NAVAL SUBMARINE MEDICAL RESEARCH LABORATORY

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Proceedings of the

SUBMARINE ATMOSPHERE CONTAMINANT WORKSHOP

held at

NSMRL

September 7-8, 1983

M. L. Shea, Ph. D., Coordinator

Released by:

W. C. Milroy, CAPT, MC, USN
Commanding Officer
Naval Submarine Medical Research Laboratory

30 July 1984

PROCEEDINGS

of

The Submarine Atmosphere Contaminant Workshop

at

Naval Submarine Medical Research Laboratory
Naval Submarine Base New London
Groton, Connecticut

September 7-8, 1983

Compiled and Edited from Papers and Recorded Transcripts

M. L. Shea, Ph. D., Coordinator

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September 7 and 8,'83

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SUBMARINE ATMOSPHERE WORKSHOP

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Introduction to Workshop
Dr. Michael Shea

Captain William Milroy, Commanding Officer, Naval Submarine Medical Research Laboratory, welcomed the workshop participants and guests.

Dr. Michael Shea began the conference with an introduction to the problems of submarine atmosphere documentation. A memo from Captain J. D. Bloom, Commanding Officer, Naval Medical Research and Development Command to the Chief of Naval Operations was presented by Dr. Shea as criteria for conducting the submarine atmosphere contaminant study and workshop. The memo (appendix 1) summarized comments and recommendations concerning submarine atmosphere contamination between NMRDC, the operations command, and Naval Research Laboratory chemists.

Two major concerns were stated in the memo. The first was that current limits for 90 day continuous exposure to atmospheric contaminants in the closed submarine environment were never validated by actual animal or human exposures and were derived by taking existing industrial limits for 8 hour/day, 40 hour/week exposures and lowering them by some factor to convert to continuous 90-day limits. This approach was deemed unsatisfactory for several reasons. 1.) The factors used to set the limits were arbitrary and in some instances were set because of limitations in atmosphere control equipment. 2.) The limits may not be conservative enough for some substances. 3.) The standards did not address the problems of aerosols in the submarine atmosphere since aerosols can both modify the entry of contaminants and may be contaminants themselves. 4.) The current limits may be too conservative with the results that: unwarranted restrictions may be placed on materials brought aboard for use during patrols; surface ventilation to reduce contaminant levels could reveal the submarine's location; and atmosphere control equipment may be unduly complex and costly.

The second major concern was that the list of contaminants in the most recent edition of the Nuclear Submarine Atmosphere Control Manual (1979) has changed very little from the list first published in the original Submarine Habitability Data book in 1962. The general feeling was that contaminants in the submarine atmosphere have changed in the past 20 years in light of the fact that specific monitoring for contaminants has not been done for at least 10 years and it is not known what is present in the newer classes of submarines.

Recommendations included conducting a literature search to determine what is already known about the health effects of long-term exposure to contaminants encountered in submarine atmospheres and determine what factors are used by OSHA and other standard setting agencies to establish safe threshold levels or determine that no safe threshold value exists.

The response from the CNO's office (appendix 2) to the memo stated that action be taken in the areas outlined in the recommendations. Based on these memos, a work proposal was written and funded. Dr. Shea briefly described the sequence of events leading to the determination of by whom and by what criteria the limits for submarine atmospheric contaminants were set. Dr. Shea concluded his introductory remarks with a statement of the workshop goals which included 1.) determining if the atmospheric contaminant limits should be reevaluated by the NRC, 2.) amending paragraphs in the atmosphere manual to be more readable and useful to submariners and 3.) identifying areas for new or continued research to meet the immediate or long term needs of the Navy.

Keynote Address
"Early Documentation of Limits for Atmospheric Contaminants in Nuclear Submarines"
Mr. Ralph C. Wands

Since anecdotal stories of how the limits of atmospheric contaminants have been derived seem to be pervasive, we felt an elaboration in this area was needed. A call to the National Research Council requesting the methodology the board used for documentation of limits produced a response most troubling since it appeared that little thought went into the limits (appendix 3). However, further research indicated that the staff officer at the NRC was incorrect in his assessment of the board's activities and that a large effort was indeed made to produce accurate meaningful limits for submarine use. To corroborate this finding, Mr. Ralph Wands, presently chief toxicologist and industrial hygienist at the Mitre Corporation and formerly director of the advisory center on toxicology at the National Academy of Sciences from 1964 to 1977 was asked to give the keynote workshop address on the "Early Documentation of Limits for Atmospheric Contaminants in Nuclear Submarines".

In his address, Mr. Wands told how the NAS advisory center on toxicology was formed and who the principle people were in its inception. An extensive literature collection was built at the center to provide a data base for atmospheric contaminants which was used to determine health risks and safe levels for submarine atmospheric contaminants. Mr. Wands indicated that the submarine habitability work was the first effort to evaluate human health effects in relation to continuous exposure to airborne chemicals. He also indicated that the NAS/NRC committee on toxicology closely interacted with the NAVY in developing recommendations for nuclear submarine contaminants in a few days or weeks and were based on the knowledge and judgement of some of the most outstanding toxicologists at the time. He concluded that the knowledge of toxicology and of air contaminants in confined spaces has expanded greatly since this original work and it is now necessary to update and expand the list of submarine atmospheric contaminants. A complete transcript of this talk is in Appendix 4.

