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Evaluation of the Potential for Significant Ammonia Releases from Hanford Waste Tanks

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July 1996

Prepared for the U.S. Department of Energy
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Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
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Pacific Northwest National Laboratory
Richland, Washington 99352

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Executive Summary

This research, performed at Pacific Northwest National Laboratory (PNNL)^(a), focused on evaluating the hazard due to the flammability and toxicity of potential ammonia releases in Hanford nuclear waste storage tanks. The study was conducted for Westinghouse Hanford Company as part of the PNNL Flammable Gas Project. A wide range of possible ammonia release mechanisms, including natural release mechanisms and those that might occur during such planned operations as saltwell pumping, was studied and quantified to the extent possible. The Lake Nyos effervescent release scenario (limnic eruption) was studied in detail. Available tank and waste data were studied exhaustively to discover possible correlations between ammonia concentrations and those of other species, or tank conditions that might allow prediction of hazardous conditions.

Candidate mechanisms for ammonia storage and release were identified and preliminary modeling was done to characterize these mechanisms in terms of their potential ammonia hazard. Because of the high solubility of ammonia, its storage and release mechanisms are qualitatively different than those of other flammable gases such as hydrogen and nitrous oxide. In tanks containing sludge and saltcake, ammonia release is dominated by diffusion. The release rate in liquid layers can be greatly enhanced by natural convection. For most tanks, this implies that the bulk of the ammonia is stored in the sludge and saltcake layers. The release rate modeling indicates that a large ammonia release requires a high concentration of ammonia dissolved in the waste coupled with a large disturbance of the waste. This disturbance could be natural in origin, such as an earthquake or rollover, or could result from tank operations.

Waste retrieval methods such as sluicing, dilution and mixing, or transfer of liquid waste into the tank can be expected to create ammonia concentrations on the order of several percent in the tank head space for tanks with high ammonia concentrations in the waste. This represents a potential health and safety hazard that must be considered in the safety basis for such operations.

Rollovers, driven by the generation of insoluble gases such as hydrogen, nitrogen, and nitrous oxide, are bounded by the historic rollovers in Tank 241-SY-101, which yielded measured ammonia concentrations of a few percent in the dome space. Rollovers can occur only in tanks with a supernatant liquid layer whose depth is comparable to or exceeds the depth of settled solids. This condition exists in some of the double-shell tanks. No other credible mechanisms have been identified that result in large, rapid,

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spontaneous releases of ammonia. The consequences of a disturbance caused by a large earthquake would be comparable to tank retrieval operations with respect to ammonia release.

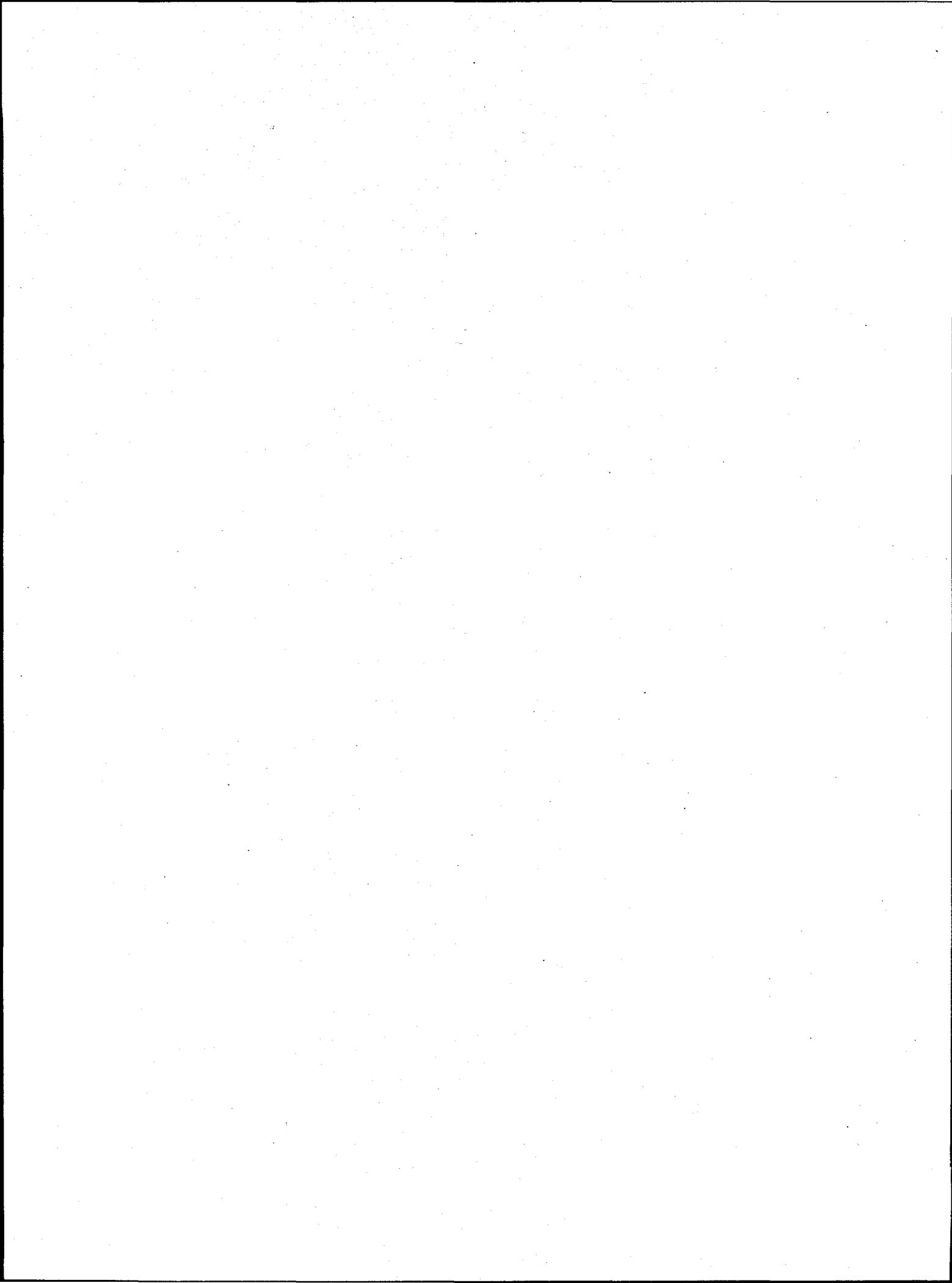
A detailed study was also performed of the conditions necessary to build up an ammonia concentration profile high enough to generate a limnic eruption. A one-dimensional model was developed that describes ammonia transport in the sludge and saltcake layers by the diffusion equation, and uses a mass transfer model to describe transport in the convective layer and in the head space. Both steady-state solutions and the time-dependent behavior of this model were investigated. The main focus of those investigations was the behavior of ammonia in the double-shell tanks, but some calculations were also done for single-shell tanks. The results indicate that in tanks with a crust or foam layer on top of a convective layer, moderate ammonia generation rates (comparable to or less than those estimated for Tank 241-SY-101) can produce ammonia concentrations in the supernatant layer that are comparable to those observed in double-shell waste tanks. However, the concentration profile in these tanks does not approach saturation at any point in the tank. For tanks with no crust or foam layer, very high ammonia generation rates are necessary to match the ammonia concentrations in the supernatant layer observed in the double-shell tanks. These generation rates are much higher than those estimated from the head space ammonia concentration in Tank 241-SY-101. The probability of a limnic eruption appears to be low, based on the modeling and the observed behavior of both single-shell and double-shell waste tanks.

All available data relevant to ammonia in both the single- and double-shell tanks were collected and analyzed. The final data set, consisting of 63 data variables, supported analysis of head space data on 37 single-shell tanks, waste data on 13 double-shell tanks, and limited exploratory analysis on the waste/head space data of 10 single-shell tanks. The data were examined both for pairwise correlations between the different data properties and for higher-order correlations using multivariate statistical techniques. For single-shell tanks, the statistical analysis supported relationships between ammonia concentration in the head space and drainable liquid volume; and between ammonia and hydrogen, nitrous oxide, and carbon dioxide concentrations in the head space. The analysis also showed a relationship in the SSTs between ammonia concentration in the head space and aluminum and nitrate concentration in the waste. Analysis of the double-shell tanks indicates that tanks with high ammonia concentrations in the waste are identifiable from the concentrations of aluminum, nitrate, total organic carbon, nitrite, and strontium.

The overall conclusion is that there is no serious potential for a large spontaneous ammonia release event, including releases resulting from limnic eruptions and earthquakes. However, rollovers and tank operations such as rapid sluicing or pumping of the supernatant could result in head space concentrations of ammonia that represent a significant fraction of the lower flammability limit for ammonia in air, and that would be a human health and safety concern.

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1.0 Introduction

Ammonia is ubiquitous as a component of the waste stored in the Hanford Site single-shell tanks (SSTs) and double-shell tanks (DSTs). Because ammonia is both flammable and toxic, concerns have been raised about the amount of ammonia stored in the tanks and the possible mechanisms by which it could be released from the waste into the head space inside the tanks as well as into the surrounding atmosphere. Ammonia is a safety issue for three reasons. As already mentioned, ammonia is a flammable gas and may contribute to a flammability hazard either directly, if it reaches a high enough concentration in the tank head space, or by contributing to the flammability of other flammable gases such as hydrogen (LANL 1994). Ammonia is also toxic and at relatively low concentrations presents a hazard to human health. The level at which ammonia is considered Immediately Dangerous to Life or Health (IDLH) is 300 ppm (WHC 1993, 1995). Ammonia concentrations at or above this level have been measured inside the head space in a number of SSTs. Finally, unlike hydrogen and nitrous oxide, ammonia is highly soluble in aqueous solutions, and large amounts of ammonia can be stored in the waste as dissolved gas. Because of its high solubility, ammonia behaves in a qualitatively different manner from hydrogen or other insoluble gases. A broader range of scenarios must be considered in modeling ammonia storage and release.

This report is divided into five sections plus references and appendixes. The three major sections each deal with a separate aspect of ammonia storage and release in the Hanford nuclear waste storage tanks and address the issues defined in the FY96 Flammable Gas Project work scope.^(a)

1) Perform analyses to integrate the results of gas phase monitoring, in-tank sampling operations, and other tank data related to ammonia distribution and release; group and correlate ammonia vapor and waste concentration to waste type and pertinent tank parameters as data become available; incorporate operational and industrial health data wherever possible.

2) Provide analyses that demonstrate the mechanisms which control ammonia storage and release in Hanford waste tanks; develop standard screening and analysis methods for determining the potential for significant ammonia releases, particularly in tanks in which slurry growth is observed in the absence of a gas release event history.

(a) Brothers, JW, et al. April 1996. *TWRS - Waste Tank Safety Program: Waste Tank Flammable Gas Project: FY1996 Workscope*, M. McNickle, ed. TWSFG96.11, Pacific Northwest National Laboratory, Richland, Washington.

3) Model the effect of possible distributions of ammonia concentration on the potential for hazardous ammonia release; relate this behavior to known waste equilibria and experiments.

This report treats these issues in a slightly different order than originally defined in the work scope. Section 2 summarizes the proposed storage and release mechanisms. Because of its high solubility, ammonia is released predominately by diffusion through the waste, if the waste is a sludge or saltcake with a finite yield stress. In a liquid layer, the release rate can be speeded up considerably by natural convection, unless blocked by a floating crust layer. For most tanks, this means that the bulk of ammonia is expected to be stored in sludge and saltcake layers. To release a large amount of ammonia requires a considerable disturbance of the waste. Both natural disturbances and the effects of current or proposed tank operations are considered. Mechanisms that result in minor releases are also reviewed. A methodology for assessing the ammonia hazard in tanks is proposed and related to the different storage and release mechanisms.

Section 3 deals with the development of ammonia concentration distributions in the tanks. This work is focused primarily on understanding whether ammonia concentrations can reach saturation in the tanks. At saturation the tank becomes a candidate for a Lake Nyos-type effervescent eruption (termed a limnic eruption), which has the potential for releasing a huge quantity of ammonia in a very short time. A model is presented that combines the effects of diffusion in the sludge or saltcake with convection in the liquid layer and evaporation into the tank head space. The effects of tank ventilation and the presence of a crust on top of the convective layer are also incorporated into the model. This model is used to determine the steady-state concentration distribution in the tanks for several different waste configurations, given an initial generation rate for ammonia. The time-dependent version of the model is also solved to estimate the time scales required to approach steady-state.

Section 4 focuses on the data currently available on ammonia in the waste tanks. All recent data on ammonia in both the SSTs and DSTs were collected and compiled, along with data that may be related to possible mechanisms for ammonia generation and storage. These data were then subjected to statistical analysis to determine whether any correlations exist between ammonia measurements in the waste and head space and other tank parameters. The data were also examined to see if there is statistical evidence to support other proposed relationships between tank parameters.

The report concludes with a summary of the findings (Section 5) followed by the cited references (Section 6) and appendices containing the detailed supporting information.

2.0 Ammonia Retention and Release

This section categorizes and describes possible mechanisms that could result in large ammonia releases from the Hanford single-shell (SST) and double-shell (DST) waste storage tanks. These mechanisms were compiled after extensive discussions with personnel at both Pacific Northwest National Laboratory (PNNL) and Westinghouse Hanford Company (WHC). An overview of ammonia in the tanks and a discussion of the role played by Henry's Law in determining the ammonia vapor concentrations is followed by a discussion of ammonia transport in the waste via diffusion and natural convection and the effects of these mechanisms on the rate of ammonia release. Natural storage and release mechanisms are summarized and grouped according to whether they are likely to result in an ammonia release, and whether the release is large or small. The impact of tank operations on ammonia release rates is described, and methods of assessing the ammonia hazard for individual tanks are discussed.

None of the mechanisms discussed in this report are likely to represent a significant hazard unless there is a substantial concentration of ammonia in the waste itself and the waste is extensively disturbed. Unlike hydrogen and nitrous oxide, ammonia is highly soluble in aqueous solutions and is likely to remain in solution at low concentrations. There is no easy way to substantially lower the solubility of ammonia and force its release from the waste except by raising the temperature or possibly by a large increase in pH. However, while it may be possible to increase the ammonia vapor pressure in the waste by changes in the solubility induced by an increase in temperature or pH, it is unlikely that the solubility can be decreased to the point at which ammonia actually bubbles out of solution. The concentration of ammonia in the waste also determines the maximum concentration of ammonia that can be achieved in the dome head space. The maximum concentrations of ammonia in the head space and in the waste are related by the Henry's Law constant. The solubility of ammonia decreases as electrolytes are added to the solution; the Henry's Law constants for the concentrated solutions in the Hanford waste tanks are a factor of 10 lower than for ammonia in pure water at the same temperature (Norton and Pederson 1994, 1995).

At present, only limited data on ammonia concentrations in tank waste are available, and the accuracy of the concentration determinations from core samples is a matter of some controversy (concentration determinations from supernatant grab samples are considered more reliable). Determining the concentration of ammonia in the waste by examining other factors, such as the ammonia concentration in the head space, is problematic. The relationship between the ammonia concentration in the waste and the ammonia concentration in the head space is complicated by several factors, even if the appropriate Henry's Law constant is known. The concentration of ammonia in the tank head space is almost always much less than the equilibrium vapor pressure corresponding to the average concentration of ammonia in

the waste, because diffusion through the liquid severely limits mass transfer. In those tanks that are actively ventilated (primarily DSTs), the concentration of ammonia in the head space will be further lowered by dilution. However, although low levels of ammonia in the head space do not necessarily imply low concentrations of ammonia in the waste, high concentrations of ammonia in the head space are probably indicative of elevated concentrations of ammonia in the waste.

Estimates of the ammonia concentration based on generation rates are also impossible at the present time, because relatively little is known about the generation mechanisms of either insoluble flammable gases such as hydrogen and nitrous oxide or soluble flammable gases such as ammonia (The steady-state ammonia concentration profile in the waste is generally a sensitive function of generation rate, as discussed in Section 3). The presence in the original waste streams of the complexants EDTA and HEDTA, as well as high levels of other organic carbon-containing species, indicates high levels of flammable gas generation, provided that other conditions such as temperature and radioactive dose rate are favorable. However, there is no method available to quantitatively relate the composition of the waste, if known, with the gas generation rate in general or with ammonia generation in particular. The concentration of other flammable gases in the tank head space is not a good indicator of the concentration of ammonia in the tank. The generation rates of other gases such as hydrogen and nitrous oxide relative to the generation rate of ammonia have not been determined, nor is it clear that the relative generation rates remain fixed from one tank to the next.

2.1 Introduction

The maximum ammonia concentration that can be achieved in the vapor phase is the equilibrium vapor pressure of ammonia over the waste, which is governed by the concentration of ammonia in the waste and the value of the Henry's Law constant. Major factors that can influence the Henry's Law constant are the levels of dissolved electrolytes, the pH, and the temperature. Once the concentration of ammonia in the head space reaches the level dictated by the concentration of ammonia in the waste and the Henry's Law constant, it will go no higher. Further release of ammonia from the waste must be accompanied by venting from the dome space.

