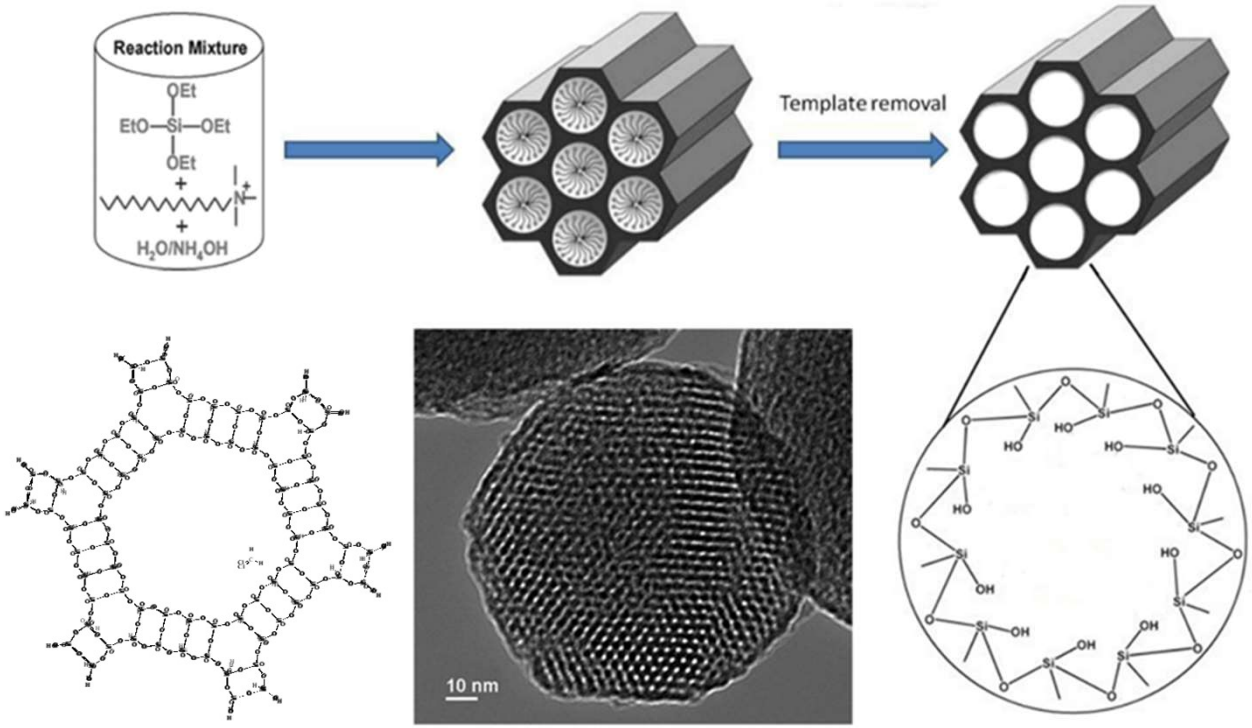
Specific Objectives

1. Determine uptake rates and equilibrium time of contaminants onto novel media.
2. Compare contaminates detected by novel media to SAHAP dosimeters during a prolonged exposure.
3. Determine if novel media detect differences in contaminants across different areas of boat.
4. Future Study: Determine if there are individual differences in exposure to contaminants among different submariner rates during a prolonged patrol.

Proprietary Mesoporous Silica Sorbent OSU-6

Advantages

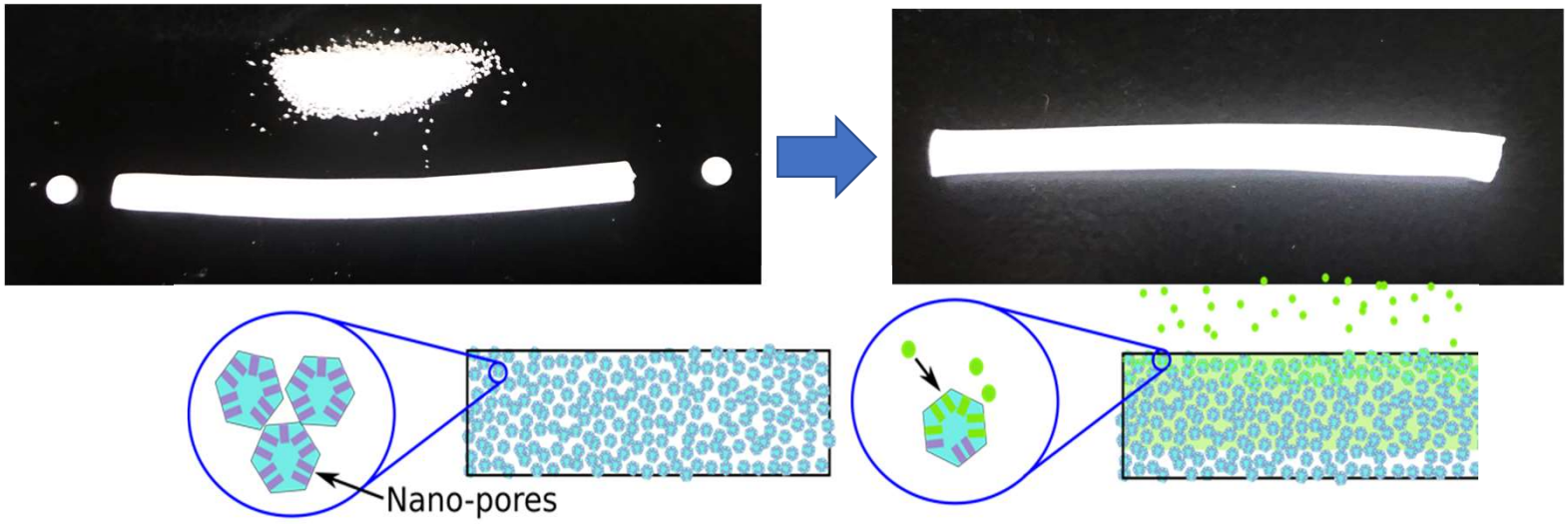
- Inorganic, high surface area sorbent with high thermal stability
- No volatiles released upon heating
- No chemical reactivity that degrades analytes
- No interference with GC/MS analyses
- Strong binding of organic vapors
- Adsorbs many different classes of volatile organic compounds
- Expect high sorption capacities