"History of Submarine Atmosphere Control"
Dr. Homer Carhart

Dr. Homer Carhart from the Naval Research Laboratory Chemistry Division explained that the atmosphere contaminant limits for the first atmosphere manual were derived by an ad hoc committee and the TLV numbers were approved by the National Academy of Sciences. The list also provided limits for contaminants for which no on-board measuring method existed but were included just in case an onboard measuring method was developed. Dr. Carhart cited a number of examples of how contaminants get into the submarine atmosphere e.g., arsine and stibine from impurities in lead. He also cited a number of contaminant limits based not on parent compounds (such as methyl chloroform, ammonia, and freon 11) initially introduced into the atmosphere but on their breakdown products resulting from decomposition in the H_2 burner. Dr. Carhart introduced to the workshop the concept of lowering O_2 concentration in submarines to reduce fire potential. He explained how O_2 partial pressure sustains life and O_2 concentration is critical to sustain fires. He recommended the O_2 concentration on submarines would be best kept at 17% but would need at least 19% for cigarette smoking. He strongly recommended that the NRC evaluate the consequences of lowering O_2 to 19%. Correlated with this would be possible synergistic health effects of contaminants on humans. Dr. Carhart predicted that it's not a matter of <u>if</u> we're going to lose a submarine due to fire, but <u>when</u>, the situation becoming especially worse in wartime.

"Status of the CAMS II Atmosphere Analyzer"
<u>Dr. Jeffrey Wyatt</u>

Dr. Jeffrey Wyatt, diagnostics section head of the Chemistry Division of NRL discussed the current status of the CAMS II system (Central Atmosphere Monitoring System II). Since real-time measurements for many submarine atmospheric contaminants is presently impossible with the current CAMS I unit, the CAMS II program was started 4 years ago. The CAMS II was designed to have the high reliability of CAMS I yet be programmable to detect and record numerous contaminants. It will be deployed in the fleet in the late 1980's and replace not only the CAMS I but also the THA (Total Hydrocarbon Analyser) which has proved totally unreliable. Dr. Wyatt compared the CAMS I and II explaining that the CAMS I is a fixed analyser with analog controls whereas the CAMS II is a variable analyser with micro-processor controls. Every seven hours the CAMS II records all mass spectra on a tape cassette which can later be analysed and used for archival storage, one tape sufficing for a 90 day patrol. Dr. Wyatt further explained the operational technology of the mass spectrograph collectors of both the CAMS I and CAMS II. The CAMS II can be programmed to read certain atmospheric components of interest. The CAMS II infrared system for CO detection was also explained. The discussion briefly touched on the detection of O_2 which Dr. Wyatt feels should be held at 155 Torr. The newly designed O_2 generator in conjunction with CAMS II could hold the O_2 very accurately. He indicated that the unit passed all the strenuous shock and environmental tests all the while maintaining its factory calibration. The CAMS II using two detectors for high and low sensitivity can easily measure 1 PPM of a gaseous substance since 1PPM equals about 6000 ion counts/min and normal background for the instrument is about 6 ion counts/min which equals 1 PPB. Dr. Wyatt also indicated that contaminants can be transported through the sampling lines and accurately measured by the CAMS II unit if the line is equilibrated and the substance is in a steady state concentration. Dr. Wyatt concluded that the future looks good for monitoring atmospheric gases in the submarine with CAMS II and a permanent archive of contamination will be available to medical researchers.

"Submarine Fire Simulation"
Dr. Fred Williams

Dr. Fred Williams from the Chemistry Division at NRL presented a talk about "serious fire scenarios" aboard submarines. Dr. Williams initially discussed basic background information about submarine fires explaining that most are class C in origin, i.e., electrical, whereas liquid fuel is class B and solid trash is class A. He also showed a diagram of documented fires in submarines from 1977-81. The discussion narrowed to hull insulation fires involving the PVC nitrile rubber used on the inside of submarine hulls. Dr. Williams described documented hull insulation fires on the SSN Snook, Batfish, Finback and Liscomb. The fires all occurred while the submarines were in port. In the case of the Snook, a truck with 3500 pounds of CO_2 was backed on the dock, the entire contents of CO_2 dumped on the fire and this was still not enough to put the fire out. Water was finally used which put the fire out quickly but Dr. Williams explained that sailors don't like to use it since it can damage sensitive electronic components. In the Finback fire, carbon arcing on the deck of the fan room caused a penetration through the PVC nitrile rubber which had been used in a clandestine manner. Flames penetrated the nucleonics lab where trash in the frame bay caught fire, melted some aluminum, burned up the frame bay and ruptured a 100 psi airline used for EABs. Because of the four hull insulation fires, Dr. Williams expressed an apprehension about the flammability of the PVC nitrile rubber. He indicated that the National Bureau of Standards (NBS) had a program to study the intumescent paint as a fire protective agent for the insulation since a replacement material is currently unavailable and large quantities are used aboard submarines. The 1 to 1.5 acres of PVC nitrile rubber insulation for a small attack sub and up to 2.5 acres for a Trident provide a big fuel load of this material. Dr. Williams went on to describe the fire test facility at NRL called FIRE I. The apparatus was developed at NRL in 1981 under the auspices of the NAVSEA steering committee on submarine damage control. FIRE I is a 10,000 cu. ft. chamber in which investigators can build fires under pressure conditions similar to a potential submarine environment. The chamber has two decks and 3 frame bays with 4 frame members. The insulation used in the fire experiments have the same mil specs as that used on the submarines. This is also true of the paints and intumescent coatings. FIRE I also has nozzles for a nitrogen fire suppression system, ports for sampling devices, radiometers, and a trailer with associated equipment. since each fire experiment costs about $80,000, all the equipment is redundant. Dr. Williams alluded to a NBS test of the PVC nitrile rubber with intumescent coatings. Based on this test the researchers thought they had "bought" an additional 7 minutes of fire protection with the intumescent paint coating the PVC nitrile rubber but in July 1981 they found out differently. The test used 4 gallons of fuel which when ignited raised the pressure from 1 to 1.7 ata and the temperature to 800 degrees C in under 1 minute. A video tape of the fire showed that within 6 to 8 seconds the fire had spread to the 2nd deck and within 20 seconds there was no visibility on the 2nd deck although the infrared camera still showed the raging fire. Other video tapes shown included a class A trash fire in a frame bay with 40 milk cartons and 70% destruction of the insulation material and a hydraulic fluid leak fire. The first and third FIRE I test simulated closed boat conditions and the fourth fire test simulated open boat conditions. The open boat fire test showed that temperature and smoke are not such a problem as in the closed boat and that the destruction of the hull insulation in test 4 was about equal to the Finback fire. Dr. Williams showed graphs of temperatures, pressures, and contaminant gases resulting from the various fire scenarios in FIRE I. He also indicated that in the 2nd test of July 1981, the intumescent paint definitely contributed to the fire spread and fire load. Because of these potential fire problems on submarines, 5 contracts for the development of new materials for new submarine construction are being implemented. Two new materials include a poly-imide and a poly-phosphazine. The poly-imide is good but may not be good enough since it burns down about 50% whereas the poly-phosphazine is very good burning down only 3 to 4% into the material. Unfortunately there is no commercial base to produce the material in large quantities. Also, a new fiberglass material is being developed which can be glued up to bulkheads. Dr. Williams indicated that in FIRE I, he can stop any fire in 8 seconds with the nitrogen pressurization system, the nitrogen stopping flaming combustion but not smoldering combustion which can occur at 4 to 5% O_2. He also indicated in the question period that there are several reasons for not presently having the nitrogen pressurization system on submarines. First is the triggering problem, i.e., who makes the decision to use the system. Secondly, the 20,000 to 30,000 cu. ft. of nitrogen which is stored in flasks and quickly dumped into the submarine represent a radical change in operational procedure. He also mentioned that fire stops will be tried in specific frame bays for 1989 authorization. Since the frame bays are used as air return ducts, the fire stops could impede the air flow. Also the decks "float" to eliminate both sound transmission problems and expansion and contraction problems so fire stops can pose engineering problems as well. Dr. Williams concluded by saying an excellent opportunity exists for this group (workshop attendees) to have an impact on new designs for air revitalization equipment and contaminants and that a materials system approach is currently being evaluated by the National Academy for materials such as mattresses and cabling.