The Henry's Law constant is the proportionality constant between the concentration of ammonia in the waste and the equilibrium vapor pressure of ammonia, and is given by the formula

$$K_{NH_3} = \frac{\gamma_{NH_3} m_{NH_3}}{P_{NH_3}}$$

where K_{NH_3} is the Henry's law constant, γ_{NH_3} is the activity coefficient for ammonia, m_{NH_3} is the molality of ammonia, and p_{NH_3} is the partial pressure of ammonia. At low concentrations of ammonia in pure water, the activity coefficient can be assumed to be equal to one. As electrolytes are added to the solution, the value of the activity coefficient changes. These changes are a complicated function of the electrolytes in the solution, as well as the temperature, and no analytic models exist that can accurately predict them. However, experimental correlations are available that can model the behavior of the activity coefficient under certain circumstances.

Norton and Pederson (1994) have obtained parameterized correlations for K_{NH_3} / γ_{NH_3} for some of the nonradioactive test mixtures used to simulate the physical characteristics of the wastes in Tank 241-SY-101. For the simulant SY1-SIM-93B, a homogeneous simulant, they obtained the correlation

$$\ln(K_{NH_3} / \gamma_{NH_3}) = -7.357 + 3330.1/T - 0.002139T$$

where T is the temperature in Kelvin and the Henry's Law constant is reported in units of mol/(kg H₂O-atm). A second correlation for a heterogeneous, slurry-type simulant, SY1-SIM-91A, was also reported:

$$\ln(K_{NH_3} / \gamma_{NH_3}) = -7.577 + 2571.3/T + 0.003076T$$

These expressions can be used to calculate the vapor pressure of ammonia as a function of moles of ammonia per kilogram of water in the waste. Unfortunately, at present it is difficult to assess how applicable these numbers are to tanks other than Tank 241-SY-101, but they at least provide order of magnitude estimates for the expected range of Henry's Law constants.

The equilibrium ammonia vapor pressure for a hypothetical tank waste that is 0.2 wt% ammonia can be estimated from these correlations. Using the correlation for the 91A simulant, which gives a lower solubility for ammonia than that for the 93B simulant, and assuming a waste temperature of 40°C, the ratio of the Henry's Law coefficient to the activity is 5.0 mole/kg-atm. Further assuming that the waste is 30 wt% water, the equilibrium vapor pressure is about 0.079 atmospheres, or 7.9 volume percent. This is roughly half the lower flammability limit (LFL) for ammonia in air and well over the concentration at which ammonia must be considered a hazard to human health. Small adjustments in any of the values used in this calculation could push the equilibrium ammonia vapor concentration over the LFL. Norton and Pederson (1995) obtained estimates of K_H / γ for Tank 241-SY-101 up to a factor of two lower than the value used here. The value of 0.2 wt% may also not be an upper bound for the concentration of ammonia. However, concentrations on the order of a few volume percent of ammonia are almost never observed in the tank head spaces. This is discussed in more detail below.

2.2 Diffusion-Limited Release

Diffusion-limited release applies to all tanks, both SSTs and DSTs. Ammonia diffuses to the surface of the waste, where it subsequently evaporates into the head space. Ammonia that is lost from the top layer of the waste must be replaced by ammonia diffusing up from lower layers in the waste. For longer time periods, the ammonia at the surface of the waste must be replenished from increasingly deeper in the waste. The longer distances that ammonia must diffuse in order to reach the surface causes the concentration near the surface to drop, and the release rate of ammonia into the head space of the tank decreases as time increases, provided that the waste is not subjected to natural convection or disturbed in some way. The simplest model for diffusion-limited release is to assume that the waste is a homogeneous material characterized by a single diffusion coefficient. Models of this scenario have been reported by Allemann (1994) and Palmer.^(a) If no other factors are present to enhance the rate of ammonia transport to the surface, and the tank remains completely undisturbed for a long period of time, this mechanism is very inefficient for releasing ammonia from the waste. After the surface region is depleted, the release rate drops rapidly. The time scale for depletion of an initial surface region approximately 1-cm thick is on the order of several hours, but the time scale to deplete a region 1-m thick is on the order of decades.

Tanks that contain mostly sludge and that have remained undisturbed for long periods will probably show very little ammonia in the head space, because the ammonia near the surface has all evaporated from the waste. Tanks that have been disturbed recently so that fresh waste has been brought to the surface will show much higher ammonia head space concentrations -- if the waste itself contains a high concentration of ammonia.

Assuming that the concentration of ammonia in the dome space is fairly low, on the order of ppm, the flux per unit area of freshly exposed surface can be estimated from the formula

$$J = C_0 \sqrt{\frac{D}{\pi t}} \quad (2.1)$$

where C_0 is the concentration of ammonia in the waste, D is the diffusion coefficient of ammonia in the waste, J is the flux of ammonia from the waste surface, and t is time. The diffusion coefficient is expected to be on the order of $2 \times 10^{-5} \text{ cm}^2/\text{s}$ (Cussler 1984). Equation (2.1) is valid only if the waste

(a) Palmer, B.J. 1995. *Calculation of Ammonia Release by Diffusion from Waste Surface of Tank 241-SY-101*. PNLMIT:012595, Pacific Northwest Laboratory, Richland, Washington.

surface can be considered flat and uniform on a length scale on the order of \sqrt{Dt} . Equation (2.1) cannot be applied at very long times, but it provides a convenient starting point for analyzing many systems. For ammonia in waste, the diffusion length scale after 20 days is only about 6 cm.

As the concentration of ammonia in the dome space increases, the assumption of zero ammonia concentration in the dome space breaks down, and the flux defined by Equation (2.1) is no longer correct. However, Equation (2.1) should still represent an upper bound to the flux from the waste, because the effect of ammonia in the dome space is to decrease the net evaporation rate of ammonia from the waste surface. For an unventilated dome space, an upper bound N_0 to the concentration of ammonia in the dome space due to diffusion and evaporation from a freshly exposed waste surface, is

$$N_0 = \frac{\phi A}{V_D} \int_0^t J(s) ds \quad (2.2)$$

where A is the total surface area of the waste, ϕ is the fraction of the waste with a freshly exposed surface, and V_D is the volume of the tank dome space. If the waste surface is flat, then $A = \pi R^2$, where R is the tank radius. An equivalent height of the dome head space can be defined as $h = V_D / A$. Combining Equations (2.1) and (2.2), as well as the formulas for A and V_D , results in the expression:

$$N_0 = \frac{2\phi}{h} C_0 \sqrt{\frac{Dt}{\pi}} \quad (2.3)$$

For an equivalent head space height of 5 m, a completely exposed surface ($\phi=1$), and a concentration of ammonia in the waste of 2×10^{-4} moles/cm³ (corresponding to about 0.2% ammonia by weight in a typical sludge), the time required to reach a value of 5% ammonia in the head space is approximately 11 days (assuming a dome temperature of 32°C). For an unventilated tank, this time scale suggests that the head space in a tank with a freshly exposed waste surface can reach the equilibrium vapor pressure of ammonia in the tank waste in a relatively short time. However, even passive ventilation may significantly reduce the maximum head space concentration that can be achieved. The time constant for ventilating the tank head space assuming a passive ventilation rate of 5 cfm is about 10 days, which is the same time scale for achieving a substantial concentration of ammonia in the head space.

There is evidence that ammonia release in many of the SSTs is diffusion-limited. Concentration values of ammonia in both the waste and the head space are available for six of the SSTs. These numbers can be combined with the weight percent water in the waste to calculate an apparent Henry's Law constant, K_H / γ^* , for each tank. If the Henry's Law constant is high, implying that the tank head

space concentration is low, this is a sign that the concentration of ammonia in the head space is diffusion-limited. The scale for determining whether the Henry's Law constant is high or low can be set by comparing the Henry's Law constant for the tank with the Henry's Law constant for pure water at the same temperature as the tank. The value for water is a maximum, and the effect of adding electrolytes is to lower the Henry's Law constant. This calculation is summarized for the six SSTs in Table 2.1. Except for Tanks 241-C-110 and 241-C-112, all tanks show values of the Henry's Law constant that are substantially greater than the value for pure water, suggesting that most of the tanks are transport-limited. Even Tanks 241-C-110 and 241-C-112 have values that are a little high compared with the value that would be obtained from Norton and Pederson's simulant correlations. Tanks 241-AX-102 and 241-C-109 stand out by having Henry's Law constants that are at least an order of magnitude larger than those of the other tanks. Interestingly, these tanks contain the least waste among the six SSTs. The waste levels in Tanks 241-AX-102 and 241-C-109 are 0.36 and 0.61 m, respectively.

Natural Convection

While the diffusion of ammonia through quiescent waste to the surface is a very slow method of releasing ammonia, almost any amount of natural convection will speed up the release rate substantially. The presence of free liquid at the top of the waste and natural convection within the liquid layer can increase the release rate of ammonia by constantly replenishing the depletion zone near the waste

Table 2.1. Henry's Law Constants for Hanford SSTs. K_H/γ^* is the Henry's Law constant calculated from the tanks, K_H/γ^0 is the Henry's Law constant for pure water. (Clegg and Brimblecombe 1989.)

Tank	[NH ₃] mg/g	P(NH ₃) atm	K_H/γ^* molal/atm	T °C	K_H/γ^0 molal/atm	Depth meters
T-111	400	226	135	19	-81.7	4.14
T-107	122	125	100	19	-81.7	1.63
C-110	86.4	124	71	20	77.8	1.70
AX-102	500	34	2800	33	42.3	0.36
C-112	5	23	31	26	58.4	0.94
C-109	53	10.1	1500	24	64.2	0.61

surface. An order of magnitude estimate of the effect of natural convection can be obtained from simple dimensional analysis. To determine whether convection is dominated by inertia or by viscosity, it is necessary to calculate the Grashof number

$$\text{Gr} = \frac{g(\Delta\rho/\rho)L^3}{\nu^2}$$

where g is the acceleration of gravity, 980 cm/s^2 , $(\Delta\rho/\rho)$ is the fractional change in the density between the top and the bottom of the liquid layer, L is the thickness of the liquid layer, and ν is the kinematic viscosity of the liquid. The fractional change in the density is usually induced by a temperature gradient and can be determined from the temperature change across the liquid layer and the thermal expansion coefficient. A typical value for the kinematic viscosity of the supernatant is $0.3 \text{ cm}^2/\text{s}$. Assuming that the fractional change in the density is 0.0002, which is approximately the fractional change in the density of water over a 1°C interval at 20°C , and a 1-m-thick liquid layer, the Grashof number is approximately 2×10^6 . This puts convection clearly in the inertial regime ($\text{Gr} > 1000$; see Gebhardt et al. 1988), and the uncertainties in $(\Delta\rho/\rho)$ and ν are unlikely to change this.

Once the convection has been determined to be inertial, the time constant, τ_c , for convection can be estimated from the relation

$$\tau_c = \frac{L}{v_c}$$

where v_c is the inertial velocity and is given by

$$v_c = \sqrt{g(\Delta\rho/\rho)L}$$

The inertial velocity is essentially due to the buoyant forces on the liquid at the bottom of the convective layer. Combining the expressions for τ_c and v_c :

$$\tau_c = \sqrt{\frac{L}{g(\Delta\rho/\rho)}}$$

Using the same numbers as those used to calculate the Grashof number, the time constant for convection is about 23 seconds. Granting a high degree of uncertainty in this number, it still seems clear that the time constant for natural convection is likely to remain under an hour.

For times less than τ_c , the supernatant layer can be considered stationary, and a thin depletion layer with a thickness on the order of $\sqrt{D\tau_c}$ can form at the top of supernatant. Assuming that convection prevents the depletion layer from becoming much larger than $\sqrt{D\tau_c}$, the flux evaporating from the surface of the liquid waste becomes

$$J = C_0 \sqrt{\frac{D}{\pi\tau_c}}$$

If the concentration of ammonia in the waste does not change much in the time required for the dome space to reach saturation, the concentration of ammonia in the dome space at time t can be approximated by

$$N_0 = \frac{\phi}{h} \sqrt{\frac{D}{\pi\tau_c}} C_0 t$$

Using 1 hour for the convection time constant and the values used above for the remaining constants, the time required to reach 5% concentration of ammonia in the head space is about 33 hours. This short time scale suggests that convection will most likely wipe out the effects of diffusion unless the liquid is trapped in some sort of sludge or porous medium. For Tank 241-SY-101, the liquid near the surface was immobilized by a 1.2-m-thick crust, which reformed within a few hours of a rollover (see Rollovers section below). This may explain the apparent success of a diffusion-based model in explaining the decay of ammonia concentration after a rollover^(a) even though a substantial liquid layer is present in this tank.

Other factors may also play a role in enhancing the rate of ammonia transport to the surface. The movement of gas bubbles through a liquid layer at the top of the waste can increase the release rate by agitating the liquid layer and replenishing the depletion zone at the waste surface. Gas bubbles will also transport ammonia directly from the lower regions of the tank. The ammonia inside these bubbles will be at or close to the equilibrium vapor pressure. The calculations outlined above suggest that these effects are negligible compared with natural convection. Convection of fluid within sludge or saltcake layers may increase ammonia transport significantly, if it occurs.

(a) Palmer, BJ. 1995. *Calculation of Ammonia Release by Diffusion from Waste Surface of Tank 241-SY-101*. PNL/MIT:012595, Pacific Northwest Laboratory, Richland, Washington.

2.3 Large Ammonia Release Mechanisms

This section reviews ammonia release mechanisms that could result in a substantial ammonia release even in the absence of any active intervention (pumping, sampling, etc.) with the tank contents.

Only three postulated natural release mechanisms are expected to result in substantial ammonia releases: rollovers, limnic eruptions, and earthquakes. Rollovers are known to occur in tanks with a substantial supernatant liquid layer; a limnic eruption or a sizable earthquake in the area must also be considered possibilities.

2.3.1 Rollovers

A rollover, which is generated by the buildup of insoluble gases such as hydrogen, nitrogen, and nitrous oxide in the sludge, provides a very effective mechanism for evacuating a large amount of gas from the waste in a short time. With respect to ammonia, a rollover has two components. The first is the initial release of ammonia entrained in bubbles containing the insoluble gases; the second is evaporation of ammonia from the fresh liquid surface that is exposed by the rollover event. A rollover occurs when gas bubbles are trapped in a sludge layer at the bottom of a tank beneath a layer of liquid. If no gas is present, the sludge is denser than the liquid and a waste configuration with the sludge at the bottom of the tank covered by a layer of liquid is mechanically stable. As gas bubbles accumulate in the sludge, however, the density decreases until it is lighter than that of the liquid layer above it, and the waste configuration becomes unstable. When the global buoyant force exceeds the yield strength of the sludge, the sludge layer breaks free from the bottom and the tank contents are inverted. The violent motion of large volumes of sludge breaking the waste surface, and the subsequent abrupt deceleration, disrupts the sludge and frees a large fraction of the gas contained therein. This results in a large volume of gas being released to the dome. The fraction of ammonia in this gas release is governed by the concentration of ammonia in the waste. The rollover also results in the exposure of a fresh liquid surface and the removal of the ammonia depletion region that may have built up at the surface before the rollover. Ammonia release via diffusion and evaporation from this surface will then proceed as discussed above.

Allemann and Terrones^(a) recently proposed a buoyancy criterion for estimating when a rollover can occur. This criterion is based on the ratio DR of the yield stress of the sludge to the buoyancy forces on the sludge. This ratio is given by the expression

(a) Personal communication with G. Terrones, Pacific Northwest National Laboratory, 1996.

$$D_R = \frac{\beta \tau_y}{g[\rho_L - (1 - \alpha)\rho_s]}$$

where τ_y is the yield stress of the sludge, α is the void fraction, ρ_L is the density of the supernatant liquid, ρ_s is the density of the sludge, and g is the acceleration of gravity. The parameter β is a numerical factor between 1 and $\sqrt{3}$ that depends on whether the sludge yields in tension or in shear. The void fraction at which a rollover can occur can be obtained by setting D_R equal to 1 and solving for α . The yield strength may also have a sensitive dependence on the void fraction; in this case, the point at which a rollover occurs is determined by a combination of the increasing buoyancy of the sludge due to retained gas and the decreasing mechanical strength of the sludge due to the voids.

