

AIRBORNE TRACE CONTAMINANTS OF POSSIBLE INTEREST IN CELSS

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ABSTRACT

One design goal of CELSS for long duration space missions is to maintain an atmosphere which is healthy for all the desirable biological species and not deleterious to any of the mechanical components in that atmosphere. CELSS design must take into account the interactions of at least six major components; (1) humans and animals, (2) higher plants, (3) microalgae, (4) bacteria and fungi, (5) the waste processing system, and (6) other mechanical systems. Each of these major components can be both a source and a target of airborne trace contaminants in a CELSS. A range of possible airborne trace contaminants is discussed within a chemical classification scheme. These contaminants are analyzed with respect to their probable sources among the six major components and their potential effects on those components. Data on airborne chemical contaminants detected in shuttle missions is presented along with this analysis. The observed concentrations of several classes of compounds, including hydrocarbons, halocarbons, halosilanes, amines and nitrogen oxides, are considered with respect to the problems which they present to CELSS.

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INTRODUCTION

The ultimate objective of the CELSS research program is to construct a life support system for long duration space missions capable of providing food, water and oxygen and of recycling wastes. The major problem in developing such a system can be viewed as achieving mass balance between subsystems by controlling flows of matter, energy and information. Before that ultimate goal is reached, a preliminary objective for the CELSS research program would be to construct a life support system for long duration space missions capable of maintaining an atmosphere healthy for all the desirable biological species and not deleterious to any of the mechanical components. In order to approach this preliminary objective it will be necessary to predict, identify and control the trace contaminants which any CELSS components could release that would be harmful to any other component.

The inclusion of higher plants or microalgae in a CELSS system almost certainly guarantees that there will be problems with trace contamination. That is because many species of plants and algae have evolved allelopathic responses; they excrete or emit substances which have the effect of lessening the competition for local resources by other individuals (J. Friedman and G. R. Waller, 1985, TIBS 10, 47-50). Early experiments with closed systems including both plants and algae revealed that the algae released a volatile substance that could seriously damage or kill the plants (M. M. Korotayeu, et al., 1964, Problemy Kosmicheskoy Biologii 3, 204), a result that could be attributed to allelopathy and autotoxicity in the the algae (R. Pratt, et al., 1944, Science 99, 351-352).

At a CELSS workshop conducted in September 1984 some concern was expressed that the problems of controlling of trace contamination deserved more study and research. When data on trace contaminant detection, identification and control on space shuttle missions became available, it seemed reasonable to approach the study of potential trace contamination problems in CELSS by examining actual trace contamination problems on the shuttle.

APPROACH

Identification of Major Subsystems

There are many ways in which the components of a life support system can be grouped into subsystems depending on the objectives of the analysis. For the purposes of analyzing sources and targets of airborne trace contaminants, six major subsystems of a CELSS are identified. These subsystems are referred to in Table 1.

- H -- Humans and possibly other animal species consume O_2 , H_2O , food, energy and information and generate CO_2 and waste.
- P -- Higher plants consume CO_2 , H_2O and energy, and generate O_2 , food and waste.
- A -- Microalgae also consume CO_2 , H_2O and energy, and generate O_2 , food and waste.
- B -- Bacteria, virus and fungi will in most cases themselves be considered as potential airborne trace contaminants. However, some may be intentionally introduced as sources of food, as aids in processing either food or waste, or as controls to inhibit the growth of other more harmful bacteria and fungi.
- M -- Machines, including specifically all the surfaces enclosing and connecting the other subsystems, may potentially outgas, degrade or react to release volatile contaminants. The machine subsystem may also accumulate and concentrate volatile contaminants released by other subsystems.
- W -- The waste processing system considered separately from the machine subsystem includes the waste products of the biological subsystems and all the intermediate materials of that processing. Inherently this subsystem would be a major source of volatile contamination should it malfunction. It could also be a highly vulnerable target for unanticipated volatile contaminants.

The chemical elements involved in the mass balance problem can be grouped according to their biological significance. Of primary importance are C, O, H, and N; of lesser importance are P and S; and of minor importance are Na, K, Mg, Ca, Fe, Cu, Zn, Cl and maybe a few others such as Br, I, Si, Mo, V and W. The other 84 chemical elements will probably not enter the mass balance problem but may be of interest as trace contaminants. The major chemical species involved in the mass balance problem are O_2 , CO_2 , H_2O , food (CHNO) and to a lesser extent N_2 .