"Physiology of Combustion Products" Dr. Irving Einhorn

Dr. Irving Einhorn spoke on the physiology of combustion products from fires that are survivable. He indicated that combustion toxicology is an area that is most complicated and the least understood since materials usually perform differently in various types of fires. He also said that too often death is usually judged the end point, but incapacitation and faulty judgement are more important to consider in fires and of equal importance is the question of whether fire victims return to normal. Dr. Einhorn explained that CO is the major cause of fire related deaths and that cyanide is a co-contributer. He diagrammed the mechanisms of CO poisoning and the compounding problems of coronary vascular disease. The effects of smoke irritation were also described, the smoke being defined as a mix of gases, particulates, aerosols, and material fragments which may be hot, contain sensory and respiratory irritants, and cause obscuration. He also described the intoxication syndrome of graded toxicants to which humans will respond over a wide concentration range, e.g. CO, and limiting toxicants which can cause histotoxic anoxia, e.g. cyanide. He showed slides of pyrolysis products of both simple and complex plastics and indicated that small scale tests will not adequately show toxic combustion products. Needed are real full scale fires to show how products will burn along with the chemical analysis of smoke and experimental animals as models for the determination of combustion toxicity. He also explained about the histopathology of brain tissue resulting from exposure to smoke and toxic products and factors involving incapacitation. Dr. Einhorn summarized by saying that fire toxicology is a complex situation because it, like fire, dynamically changes. Also, in submarines, we have a different set of criteria than in the civilian sector where escape from a fire is possible. In submarines, a person must maintain his function or threaten the lives of the entire crew. While fires can be toxic, the toxicity aspects are secondary when considering the tremendous heat and lack of O_2 that can occur in a closed hatch situation as shown by Dr. Williams. In screening materials for small fire scenarios, then the combustion toxicology approach is important in order to determine the toxic contribution of materials or product assemblies in real fire situations.

"Historical Perspective of the Submarine Atmosphere" Manual Mr. Robert Nyers

Mr. Robert Nyers from NAVSEA related a history of the Submarine Atmosphere Manual, which is considered the "bible" of atmosphere control. Modern submarine atmosphere control began with the Nautilus, which initially could submerge for only about 44 hours due to atmospheric contamination of CO and CO_2, which were difficult to remove. In 1956, the "Submarine Habitability Cruise" was conducted on the Nautilus for 11 days with NRL scientists, Electric Boat and BUSHIPS personnel. They found that levels of CO ranged from 40 to 55 PPM, CO_2 from 1.2 to 1.5% and Freon-11 at 500 PPM. Although there was no atmosphere control in the early nuclear submarine program, the data generated by the "Submarine Habitability Cruise" led to the BUSHIPS instruction 91A90.4 discontinuing the use of organic solvents on submarines, limiting painting to 30 days prior to going to sea and directing the use of water based paints. Also the building of plastic models was prohibited during the cruise because of the styrene cement and solvents. The CO of the SSBN George Washington, after its first patrol in 1960, requested that the scattered submarine atmosphere information be put into one comprehensive document, this being endorsed by the commander of submarine squadron 14 and others. Requirements were that the manual teach the fundamentals and principles of submarine atmosphere control, set standards and limitations associated with atmospheric control, establish proper atmospheric operating procedures for normal and emergency use and establish a basis for the development and improvement of atmospheric control techniques by operational personnel. The Submarine Habitability Data Book first appeared in April, 1961 for comment on by forces afloat, the book being in a loose leaf format to effect easy amending. In September, 1962, the first book was issued to the fleet. In 1967, the book was revised and classified, the limits being lowered for some contaminants. Also, 5 pages were included on a materials list that was permitted, limited, or prohibited, the use of aerosols being prohibited. In 1974, a revised issue appeared and the 1976 issue described new equipment being installed on submarines. The current 1979 issue is structured the same as previous issues, however, the materials list has grown to 30 pages. When a new substance is evaluated for the list, NAVSEA gives the request to a Navy lab for review and analysis and then channels the information through the medical community and finally NEHC determines if the substance should be permitted, limited, or prohibited, the entire process taking about 2 years and costing about $10,000. An extensive question and answer period followed Mr. Nyers talk in which he addressed numerous problems associated with hardware, painting, compressing diving air in submarines, and AFFF fire extinguishers. Mr. Nyers ended by saying that not enough information exists in certain parts of the manual, e.g., in the medical aspects and should be revised.