For a rollover to occur, several conditions must be satisfied. The tank must contain a sludge layer with a finite yield strength so that gas can accumulate at the bottom of the tank. The tank must also have a layer of supernatant on top of the sludge. The magnitude and speed of the rollover depend on the thickness of the supernatant layer. A thin layer will result in either a small, slow rollover or no rollover at all, as observed in experiments on clay simulants.^(a) Meyer has recently proposed an energy criterion for a rollover which suggests that a rollover is not possible in a tank without a supernatant layer.^(b) In addition to having both a sludge and a supernatant layer in the waste, the tank must also be generating and retaining insoluble gases such as hydrogen and nitrous oxide. The presence of retained gas can be detected by a level rise in the waste or by a negative value of the response of waste level to barometric pressure, dL/dP (Whitney 1995). Another indicator that insoluble gas is being generated, although not necessarily retained, is the presence of relatively high concentrations of hydrogen or nitrous oxide in the tank head space.

The total ammonia released directly by the rollover can be calculated from the fraction of sludge that is disturbed in the rollover event, the void fraction of the sludge, and the percent ammonia in the gas bubbles. The percentage of ammonia in the bubbles can be calculated if the Henry's Law constant and the concentration of ammonia in the waste are known. The effects of pressure can easily be incorporated into the calculation using the ideal gas law.

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- (a) Gauglitz, PA. 1996. From video, *Gas Release Mechanisms in Single-Shell Tanks: Effects of Supernatant Layer Thickness on Rollover Dynamics*. Presented at the Flammable Gas Technical Exchange, March 7, 1996, Richland, Washington.
- (b) Meyer, PA. 1996. *An Energy Criterion for Predicting Gas Release During Rollover in Double- and Single-Shell Hanford Waste Tanks*. TWS96.2, Pacific Northwest National Laboratory, Richland, Washington.

The amount of gas released by evaporation of ammonia from the fresh liquid surface may be a more complicated calculation. If no crust reforms, then ammonia release would be dominated by convection, and the convective layer will release gas at a fairly high rate until the concentration of ammonia in the liquid is uniformly depleted. If a crust reforms shortly after the rollover that is sufficient to suppress convection in the top 30-50 cm of tank fluid, then the release of ammonia will be dominated by diffusion.

2.3.2 Limnic Eruption (Lake Nyos Effervescence)

This mechanism is modeled after the Lake Nyos event, which resulted in the catastrophic release of large quantities of carbon dioxide dissolved in the bottom of a deep lake. Carbon dioxide was dissolved in the lake up to the saturation point, resulting in an unstable equilibrium. It is believed that water at the bottom of the lake began moving upward, causing the saturation concentration of carbon dioxide to decrease and bubbles of carbon dioxide to begin nucleating in the water. The upward motion of the bubbles entrained more water from the bottom of the lake, resulting in further carbon dioxide release. This process has been termed a 'limnic eruption' and is capable of releasing enormous quantities of gas, provided that the gas is dissolved up to the saturation point. For ammonia, this would require very high concentrations of gas in the waste.

A simple model of the limnic eruption requires that all the waste is saturated with respect to ammonia (it is also possible that only the bottom layers of the waste are saturated and the upper layers are unsaturated). The saturation concentration can be obtained from the Henry's Law constant and the pressure profile inside the waste. If the waste is at a uniform density, ρ , then the pressure is a linear function of depth inside the tank:

$$P(z) = (h - z)\rho g + P_{ext}$$

where h is the elevation of the waste surface, z is the elevation at which the pressure is to be calculated ($h - z$ is the depth of that point), and P_{ext} is the external atmospheric pressure. For a 10-m depth of waste with a density of 1.4 g/cm^3 and an external pressure of 1 atmosphere, the pressure varies linearly from 1 atmosphere at the top of the tank to about 2.4 atmospheres at the bottom. Assuming that the tank is all liquid, that it is at a uniform 30°C , and that the Henry's Law constant is well described by the correlation for the simulant SY1-SIM-93B, then the saturation profile for ammonia in this waste is

$$C_{sat}(z) = (K_{NH_3} / \gamma_{NH_3}) P(z)$$

Under these conditions, the value of K_{NH_3} / γ_{NH_3} is 6.3 moles-NH₃/(kg-H₂O-atm). The saturated concentration of ammonia in the waste varies from 6.3 moles per kg of water at the top to 15.1 moles of ammonia per kg of water at the bottom. Assuming that the water content of the waste is 35 wt%, the saturation concentration of ammonia in the waste is about 3.7 wt% at the top and 9.0 wt% at the bottom. The worst-case effervescence scenario is that all the waste passes close to the surface and its concentration of ammonia is reduced to the saturation concentration at one atmosphere. For the standard 22.9-m tank, this involves 4100 m³ of waste. If this is all returned to a concentration of 3.7% ammonia, a total of 8.9×10^6 moles of ammonia must be released. This is 2.2×10^5 m³ of ammonia.

Because of the very high ammonia concentrations required in the waste for a limnic eruption, a high ammonia concentration in the head space would almost certainly occur in tanks that are at risk for this type of release. This mechanism also probably requires both a sludge and a convective layer in the tank. The convective layer is necessary so that vertical displacement of the waste required to initiate the eruption is possible. However, because of natural convection, an all-liquid tank cannot develop a supersaturated concentration profile. A sludge layer that allows ammonia to be transported only by diffusion would allow the ammonia concentration to build up to the saturation limit. High temperatures in the tank may lower the threshold for a limnic eruption by decreasing the value of the Henry's Law constant, or, equivalently, by raising the vapor pressure of ammonia in the waste.

Although a limnic eruption would result in a catastrophic release of ammonia, the extremely high concentrations of ammonia required make it unlikely that such a release will occur. Concentrations on the order of 2-3% are almost an order of magnitude larger than the ammonia concentrations that have been measured recently in the tank waste (PNL 1994). The conditions necessary to achieve these kinds of concentrations are explored in more detail in Section 3.

2.3.3 Earthquakes

Earthquakes can contribute to a large ammonia release by severely agitating the waste tank contents and exposing fresh liquid to the head space. They may also create a breach in the tank, allowing ammonia vapor to escape to the environment. For the earthquake to have a significant effect on the waste, the waste must contain a reasonable amount of water. This waste can then be liquefied by the earthquake, resulting in both the release of gas trapped in the waste and the exposure of the surface of the tank to fresh waste. For tanks with a high concentration of ammonia in the waste, this can bring the concentration of ammonia in the head space to high levels.

Reid et al. have done calculations on tanks to determine the stresses induced in the waste by an earthquake.^(a) Starting with the spectrum for a Hanford design basis earthquake, they calculated the stresses in the waste for both vertical and horizontal shaking of the tank. These stresses were then used to calculate the available energy per unit volume of sludge. This energy was compared with the stress-strain properties of the waste to determine whether or not enough energy is available from the earthquake to yield the sludge. If the energy surpasses the yield threshold of the sludge, it is assumed that liquefaction of the waste occurs. If the energy is below the yield threshold, it is assumed that no large-scale deformation or disturbance of the waste occurs. The calculations indicate that over a plausible range of sludge properties, both outcomes are possible. Low-strength sludges will yield for both 100-year and 1000-year earthquakes, while high-strength sludges are expected to remain more or less solid.

2.4 Small Ammonia Release Mechanisms

This section focuses on release mechanisms that are expected to result in only small releases of ammonia. Such mechanisms include chimney mudpots, fracture and dryout, bubble migration, and subsidence.

2.4.1 Chimney Mudpots

A chimney mudpot forms when insoluble gas is generated inside a sludge, or possibly a saltcake, causing bubbles to form and coalesce. Eventually these bubbles can form a connected, dendritic bubble network that may extend over a large volume. When this network breaches the waste surface, a fraction of the gas contained inside is released. Because the gas inside the network is expected to be saturated with respect to ammonia, the gas released when a mudpot reaches the surface will be ammonia-rich if the tank waste has a high ammonia concentration; and the concentration of ammonia in the head space will increase if the head space concentration is initially below saturation.

The maximum height of the dendritic network is limited by the yield stress of the sludge or saltcake in which the network forms. The European Study Group arrived at the following estimate for the maximum size bubble that can occur in a sludge with yield stress τ_y ^(b)

$$\rho_s a g = \tau_y$$

(a) Reid, H, P Meyer, and J. Phillips. 1996. *Waste Tank Sludge Yielding Estimates with Design Base Earthquake Spectrum Shock Analyses*. Presented at Flammable Gas Quarterly Review Meeting, May 1, 1996.

(b) European Study Group held at Oxford, UK, March 1996. Results communicated to M. E. Brewster.

where ρ_s is the sludge density and a is the radius of the bubble. This formula is derived from the fact that the yield stress must compensate for the vertical hydrostatic pressure imbalance across the bubble. This formula actually applies to any gas-filled region, simply by replacing a with $h/2$, where h is the vertical height of the gas-filled region. For a sludge with a yield stress of 1000 Pascal and a density of 2 g/cm^3 , this height is about 10 cm. For stronger sludges, this height increases proportionately. These estimates may also have to be modified if the network is highly branched, since branching could lower the effective density of the sludge. However, branching is unlikely to decrease the sludge density by more than 30%. Unfortunately, not much is known about how the network develops in the horizontal direction. Specifically, it is unclear what maximum void fraction can be achieved in a dendritic network that is growing horizontally, before it fails and releases its gas. The vertical growth of the network is limited by the yield strength of the sludge. However, a network that fails deep within the sludge may breach a second network above it, causing that network to fail, which then causes another network to fail, and so on. This cascade of network failures may ultimately result in a sizable gas release, depending on how much of the gas stored in the layer can flow to the breach point before the network is sealed off again.

While a series of vertical failures for a set of dendritic bubbles is possible, it is not clear what the extent of gas release in the horizontal direction would be. Unless the connected dendritic volume has a considerable lateral extent, an upward cascade of mudpot failures will not result in a large gas release. Assuming that the probability of vertical fingering is not significantly different from the probability of horizontal fingering, then it is unlikely that an extended dendritic network can form in the horizontal direction without a vertical failure. A bubble network that is gradually growing outward horizontally will fail when its vertical dimension surpasses the vertical failure criterion. The horizontal extent will be comparable to the vertical extent, so only a small portion of the waste is likely to release gas. Even if there is a significant bias toward fingering in the horizontal direction, vertical failures, possibly resulting from an intersection with another dendritic region centered at a different height, will prevent the formation of large, connected regions that are significantly extended in the horizontal direction. Only fingering mechanisms with a bias of more than 20% favoring horizontal over vertical growth are likely to result in the flat, extended dendritic regions that are necessary for a large release across the tank.

Even if a large, horizontally extended region were to form, nonuniformities in the growth of the dendritic region will cause it to break up into smaller regions. Assuming that a large, flat, connected region forms and continues to grow upward and outward, the portion of the upper or lower surface that initially exceeds the vertical failure criterion will be fairly localized. For the entire connected dendritic region to exceed the vertical failure criterion, a large, flat portion of the dendrite would need to fail.

However, a small localized failure in the region of the initial intrusion, which breaks the intrusion off from the rest of the dendrite, could cause both resulting dendrites to fall back under the vertical failure criterion.

An alternative to having the chimney mudpot acting in a sludge layer is to have a sludge layer deposited on top of saltcake. This has been seen in core samples of Tank 241-S-102.^(a) The sludge acts as an impermeable barrier to gas formed in the saltcake, which would otherwise migrate as bubbles through the saltcake until they escaped into the tank head space. The maximum overpressure that can be retained by the sludge is governed by the yield stress criterion described above, which dictates that the maximum height of the column of gas retained under a sludge pressure seal is proportional to the yield stress of the sludge. For a 1000-Pascal sludge, the column of gas trapped under the pressure seal is about 10 cm. For a standard 22.9-m-diameter tank, assuming a void fraction of 0.1 in the layer of gas trapped below the pressure seal, this works out to a total release volume of 41 m³. If the seal is located near the bottom of the tank, the release volume will increase because of expansion of the released gas.

The formation of dendritic bubble networks and chimney mudpots requires the presence of a finite yield stress sludge or saltcake and the generation of insoluble gas. Insoluble gas can be detected by a level rise, a negative value of the pressure response dL/dP , or the presence of insoluble gases such as hydrogen or nitrous oxide in the head space. The presence of active mudpots can be detected by the appearance of obvious venting structures such as fumeroles on the surface of the waste. However, fumeroles have been positively identified only on the surface of Tank 241-SY-101.^(b)

2.4.2 Fracture and Dryout

This mechanism acts to increase the volume of sludge that is close to the surface and therefore minimizes the effect of the depletion zones on the release rate. Cracks that form on the waste surface as it dries propagate downward into the waste, increasing the effective surface area of the waste. Fractures may also be instrumental in releasing pockets of concentrated or pressurized gases that form under the waste surface.

Except under certain narrowly defined conditions, it is unlikely that fracture and dryout will significantly enhance the rate of ammonia release due to evaporation. The increased rate of release would be due primarily to the increase in waste surface area resulting from the cracks. However, under most

(a) Recknagle, KP. 1996. *Analysis of Visual Observations for Single Shell Tanks*. TWS96.3, Pacific Northwest National Laboratory, Richland, Washington.

(b) *ibid.*

conditions, fracturing will not increase the surface area of waste that is already saturated with liquid. The fractures resulting from waste dryout will extend through the dry region of the waste and will terminate when the waste becomes moist. Moist waste will most likely exhibit some plastic behavior that will allow it to 'heal' when a crack forms. Increasing the surface area of dry waste will have no effect on the ammonia release rate, because dry waste is not expected to retain ammonia. The dry waste would also be expected to be fairly permeable with respect to diffusion of ammonia vapor, so cracks that form in the dry layer would not significantly increase the ammonia release rate.

The one scenario in which surface cracks will increase the surface area of moist waste is if the moist waste below the surface is very rigid, which might happen if the waste forms a very stiff gel. For this case, cracks appearing at the surface could be assumed to penetrate straight through the rigid waste layer. If the rigid waste layer is extremely thick, then this assumption may break down.

A secondary effect of extensive cracking of the waste is that narrow cracks will suppress convection, and the release of ammonia will be limited by gas phase diffusion. However, because gas phase diffusion constants are orders of magnitude larger than the diffusion constants for aqueous solutions, this is expected to make only a small difference in the overall release rate of ammonia, particularly if the cracks do not extend far into the waste.

Surface cracking has been proposed as a method of breaching large volumes of stored gas below the surface of the waste. However, no method of generating these large gas volumes has been proposed. Even if a void or cavern were formed, if it occurs in dry waste it cannot retain significant amounts of flammable gas because of the high porosity and poor gas retention characteristics of dry waste. Surface cracking is easily detected by examining the waste surface.

2.4.3 Subsidence

Subsidence is the collapse of one layer of waste and the subsequent forcing of liquid or gas up to the surface. This can occur if one of the lower waste layers is a mechanically weak porous solid or possibly a gel. If the liquid level is at or above the top of the waste surface, the upper portions will be partially supported by buoyant forces, and the weak solid or gel layer may be strong enough to support the material above it. If some of the liquid is removed during an operation such as salt well pumping, or by leakage, the drop in liquid level will increase the stress on the weak layer, possibly resulting in a collapse. Assuming that the weak layer is saturated with liquid, the collapse may displace liquid to the top of the tank, resulting in exposure of a fresh liquid surface and a temporary increase in the evaporation rate for ammonia.

Suppose a layer of dense material is lying on top of a completely submerged layer which is mechanically fairly weak. This may be due to a high density of cavities in the weak layer or it may be because the layer is formed from a low-density gel. The liquid level is assumed to be above the weak layer and lies somewhere within the layer above it. Assume that a height h_u of the upper layer is exposed and a height h_l is covered by liquid. The geometry of the situation is shown schematically in Figure 2.1.