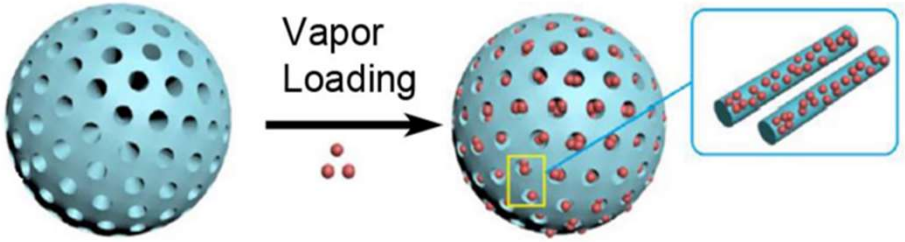
Images by XploSafe LLC (with permission)

Apblett A, Materer N, Kadossov E, Shaikh S. Superior Monitoring of Chemical Exposure Using Nanoconfinement Technology. Mil Med. 2021 Jan 25; 186 (Suppl 1): 795-800. doi: 10.1093/milmed/usaa372. PMID: 33499467; PMCID: PMC7980483.

OSU-6 Sorbent Tokens



Close-up illustration of the nano-confinement in the nano-pores



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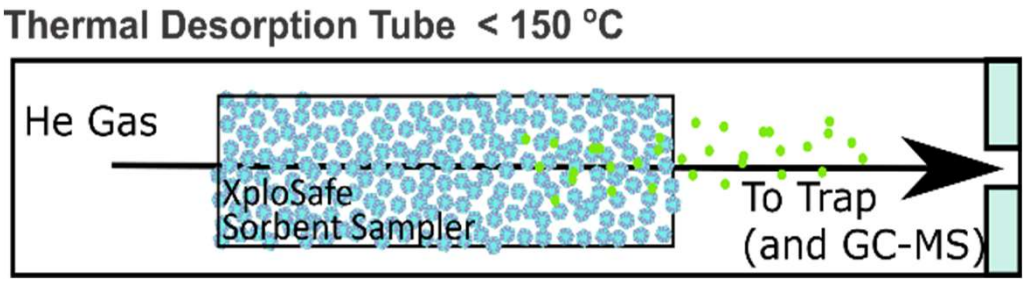
Analysis of the OSU-6 sorbent tubes using thermal desorption and GC-MS



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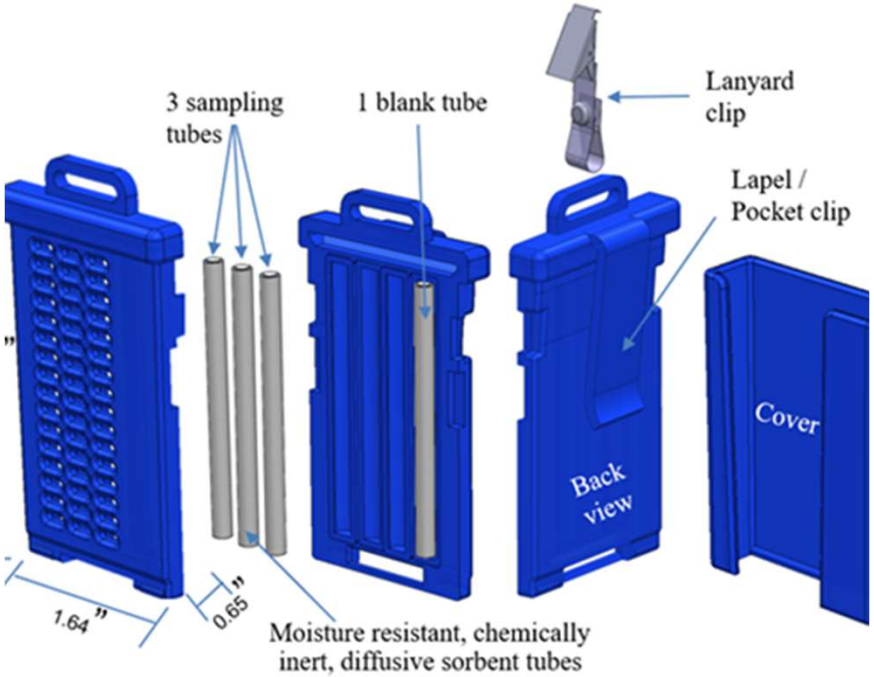
XCel+ Passive Dosimeter