Summary of First Session

CDR Kenneth R. Bondi

At the beginning session of the second day, Dr. Bondi asked the workshop group to consider the following areas for discussion after the formal presentations. 1.) Is it necessary to have the limits revised? 2.) What is the correct chain of command action for implementing a tasking document? 3.) What do we want to do specifically or what do we specifically want and don't want, e.g., in terms of listing limits and compounds. 4.) When should we do this? When is the appropriate time--this year? or when CAM II comes on line so we can get data and feedback from it. 5.) Do we need further input or do we need another meeting like this? 6.) Should we discuss other items such as an update of the Atmosphere Control Manual? 7.) Should we include other items into the manual or more medical input into the manual and/or more items on fire protocols, etc? 8.) Is there further research to be done?

"Development of Novel Theshold Limit Values for Submarines"
Mr. Jesse Lieberman

Mr. Jesse Lieberman discussed threshold limit values (TLVs) on submarines. First he explained how the ACGIH TLV committee is set up and organized into 3 specialized subcommittees which consider limits for organic compounds, hydro-oxy carbon compounds, and meso-halocarbon compounds. Committee members review and update present TLVs and develop new TLVs and documentation for chemical substances. Ad hoc committees are formed to address special problems, e.g., to establish short term exposure limits (STELs). The full committee meets twice annually and the sub-committee meets once annually with the results of all the committees discussed and reviewed by the ACGIH board of directors who submit committee recommendations to the ACGIH membership for final approval at the annual meeting. The preface to the ACGIH handbook outlines the general philosophy and policy of the committees. Sources of data the committees use include: 1.) industrial experience although the accuracy of the field measurements in some cases may be questionable, 2.) human experimental data, studies being limited in number, and 3.) animal experiments in which extrapolation to humans is necessary but subjective. Novel and unusual work schedules were discussed where TLVs for these exposures are obtained by multiplying the current TLV by some factor. Mr. Lieberman also discussed how ceiling values are calculated and how the ad hoc committees derive STEL values which can exceed the TLV by 5 times for brief periods, the STEL value being the concentration for which no effects are seen and the time weighted average (TWA) is not exceeded and the exposures repeated not more than 4 time/day with at least 60 minutes between exposures. A point he made very clear is that TLVs are arbitrary and are not to be used as an index for a toxicity hazard. TLVs are really designed to prevent gross over exposures to hazardous materials. He went on to describe the Brief and Lascala concept of novel exposures but indicated that since it was a new idea good medical surveillance is necessary. He also indicated that for continuous exposure some TLVs can be used but for others a safety factor would need to be considered. Mr. Lieberman summed up by saying that more data are needed to confirm the adequacy of a continuous exposure model keeping in mind the model's limitations. If one recognizes that TLVs are not fine lines between what is safe and what is dangerous then a model can be used to predict equal protection during special exposures particularly where good toxicological data are absent.

"Considerations in Setting Threshold Limit Value Standards" for Submarines
Mr. Christopher Eident

Mr. Christopher Eident, industrial hygienist at the Submarine Medical Center, presented his ideas on what should be considered in setting standards for submarine use. Mr. Eident talked of his experience with the submarine fleet for evaluating and monitoring workplace health hazards in the areas of asbestos removal and control, gas free engineering, hearing conservation, painting, and general repair work. He indicated that generally, the measureable contaminants on submarines during the times he has made measurements are well within the set limits. Mr. Eident went on to list the things he felt should be incorporated or amended in the Nuclear Powered Submarine Atmosphere Control Manual to make it a more informative document for use by the fleet. 1.) Determine if the standards are currently up to date with present toxicological knowledge. 2.) A rational or criteria should be established for setting individual standards which would allow flexibility. 3.) Added to the 90 day, 1 day and 1 hour limits should be STELs and IDLH (immediately dangerous to life and health) values. 4.) Incorporation of scenarios in the Atmosphere Manual to show what can happen (medically) if you exceed the TLV standard, the format being similar to NIOSH and OSHA manuals. 5.) Should the Atmosphere Manual be written as 2 documents, i.e., one for research with expanded technical and materials sections and the other as a working manual for fleet distribution? 6.) Should a committee add or delete substances from the list of TLVs now in the Atmosphere Manual? 7.) The materials list for prohibited and limited use items on submarines could be improved similar to the British list in which some information is given about the product. 8.) How to properly label and store potentially hazardous items aboard submarines could be added to the Atmosphere Manual. Mr. Eident followed these suggestions with an in depth description of the Submarine Base Hazardous Materials Management PROGRAM WHICH INVOLVES A computer generated list used in labeling hazardous products.