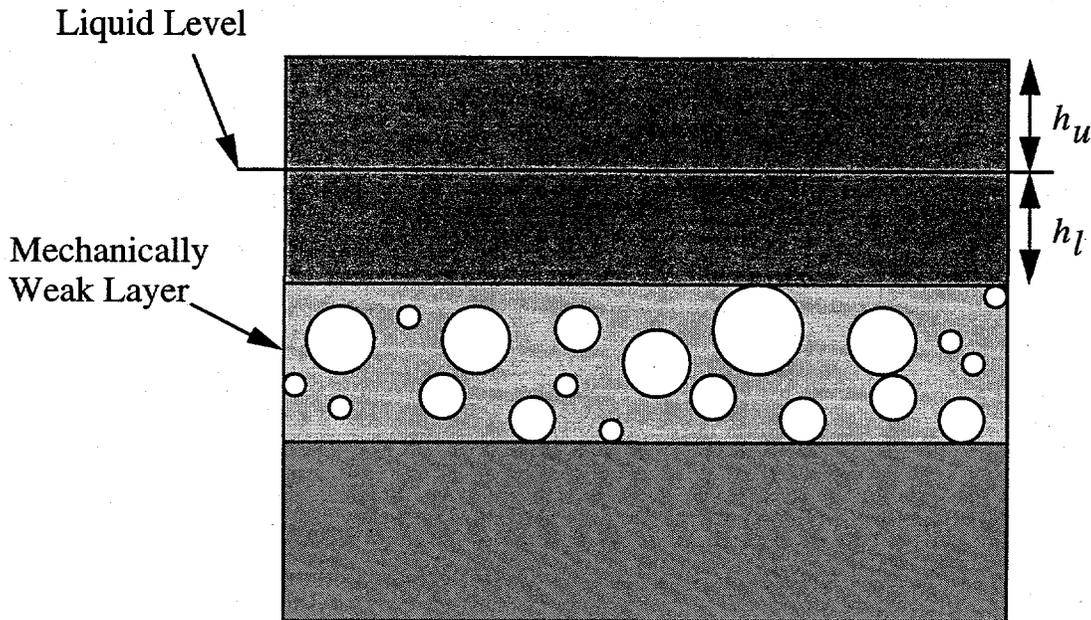


Figure 2.1. Schematic of Subsidence in Tank Waste

The upper layer has a density ρ_s and a void fraction α and the liquid has a density ρ_l . The total force this layer exerts on the weak layer below is

$$h_u(1 - \alpha)\rho_s g + h_l(1 - \alpha)(\rho_s - \rho_l)g$$

This force must be supported by the weak layer. As the liquid level drops, h_u increases and h_l decreases. Because $\rho_s \gg \rho_s - \rho_l$, a drop in the liquid level will result in an increasing force on the weak layer underneath. If this force exceeds the compressive yield stress of the weak layer, the weak layer will collapse and the liquid it contains will be forced through the upper layer. This will expose fresh liquid to the tank dome space and may even result in the appearance of a fresh convective layer on top of the waste, resulting in enhanced evaporation of ammonia. However, in order for this to result in a substantial increase in the head space ammonia vapor concentration, the subsidence would have to occur rapidly over a large portion of the tank. This has not been observed. Subsidence of dry waste may force a small

volume of gas into the head space. However, because dry waste is expected to be fairly permeable, the gas forced into the head space by this type of subsidence is unlikely to differ much from the gas already in the head space.

2.5 Consideration of Tank Operations

Operations on the tanks such as core sampling, mixing or sluicing, saltwell pumping, etc., can all be expected to affect the ammonia release rate in tanks with high ammonia concentrations. Each of the major tank farm activities and its possible impact on ammonia release is reviewed below.

2.5.1 Intrusion

Intrusion refers to any activity that penetrates the surface of the waste. This includes core sampling and the placement of probes. Because of the small surface area involved, intrusion is not expected to greatly affect the concentration of ammonia in the head space by exposing fresh waste. However, intrusion may trigger a substantial release if an unstable situation exists in the tank. This could occur in a tank that is about to rollover or in a tank that is approaching the saturation concentration of ammonia and is a candidate for a limnic eruption. Intrusion into a tank with an active chimney mudpot mechanism could also result in a release, albeit a small one.

2.5.2 Dilution

Dilution can affect the head space ammonia concentration in two opposing ways. The act of introducing the diluent itself is expected to result in significant agitation of the waste and the exposure of the tank surface to fresh waste. For tanks with a high ammonia concentration in the waste, this will result in a significant increase in ammonia concentration in the head space – provided the head space ammonia concentration is below the equilibrium vapor concentration. On the other hand, if the diluent is water, the solubility of ammonia in the waste will increase, which will lower the equilibrium vapor pressure of ammonia in the waste. This will lower the equilibrium concentration of ammonia in the head space for the diluted waste relative to the original waste. The decrease in the equilibrium concentration is expected to be proportional to the dilution ratio, which is unlikely to be more than a factor of 3:1. If the ammonia in the head space of the undisturbed tank was substantially below the equilibrium concentration, dilution will likely result in an increase in head space ammonia concentration, primarily due to the exposure of fresh waste. Because it represents a severe disturbance of the waste, dilution could also initiate a release in an unstable tank, just as in the case of intrusion.

2.5.3 Saltwell Pumping

Saltwell pumping is potentially a very effective method of achieving the equilibrium vapor pressure of ammonia in the head space. As fluid drains from the saltcake, a thin coating of fluid is left on the pore walls. The total volume of this fluid can be quite large, and it is dispersed so that the surface area of the liquid is very large. The ammonia in the thin liquid layer coating the pore wall needs to diffuse only a short distance before reaching the liquid surface and evaporating. The empty pore spaces are generally expected to be connected to the tank head space, so the movement of ammonia through the drained saltcake will be characterized by gas phase diffusion constants, which are orders of magnitude larger than those for the liquid. These conditions will allow rapid equilibration of a large volume of liquid with the tank head space. If the liquid fraction of the waste has a high ammonia content, then high head space concentrations of ammonia can be expected. This behavior was observed by Peurrung and Gauglitz^(a) in simulations of saltwell pumping using the STOMP hydrology simulator code.

2.5.4 Tank Mixing/Sluicing

Tank mixing and sluicing operations can be expected to create large-scale disturbances and agitation of the waste; this can result in large ammonia releases both by liberating bubbles of trapped gas in the sludge and by constantly exposing fresh waste surfaces to the dome head space. The constant renewal of the waste surface minimizes the effect of local depletion due to diffusion and evaporation of ammonia. Tank operations may also precipitate a release if an unstable equilibrium exists. If a mixing time τ_M is assigned to the sluicing or mixing operation to represent the amount of time required to turn over the tank contents, then the ammonia release rate can be estimated in a manner similar to that used to examine the effect of natural convection. Because the mixing time is likely to be short, operations of this type will probably result in very rapid release of ammonia. The concentration of ammonia in the dome head space will probably be close to the equilibrium concentration, even for ventilated tanks.

Tank mixing operations might be expected to result in large ammonia releases if two types of tank waste are combined so that the mixture reflects a large drop in the Henry's Law constant compared with its value for one of the original wastes. If the waste also contains a significant concentration of ammonia, then a potential problem might occur due to the abrupt increase in the ammonia vapor pressure, which might result in a limnic eruption of ammonia. However, an eruption of this kind would require that the Henry's Law constant of the mixed waste be sufficiently low and the concentration of

(a) Peurrung, LM. and PA Gauglitz. 1996. *Gas Release During Salt Well Pumping: Model Predictions from the STOMP Hydrology Simulator*. TWSFG96.14, Pacific Northwest National Laboratory, Richland, Washington.

ammonia in the mixed waste sufficiently high that the vapor pressure of ammonia in the mixture is at least one atmosphere. Both of these conditions may be extremely difficult to achieve if the separate waste streams are already below saturation.

The most likely scenario for lowering the Henry's Law constant is to suddenly increase the pH in one of the tanks. The conversion of ammonium ion to dissolved ammonia would be expected to substantially lower the solubility of ammonia in the waste. From Norton and Pederson (1994, 1995), the Henry's Law constant for a 4 M solution of sodium hydroxide is about a factor of three smaller than the Henry's Law constant for pure water at the same temperature (This is true over the temperature range 20°C to 70°C). This ratio may change as other electrolytes are added to the solution. Starting with a tank that is 0.2 wt% ammonia and is at a low pH, and then suddenly increasing the hydroxide concentration to 4 M may decrease the solubility of ammonia by a factor of three, and increase the equilibrium vapor pressure of ammonia over the waste by a factor of three (assuming this change in hydroxide could be done without a significant dilution of the waste). However, the ammonia would still be quite soluble. From the calculations done above for the limnic eruption, the 0.2 wt% solution is well below the saturation concentration. This calculation is based on the correlation for the SY1-SIM-93B simulant, which is expected to have a hydroxide concentration of about 2 M (Norton and Pederson 1994). At this concentration of hydroxide, the ammonia is already present in the waste as ammonia and not ammonium ion, and further increases in the hydroxide concentration are unlikely to have a large effect on the ammonia solubility.

2.6 Ammonia Hazard Evaluation

Determining the ammonia hazard in the SSTs and DSTs is complicated by the lack of reliable and detailed information for many of the tanks. However, most of the hazard can be classified by obtaining answers to the following three questions:

1. What is the waste configuration?
2. Is there a significant amount of insoluble gas being generated and retained?
3. What is the ammonia concentration in the waste?

With the possible exception of Question 3, a complete or partial answer to each of these questions is available for almost all of the tanks at Hanford. To evaluate ammonia hazards, the waste configurations can be divided into the following four classes:

Configuration A: Sludge/saltcake under supernatant liquid, with or without crust above the supernatant.

Configuration B: Wet sludge/saltcake with little or no supernatant (i.e., free liquid level approximately equal to solid waste level).

Configuration C: Dry saltcake over a wet sludge/saltcake layer. For this configuration, the liquid level is below the waste surface (see Figure 1).

Configuration D: All liquid, or a suspension of solids with zero yield stress.

Information on the waste configuration is available from historical fill records, core sampling, in-tank photographs, and ball rheometer measurements.

Configuration A is an indicator for either a potential rollover or a limnic eruption. It may also present a hazard with respect to seismic disturbances and various tank operations such as dilution and retrieval. Any of these activities can be expected to turn over large volumes of waste, exposing the surface to fresh waste as well as releasing any trapped gas. If the tank is a candidate for either a rollover or a limnic eruption, then intrusive activities, such as core sampling, present a hazard because they may initiate these events. In Section 3 it will be shown that this configuration is more likely to retain large amounts of ammonia if there is a crust or some other diffusion barrier floating on the supernatant layer.

Configuration B is not a likely candidate for either a rollover or a limnic eruption because it lacks a supernatant layer that would make significant motion of the sludge layer possible. A seismic event could still liquefy the tank contents, releasing trapped gas and exposing the surface to fresh waste. If a tank containing this waste configuration is saltwell-pumped, a high head space ammonia concentration may result if the interstitial liquid has a high ammonia concentration. Tank operations such as retrieval and dilution may also result in high head space concentrations.

Configuration C can pose a significant ammonia hazard only if the wet sludge/saltcake layer is relatively thick. The dry saltcake layer cannot retain much ammonia. If this configuration is saltwell-pumped, high head space ammonia concentrations can result if the concentration of ammonia in the interstitial liquid is high. Tank retrieval and dilution operations can also result in high head space ammonia concentrations.

Configuration D is not expected to present an ammonia hazard under most circumstances. This configuration cannot retain insoluble gas, so any mechanism requiring corelease of ammonia with insoluble

gas can be ruled out. Further, because the waste is subject to natural convection, the release rate of ammonia due to evaporation from the surface should remain relatively high, and the steady state concentration of ammonia in the waste should be low. The only way to achieve a high ammonia concentration for this configuration is a high ammonia generation rate in the waste or direct addition of ammonia to the waste stream. With direct addition, high ammonia concentrations would persist for only a short time.

Information about whether insoluble gas is being generated and retained (Question 2) can be obtained from three sources:

- A negative value of dL/dP for the tank.
- An observable level rise over time, not attributable to water intrusion or addition.
- High concentrations of insoluble gases such as hydrogen and nitrous oxide in the tank head space.

Only the first of these, dL/dP , is a good indicator that the tank is generating and retaining gas (Whitney 1995). A level rise may be due to other factors such as a tank intrusion, and a high concentration of insoluble gas in the head space does not imply that the gas is being retained. However, in the absence of additional information, the presence of one or more of these conditions can be taken as an indication of gas generation and retention, and additional measurements and study are in order.

Gas generation and retention is an indicator for rollover in configuration A. Retained gas can also be released as a consequence of retrieval and dilution operations, as well as by a seismic event. However, the volume of ammonia released as part of the gas trapped inside the bubbles is probably a small fraction of the amount of ammonia released as a consequence of mixing and exposure of fresh waste at the surface of the tank. The release of trapped gas may contribute to an overall flammability hazard, since one of the insoluble gases generated by the tanks is hydrogen, which is much more flammable than ammonia.

Information about the concentration of ammonia in the tanks (Question 3) can be obtained from direct measurement of ammonia in the waste or in the head space. High ammonia vapor measurements in the head space probably indicate significant ammonia in the waste, but because of mass transport limitations, low ammonia head space measurements do not necessarily imply a low concentration of ammonia in the waste. If transport of ammonia in the waste is limited by liquid phase diffusion, then it is possible for high concentrations of ammonia to exist in the waste while only a low ammonia vapor concentration appears in the head space. If it is possible to determine that there is little or no ammonia dissolved in the waste, then the ammonia hazard in the tank can be assumed to be small. However, in most tanks very

little is known about the ammonia concentration, and the ammonia concentration must therefore be assumed to be substantial until more data can be collected.

A very high ammonia concentration, on the order of 1 wt% or greater, is an indicator for a potential limnic eruption in tanks with waste configuration A. No concentration this high has ever been observed in a Hanford tank. Ammonia concentrations on the order of 0.2 wt% are indicative of potential problems from the viewpoint of human safety and would be expected to achieve equilibrium vapor pressures that represent a substantial fraction of the LFL for ammonia. Concentrations in this range have been observed for several tanks. Ammonia concentrations in this range would also indicate potential problems for tank operations, such as dilution, retrieval, and saltwell pumping, that might disturb large fractions of the waste. This concentration range could also lead to high ammonia vapor concentrations in the head space in the event of a rollover or an earthquake that managed to disturb large volumes of the tank waste.

2.7 Summary of Ammonia Retention and Release

The key to characterizing the ammonia hazard in both SSTs and DSTs is determining the concentration of ammonia in the waste. This, combined with estimates of the Henry's Law constant, provides an upper bound on the concentration of ammonia in the head space in any release scenario. Current upper bounds on the concentration of ammonia in the waste and estimates of the Henry's Law constant lead to equilibrium concentrations in the head space that are on the order of 5 to 10% ammonia by volume, i.e., less than the LFL of ammonia in air of 15%.

Tanks that remain undisturbed for long periods of time will have concentrations of ammonia in the head space that are substantially below the equilibrium vapor concentration based on the concentration of ammonia in the waste. This occurs because transport of the ammonia to the waste surface is diffusion-limited. As longer periods of time pass, the difference between the measured head space ammonia concentration and the expected equilibrium concentration increases. For this reason, head space measurements of ammonia may lead to considerably underestimating the concentration of ammonia in the waste.

Only three natural release scenarios are expected to result in high concentrations of ammonia in the head space: rollovers, earthquakes, and limnic eruptions, and only in tanks that already contain a high concentration of ammonia in the waste. Of the three, only rollovers have been observed to occur in the Hanford waste tanks. A rollover can generate high ammonia concentrations via a combination of 1) direct release of ammonia along with other insoluble gases and 2) evaporation of ammonia from the fresh waste surface that is produced as a consequence of the rollover. Earthquakes can potentially achieve a high ammonia concentration by creating a fresh waste surface, but only in tanks containing a fairly weak sludge. Further modeling of earthquakes in the waste tanks may clarify the probability of an earthquake

releasing a significant amount of ammonia. A limnic eruption will result in an enormous release of ammonia; however, the probability of achieving the conditions necessary for a limnic eruption to occur appear small. This scenario will be discussed in more detail in the next section.

Tank farm operations can lead to high ammonia concentrations in the head space by agitating the waste and allowing the head space concentration of ammonia to reach the equilibrium value. This is particularly true for such operations as dilution, saltwell pumping, and tank mixing/sluicing. Intrusions such as would occur during sampling are much less likely to result in large ammonia releases unless the tank is already primed to release a large amount of gas due to a natural release event like a rollover. Adjustment of the pH in the tanks may also result in an elevation of the ammonia levels in the tank by decreasing the solubility of ammonia. This is particularly true if the tank is originally at low pH. However, it is unlikely that a pH adjustment will lower the ammonia solubility to the point at which ammonia vapor begins to bubble out of the waste.

A reasonable assessment of the ammonia hazard can be made by determining 1) the waste configuration, 2) whether insoluble gas is being retained and generated in the waste, and 3) the concentration of ammonia in the waste. This information is enough to identify tanks with a high ammonia hazard and to roughly categorize the hazard. This information is either available or will be available in the future.

2.8 Recommendations

The key to resolving ammonia safety issues in the tanks is a better understanding of the concentration of ammonia in the tanks and more complete characterization of the Henry's Law constant for actual tank waste. At present, values of the ammonia concentration in the waste are relatively scarce, particularly for the SSTs. A higher priority should be put on obtaining these numbers from waste samples in future core sampling operations. More information about the vertical distribution of ammonia in both SSTs and DSTs would provide an opportunity to make a quantitative comparison between the retention scenarios described here and the behavior of ammonia in the tanks.

3.0 Ammonia Concentration Modeling

An effervescence of the type experienced at Lake Nyos (Kantha and Freeth, 1996; Zhang, 1996; Kling, et al., 1994) has been suggested as a possible scenario that might produce unusually large and dangerous releases of ammonia from the single-shell and double-shell waste tanks at Hanford. The Lake Nyos effervescence (which is referred to as a limnic eruption) involved a rapid release of carbon dioxide from saturated solution in the lake water. The Hanford tanks are not as deep as lake Nyos, but ammonia is significantly more soluble in water than is CO_2 , which results in the concern that a similar violent effervescence could occur with ammonia under some conditions in the tanks.