Limits of Detection:
low nanograms

Sampling for over 80 compounds:
capacity for both short or long sampling efforts (minutes/hours or days/weeks)

Images by XploSafe LLC (with permission)

Sample rates for Navy compounds of concern (COC) for the XCel+ Passive Dosimeter

#	Compounds of Concern (COC)	Linear exposure range (ppm*h)	Sampling rate per token (mL/min)
	Navy compounds		
1	Acetaldehyde	25.9	6.0±0.9
2	Acetone	180	9.3±0.6
3	Acetonitrile	>5	14±5
4	Acrolein	>0.2	9.0±0.4*
5	Acrylonitrile	25	14.2±0.4
6	Benzene	>4	5±2
7	Crotonaldehyde	>1	2.5±0.1
8	1,2-Dichlorotetrafluoroethane	>5	1.5±0.7
9	Ethanol	70	16±2
10	Formaldehyde	>8	17±2
11	Isopropanol	69	10.3±0.7
12	Methanol	>4	20±2
13	Methylene chloride	>5	4±2
14	Methyl ethyl ketone	>0.9	2±1*
15	Methyl isobutyl ketone	>0.2	1.9±0.5*
16	Monoethanolamine	6810	0.06±0.02**
17	1,1,2,2-Tetrachloroethane	>0.2	16±4*
18	Toluene	>10	5.6±0.5
19	1,1,2-Trichloroethane	>0.3	6.0±0.2*
	Additional compounds completed so far		
20	n-Hexane	31	2±1
21	1,3-Butadiene	0.03	4±1

The mass (M) gain obtained after exposure:

$$M = SR \times C \times t$$

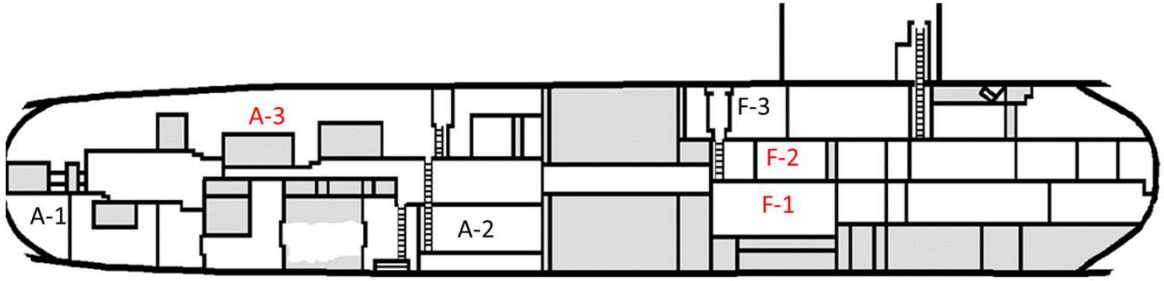
SR – Experimental sampling rate
C – Air Concentration
t – Time

Assumes linear adsorption (linear range)

*Determined at RH = 0% using a pre-calibrated 1-ppm 74-component gas mixture.
** Analyzed using solvent extraction

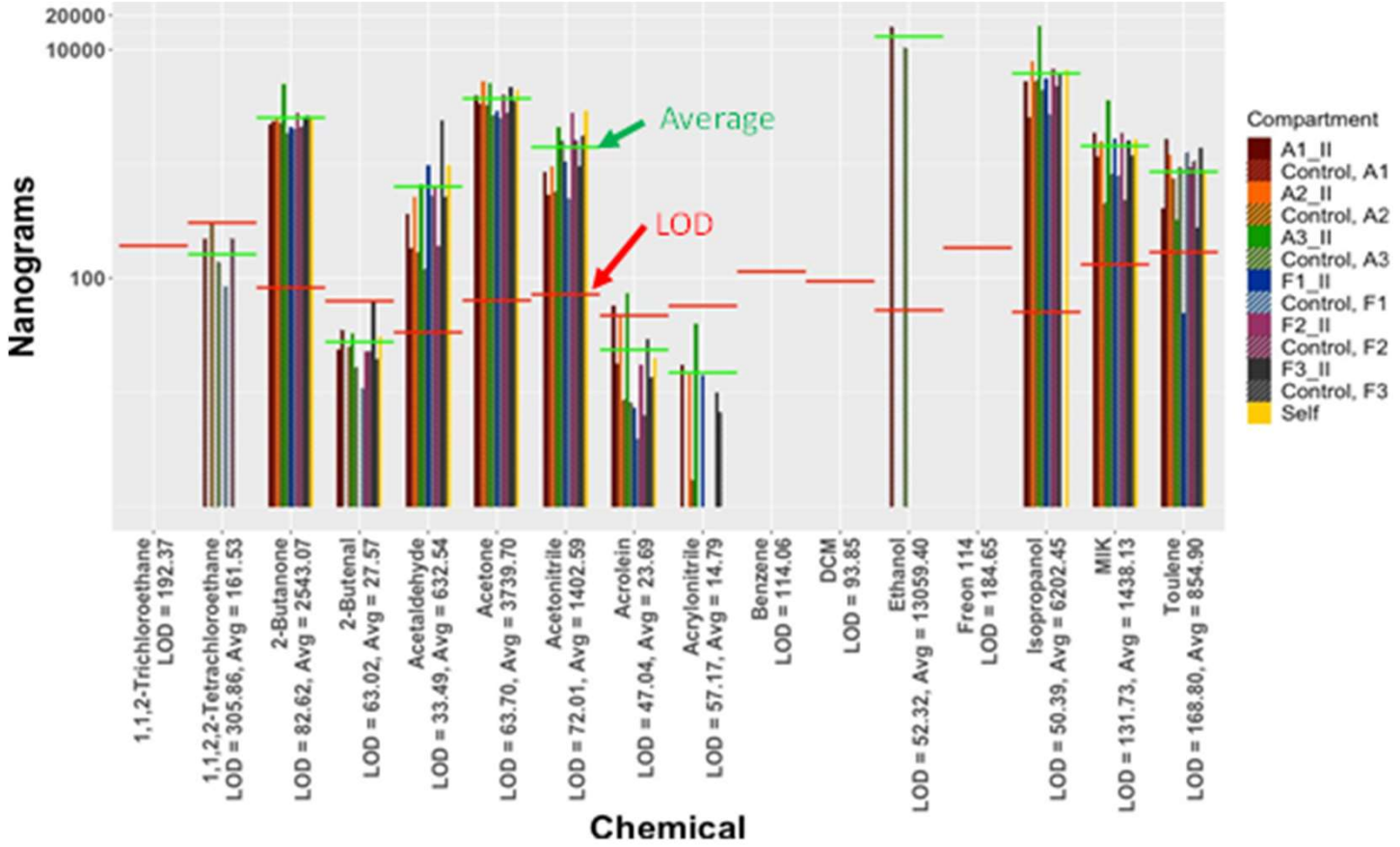
Comparison of SAHAP Assay Technology badges to XCel+ Passive Dosimeter