Discussion of Recommendations for Submarine Atmosphere Contaminant Limits Workshop Attendees

The formal presentations provided a core of knowledge, ideas, and needs from which the workshop group formulated recommendations. After several hours of discussion, major recommendations were worked out and include the following:

Major Recommendations

The major recommendation of the workshop committee was that parts of Chapters 2 and 3 of the Nuclear Powered Submarine Atmosphere Control Manual be revised. Ad hoc committees would be convened to revise or compose pertinent paragraphs to be incorporated into the atmosphere manual. The areas covered by the committees and their respective sponsors would include:

1) recommending lists of items which should be put in and taken out of the atmosphere manual (NRL),

2) format changes to aid in making Chapters 2 and 3 more concise (NAVSEA),

3) labelling and logging of hazardous materials with particular attention given to the type of packaging and quantity of material to be used on submarines (NEHC), and

4) the elaboration of scenarios for particular types of spills of hazardous materials and the proper corrective action to be taken when in port as well as at sea (integration of committees from NRL, NAVSEA, NEHC with NSMRL).

The charge to all committees would be to produce definitive statements which would be presented to the National Research Council for final approval before being incorporated into the Submarine Atmosphere Manual.

The workshop committee also recommended that a future Needs Committee be convened to study the feasibility of investigations in areas such as epidemiology and smoking on submarines and the health effects of 19% O_2 with respect to reducing the potential for fires at sea.

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IN REPLY REFER TO
NMRDC-41:sas
3910
Ser 41/65
27 May 1980

From: Commanding Officer, Naval Medical Research and Development Command
To: Chief of Naval Operations (OP-21)

Subj: Submarine Atmosphere Control

Ref: (a) Discussion, CAPT J. Vorosmarti (NMRDC-41) and CAPT C. Biele (OP-212), 22 December 1979

1. The following comments and recommendations concerning submarine atmosphere contamination are a result of reference (a) and subsequent discussions between CAPT J. Vorosmarti, Dr. H. Carhart and Dr. J. DeCorpo of NRL and are forwarded for your information.

a. The current limits for 90-day continuous exposure to atmospheric contaminants in the closed submarine environment have never been validated by actual animal or human exposures. They have been derived by taking existing industrial limits for 8 hr/day, 40 hr/wk exposures and lowering them by some factor to convert to continuous 90-day exposure limits. This approach is unsatisfactory for several reasons:

(1) The factors used to set up the limits are arbitrary and, in case of some substances, were set because of limitations in atmosphere control monitoring equipment.

(2) The limits may not be conservative enough for some substances. Although no long-term health problems have been detected in submariners, a large scale retrospective epidemiological study is now being conducted to ascertain if any disease states can be attributed to submarine duty.

(3) The standards do not address aerosols in submarine atmospheres; since the presence of aerosols can modify the route of entry of contaminants, as well as being contaminants themselves, they must also be investigated.

(4) The current limits may be too conservative, with the result that: unwarranted restrictions may be placed on materials that are brought aboard for use during patrols; unnecessary ventilation may be undertaken with the possibility that the location of the submarine is revealed; or atmosphere control equipment may be unduly complex and costly.

2. One of the problems encountered in reviewing this situation is that the list of contaminants in the recent Nuclear Submarine Atmosphere Control Manual has changed very little from the list published in the original Submarine Atmosphere Habitability Data Book. There is good reason to believe that over the past 20 years, the contaminants present in submarine atmospheres

have changed. However, since routine monitoring of atmospheres for contaminants has not been done for 10 years, it is not known what is present in the newer classes of submarines.

3. The following actions are recommended to address the problems discussed above.

a. Conduct a literature search to determine what is already known about the health effects of long-term exposure to contaminants encountered in submarine atmospheres; determine what factors are used by OSHA and other standard-setting agencies to establish safe threshold levels or to determine that no safe threshold value exists.

b. Using methodology already developed by NRL, reinstate sampling of submarine atmospheres to determine what contaminants are present.

c. Develop a priority list of contaminants known to be present in submarine atmospheres.

d. Perform toxicologic studies in animals on high priority contaminants.

4. Your comments concerning these proposed actions are requested.

J. D. BLOOM

Copy to:
NSMRL
BUMED 3C2
NRL 6180, 6110

DEPARTMENT OF THE NAVY
OFFICE OF THE CHIEF OF NAVAL OPERATIONS
WASHINGTON, D.C. 20350

IN REPLY REFER TO

Ser 212F/714221
AUG 22 1980

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CO	
AO	
03	
20	

From: Chief of Naval Operations
To: Commanding Officer, Naval Medical Research and Development Command

Subj: Submarine Atmosphere Control

Ref: (a) NMRDC ltr 3910 ser 41/65 of 27 May 1980 (NOTAL)
(b) Discussion, CAPT J. Vorosmarti (NMRDC-41) and CAPT C. Biele (OP-212), 22 December 1979

1. Reference (a) provided recommended actions concerning submarine atmosphere concerns discussed during reference (b). The recommendations were reviewed and were found to fulfill the submarine community's current needs to identify significant problem areas in submarine atmosphere control.

2. Request you take paragraph 3 of reference (a) for action within present budget.

3. By copy of this letter, CHNAVMAT and ONR are requested to provide available support to this program.

F. B. KELSO, II
By Direction

Copy to:
ONR
CHNAVMAT
NSMRL
BUMED 3C2
NRL 6180, 6110

NATIONAL RESEARCH COUNCIL
ASSEMBLY OF LIFE SCIENCES
2101 Constitution Avenue Washington, D. C. 20418

BOARD ON TOXICOLOGY AND
ENVIRONMENTAL HEALTH HAZARDS

May 26, 1982

Kristopher M. Greene
Captain, Medical Corps, U.S. Navy
Submarine & Diving Medicine Program Manager
Department of the Navy
Naval Medical Research and Development Command
National Naval Medical Center
Bethesda, MD 20014

Dear Captain Greene:

This letter is to confirm our phone conversation of today, and provides information in relation to your earlier request for information in the phone conversation of April 29, 1982. The basis of your request was an attempt to determine whether there is information in the Committee on Toxicology records which identifies the approach and method used by Committee members in identifying exposure limits for contaminants in submarine atmospheres.