In the Lake Nyos event, liquid saturated with CO_2 was disturbed in such a way that it could no longer hold the dissolved gas in solution. The CO_2 came out of solution very rapidly, releasing a very large volume of gas in a short period of time. In order for such an event to occur, two conditions must be met. First, the liquid must be saturated with the gas; and second, something must disturb the equilibrium condition of the solution. In the case of the waste tanks, a number of mechanisms have been postulated as potential triggers for such an event, including earthquakes, rollovers, and waste handling activities. For tanks that have become fully saturated, even minor disturbances, such as those caused by thermal variation or changes in the ambient air pressure, may be sufficient to trigger a release.

This section will focus on developing a model of the ammonia concentration profile within the tank. Understanding the behavior of the concentration profile is the key to assessing the likelihood of a limnic eruption in the Hanford waste tanks. A time-dependent one-dimensional model of the ammonia distribution as a function of height in the tank has been developed. The concentration profiles predicted by this model can then be compared with the ammonia saturation profile. If the ammonia concentration profile reaches or exceeds the saturation profile at any point in the tank, the tank can be considered at risk for a limnic eruption. If the ammonia concentration profile is below the saturation profile throughout the tank, then a limnic eruption is unlikely.

The saturation concentration of ammonia in a tank can be calculated from Henry's law, assuming that the partial pressure of ammonia in the crust, supernatant, and the sludge is equal to the hydrostatic pressure. It is also assumed that the interstitial space in the sludge layer is filled with supernatant fluid. Figure 3.1 shows a plot of the steady state saturation concentration of ammonia as a function of elevation for a typical tank with sludge under a supernatant layer. (Additional details on the calculations for this figure are given below). Ranges of ammonia concentration values measured in the head space (for

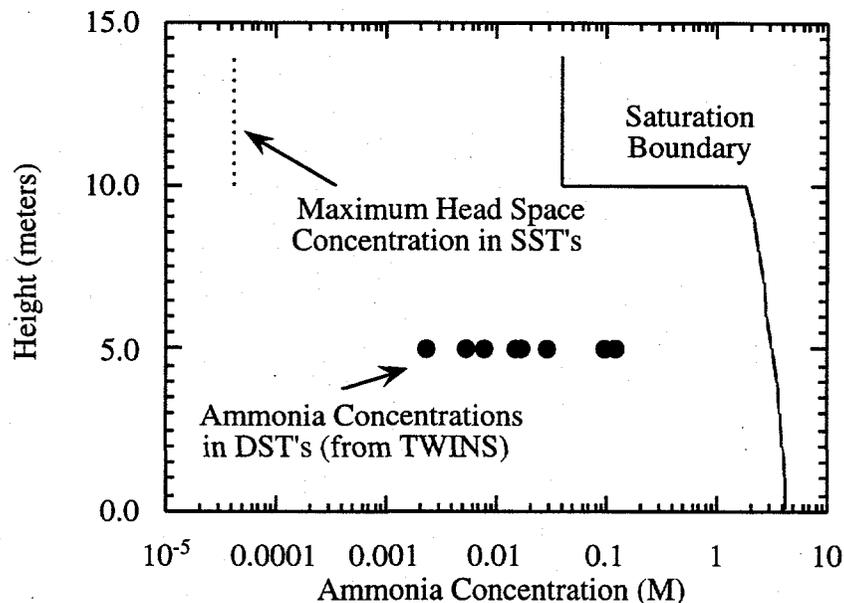


Figure 3.1. Ammonia saturation boundary (solid line) for a tank containing 10 meters of sludge and supernatant. For comparison, the maximum head space concentration of ammonia seen in the SST's (dotted line) and the ammonia concentration values measured in the DST supernatants (dots) are also included.

SSTs) and in the supernatant (for DSTs) are also shown on the plot. These data indicate that the conditions are far from saturation, at least for the supernatant, and therefore suggest that a limnic eruption in the waste tanks is unlikely. However, no data is available on ammonia concentrations in the sludge layer of DSTs.

To make a categorical statement that such an event is unlikely in any of the tanks under any expected conditions however, it is necessary to determine what the concentration of ammonia is in any given tank at any given time. If it can be shown that the ammonia concentration in a tank is not at or near saturation at any time in the tank's history, then it is reasonable to suppose that a limnic eruption cannot occur. If the ammonia concentration does approach saturation, then further analysis is in order to evaluate the effects of proposed trigger mechanisms. In either case, this approach requires a dynamic model that can determine the ammonia concentration profile in the tank over time with some reasonable degree of accuracy.

Three one-dimensional mathematical models of ammonia transport in the tanks due to convection and diffusion processes have been developed, which predict the ammonia concentration as a function of time. These are simple transport models which make use of several parameters, including source terms for ammonia generation and mass transport across the fluid-fluid and fluid-air interfaces. Few of the model parameters are known or can be determined with reasonable accuracy using currently available tank instrumentation. The remaining parameters can be estimated using reasonable engineering assumptions or experimental correlations, which will at the very least allow bounding calculations to determine the greatest possible ammonia concentration profile that can be expected in a tank. The results of calculations using the model are then compared to the saturation boundary to assess whether a limnic eruption hazard exists. The models are described in detail in the following subsections, along with discussions of the assumptions used to estimate the model parameters.

3.1 Introduction

For the purposes of ammonia concentration modeling, three tank waste configurations will be investigated. These correspond to waste configurations A (with and without a crust) and B, described previously in Section 2.6. The three configurations, illustrated in Figure 3.2, are

- a) sludge, with gases in the dome space
- b) sludge and supernatant liquid, with gases in the dome space
- c) sludge and supernatant liquid capped with a crust, with gases in the dome space

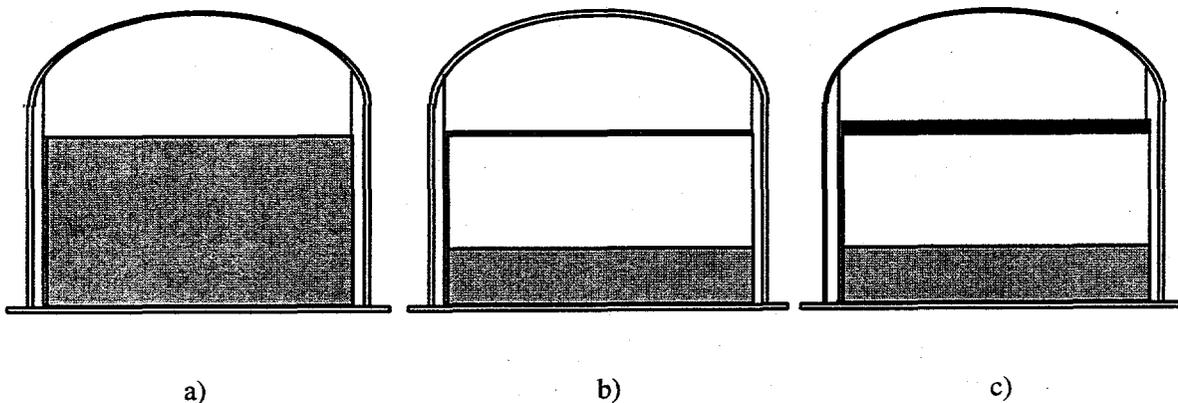


Figure 3.2. Tank Waste Configurations, a) All Sludge, b) Sludge-Supernatant, c) Sludge-Supernatant-Crust.

In a limnic eruption, fluid saturated with the dissolved gas must be disturbed by some event that causes an upward motion of fluid, resulting in a local pressure change that upsets the equilibrium condition of saturation. The sludge is a shear-thinning material with a yield stress (Stewart et al. 1995, Shepard et al. 1995), and would therefore be resistant to induced motion in response to a trigger event. The supernatant liquid is similar to water, and therefore can move in response to an applied force. Because they contain both sludge and supernatant, configurations (b) and (c), are more interesting in this analysis. However, insoluble gases in the sludge layer may be able to overcome the yield stress of the material, so the possibility of an upwelling in configuration (a) cannot be totally discounted.

The governing equations for all three configurations are given in Section 3.3. The models account for ventilation of the dome space, and assume that ammonia is generated by a combination of radiolytic and thermal reactions occurring at different rates within the sludge and supernatant layers. Forced convection in the dome space and buoyancy-driven convection in the supernatant layer are assumed to produce a uniform concentration of ammonia in the head space and in the liquid layer. The primary mechanism for mass transport in the sludge layer is assumed to be diffusion. To evaluate the likelihood of a limnic eruption, the concentration profiles predicted using these models for the three configurations are compared to the ammonia saturation concentration profile in the tanks. An ammonia concentration profile that touches the saturation profile at any point represents a tank in an unstable configuration that could spontaneously release a large quantity of ammonia in response to a small disturbance of the tank contents. The components of the models and the boundary conditions are presented in Sections 3.3 through 3.7 below.

Results for sample calculations with these models, spanning a range of conditions, are presented in Section 3.8. The calculations show that tanks with a foam or crust layer floating on top of the supernatant can account for measured ammonia concentrations in the DSTs. The local ammonia concentration, however, does not exceed the saturation limit at any point inside the tank.

3.2 Saturation Concentration

A necessary but not sufficient condition for effervescence is that saturation concentration must be attained at some region of the waste in the tank. The saturated concentration can be calculated from Henry's law, assuming that the partial pressure of ammonia in the crust, the supernatant and the sludge is equal to the hydrostatic pressure. It is also assumed that the interstitial space in the sludge layer and crust is filled with the supernatant fluid. Therefore, the saturation concentration C_{sat} (in kg ammonia / m^3 solution) as a function of elevation z (in m from the bottom of the tank floor) is

$$C_{\text{sat}}(z) = \frac{K_H [p_0 + \rho g(H - z)] M \rho \omega_w}{\gamma_1} \quad (1)$$

where K_H is the Henry's law constant for ammonia in pure water (in moles / kg-atm), p_0 is the dome space pressure (in atm), ρ is the density of the supernatant (in kg / m³), H is the combined depth of supernatant and sludge layers (in m), M is the molecular weight of ammonia (in kg / moles), g is the gravitational acceleration, γ_1 is the activity coefficient for ammonia in the supernatant, and ω_w is the mass fraction of water in the supernatant. This formula assumes that the solid particles in the sludge layer are settled, so that their weight is mechanically transmitted through the particle grains to the bottom of the tank. If the particles were instead suspended in the sludge layer, this formula would have to be modified to account for the effective increase in the density of the supernatant. Because of this, this formula cannot be applied to tanks with a crust, but the crust has only a small affect on the saturation profile. A discussion of the Henry's law and activity coefficients for ammonia in a simulated waste for Tank 241-SY-101 can be found in Norton and Pederson (1995). Equation (1) was used to obtain the saturation boundary shown in Figure 3.1.

3.3 Mathematical Model

Three models are proposed to calculate the time history of the ammonia concentration profile for any particular tank that conforms to any of the three configurations shown in Figure 3.2. Based on available data (temperature, ventilation flow rate, etc.) for various tanks, estimates of the parameters in these models and the assumptions used to obtain them will be described. The remainder of this section presents some calculations to illustrate the application of the models in each tank configuration.

In all three configurations, ammonia generation within the tank is modeled with a source term representing the thermal and radiolytic generation of ammonia within the waste. This generation rate is assumed to be constant, although it may actually have a time dependence in the tanks, particularly if the generation rate is related to the level of radioactivity. The generation rate is assumed to be correlated with the fraction of liquid in the waste. The supernatant layer is therefore assigned a higher generation rate than the sludge layer. The relative ratio of ammonia generation in the sludge and supernatant layers is kept fixed in these calculations. Only the overall generation rate is varied.

The effect of ammonia degradation is also incorporated in the model. Bryan and Pederson (1996) calculated that 0.15% of ammonia is degraded in the course of one year. This is equivalent to a decay rate constant of $4.8 \times 10^{-11} \text{ sec}^{-1}$. The mass flux of ammonia between the supernatant and the gas in the dome space is estimated from penetration theory. The mass flux between the sludge or crust and

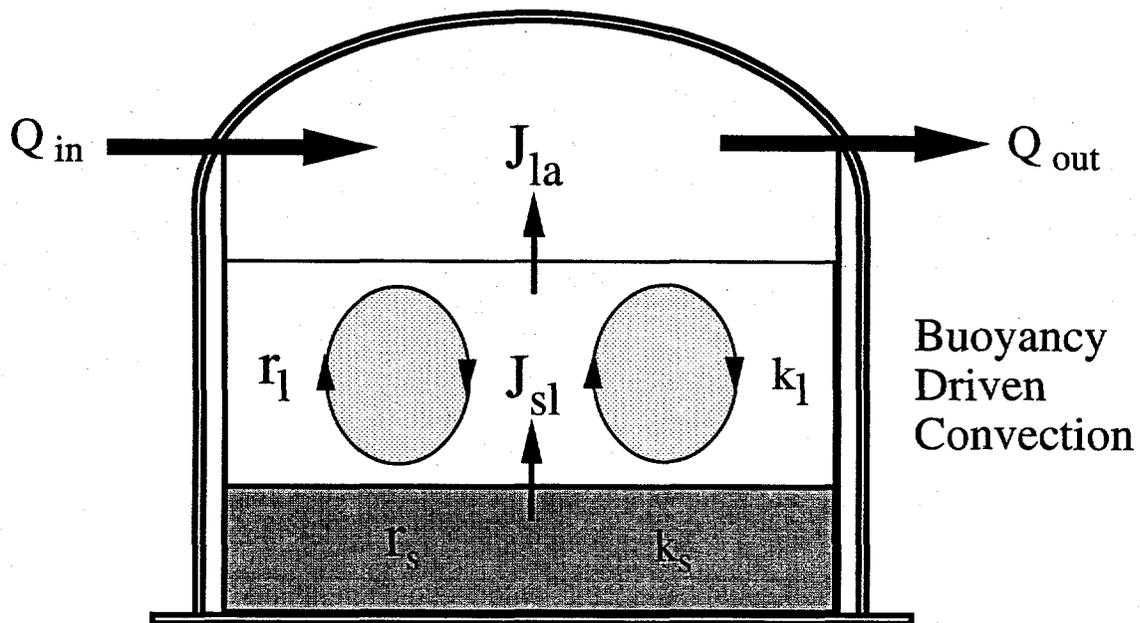


Figure 3.3. Schematic Diagram for the Ammonia Concentration Distribution Model.

the supernatant is estimated from correlations for buoyancy-driven convection in horizontal containers, and by applying the analogy between heat transfer and mass transfer. Because there is convection in the dome space and in the supernatant, the ammonia concentrations are assumed to be uniform in each phase. The dome space is assumed to be ventilated at a constant air flow rate, Q . It is assumed that the initial concentration is known throughout the tank.