An analysis of airborne trace contaminants will focus on minor components in this mass balance problem: those very minor components which might be missed even if the mass equations were balanced to the fourth or fifth significant figure, but components which could nonetheless have a serious detrimental effect on at least one major subsystem. Drawing an analogy from toxicology, the concentration dependence of the detrimental effects of such trace contaminants can be characterized in two ways.

- (1) A contaminant will damage a subsystem when it persists above a minimum atmospheric concentration for a period on the order of days: a condition analogous to chronic toxicity.
- (2) A contaminant will damage a subsystem when it is released in such quantities that it exceeds a minimum atmospheric concentration: a condition analogous to acute toxicity.

The airborne trace contaminants are defined to be those components which are gases or can be volatilized at normal temperatures and pressures, or which can be transported on normal atmospheric currents. Table 1 is a listing of classes of chemical compounds which are potential airborne trace contaminants in a CELSS. The table includes an evaluation of which major subsystems could be sources and which could be targets for each class of compounds. It would be appropriate to offer a

few comments on how these airborne trace contaminants might be detected and eliminated in a CELSS.

Methods of Detection

Only two methods of airborne trace contaminant analysis will be generally applicable, IR and GC/MS. Visible and UV light monitoring of airborne bacteria, fungi and their spores will be important. Monitoring of toxic, volatile trace contaminants should be done at a frequency proportional to their toxicity, and that requirement well mean that monitoring will have to be done in real time, on board the space craft. In addition some compounds might be monitored as indicators of stress on particular subsystems, for example ethylene, ethane and methane could be monitored to indicate stress on the higher plants.

Methods of Elimination

In order to remove airborne trace contaminants it will be necessary to collect and chemically transform them selectively. In a completely closed system regeneration of the constituent elements of trace contaminants would be necessary. For incompletely closed systems chemical transformation of trace contaminants is not necessary only insofar as their loss does not significantly affect the mass balance. Storage of collected contaminants would be inherently hazardous, but jettisoning of that material might be unacceptable because it would compromise experiments or procedures dependent on vacuum conditions near the space craft.

OBSERVATIONS

Table 2 is a listing of the airborne trace contaminants which have been observed on the shuttle missions to date. They are grouped according to the classification scheme in Table 1. These trace contaminants were collected on space shuttle missions either in gas sample bottles manually operated by the astronauts, or in activated charcoal filters or canisters of lithium hydroxide which were components of the environmental control system. The contaminants were later identified in ground laboratories by GC/MS. A few particular contaminants which have been observed, and some which have not been observed, require special comment.

Methane is assumed to have a biological origin, the humans and their associated bacteria. It has a low toxicity, so it not dangerous in that respect. However it is not readily adsorbed by charcoal and in some simulations its atmospheric concentration has risen high enough to present a fire hazard.

Dimethyl benzene (toluene), which is carcinogenic, has been observed as an airborne contaminant on every shuttle mission. On one shuttle mission the amount of toluene in the gas bottle samples indicated that the spacecraft maximum allowable concentration (SMAC) had been exceeded. Although the source of the toluene was not positively identified, it is thought that an astronaut had taken gas bottle samples while holding an uncapped marking pen.

A large number of silicone compounds have been observed in fairly high concentrations. These compounds are notoriously difficult to remove once they have been applied to surfaces. Contamination from them is generally not considered to pose a problem because of their low toxicity to humans. Two silicone contaminants which are toxic and have been observed are propylfluorosilane and propyldifluorosilane.

On several occasions relatively large amounts of bromotrifluoromethane have been observed. This mildly toxic compound is released by leaking fire extinguishers. Twenty-three other halocarbons have also been observed, some of them at relatively high concentrations. Most of these halocarbons are thought to arise from the outgassing of residual solvents used for degreasing and removing excess silicones.

Dichloroethyne (C_2Cl_2) is an extremely toxic compound not known to be a contaminant or an outgassing product of any substance present in the shuttle. However it can be produced by dehydrohalogenation of trichloroethene (C_2HCl_3) in strong base. This latter compound is commonly used as an industrial solvent, for degreasing and dry cleaning. Undoubtedly it has been used inside the shuttle because it has also been trapped and detected in the activated charcoal filters. However, the activated charcoal filters did not collect all the trichloroethene. Some of it must have passed through the charcoal to the lithium hydroxide canisters which are next in the air flow path and are used to scrub carbon dioxide from the air. The trichloroethene reacted in the lithium hydroxide canisters to form dichloroethyne which passed back out into the cabin atmosphere. It was then picked up in a subsequent pass through the activated charcoal filters.