We have reviewed the files and reports of the Committee back to its beginnings in the mid-1950s. At no time have we found any information or reports which suggest a methodological approach in determining acceptable exposure limits for extended periods of time in confined environments, i.e., submarines.

Attached is a memorandum dated May 17, 1966 from N.E. Rosenwinkel, then Chief of the Bureau of Medicine and Surgery, Department of the Navy. This memorandum requests the Advisory Center on Toxicology of the Academy to update the Navy's 1962 document, Submarine Atmosphere Habitability Data Book, with regard to acceptable concentrations of various contaminants found in nuclear submarines. The NAS Advisory Center's reply, with accompanying Committee on Toxicology tables, from May 1966 are also appended.

There is also enclosed a copy of a 1979 Committee on Toxicology publication, Criteria for Short-term Exposures to Air Pollutants. This report describes the various factors which are taken into consideration when developing acceptable concentrations of air pollutants under various environmental situations.

I hope this information will be of use and assistance to you. Please contact me if further information is needed.

Very truly yours,

Gordon W. Newell

Gordon W. Newell, Ph.D.
Associate Executive Director

GWN/cvs

Enclosures

KEYNOTE ADDRESS

EARLY DOCUMENTATION OF LIMITS FOR ATMOSPHERIC CONTAMINANTS IN NUCLEAR SUBMARINES

RALPH C. WANDS

The MITRE Corporation
McLean, Virginia 22102

PRESENTED AT THE WORKSHOP ON ATMOSPHERIC CONTAMINANTS IN NUCLEAR SUBMARINES, NAVAL SUBMARINE BASE, NEW LONDON

September 7-8, 1983

At 10:00 AM on January 29, 1957, a meeting was called to order at the National Academy of Sciences that has had a beneficial effect, to some degree, on every resident of the United States and, to a greater degree, on those serving in the isolated and confined spaces of nuclear-powered submarines and of manned spacecraft. At this meeting, Dr. Douglas Cornell, speaking for the Academy, announced the formation of a new office, the Toxicology Information Center, and introduced its Director, Dr. Harry W. Hays. The task of Dr. Hays and the Center was to provide "advice, information and interpretations" regarding toxicological information to the Armed Forces and the Atomic Energy Commission. These agencies provided $5,000 each to support the Center for its first year of activity. A Committee on Toxicology, chaired by Dr. Harold C. Hodge of the University of Rochester, provided its knowledge and experience without fee to the service of the Center. In 1958, the budget for the Center was increased to $60,000 and an additional $20,000 was contributed by the Bureau of Ships for the Center's use in evaluating "a large number of potentially toxic materials which might be used aboard nuclear submarines." Already by that time the Center had submitted five reports on chemicals of concern to the submarine fleet.

VIEWGRAPH #1

Let me introduce you to some of the people (Table I) who served in this program of collecting and evaluating toxicology information related to submarine atmospheric habitability. This Table lists the members of an informal working group that met weekly to review lists of items going on board these submarines. They weeded out the hardware items and suggested priorities for toxicological evaluation of chemicals by the NAS/NRC Committee on Toxicology.

Mr. Morris Alpert, known to all as "Mickey", was the key person in code 620 of BuShips who provided the lists of materials and the funding of the project, as well as serving as liaison to the other vital parts of the Navy's program, such as the Naval Research Laboratory and its analytical chemistry capabilities.

Captain Jacob Siegel created and directed the Navy Toxicology Unit (NTU) at the Naval Medical Research Laboratories in Bethesda, MD. He arranged, with the help of Mr. Bluntchli of Ciba, for the fabrication and installation of five chambers at NTU for continuous exposure of experimental animals by the inhalation route for the evaluation of the chronic toxicity of air contaminants in the submarines. These chambers were designed by Dr. Hodge and his colleagues at the University of Rochester and they are still the basic tool for inhalation studies in most of the laboratories today. These chambers are designed to assure uniform flow patterns and distribution of gases. They are equipped with several ports for monitoring the concentration of the test material throughout the chambers.

Dr. Hays, by means of the extensive collection of literature which he built at the Center, was able to provide the data base for prioritizing the toxicological testing of atmospheric contaminants in the submarines. Dr. Hays also served as the facilitating staff officer for bringing the best brains in toxicology in the country to bear on the questions of health risks and safe levels of these materials in the air of the submarines. To the best of my knowledge, this was the first effort to evaluate the human health effects of continuous exposure to airborne chemicals. In the perspective of EPA's current problems with air pollution, this submarine program may seem simple. However, this submarine atmospheric habitability work was indeed pioneering, and without it and subsequent similar programs at NASA, the EPA would not have been as far ahead as it is now in addressing the air pollution problems of today.

VIEWGRAPH # 2

I would like to introduce you (Table II) to those members of the scientific community at large who donated their knowledge and their time to serve on the Academy's Committee on Toxicology during the busiest years of the submarine habitability program while, at the same time, serving the needs of the other sponsors of the Center. As is customary for all committees of the NAS/NRC, these people were only reimbursed for their travel and living expenses.

There were three chairmen of the Committee on Toxicology for the years 1958 through 1966 which were the peak years of these submarine studies. These chairmen were Dr. Harold C. Hodge, University of Rochester; Dr. Norton Nelson, New York University; and Dr. Arnold J. Lehman, U.S. Food and Drug Administration.