Forced convection in the dome space, and buoyancy-driven convection in the supernatant layer, contribute to turbulent mixing that leads to uniform concentration (independent of the spatial coordinate) within these regions. The absence of convection in the sludge and crust layers implies that ammonia concentration there is governed by molecular diffusion. The concentration in these layers will be nonuniform. In all cases, the flux of ammonia across each interface is continuous and can be expressed in terms of an overall mass transfer coefficient. At the bottom of the tank, a no mass flux boundary condition is enforced. Application of the above assumptions to each tank configuration, together with the conservation of mass equation, leads to the following convection-diffusion equations and boundary conditions for the ammonia concentration:

Sludge with Gases in the Dome Space

$$\frac{dC_a(t)}{dt} = \frac{A}{V_a} J_{sa} - \frac{Q}{V_a} C_a(t) \quad (2a)$$

$$\frac{\partial C_s(z,t)}{\partial t} = D_s \frac{\partial^2 C_s(z,t)}{\partial z^2} + r_s - k_s C_s(z,t) \quad (2b)$$

$$J_{sa} = -D_s \left. \frac{\partial C_s}{\partial z} \right|_{z=Sludge\ Top} \quad (2c)$$

$$0 = -D_s \left. \frac{\partial C_s}{\partial z} \right|_{z=Sludge\ Bottom} \quad (2d)$$

Sludge and Supernatant liquid with Gases in the Dome Space

$$\frac{dC_a(t)}{dt} = \frac{A}{V_a} J_{la} - \frac{Q}{V_a} C_a(t) \quad (3a)$$

$$\frac{dC_l(t)}{dt} = \frac{A}{V_l} (J_{sl} - J_{la}) + r_l - k_l C_l(t) \quad (3b)$$

$$\frac{\partial C_s(z,t)}{\partial t} = D_s \frac{\partial^2 C_s(z,t)}{\partial z^2} + r_s - k_s C_s(z,t) \quad (3c)$$

$$J_{sl} = -D_s \left. \frac{\partial C_s}{\partial z} \right|_{z=Sludge\ Top} \quad (3d)$$

$$0 = -D_s \left. \frac{\partial C_s}{\partial z} \right|_{z=Sludge\ Bottom} \quad (3e)$$

Sludge, Supernatant Liquid and Crust with Gases in the Dome Space

$$\frac{dC_a(t)}{dt} = \frac{A}{V_a} J_{ca} - \frac{Q}{V_a} C_a(t) \quad (4a)$$

$$\frac{\partial C_c(z,t)}{\partial t} = D_c \frac{\partial^2 C_c(z,t)}{\partial z^2} + r_c - k_c C_c(z,t) \quad (4b)$$

$$J_{ca} = -D_c \left. \frac{\partial C_c}{\partial z} \right|_{z=Crust\ Top} \quad (4c)$$

$$J_{lc} = -D_c \left. \frac{\partial C_c}{\partial z} \right|_{z=Crust\ Bottom} \quad (4d)$$

$$\frac{dC_l(t)}{dt} = \frac{A}{V_l} (J_{sl} - J_{lc}) + r_l - k_l C_l(t) \quad (4e)$$

$$\frac{\partial C_s(z,t)}{\partial t} = D_s \frac{\partial^2 C_s(z,t)}{\partial z^2} + r_s - k_s C_s(z,t) \quad (4f)$$

$$J_{sl} = -D_s \left. \frac{\partial C_s}{\partial z} \right|_{z=\text{Sludge Top}} \quad (4g)$$

$$0 = -D_s \left. \frac{\partial C_s}{\partial z} \right|_{z=\text{Sludge Bottom}} \quad (4h)$$

where t is the time variable; z is the vertical coordinate (elevation from the tank floor); the subscripts a, c, l, and s refer to quantities in the dome space, crust, supernatant, and sludge, respectively; C represents concentration (in kg ammonia / m³ solution); V represents volume (in m³); r represents generation rate (in kg of ammonia / m³ solution-sec); k represents decay rate (in sec⁻¹); A is the cross sectional area of the tank (in m²); Q is the ventilation flow rate in the dome space (in m³/sec); J_{la} is the mass flux of ammonia across the supernatant into the dome space (in kg / m²-sec); J_{sl} is the mass flux of ammonia across the sludge-supernatant interface (in kg / m²-sec); J_{sa} is the mass flux of ammonia across the sludge into the dome space; J_{ca} is the mass flux of ammonia across the crust into the dome space; J_{lc} is the mass flux of ammonia across the supernatant into the crust; and D_s is the diffusion coefficient of ammonia in the sludge (in m² / sec). The initial concentration profile must be assumed for time zero. For most of these calculations, the initial concentration is assumed to be zero everywhere.

3.4 Convection in the Supernatant

Measurements in several double-shell tanks indicate that there is a temperature difference ranging from 4 °C to 8 °C between the sludge-supernatant interface (hot) and the supernatant-gas interface (cold). When a fluid layer is heated from below, buoyancy-driven convection will occur if the Rayleigh number for the layer exceeds 1100 (Chandrasekhar 1981). The Rayleigh number Ra is defined as

$$Ra = \frac{\beta_l \Delta T \rho_l g L^3}{\kappa_l \mu_l} \quad (5)$$

where β_l is the thermal expansion coefficient (in 1/°C), ΔT is the temperature difference between the bottom and the top of the fluid layer (in °C), ρ_l is the density (in kg/m³), g is the gravitational constant, L is the depth of liquid (supernatant) layer, κ_l is the thermal diffusivity (in m² / sec), and μ_l is the viscosity (in Pa-sec). Using the thermophysical properties of water for β_l and κ_l , a density of 1460 kg/m³, and a viscosity of 20 cP, the Rayleigh number in a layer 6 m deep with a 4 °C temperature difference between top and bottom is 1.7×10^{12} . In this case, the buoyancy driven flow will be in the turbulent regime.

A characteristic velocity U for this flow can be obtained by equating the kinetic energy per unit volume to the work per unit volume due to buoyancy (Gebhart et al. 1988);

$$U = \sqrt{\frac{2gL_1(\rho_{\text{top}} - \rho_{\text{bottom}})}{\rho_{\text{bottom}}}} \quad (6)$$

where ρ_{top} (ρ_{bottom}) is the density at the top (bottom) of the supernatant layer. With these parameters, U is 0.43 m/sec and a characteristic time τ_c is 14 sec (L_1 / U).

3.5 Convection in the Sludge

The sludge layer is comprised of a combination of sedimented material, supernatant fluid, and insoluble gas bubbles. For the purpose of analysis, this layer can be regarded as a supernatant saturated porous medium with internal heat generation. Temperature distributions in the sludge of double-shell tanks have been found to be approximately parabolic. Therefore, the rate \dot{q}_s at which energy is generated per unit volume (in W / m^3) can be estimated from the energy equation applied to the sludge layer

$$\dot{q}_s = \frac{2\phi_s}{L_{\text{max}}(L_s - L_{\text{max}})} \left[T_{\text{max}} - T_0 + \frac{L_{\text{max}}(T_0 - T_1)}{L_s} \right] \quad (7)$$

where ϕ_s is the thermal conductivity of the sludge (in $W / m\cdot C$), L_{max} is the elevation at which the maximum temperature occurs, T_0 and T_1 are the temperatures at the bottom and at the top of the sludge layer (in $^{\circ}C$), T_{max} is the maximum temperature in the layer, and L_s is the thickness of the sludge layer.

Convection of a fluid in a porous medium subjected to internal heat generation occurs whenever the modified Rayleigh number R_p exceeds the value of 31 (Tveitereid 1977)

$$R_p = \frac{P\beta_1 g \dot{q}_s L_s^3}{2c_{p1} \kappa_s^2 \mu_1} \quad (8)$$

where P is the permeability of the porous layer (in m^2), c_{p1} is the specific heat capacity of the liquid (in W / m^3), and κ_s is the thermal diffusivity of the porous layer (in m^2 / sec). Using the following temperatures^(a) $T_0 = 37.8^{\circ}C$, $T_1 = 43.6^{\circ}C$, $T_{\text{max}} = 44.4^{\circ}C$, and assuming that the thermophysical properties

(a) Memo from C.W. Stewart, 1995.

for nonmetallic solids apply to the sludge, and that the permeability is $2 \times 10^{-12} \text{ m}^2$, the modified Rayleigh number, R_p , is about 0.03. This value is well below the critical Rayleigh number; indicating that with the assumed temperature distribution, there will be no convection in the sludge layer.

3.6 Supernatant-Gas Mass Transfer

Penetration theory (Cussler, 1984) is applied to estimate the overall mass transfer coefficient at the supernatant-gas interface, h_{1a} . There is a depletion zone below the interface due to the combined effects of buoyancy-driven convection, diffusion of ammonia in the supernatant, and evaporation. The length scale of the depletion zone is $\sqrt{D_1 \tau_c}$. At equilibrium, the concentration of ammonia in the supernatant is related to that in the dome space by Henry's Law. This relationship can be written as

$$C_1(z = L_s + L_1) = \lambda C_a(z > L_s + L_1) \quad (9)$$

The term λ is the Ostwald solubility coefficient (Glasstone 1954), which is related to the Henry's Law constant K_H (in moles / kg-atm) by

$$\lambda = \frac{RT\rho_1 K_H \omega_w}{\gamma_1} \quad (10)$$

where R is the universal gas constant, and T is the absolute temperature at the supernatant-sludge interface (in K).

Applying the diffusion equation to the depletion region with appropriate boundary conditions, in conjunction with Equations (3a-b), and assuming a negligible generation and degradation rate in the depletion zone, the average ammonia concentration in the supernatant C_1 can be obtained in closed form at steady state as

$$C_1 = C_a \left(\lambda + \frac{Q}{A} \sqrt{\frac{\tau_c}{D_1}} \right) \quad (11)$$

Equations (3a-b) can also be solved by assuming that the mass flux, at the boundary J_{1a} is proportional to $(C_1 - C_a)$. With this assumption and neglecting the decay rates, the average concentration C_1 is given by

$$C_1 = C_a \left(1 + \frac{Q}{Ah_{la}} \right) \quad (12)$$

Solving for the proportionality constant h_{la} (overall mass transfer coefficient) from Equations (11) and (12)

$$h_{la} = \left[\frac{A(\lambda - 1)}{Q} + \sqrt{\frac{\tau_c}{D_1}} \right]^{-1} \quad (13)$$

The mass flux, therefore, is

$$J_{la} = h_{la} [C_1(t) - C_a(t)] \quad (14)$$

3.7 Sludge-Supernatant Mass Transfer

A one-to-one correspondence between a convective heat transfer and a convective mass transfer problem can be established when the flow pattern is the same and the dimensionless equations and boundary conditions are mathematically equivalent (White 1988). Therefore, an estimate of the overall mass transfer coefficient at the sludge-supernatant interface, h_{sl} , can be obtained by applying the mass transfer analogy to an experimental correlation for the analogous heat transfer problem.

It is assumed that the transport of ammonia takes place along a flat interface in which the characteristic velocity is imposed by buoyancy-driven convection due to a thermal gradient. Because the sludge layer generates ammonia, there is a constant mass flux at the interface. Turbulent convective motion in the supernatant transports ammonia throughout this layer. The process by which ammonia is transferred through the sludge-supernatant interface can be approximated by a turbulent convective mass transfer process over a flat plate with a constant mass flux. Applying the heat and mass transfer analogy to the turbulent boundary layer flow with constant heat flux (White 1988), we obtain

$$Sh_L = 0.0385 Re_L^{4/5} Sc^{1/3} \quad (15)$$

where Sh_L is the Sherwood number ($h_{sl} L / D_1$), Re_L is the Reynolds number ($U L / \nu_1$), and Sc is the Schmidt number (ν_1 / D_1). The velocity U is calculated from Equation (6), and ν_1 is the kinematic

viscosity of the supernatant. The length of a convection cell ($1.17 L_1$; see Chandrasekhar 1981) is used as the length scale L along the horizontal direction. Therefore, the mass transfer coefficient can be written as

$$h_{sl} = 0.0373 \left(\frac{D_1}{L_1} \right) \left(\frac{v_1}{D_1} \right)^{1/3} \left(\frac{UL_1}{v_1} \right)^{4/5} \quad (16)$$

The mass flux is

$$J_{sl} = h_{sl} [C_s(L_s, t) - C_1(t)] \quad (17)$$

3.8 Ammonia Concentration Model Calculations

The ammonia concentration models described in Sections 3.3-3.7 are expressed as a system of differential equations that can be solved numerically using a tridiagonal implicit solver. All three configurations were included in the implementation of the model in a Fortran computer code. The numerical calculations of the code were validated by comparing the numerical results obtained at long times to analytic steady-state solutions for the three configurations. Calculations were performed to assess the effect of ammonia generation rate on the ammonia concentration profile for all three tank configurations. In addition, calculations were made to assess the effect of crust thickness on the ammonia concentration in the sludge, supernatant, and in the tank head space.

To facilitate comparison between different parameterizations of the three different configurations, the same basic tank geometry was used in all calculations. The geometry parameters were as follows:

head space area = 412 m²

head space volume = 2461 m³

sludge height = 4 m

supernatant height = 6 m

Unless otherwise noted, all calculations reported here assume a tank ventilation rate, Q , of 0.14 m³/sec (300 ft³/min) for the head space. The remaining parameters describe the supernatant and the fraction of liquid in the sludge

$\Delta T = 4$ °C

$\mu_1 = 30$ cP

$$\rho_l = 1460 \text{ kg / m}^3$$

$$\omega_w = 0.361$$

The following representative parameters for the solubility of ammonia in the waste and the ammonia decay rate were obtained from studies of ammonia in waste simulants and in actual waste samples:

$$K_H = 31.12 \text{ moles / kg-atm (Clegg and Brimblecombe 1989)}$$

$$\gamma_l = 8.86 \text{ (Norton and Pederson 1995)}$$

$$k_l = k_s = 4.8 \times 10^{-11} \text{ sec}^{-1} \text{ (Bryan and Pederson 1996)}$$

These values lead to a value of 48 for the Ostwald solubility coefficient, λ . The characteristic velocity for natural convection in the supernatant layer, U , is 0.43 m/sec and the characteristic time, τ_c , is 14 sec. The corresponding mass transfer coefficients are as follows:

configuration (a):

$$\text{sludge-to-air interface} = 0.0000045 \text{ m/sec}$$

configuration (b):

$$\text{sludge-to-supernatant} = 0.0000032 \text{ m/sec}$$

$$\text{supernatant-to-air} = 0.0000045 \text{ m/sec}$$

configuration (c):

$$\text{sludge-to-supernatant} = 0.0000032 \text{ m/sec}$$

$$\text{supernatant-to-crust} = 0.0000032 \text{ m/sec}$$

$$\text{crust-to-air} = 0.0000045 \text{ m/sec}$$

The diffusivity of ammonia in the sludge and in the crust is an input parameter to the model. The values specified determine the rate of mass transfer by diffusion within the sludge and the crust. The value of the molecular diffusivity of ammonia in water is assumed to be representative of the diffusivity of ammonia in the sludge and in the crust (The diffusivity of almost all small solutes in an aqueous solution is on the order of $1-2 \times 10^{-9} \text{ m}^2/\text{sec}$ [Cussler 1984]). The following values of the diffusivity were used in these calculations:

$$\text{in the sludge: } D_s = 1.0 \times 10^{-9} \text{ m}^2/\text{sec}$$

$$\text{in the supernatant: } D_l = 2.0 \times 10^{-9} \text{ m}^2/\text{sec}$$

$$\text{in the crust: } D_c = 1.0 \times 10^{-9} \text{ m}^2/\text{sec}$$

The rate of generation of ammonia in the sludge, supernatant, and crust material is perhaps the most significant variable in the model. Unfortunately, it is also extremely difficult to characterize with any precision for the waste tanks. Therefore, in calculations with this model, a range of generation rates were investigated, representing low, medium, and high values. These rates are as follows:

	supernatant	sludge	crust
low generation rates:	45 g/day	10 g/day	0.252 g/day
medium generation rates:	450 g/day	100 g/day	2.52 g/day
high generation rates:	4500 g/day	1000 g/day	25.2 g/day

For the "high" generation rate, the corresponding volumetric generation rates are 2.1×10^{-8} kg/m³-sec for the supernatant and 7.1×10^{-6} kg/m³-sec for the sludge and crust. The volumetric generation rates in the sludge and in the crust were assumed to be equal (the table above shows mass generation rates). The remaining generation rates can be obtained by scaling by factors of 10. The generation rates in the crust listed above are for a crust layer 10 cm thick. For a 1 meter crust, also investigated in this work, the generation rates increase by a factor of 10. A scale for the generation rate can be obtained by looking at the concentration of ammonia in the head space of Tank 241-SY-101. Allemann (1994) has estimated that the base ammonia concentration in the head space for this tank due to diffusion of ammonia out of the waste is approximately 40 ppmv. The ventilation rate for Tank 241-SY-101 is about 500 ft³/min. Assuming that the 40 ppmv represents a steady-state concentration, it can be calculated that Tank 241-SY-101 is generating about 600 g/day of ammonia. This is on the same order of magnitude as the value defined above as a "medium" generation rate.

The results of calculations with the various tank configurations are presented below. Section 3.8.1 describes the configuration with sludge and supernatant, with and without a crust. Section 3.8.2 shows the concentration profiles predicted for the conditions in tanks with sludge only. Section 3.8.3 discusses the time-scale of the evolution of the concentration profiles for the various configurations considered.

3.8.1 Ammonia Concentrations in Tanks With and Without Crust

The results obtained with the low, medium and high ammonia generation rates for the tank configuration with sludge plus supernatant are shown in Figure 3.4. All three generation rates predict concentrations in the supernatant that are well below the *highest measured values of ammonia in the supernatant* layers of double-shell tanks (these values were obtained from the TWINS data base). The highest generation rate shown in Figure 3.4 leads to a concentration profile that is approaching the saturation boundary near the bottom of the tank (in the sludge). If this configuration is an accurate representation of the behavior of ammonia in the DSTs, then this result suggests that the sludge layer in

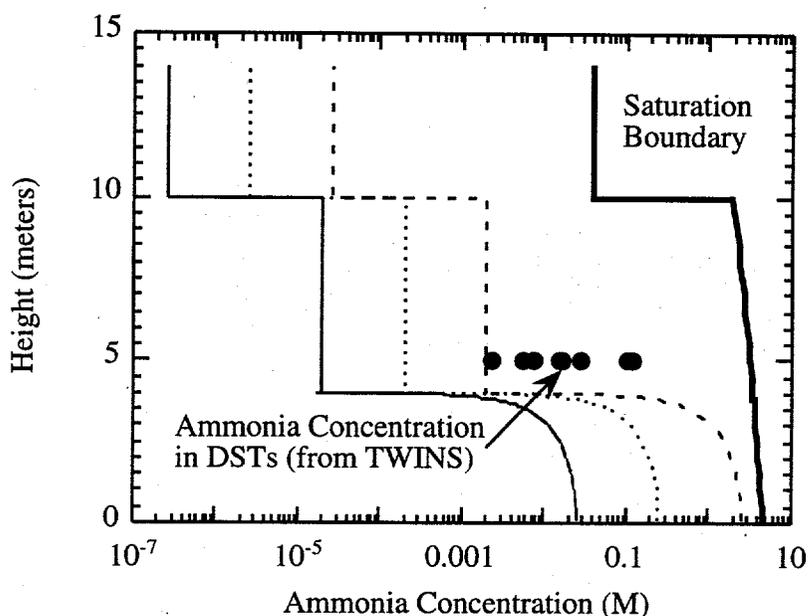


Figure 3.4. Ammonia Concentration Profiles for Tank Configuration with Sludge and Supernatant. (solid line) low generation rate; (dotted line) medium generation rate; (dashed line) high generation rate; (heavy line) saturation boundary; (dots) measured values of the ammonia concentration in the convective layer of DSTs.

some of the DSTs may be close to saturation. However, the ammonia generation rates of 1000 g/day in the sludge and 4500 g/day in the supernatant needed to generate this profile are extremely high, based on a comparison with the estimated generation rate for Tank 241-SY-101.