The shuttle missions have had some variability in the number of airborne bacteria; between 100 and 350 culture forming units per cubic meter have been observed including both aerobes and anaerobes. The spores of one major fungus, Candida albicans, have been observed, but fungal growth does not appear to be a problem on the shuttle. If there is a problem, it might not be evident until longer duration missions are undertaken. On the earth, gravity acts like a filter limiting the propagation of airborne fungal spores. In a low gravity environment the spores could be expected to propagate more readily.

Among the compounds which have not been observed are hydrogen cyanide and benzonitrile, although they have been observed in tests involving the pyrolysis of electrical insulation. Ethene (ethylene) which has diverse and striking effects on higher plants at concentrations as low as 5 ppb, has also not been observed.

DISCUSSION

The trapping of dichloroethyne in the shuttle illustrates particularly well why great care is required in studying the interactions of CELSS subsystems. The way in which it must have been generated in the space shuttle clearly illustrates how two subsystems can interact to produce hazardous trace contaminants. The possibility that chloroethyne and dichloroethyne could be generated in that way had been pointed out by R. Saunders (1967, Arch. Environ. Health 14, 380-384) in reports of very early space flight simulations.

Another lesson provided by the odyssey of chloroethyne in the space shuttle is that the activated charcoal filters have a finite capacity that can be overwhelmed with unpleasant consequences. In order to be effective, activated charcoal filters must be changed on a regular basis. For long duration space missions this means that large numbers of spent filters must either be jettisoned, stored and returned to earth, or recharged with the discharged contaminants being either evacuated or converted by the waste processing system. Only the last alternative can be considered desirable in a CELSS. The problems with activated charcoal filters can be expected to become even more critical when higher plants or microalgae are included in a CELSS because of the relatively large amounts of volatile organic compounds which they produce.

From the available trace contamination data, the class of compounds posing the most immediate danger is the haloalkanes. They meet both criteria for the definition for chronic contaminants; they are not completely adsorbed or retained by the activated charcoal filters, so they tend to persist in the shuttle atmosphere, and as a class the haloalkanes are chronic toxins to humans. It must be hoped that steps will be taken to limit the use of haloalkanes on the shuttle, on the space station and certainly in a CELSS.

Another class of compounds which presents a large potential danger as trace contaminants is the siloxanes. These compounds, like the haloalkanes, tend to be chemically inert, but unlike the haloalkanes, they are mostly nontoxic to humans. The low molecular weight compounds are easily volatilized, not readily adsorbed by activated charcoal and tend to persist in spacecraft atmospheres. They have been observed as trace contaminants in every spacecraft since the Mercury capsule. Unfortunately these compounds do present a number of problems. First, their tenacious persistence on surfaces leads to the heavy use of haloalkanes in efforts to remove them. Second, the alterations in the surface properties of silicate glass which they can produce at even low concentrations might seriously compromise cell tissue culture work envisioned for future shuttle experiments. Third, no research has been done on the long term effects of low atmospheric concentrations of these compounds on plants. Fourth, for some experimental waste processing systems, it is possible that these compounds could be difficult to handle.

Another potential source of trace contamination is aging synthetic polymers. With time all synthetic polymers suffer depolymerization which is usually accompanied by the release of a large number of gaseous compounds. Such polymers have been used extensively in the shuttle and presumably they will continue to be used in the construction of spacecraft for many years. The aging of synthetic polymers is accelerated by exposure to light, ionizing radiation, trace contaminants, water and oxygen. In spacecraft the aging processes could be worse because of high energy radiation and atmospheres of enriched oxygen. (Oxygen radical species are created in proportion to the partial pressure of oxygen, but in pure atmospheres there is less probability for destructive collisions so the radical species can reach higher concentrations.) In a CELSS including either higher plants or microalgae, the exposure to light and humidity can be expected to accelerate the aging of polymers used in the growing chambers.

An enumeration of the airborne trace contaminants observed on the shuttle is useful in determining what contamination problems can be dealt with in the current life support system, a system consisting of just human, bacterial and machine subsystems. For a CELSS including a waste processing system and either higher plants or algae, the list of trace contaminants will certainly include even more compounds from the classes listed in Table 1. With a greater variety of trace contaminants present, the probability of synergistic effects also becomes greater; several trace contaminants could react to form an even more hazardous compound, a target substance could be more susceptible to a combination of contaminants, or a contaminant could catalyze a reaction which released more contaminants. Fortunately, with more trace contaminants present, there is also an increased probability that some of them could react and become neutralized, but that is the sort of good fortune that should not be relied upon. In a CELSS it will be very important to be able to identify trace contaminants rapidly and to have a data base of chemical properties and reactions which can be used to predict the consequences of contamination.