- 56-day deployment aboard VA class submarine
- SAHAP and XCel+ badges hung next to each other in 6 locations
- One XCel+ badge worn by member of research team
- Badges exposed to submarine atmosphere for first 28 days
- SAHAP badges analyzed by Assay Technologies
- XCel+ badges analyzed by AFRL



Credit: U.S. Navy Photo, Program Executive Office Submarines Public Affairs

Results of XCel+ Badge exposures



Self vs. Average Across Locations

Confidence Interval	t-statistic	Degrees of Freedom	Mean difference	p-value	Significance
95%	1.2127	3	0.459	0.2807	ns

LOD = limit of detection

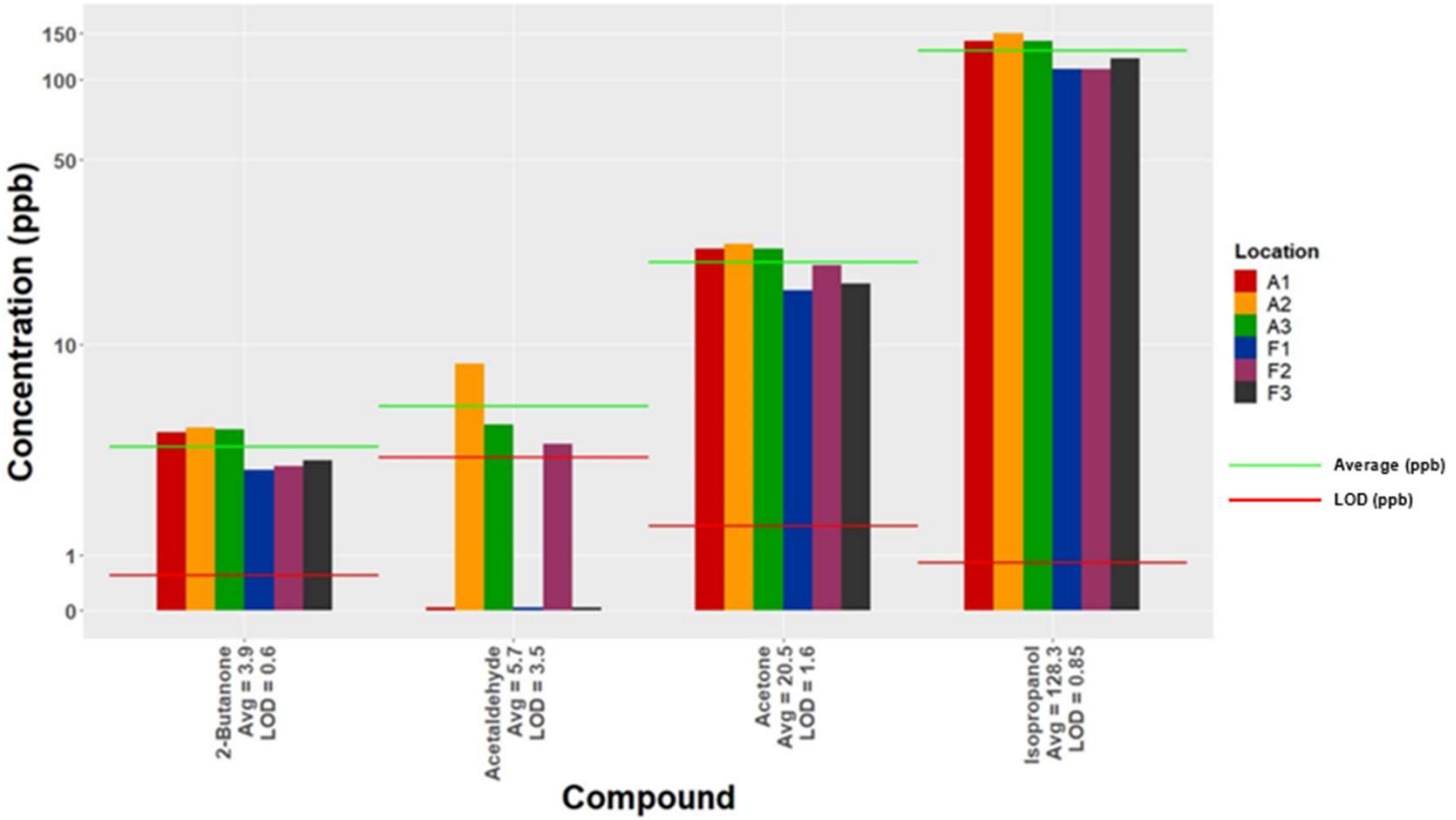
Average= mean value over 6 locations

Results SAHAP vs XCel+

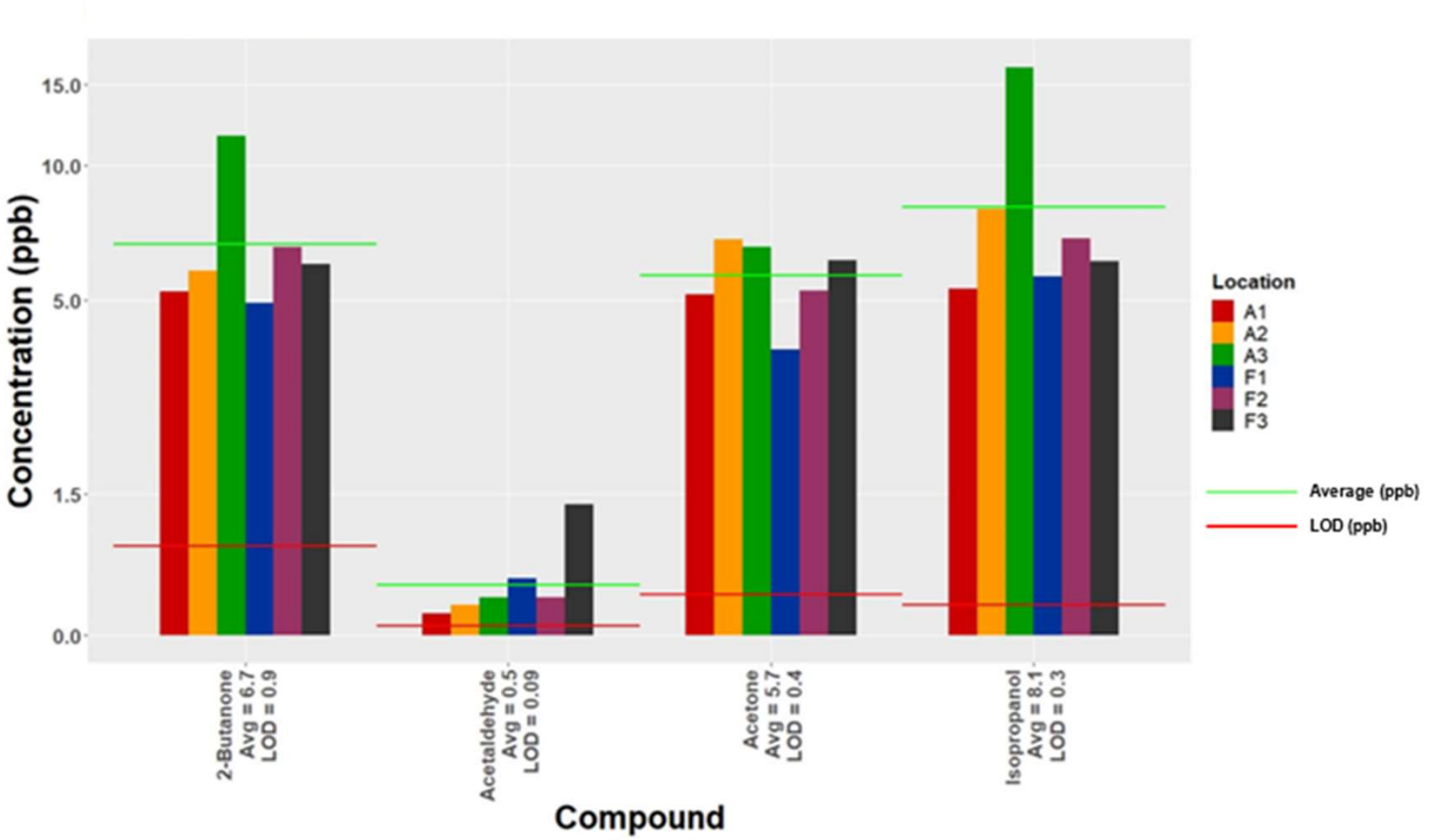
Compounds observed above the LOD (analyzed using GC-MS) on the SAHAP Assay badges (SAHAP) and XCel+ Badges. Bold = those compounds that were observed on each of the media.