Nearly all of the tanks have a crust or foam layer of some sort floating on top of the supernatant. The influence of the crust on the ammonia concentration profiles was examined by performing calculations on a tank with the same sludge and supernatant properties, but including a 10 cm crust. The generation rate of ammonia per unit volume and the diffusivity of ammonia in the crust are assumed to be the same as in the sludge. The major effect of the crust is to increase the concentration of ammonia in the supernatant.

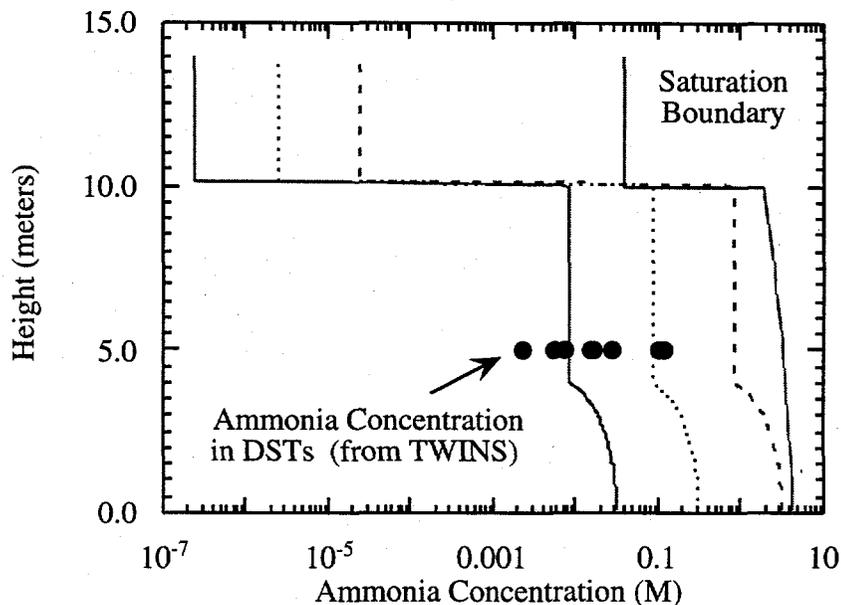


Figure 3.5. Ammonia Concentration Profiles for Tank Configuration with Sludge, Supernatant, and a 10 cm Crust. (solid line, left) low generation rate; (dotted line) medium generation rate; (dashed line) high generation rate; (solid line, right) saturation boundary; (dots) measured values of the ammonia concentration in the convective layer of DSTs.

These results suggest two important points relative to the ammonia concentration profile. For a tank with a high mass transfer rate between the convective layer and the head space (no crust), a very high ammonia generation rate is required to obtain a concentration profile in the sludge that approaches saturation. For tanks with a crust that have a low mass transfer rate between the convective layer and the head space, much lower ammonia generation rates are required to reach an ammonia concentration in the convective layer in the range that has been measured in the DSTs. However, for tanks with a crust, the difference in ammonia concentration between the supernatant and sludge layers decreases dramatically. For this case, generation rates that are sufficient to account for the highest measured concentrations of ammonia in the convective layer still result in profiles that are well below the saturation limit.

The results shown in Figure 3.5 indicate that the medium ammonia generation rate (i.e., 100 g/day in the sludge and crust, 450 g/day in the supernatant) in a tank with a 10 cm crust is near the upper range of the measured data. Using this generation rate, calculations were performed on tanks with a 1 cm thick crust, a 10 cm thick crust, and a 100 cm thick crust. The results for these cases are shown in Figure 3.6.

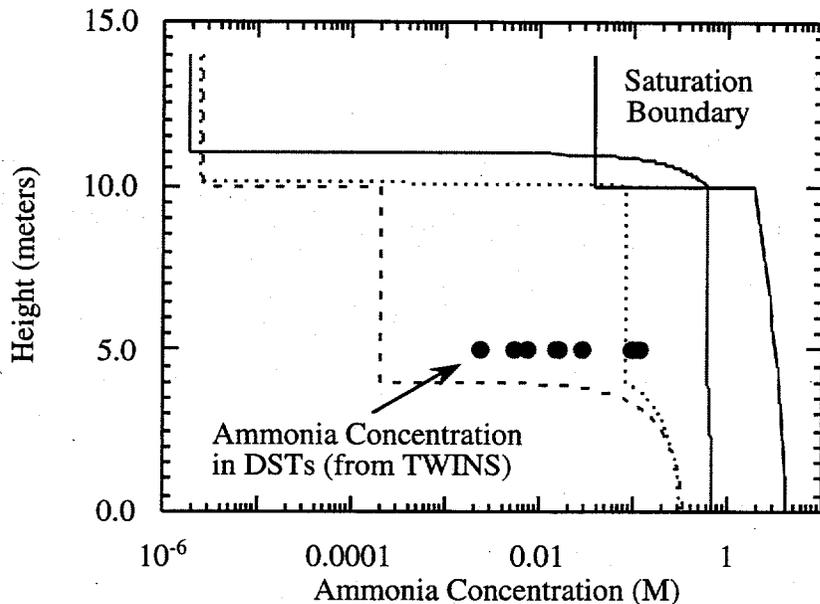


Figure 3.6. Effect of Crust Thickness on Ammonia Concentration Profiles. (dashed line) no crust; (dotted line) 10 cm crust; (solid line, left) 100 cm crust; (solid line, right) saturation boundary; (dots) measured values of the ammonia concentration in the convective layer of DSTs.

With a crust, the concentration in the supernatant is well below the measured values. The 10 cm crust results in a supernatant concentration comparable to the highest values measured in the DSTs, while the 100 cm crust results in a supernatant concentration well beyond the values measured in the DSTs. Both the 10 cm and 100 cm crust cases can account for measured supernatant ammonia concentrations, but neither case has an ammonia concentration profile that approaches the saturation boundary (only the saturation boundary for the tank without a crust is shown).

3.8.2 Ammonia Concentrations in Tanks With Sludge Only

Calculations were done on a tank with 5 meters of sludge only (no supernatant and no crust) and passive ventilation in the dome space ($5 \text{ ft}^3/\text{min}$ or $0.023 \text{ m}^3/\text{sec}$). The ammonia generation rate in the tank was adjusted to give a gas phase concentration in the range of 1000 ppmv ammonia ($4.5 \times 10^{-5} \text{ M}$), which corresponds to the highest measured head space concentration of ammonia in the SSTs. The results are shown in Figure 3.7. The ammonia generation rate used in this calculation was 212 g/day,

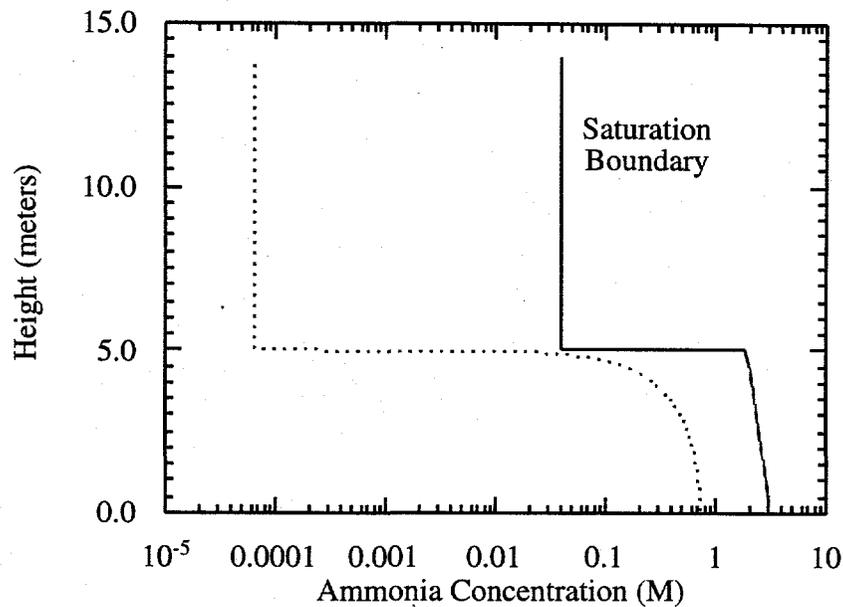


Figure 3.7. Ammonia Concentration Profile for Tank Configuration with Sludge Only. (dotted line) ammonia concentration profile; (solid line) saturation boundary.

which is in the same range as the 'medium' generation rates used in the calculations on the tanks with convective layers. The concentration profile in the sludge is again well below the saturation boundary. However, the concentration of ammonia in the waste does reach fairly high levels. If the average concentration of ammonia in the liquid fraction of the sludge is taken as about 0.5 M , then the expected concentration of ammonia in the head space should be about 0.01 M , based on an Ostwald solubility coefficient of $\lambda = 48$. This is two orders of magnitude higher than the concentration calculated here, indicating that the concentration of ammonia in the head space of a tank containing only sludge is substantially lowered because of transport limitations.

3.8.3 Time Evolution of Ammonia Concentration Profiles

The time scale required to obtain a steady state condition in all three tank configurations is on the order of 800 to 1200 years. However, the concentration profiles reach 50% of their steady state values in approximately 100 days, 80% of steady state within about 6 months, and 90% of steady state in about 80 years. The initial buildup of ammonia appears to be fairly rapid even though the final approach to

steady state is slow. It is probably safe to assume that most tanks are now within 50% of their steady-state concentrations. If the generation rates are on the order postulated (i.e., 450 g/day in the supernatant and 100 g/day in the sludge and crust), then it is unlikely that the local ammonia concentrations are approaching saturation.

In the calculations presented here, the initial concentration of ammonia in the tanks is assumed to be zero everywhere. For the configuration containing sludge plus supernatant, with no crust, calculations were done on a tank that was initially saturated with ammonia in both the sludge and supernatant layers. The evolution of the ammonia concentration in the supernatant for this case is compared to that of the case with zero initial concentration in Figure 3.8 (the 'medium' generation rate was used for both calculations). As might be expected, the two curves approach the same steady state concentration. The time scale for reaching steady state appears comparable for both initial conditions, although the total amount of ammonia released is much larger for the initially saturated case.

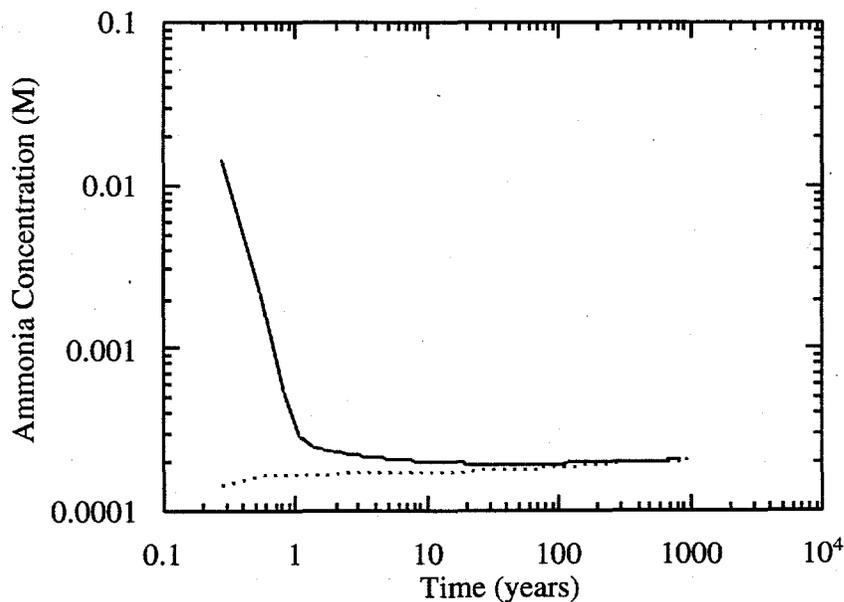


Figure 3.8. Effect of Initial Conditions on Ammonia Concentration Profiles. (dashed line) zero initial concentration; (solid line) saturated initial concentration.

3.9 Summary and Conclusions

Three tank configurations were investigated using a time-dependent one-dimensional model to calculate the ammonia concentration profiles for a range of ammonia generation rates. Three main conclusions result from this work. First, high generation rates (relative to those estimated for Tank 241-SY-101) are needed to approach the saturation boundary in the tank configurations with sludge and supernatant but without a crust (configuration [b]). Second, tanks with a crust (configuration [c]) can account for measured values of ammonia in the convective layers of Hanford DSTs with only moderate ammonia generation rates. However, in this case the ammonia concentration profiles in the tank are well below saturation, and the possibility of a limnic eruption is small. Third, the time constant for the development of the ammonia concentration profile is very slow, requiring nearly 1000 years to reach steady state. However, the profile reaches 50% of steady state in approximately 100 days, reaches approximately 80% of steady state in 6 months, and 90% of steady state in only about a century.

The calculations indicate that a key feature in understanding the distribution of ammonia in the DSTs is the rate of mass transfer between the convective layer and the tank head space. This rate can be lowered substantially by the presence of a crust, or possibly a foam, which suppresses convection at the top of the waste. Such crusts and foams are ubiquitous in the DSTs, which are the only candidates for a limnic eruption. The main effect of the crust is to lower the difference in ammonia concentration between the supernatant and sludge layer. Because a crust or foam layer appears to be present for all the DSTs currently on the flammable gas watch list, the calculations described here indicate that the potential for a limnic eruption is low.

The results of calculations for an all-sludge tank indicate that attempts to measure ammonia in the waste by sampling the ammonia concentration in the head space can substantially underestimate the ammonia concentration in the waste. This is in accord with the conclusions reached in the previous section.

3.10 Recommendations

The rate of ammonia mass transfer between the convective layer and the tank head space appears to be crucial to the concentration profile of ammonia in the tanks. Experiments to quantify the effects of a foam or crust on top of the supernatant layer would be useful for future modeling of ammonia distributions in the DSTs. The one-dimensional models used here can also be used to model ammonia distributions in both the DSTs and SSTs as more data on the spatial variation of ammonia in the tanks becomes available.

4.0 Data Collection and Statistical Analysis

The purpose of this task is to gather available data and assess relationships between ammonia and other chemical constituents and physical properties in tank waste, and use the data to understand the generation, retention and release of ammonia in the Hanford waste tanks. Specifically, this task seeks to answer the following questions:

- Is the available data sufficient to establish statistically significant relationships?
- Is there statistical evidence to support or refute relationships between ammonia concentration and other chemical and physical measurements in the liquid and/or the head space of the waste tanks?

Efforts were made to identify constituents that could affect ammonia concentration, gather the data from existing sources, assess their quality, and, where possible, apply the appropriate statistical methods to answer the questions listed above.

Section 4.1 presents an overview of the data collected for this study and an assessment of their quality. Section 4.2 presents a brief review of findings from statistical analyses of single-shell and double-shell tank data. Sections 4.3 and 4.4 summarize the conclusions and recommendations. Details of the data collection and statistical analyses are presented in Appendices A, B, C, and D.

4.1 Data Collection

A broad range of chemical, radiological, and physical properties could potentially affect the waste and head space ammonia concentrations. With the help of several chemists at the Hanford site, a list of constituents and properties of tank waste was compiled. The complete list is presented in Table A.1 of Appendix A. It proved useful to organize the data into four categories:

- Head Space Gas Concentration
- Single-Shell Tank (SST) Waste Composition
- Double-Shell Tank (DST) Waste Composition
- Tank Engineering Characteristics Data

The distinction between single- and double-shell tanks was made because double-shell tanks contain mostly liquid waste and are in active use, while single-shell tanks contain mostly solid waste and are "stabilized" (out of active use since 1980). In addition, all of the readily available head space data are for single-shell tanks, most of which are passively ventilated. Double-shell tanks are all actively ventilated.