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TABLE 1. Potential Airborne Trace Contaminants,
Sources and Targets in CELSS

G indicates that the compound is generated by the listed subsystems, E indicates that the compound has an effect on the listed subsystems, and H, P, A, B, M and W indicate the appropriate subsystems as defined in the APPROACH Section of this paper.

1) Hydrocarbons

- .1) methane, ethane, other alkanes; G:HPABM
- .2) ethene, other alkenes, terpenes; G:PAB, E:P
- .3) ethyne, other alkynes; G:PM, E:HP
- .4) benzene, alkylbenzenes, indan, naphthalene; G:M (solvents), E:HPAB

2) Nitrogen Containing

- .1) nitrogen oxides - N_2O , NO, N_2O_3 , NO_2 , N_2O_4 , N_2O_5 , NO_3 , N_2O_6 ; G:PAMW (fuels, atmospheric reactions), E:HPAM
- .2) organic nitrogen oxides - RNO (nitroso), RONO (nitrite), RNO_2 (nitro), $RONO_2$ (nitrate), R_2NNO (nitrosamine); G:M (fuels), E:HPAB
- .3) amines - NH_3 , RNH_2 , R_2NH , R_3N , R_4N^+ ; G:HPABW (cleaning and disinfecting compounds), E:HPAB
- .4) hydrazines - N_2H_4 , $RNHNH_2$, $RNHNHR$, R_2NNH_2 , R_2NNR_2 ; G:M (fuels), E:HPABM
- .5) amine oxides - NH_2OH , $RNHOH$, R_2NOH , R_3NO ; G:M (possibly atmospheric reactions), E:HPAB
- .6) amino alcohols - 2-aminoethanol; G:W (carbon dioxide scrubber), E:HPA
- .7) cyanides - HCN, RCN; G:PAM (pyrolysis), E:HPAB
- .8) cyanates (ROCN), isocyanates (RCNO); G:MW (degradation of urea and polymers), E:HPAB
- .9) thiocyanates (RSCN); G:P, E:HPA
- .10) nitrogen heterocycles - pyridine, indole, skatole; G:HPA(?)BW, E:HP

3) Oxygen Containing

- .1) oxygen (in some subsystems), ozone, oxygen radicals (O, OH); G:PAM (atmospheric reactions), E:HPABM
- .2) carbon monoxide; G:H(?)BM, E:HPAB
- .3) water (in some subsystems); G:HPBW, E:MB
- .4) alcohols and phenols (ROH), ethers (R_2O); G:HPBM, E:HP
- .5) hydrogen peroxide (H_2O_2), hydroperoxides (RO_2H), peroxides (R_2O_2); G:AM (fuels, polymerizing agents), E:HPABM
- .6) aldehydes (RCHO), ketones (R_2CO); G:HPB, E:HPB
- .7) carboxylic acids (RCO_2H); G:HPB, E:HPBM
- .8) carboxylic esters (RCO_2R); G:HPBM, E:HP
- .9) oxygen heterocycles - furan, coumarin; G:PB, E:HP

4) Halogen Containing (Fluorine, Chlorine, Bromine, Iodine)

- .1) chlorine (Cl_2), hypochlorite (ClO^-), iodine (I_2); G:M (fumigants, disinfectants), E:HPABM
- .2) hydrogen halides (HF, HCl); G:MW, E:HPABMW
- .3) phosgene ($COCl_2$); G:M (pyrolysis), E:HPABM
- .4) haloalkanes (RF, RCl, RBr, RI); G:PA(?)B(?)M (macroalgae produce organic compounds of Cl, Br and I; cleaning solvents, refrigerants, polymers), E:HPABW
- .5) fluorosilane (R_3SiF); G:M (trace contaminant in silicones), E:HPABMW