It is most important to point out that these members of the Committee on Toxicology did not operate in an isolated ivory tower. It was our practice at the Center to invite 25 regular attendees to the Committee's meetings, the representatives of the technical and administrative staffs of the sponsoring agencies, as well as others having knowledge applicable to the problems confronting the Committee. This policy provided a mechanism whereby the Committee members obtained a detailed and thorough description of the problems presented to them. At the same time, the representatives of the sponsors were given an understanding of the kind of thinking behind the formal reports of the Center. In many ways, this was the "Camelot" of Toxicology.

VIEWGRAPH #3

The next few viewgraphs (Table III) show the extensive list of 32 recommendations of limits for atmospheric contaminants in submarines as provided to the Navy by the Committee. Many of these are "crew-related" such as CO_2, cigarette lighter fluid, and methane. Others are "equipment-related" such as stibine and arsine from battery charging, ozone from the electrostatic precipitators used to remove particulates from cigarette smoking or monoethanolamine from the CO_2 scrubber. All concentrations given in this and the next Table are in units of ppm. The 24-hour values represent emergency levels which are not to be repeated until all affected personnel have completely recovered. A word of explanation is needed about the hydrocarbon limits. The total atmospheric level for hydrocarbons is 101 ppm of which 1 ppm may be benzene, 50 ppm may be other aromatic hydrocarbons such as toluene or xylene, and 50 ppm may be non-aromatic hydrocarbons including cyclohexane and heptane, but not including methane for which there is a separate standard.

VIEWGRAPH #4

It is inevitable that there will be emergencies in any complicated system of humans and machinery, especially in a military system. In a nuclear submarine, you are on your own whenever an emergency arises. You cannot call the fire department or the factory representative. Accordingly, the Navy developed a list of atmospheric contaminants which were likely to be encountered at elevated concentrations during various kinds of emergencies, including spills. This list was presented to the Committee for advice on how much might be tolerated (Table IV) without serious toxic effects for the one hour required to reduce the levels to the 24-hour standards after which the normal levels were to be achieved. It is expected that during these emergency exposures, there may be adverse effects on the crew such as increased respiratory rate from elevated CO_2, or headache from increased CO, or respiratory irritation from ammonia, phosgene or sulfur dioxide. These acceptable effects are not expected to interfere with essential functioning of crew members and all such effects are anticipated to be fully reversible. To the best of my knowledge there are no reports of adverse health effects while these standards were observed.

Let me close with one or two anecdotes indicative of the complexity of the problems and the associated decision-making that went into the selection of some of these values.

It is necessary to provide thermal insulation on the interior bulkhead of the occupied hull of a submarine. The insulation provides thermal comfort, prevents condensation and corrosion on the bulkheads, and aids in external noise reduction. This insulation was applied in the shipyard during construction of the hull. In view of the inevitability of welding and other ignition sources in the shipyard, a non-flammable solvent was required for the adhesive holding the insulation to the bulkheads. This led to the use of chlorinated solvents. Quite sometime later, it was discovered that these and other volatile components were diffusing out through the insulation into the living spaces of the submarine. These, like other gases and vapors, were being passed through the Hopcalite catalytic burner designed to convert CO to CO_2. Both irritant and toxic products resulted, such as formaldehyde from methanol and dichloroacetylene from the chlorinated adhesive solvent. The latter compound was known to be very toxic and explosive. This situation led to an urgent study at the NTU where Captain Seigel built a device to generate dichloroacetylene at a controlled rate for delivery into the inhalation toxicity chambers in various concentrations.

A similar situation developed in conjunction with the selection of electrostatic precipitators to remove small particulates, generated mostly from cigarettes, from the atmosphere. (Cigarette smoking was considered essentially uncontrollable.) There were two basic designs of precipitators available, one operated at low voltage, required a large space, and had considerable weight. The other was lightweight and small, but it produced ozone from the high voltage corona discharge. This was the reason for the ozone level shown in the last two viewgraphs.

In conclusion, the NAS/NRC Committee on Toxicology was able to interact closely with the Navy in developing, within a few days or weeks, recommendations for critical contaminants in the atmosphere of nuclear submarines. These recommendations were based on the knowledge and judgement of some of the most outstanding people in the field of toxicology at that time and upon the technical support of the staff of the Center under the leadership of Dr. Harry W. Hays. Your test of time is the witness to the effectiveness of this procedure. However, our knowledge of toxicology in general and of air contaminants in confined spaces especially, has greatly expanded. It is time to update and expand this list. I will be pleased to help in any way I can.

At this point I would like to express my sincere appreciation to Dr. Hays, Captain Siegel and my former colleagues at the Advisory

Center on Toxicology, Miss White and Mrs. Paulson for their assistance in gathering this information and in reviewing my manuscript. As a former naval officer, I consider it a great privilege to be with you today and to have served as an assistant to Dr. Hays and the Committee on Toxicology in developing these standards.

Thank you.