SAHAP Badge	XCel+ Badge
Acetaldehyde	**Acetaldehyde**
	Acrolein
Acetone	**Acetone**
	Acetonitrile
Ethanol	Ethanol (contamination) ?
Isopropanol	**Isopropanol**
2-Butanone	**2-Butanone**
2-Butanol	
	MIK
	Toluene

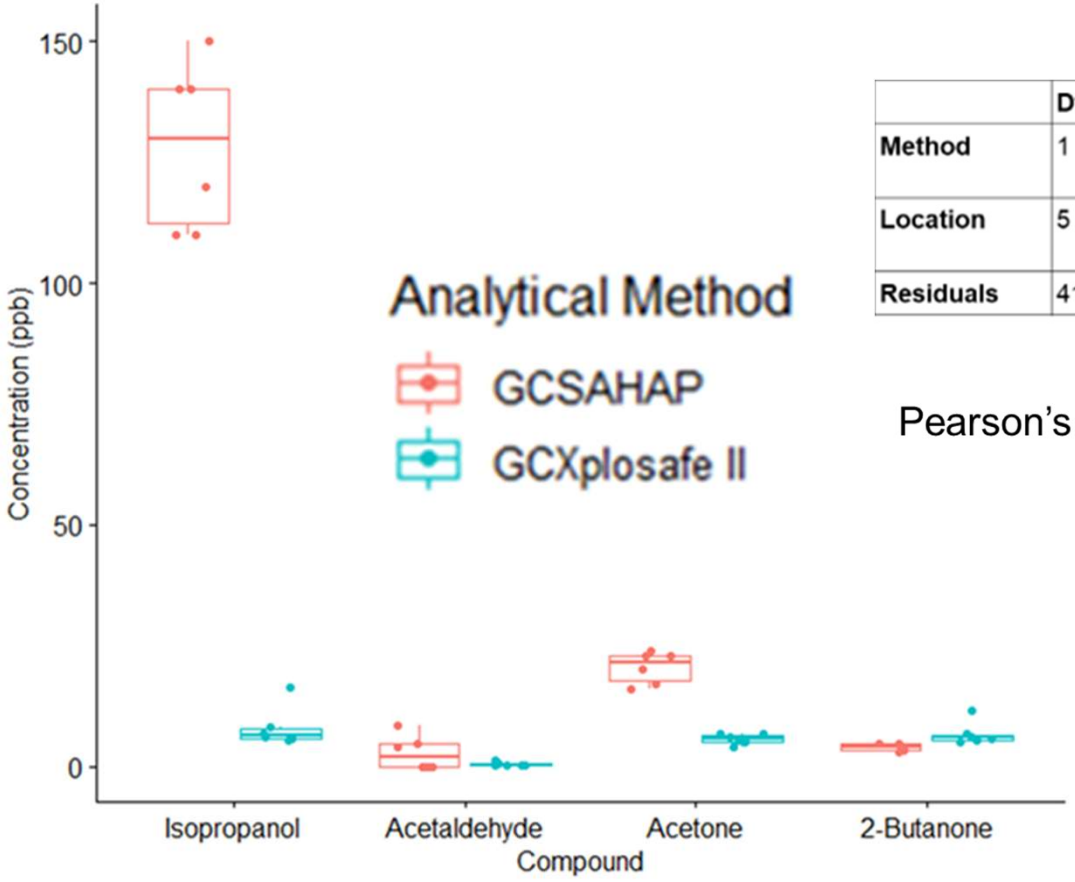
SAHAP Badge air concentrations



XCel+ Badge air concentrations



Results SAHAP vs XCel+