- 5) Silicon Containing
- .1) silanes (R_3SiH), silanols (R_3SiOH), siloxanes ($R_3SiOSiR_3$); G:M (silicones), E:P(?)W
 - .2) orthosilicate esters ($[RO]_4Si$); G:M (coolant fluid), E:HPW
- 6) Phosphorus Containing
- .1) phosphate esters ($[RO]_3PO$); G:MW (flame retardant, plasticizer, hydraulic fluid, disinfectant), E:HPAB
- 7) Sulfur Containing
- .1) sulfur oxides - S_2O , SO , SO_2 , SO_3 ; G:MW (atmospheric reactions), E:HPABM
 - .2) organic sulfur oxides - sulfoxides (R_2SO), sulfones (R_2SO_2), sulfate esters (R_2SO_4); G:M, E:HPABM
 - .3) sulfides - hydrogen sulfide (H_2S), thiols (RSH), thioethers (R_2S), disulfides (R_2S_2); G:PA(?)W, E:HP
 - .4) carbon disulfide; G:M, E:HP
 - .5) sulfur heterocycles - thiophene, thiofuran; G:B, E:HP
- 8) Macroorganics
- .1) pollen, bacteria, virus, spores; G:HPAB, E:HPABM
 - .2) hair, skin, excreta; G:H, E:HBM
 - .3) abraded material; G:M (lint, torn velcro hooks), E:HM
- 9) Metals
- Metals which might be generated in trace amounts by the machine subsystem and which would be biologically hazardous (depending on the chemical form and the biological species) are: Al, Sb, As, Ba, Be, Bi, B, Cr, Co, Ga, Ge, Au, In, Pb, Li, Mn, Hg, Ni, Pd, Pt, Re, Rh, Se, Ag, Ta, Sn, Ti, Zr.

TABLE 2. Airborne Trace Contaminants on Shuttle Missions

These compounds were recovered from gas sample bottles, activated charcoal filters or lithium hydroxide canisters after shuttle missions and were identified by GC/MS. They are grouped according to the classification scheme in Table 1.

- 1.1) methane, pentane, hexane, heptane, octane, nonane, decane, 2-methylpentane, 2,2,4-trimethylpentane, methylcyclopentane, cyclohexane, 2-methylhexane; other incompletely identified alkanes: C4-alkane, C5-alkane, C6-alkane, C7-alkane, C8-alkane, C9-alkane, C10-alkane, C11-alkane, C12-alkane, C13-alkane, C14-alkane, methylethylcyclopentane
- 1.2) 1-pentene, 2-methyl-1,3-butadiene, limonene; other incompletely identified alkenes: butene, pentene, C4-alkene, C7-alkene, C8-alkene, C9-alkene, C10-alkene
- 1.4) benzene, methylbenzene, 1,2-dimethylbenzene, 1,3-dimethylbenzene, 1,4-dimethylbenzene, butylbenzene, ethylbenzene, ethenylbenzene, propylbenzene, indan, 2-methylindan, naphthalene; other incompletely identified alkylbenzenes: C3-substituted benzene, C4-substituted benzene, dimethyl ethenylbenzene
- 2.3) ammonia
- 2.7) ethanenitrile
- 3.2) carbon monoxide
- 3.4) methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, 2-methyl-2-butanol, 1,2-ethanediol, diethoxymethane, 2-ethoxyethanol, 3-ethoxy propene
- 3.6) ethanal, propanal, propenal, butanal, pentanal, hexanal, heptanal, 2-ethylhexanal, 2,4-hexadienal, benzaldehyde, propanone, 2-butanone, 2-hexanone, 2-heptanone, 3-heptanone, 4-methyl-2-pentanone, 6-methyl-2-heptanone; an unidentified C7-ketone
- 3.7) acetic acid, 3-oxobutanoic acid
- 3.8) ethyl formate, ethyl acetate, propyl acetate, butyl acetate, 2-butyl acetate, 2-methylpropyl acetate, 2-ethoxyethyl acetate, ethyl propanoate, methyl 2-methylpropenoate, ethyl butanoate, diethyl o-phthalate; an unidentified C5-ester
- 3.9) 1,4-dioxane, furan, benzofuran, 2-methylbenzofuran
- 4.4) 1,1,1-trichloroethane, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,1-dichloroethane, 1,1-dichloroethene, 1,1-dichlorotetrafluoroethane, 1,2-dichloroethane, 1,2-dichloropropane, bromotrifluoromethane, chloroethane, chloroethene, chlorofluoromethane, chloromethane, chlorotrifluoroethene, dichlorodifluoroethene, dichlorodifluoromethane, dichloroethane, dichloroethyne, dichlorofluoromethane, dichloromethane, tetrachloroethene, trichloroethene, trichlorofluoromethane, trichloromethane, trifluoromethane
- 4.5) propylfluorosilane, propyldifluorosilane
- 5.1) hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane, tetradecamethylhexasiloxane, hexadecamethylheptasiloxane, octadecamethyloctasiloxane, eicosamethylnonasiloxane, docosamethyldecasiloxane, hexacosamethyldodecasiloxane, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, tetradecamethylcycloheptasiloxane, hexadecamethylcyclooctasiloxane, propylsilane, triethylsilane, trimethylsilanol
- 7.3) dimethylsulfide
- 7.4) carbon disulfide