TABLE I

INFORMAL SCREENING GROUP FOR ATMOSPHERIC CONTAMINANTS
IN NUCLEAR SUBMARINES
(ca 1960)

MR. MORRIS ALPERT - BUSHIPS

DR. HARRY HAYS - NAS/ACT

CAPTAIN JACOB SIEGEL, USN-NTU

TABLE II

COMMITTEE ON TOXICOLOGY
NATIONAL ACADEMY OF SCIENCES
(1958-1966)

HAROLD C. HODGE, UNIVERSITY OF ROCHESTER, CHAIRMAN	1950-58
ARNOLD J. LEHMAN, FDA, CHAIRMAN	1950-70
NORTON NELSON, NEW YORK UNIVERSITY, CHAIRMAN	1952-61
MERRIL EISENBUD, NEW YORK UNIVERSITY	1952-62
DAVID FASSETT, EASTMAN KODAK	1955-58
RICHARD FORD, TEXAS MEDICAL CENTER	1955-58
WILLIAM G. FREDERICK, UNIVERSITY OF MIAMI	1962-64
HORACE W. GERARDE, ESSO RESEARCH AND ENGINEERING	1958-66
CHARLES H. HINE, UNIVERSITY OF CALIFORNIA	1955-58
ELLIOTT A. MAYNARD, UNIVERSITY OF ROCHESTER	1958-61
CARL A NAU, TEXAS MEDICAL CENTER	1958-61
VERALD K. ROWE, DOW CHEMICAL	1964-72
LESLIE SILVERMAN, HARVARD UNIVERSITY	1952-57
HENRY F. SMYTH, JR., CARNEGIE INSTITUTE OF TECHNOLOGY	1964-70
HERBERT E. STOKINGER, U.S.P.H.S.	1952-75
WILLIAM L. SUTTON, EASTMAN KODAK	1964-69
JAMES L. WHITTENBERGER, HARVARD UNIVERSITY	1958-61
JOHN A. ZAPP, JR., DUPONT-HASKELL	1952-64

TABLE III

DESIGN CRITERIA FOR ATMOSPHERIC CONTAMINANTS
IN NUCLEAR SUBMARINES

COMPOUND	RECOMMENDED CONCENTRATIONS[a]	
	24 HOURS[b]	90 DAYS
ACETONE	2,000	300
ACETYLENE	2,500	2,500
AMMONIA	50	25
ARSINE	0.1	0.01
BENZENE	100	1.0[c]
CARBON DIOXIDE	10,000	5,000
CARBON MONOXIDE	200	25
CHLORINE	1.0	0.1
DICHLORODIFLUOROMETHANE (R-12)	20,000	1,000
1,2-DICHLORO-1,1,2,2-TETRA-FLUOROETHANE (R-114)	20,000	1,000
ETHANOL	500	100
FLUOROTRICHLOROMETHANE (R-11)	20,000	1,000
HYDROCARBON SOLVENTS (STODDARD SOLVENT, MINERAL SPIRITS, PAINT THINNER, LIGHTER FLUID, KEROSENE)	500	50[c]
HYDROGEN	3,000	3,000
HYDROGEN CHLORIDE	4.0	1.0
HYDROGEN FLUORIDE	1.0	0.1
ISOPROPANOL	200	50

TABLE III (concluded)

COMPOUND	RECOMMENDED CONCENTRATIONS[a]	
	24 HOURS[b]	90 DAYS
MERCURY	2.0 mg/m^3	0.01 mg/m^3
METHANE	5,000	5,000
METHANOL	200	10
METHYL CHLOROFORM	500	200
MONOETHANOLAMINE	3.0	0.5
NITROGEN DIOXIDE	1.0	0.5
OZONE	0.1	0.02
PAINT THINNER	--SEE HYDROCARBON SOLVENTS--	
PHOSGENE	0.1	0.05
STIBINE	0.05	0.01
SULFUR DIOXIDE	5.0	1.0
TOLUENE	100	50[c]
TRIARYL PHOSPHATES[d]	50 mg/m^3	1.0 mg/m^3
VINYLIDENE CHLORIDE	25	2.0
XYLENE	100	50[c]

[a]All concentrations are parts per million (ppm) by volume unless otherwise noted.

[b]All 24-hour values represent emergency levels and are not to be repeated until all affected personnel have completely recovered.

[c]Total non-aromatic hydrocarbon solvents shall not exceed 50 ppm. Total aromatic hydrocarbon solvents other than benzene shall not exceed 50 ppm. Thus, the total atmospheric concentration of all hydrocarbons may be as high as 101 ppm provided no more than 50 ppm are aliphatic hydrocarbons, no more than 1 ppm is benzene, and no more than 40 ppm are aromatic hydrocarbons other than benzene.

[d]Assumes maximum of 2.0% ortho isomer.

TABLE IV

EMERGENCY EXPOSURE LIMITS FOR ATMOSPHERIC CONTAMINANTS
IN NUCLEAR SUBMARINES

COMPOUND	60-MINUTE EEL (ppm)[a]
AMMONIA	400
CARBON DIOXIDE	25,000
CARBON MONOXIDE	200
DICHLORODIFLUOROMETHANE (R-12)	30,000
1,2-DICHLORO-1,1,2,2-TETRA-FLUOROETHANE (R-114)	30,000
FLUOROTRICHLOROMETHANE (R-11)	30,000
HYDROGEN CHLORIDE	10
HYDROGEN FLUORIDE	8.0
HYDROGEN SULFIDE	50
METHYL CHLOROFORM	1,000
MONOETHANOLAMINE	50
NITROGEN DIOXIDE	10
OZONE	1.0
PHOSGENE	1.0
SULFUR DIOXIDE	10

[a]These are true emergency exposure limits and it is assumed that the engineering facilities will reduce these values to no more than the 24-hour levels within the 60-minute period.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Scientists and engineers from several Naval laboratories and representatives of various government contracting organizations attended this two-day workshop on submarine atmosphere contaminants.

Subjects discussed in the first session were: limits for atmosphere contaminants in nuclear submarines; the history of submarine atmosphere contaminants; the CAMS II Atmosphere Analyzer; submarine fire insulation, and combustion products,

item no. 20--continued

During the second session, discussions concerned the development of novel threshold limit values for submarines, and setting of threshold limit value standards for submarines. Recommendations for submarine atmosphere contaminant limits were offered by workshop attendees.