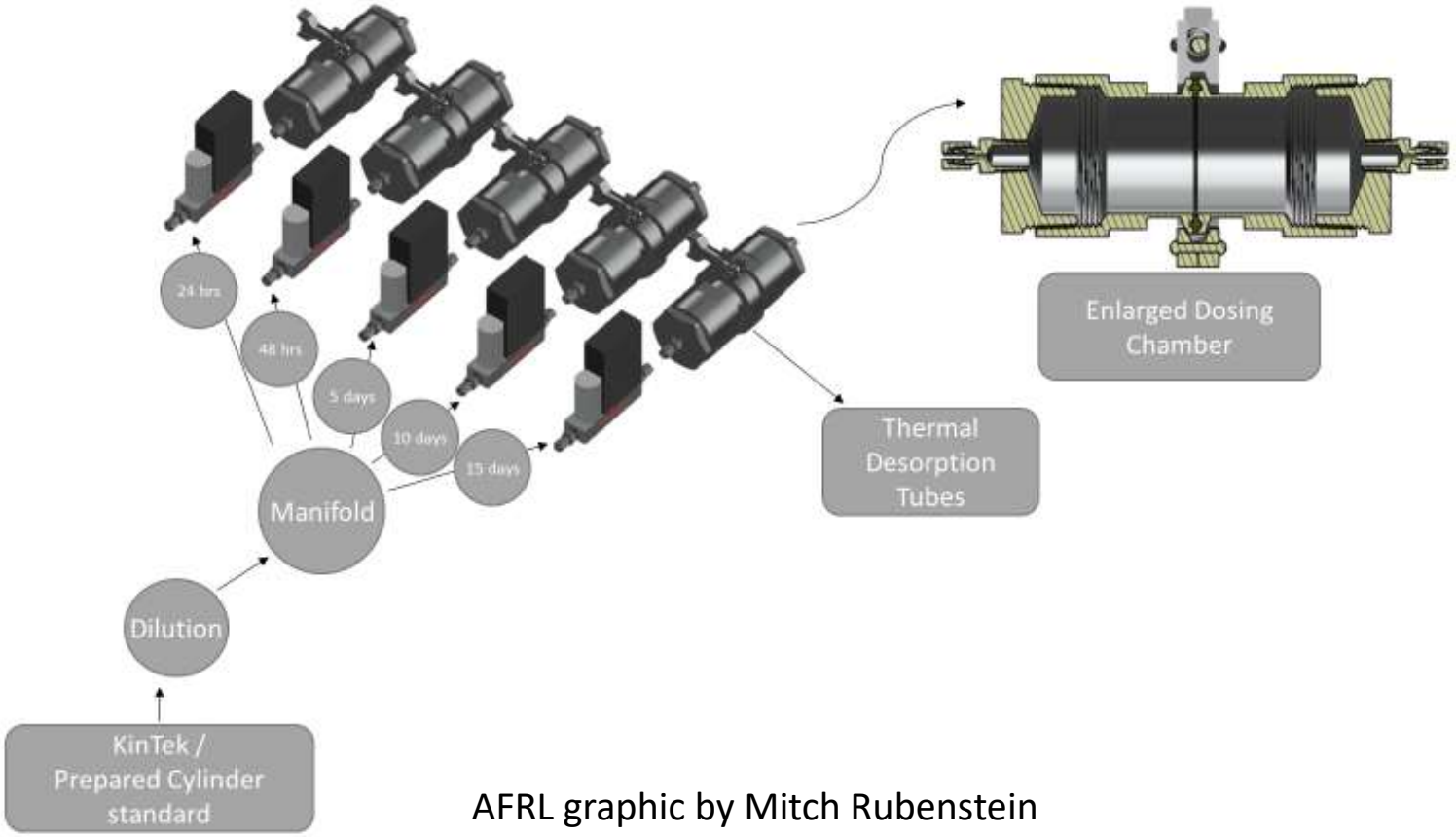


	Df	Sum Sq	Mean Sq	F Value	p-value	Significance
Method	1	13602	13602	8.374	0.00607	** (p<0.01)
Location	5	465	93	0.057	0.99773	ns
Residuals	41	66602	1624			

Pearson's Correlation Coefficient (r): 0.505 P-value: 0.012

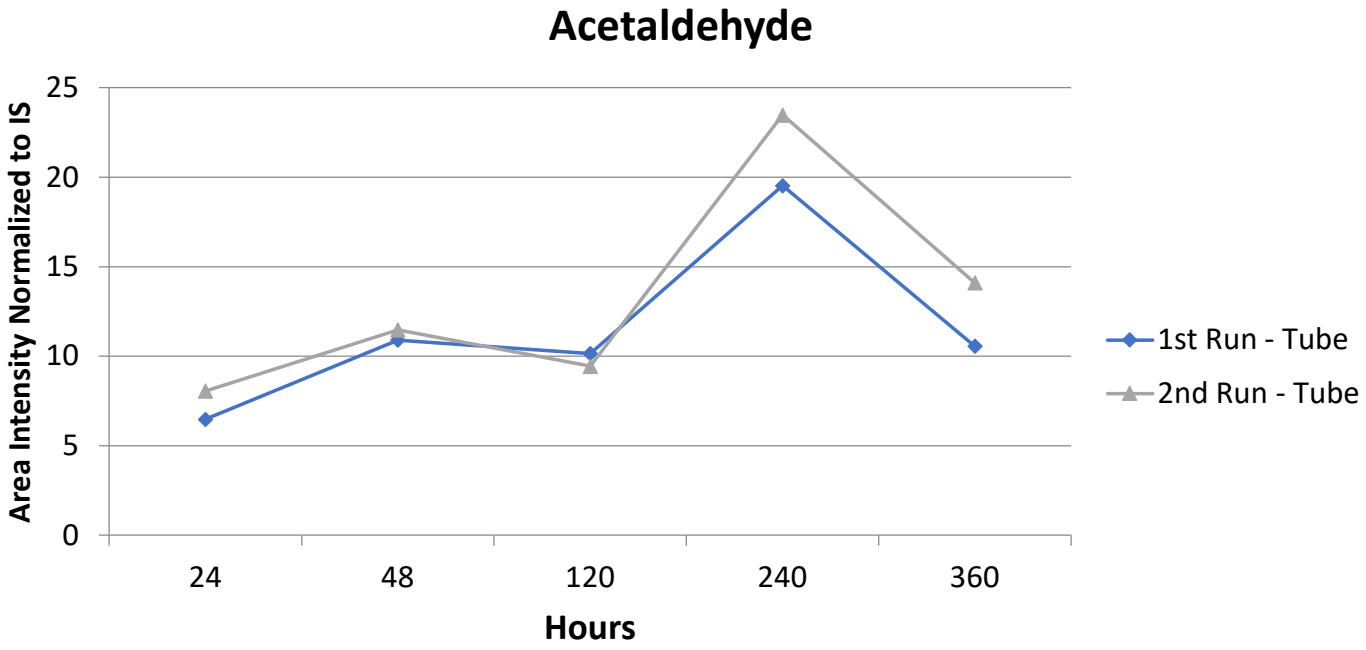
- Why are XCel+ air values lower than SAHAP air values?

Equilibrium Exposure Experiments

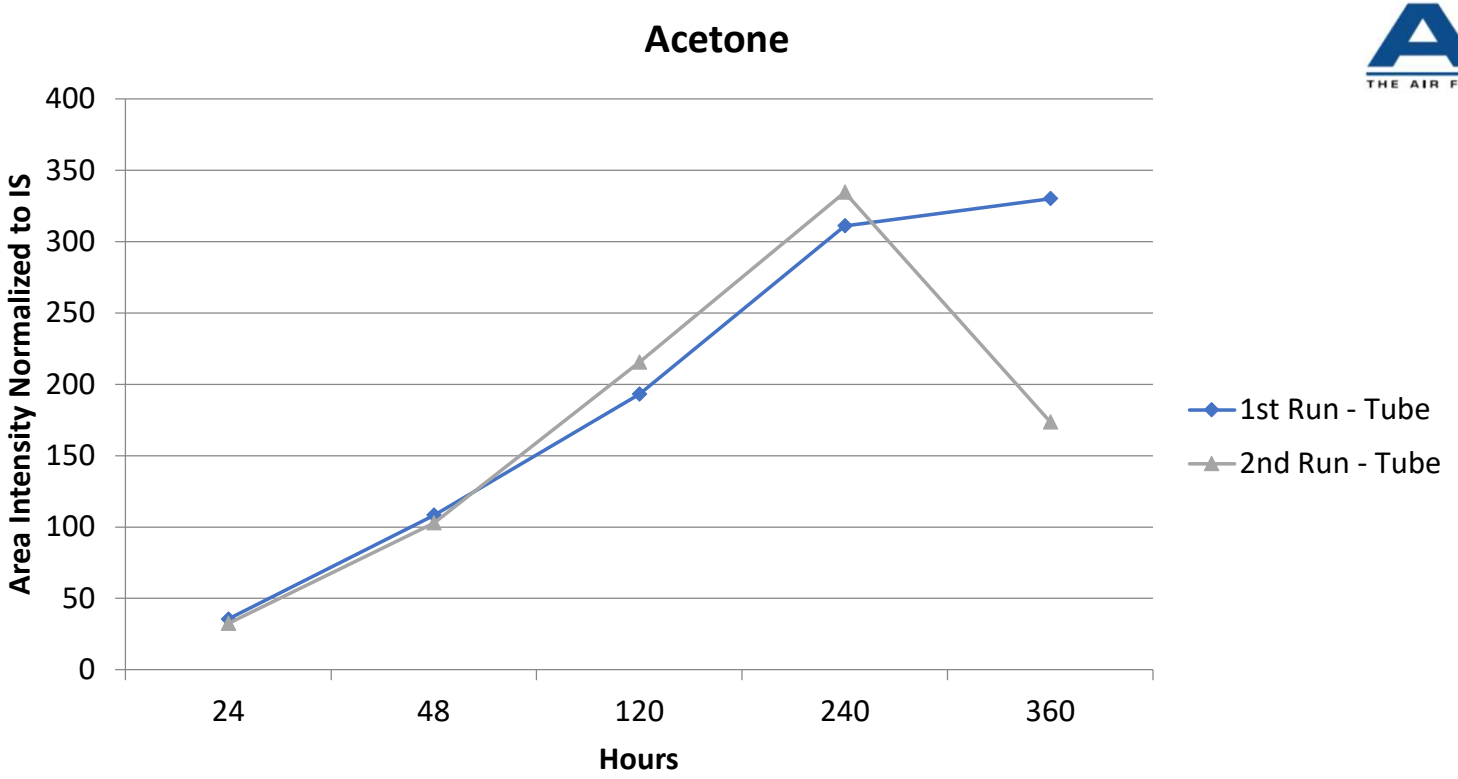


AFRL graphic by Mitch Rubenstein

Why are XCel+ air values lower than SAHAP air values?



Acetaldehyde Fifteen Day Dosing Study and Analysis by TD-GCMS. Linearity is observed for 10 days.



Acetone Fifteen Day Dosing Study and Analysis by TD-GCMS. Linearity is observed for 10 days.

Conclusions

- 15 of the COCs at or close to the LOD
- Four compounds above the LOD for both SAHAP and XCel+ media
  - Acetaldehyde; 2-Butanone; Acetone and Isopropanol
- Ethanol also observed above the LOD but may be contamination from hand sanitizer
- Levels of the four COC detected on both media did not differ significantly across the 6 sample locations
- The four COC detected on the XCel+ badge worn by the rider closely matched the mean concentration for that COC found across the 6 sample locations.

Next Steps

- Validate current results on another submarine shorter duration of exposure (approx. 10 days)
- Complete equilibrium dosing experiments for all COC for XCel+ badge
- Deploy XCel+ badges on individuals to measure personal environmental exposures during a deployment.
  - Difference in exposure by submariner rate/location of watch station (foreword vs aft compartment)?
  - Do individual exposures track mean boat exposures for all COC?