An intensive effort was made to collect data according to the originally proposed list. However, data were found for only a portion of the list (see Table A.2 in Appendix A). Furthermore, even when measurements of a particular constituent or property were available, values for the measurement were not necessarily available for all tanks. The final data set was compiled after dealing with such issues as missing data and less than detection limit measurements. This section describes the identified data sources, the steps taken to compile the final data set, and the data selection criteria.

4.1.1 Data Sources

Several data sources were used to gather the data in Table A.2. The data from these sources are of varying quality.

Tank Characterization Reports (TCRs)

These are generally taken to be high quality sources of data. However, the accessibility was limited because it was necessary to create a data set manually by extracting the pertinent numbers from the document. In addition, TCRs are available for only a limited number of tanks. TCRs were considered as the primary source for tank waste data since they provide estimates of concentrations after accounting for the variability structure of the data due to sampling, analytical procedures, and spatial variability.

Tank Waste Information Network System (TWINS) (TWINS, 1990)

This database system is easily accessible and of good quality. This is the primary data source for head space data, where the sampling schemes were relatively simple.

Tank Waste Source Term Inventory Validation Report (TWSTIVR) (ICF Kaiser, 1995)

Data from this report were reviewed. Most of the values reported data already accessed from TWINS. Some values were not duplicated in TWINS, but information on the sampling date and/or the analysis method indicated that data from this source would require verification before use, which is not within the

current scope of this work. Only a few numbers were used from this source, when the corresponding measurements were missing from other data sources.

Surveillance Analysis Computer System (SACS) Database (Glasscock, 1993)

This database is easily accessible and is of good quality. This data source was used to compute head space and waste temperatures and volumes at the time of the head space sampling events for each tank.

Tank Farm Surveillance and Waste Status Summary Report (Hanlon, 1994)

This report was used to obtain drainable liquid volumes.

Summary of Single-Shell Waste Tank Stability (Wodrich, 1992)

This report was used to obtain pH values. However, because of the high ionic strength of most of the Hanford waste, most of these values are suspect. These data were used because they were the only comprehensive data available to the authors at the time of the work.

The Industrial Health Data (IH)

This data set was collected at tank ventilation outlets and other above ground locations to monitor ammonia content. However, the relationship between the ammonia concentration at the location of measurement and that in the tank head space is not always clear. Due to these complicating factors, this data set was not used.

4.1.2 Data Selection and Conversion

To improve the usability of the data for statistical analysis, further steps were required to eliminate certain constituents and/or tanks and to deal with several data issues. This effort is briefly summarized here. For more details, see Appendix A.

A constituent was excluded from the final data set under any of following conditions:

- Many missing values. For example, total beta, total gamma, and chromium concentrations in tank waste were excluded by this criterion.

- Measured characteristic similar to other measurements. For example, water vapor and relative humidity both measure the water content in the head space. Since water vapor measurements were used to convert other vapor concentrations from a dry air basis to a wet air basis, relative humidity was eliminated from the final list.
- Limited number of tank measurements available. Ammonia measurements in liquid waste are available for only seven SSTs and 13 DSTs. Several constituents considered to be less significant than others were excluded to facilitate analysis with this small number of tanks.

Several tanks were excluded from the analysis for one or more of the following reasons:

- The tanks are actively ventilated and their head space concentrations are therefore not comparable with those of passively ventilated tanks. Seven actively ventilated SSTs were eliminated from the head space data set.
- Many missing values. More than 70% of head space data for Tanks 241-U-203 and 241-U-204 were either missing or less than the detection limit. These two tanks were eliminated from the head space data set.
- Data quality is suspect. Tank 241-C-103 head space was sampled over several days early in the history of the vapor program. The measured head space concentrations of this tank are distinctly different from other available tank measurements. Therefore, this tank was determined to be an outlier and was excluded from the analysis.

Conversion and other data issues that have been addressed include:

- Determining the appropriate sample method. Three methods were used for head space sampling. Many constituents had measurements from two of the three methods. Some exhibited widely differing results. With the help of chemists, data was selected from a specified single or combined sample method for each constituent.
- Determining the appropriate analytical method. The preferred analytical method indicated by the TCRs was used for each constituent.
- Converting data to comparable units. This includes converting the measurement units and converting vapor concentrations from a dry air basis to a wet air basis. The units used in the final data set are shown in Tables A.8 to A.11 in Appendix A.

- Addressing missing values. The multivariate analysis techniques used in this study do not allow a single missing value in the data set, so an incomplete data set for a given tank must be either filled in or dropped from the analysis. Dropping data sets that are nearly complete was undesirable, since a significant fraction of the data fell into this category. For head space data, missing values were treated as “less-than-detection” (LTD) values. The justification for this treatment is that if a compound was present and showed up as a significant reading, it would be reported even if it was not specifically being looked for. If the compound was not specifically being looked for and did not show up in the analyses, it would not be reported.^(a)
- Addressing “less-than-detection” values. This issue was dealt with on an analyte-by-analyte basis. Details on how the LTD values were addressed for head space data are presented in Appendix A.

4.1.3 Overview and Features of Collected Data Sets

In general, the quality of the collected data is fairly good, since considerable efforts were made to select the best available data sources and to exclude measurements of suspect or unknown quality. However, several pieces of data are missing or quite incomplete. Figure 4.1 shows graphically what data is available on a tank by tank basis. Each row denotes a specific tank, with the single-shell tanks listed first. Each column is a specific chemical constituent as listed in Table A.2. The cell for each tank and constituent combination is shaded to represent whether or not data exists for that combination: medium gray indicates that data exists, black indicates that the data exists and is an ammonia concentration, and light gray indicates the data does not exist. The figure indicates the following:

- Head space concentration data are available for 37 single-shell tanks (excluding the 10 tanks previously eliminated as described in Section 4.1.2). All have ammonia measurements. The available DST head space data were not consistent with the SST data, and thus could not be used for this portion of the work.
- Waste composition data are available for 17 double-shell tanks. Among them, 13 tanks have ammonia measurements.
- Sixteen single-shell tanks have both head space and waste composition data. Only seven of those, however, have ammonia measurements in liquid waste. Several tanks have only one or two waste composition measurements.

(a) Based on personal communication from John Huckaby, PNNL.

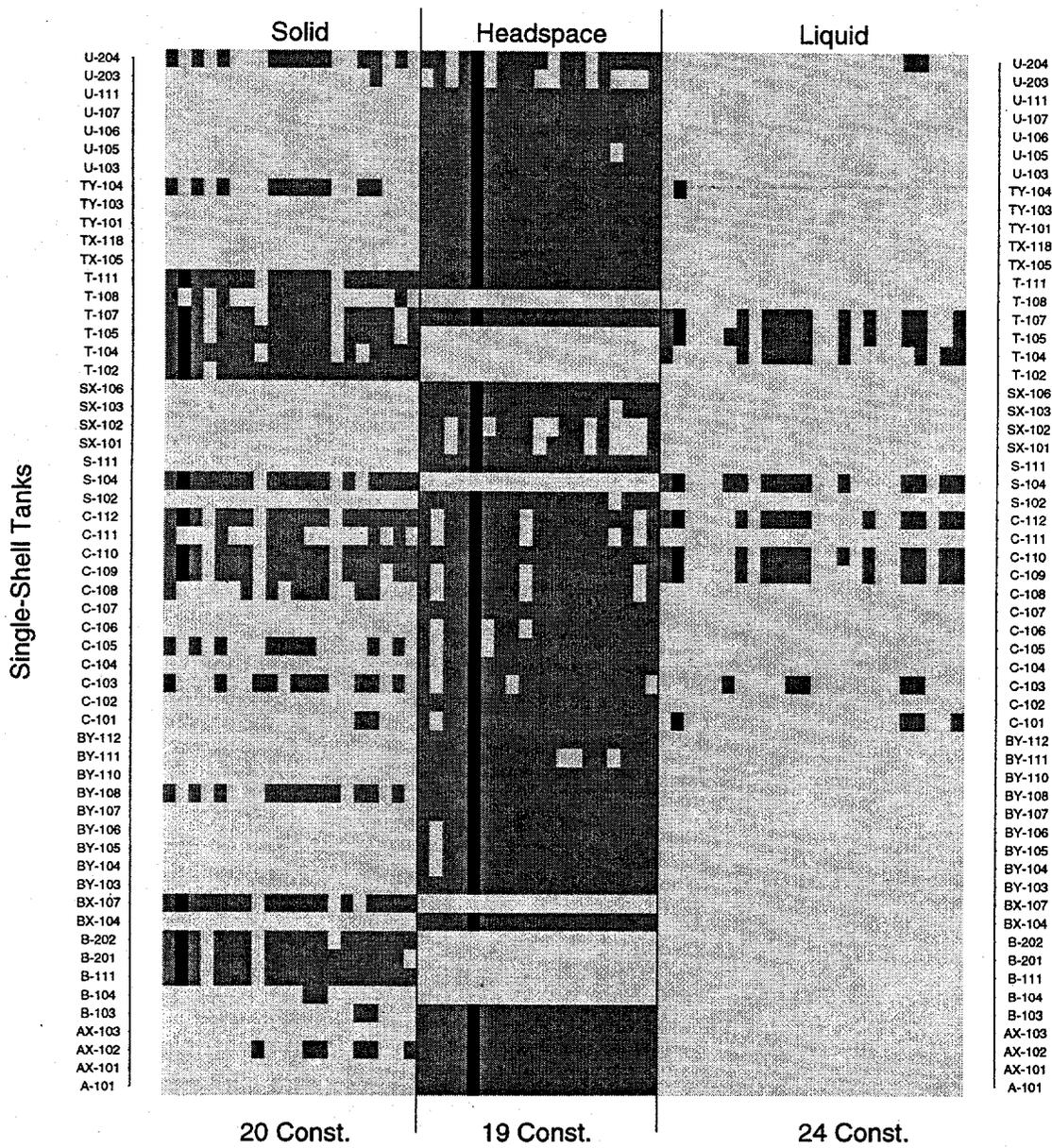


Figure 4.1. Available Data for Constituents of Interest

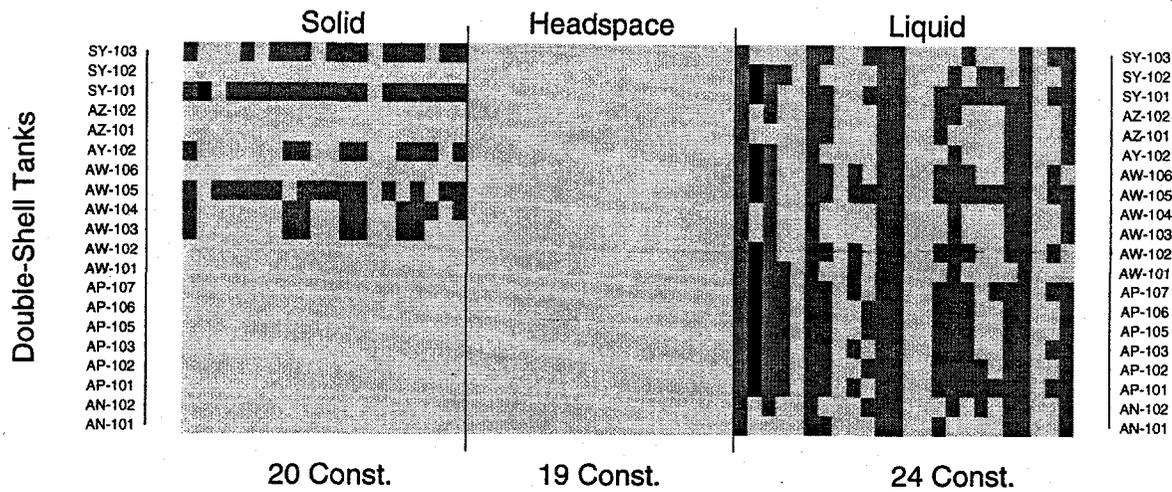


Figure 4.1. (Contd)

Based on these observations, the data set supports simple and advanced statistical analyses within the head space (for SSTs) or within the liquid waste (for DSTs) to identify relationships between ammonia and other constituents. However, the data set supports only a very limited analysis to establish a relationship between ammonia concentrations in the head space and in the liquid waste.

4.2 Statistical Analysis

Statistical analysis was performed using Splus and SAS programs. The significant findings are related below.

It is important to note that the statistical analyses presented here are based on the use of the waste tank data as a basic observation. This differs from the typical laboratory analysis where conditions are more tightly controlled. While one may "know" from laboratory analysis that higher temperatures generally lead to more ammonia in the head space, this conclusion is based on a laboratory experiment that modifies one factor to see the effect on another factor. The statistical analysis of the waste tank data is distinctly different. The fact that ammonia in the head space and temperature of the head space do not show any association does not imply a finding opposite to the laboratory experiment. It simply means that with many factors varying in the tanks, the ammonia and temperature data don't show such a relationship. If one tank has little ammonia in it, there will be little ammonia in the head space, no matter what the temperature. Also, note that we are not modifying experimental conditions and taking multiple measurements so as to detect changes.

The data quality is a major issue in any study of this kind. It is important to assess the impact of data quality, to make the data quality as high as practicable, and to use robust and multiple statistical analysis techniques to mitigate the impact of poor data quality. (The word "robust" is used here in the statistical sense. A technique is said to be robust if it is relatively unaffected even when all of its underlying assumptions are not met. Since we are concerned with measurement errors that may be large, and with other uncertainties in the data, the use of robust statistical techniques enhances our confidence in the findings.)

Two types of error are of concern: (1) identifying a relationship as existing when it does not and (2) not identifying a relationship that does exist. Two major factors can adversely influence the likelihood of making these mistakes: poor data quality and inappropriate use of statistical techniques. Generally, the poorer the data quality, the more likely the second error. That is, relationships that exist will not be identified. Inappropriate use of statistical techniques, such as using regression with too many variables, can lead to misidentifying relationships that do not exist.

To minimize the adverse impact of data quality, the techniques described in Section 4.1 were employed. Also, a carefully selected variety of statistical tools was applied. The tools include such simple techniques as scatter plots, which present conceptual relationships to the analyst without assumptions, and where any gross outlier values can be identified and discounted from the conceptual conclusions. Techniques which do not impose assumptions about the shape or form of the data were also used to search for general relationships. Kendall's Tau was applied to identify pairwise correlations because it simply looks at the relative sizes of pairs of values (Randles and Wolfe 1991, p. 108). If no relationship exists, then about half of the pairs should have one type of relative size relationship (both elements of the pair higher or lower than the elements of the other pair); and the other half of the pairs should have the other kind of relationship (one element of the pair higher but the other lower). If this simple statistical tool finds association between two analytes, since it is not sensitive to measurement errors, one can be relatively confident such an association exists. Two other tools used were the multivariate principal component analysis and discriminant analysis. These tools are distinctly different, and yet provide a graphically similar conclusion, thus strengthening the confidence one can have in the conclusion.

It may be helpful to the reader to view the approaches used to disclose relationships in the data as "bottom up" or "top down", referring to the search for constituents that relate to ammonia. The "bottom up" approach refers to the use of a single constituent, then two, then three constituents and so on, to search for relationships. The term "top down" refers to starting with all possible constituents and dropping constituents out of consideration as they are judged insignificant by a statistically based criterion. Both approaches are acceptable practices and are often referred to with the terms: "forward", "backward" or "stepwise."

The "bottom up" approach searches for simple relationships, sometimes confirming relationships suspected to exist, and sometimes coming up with new relationships. Unfortunately, the combinations grow very rapidly and it becomes impractical to present all possible constituent analyses. Selected comparisons using a few constituents are presented in Section 4.2.2. An investigation into ammonia in the head space as related to constituents in the waste is presented in Section 4.2.3.

In Section 4.2.4, the "top down" approach is described. Top down analysis techniques look for complex relationships. An analysis is presented using all available constituents and ammonia. The technique removes the most insignificant constituents to identify the possible relationships among the remaining ones.

4.2.1 Exploratory Data Analysis

The primary tools used to search for pairwise relationships between ammonia and one other constituent are the scatter plot and Kendall's Tau. The scatter plot provides a visual image of the relationship between the constituents. Scatter plots for ammonia concentration and each of the constituents are presented in the appendices. Figure 4.2 presents a histogram for ammonia in the head space of the 37 SSTs used in the analysis. It also presents two scatter plots. The scatter plots illustrate the relationship apparent between ammonia and propanol, which had a Kendall's Tau value equal to 0.43; and between ammonia and nitrous oxide, which had a Kendall's Tau value equal to 0.34. Notice that the scatter plots are on a log-log scale. Histograms and scatter plots for all constituents are in the appendices.

Kendall's Tau was used to investigate relationships between sets of data, with pairs of values associated with each observation. The value of Tau will always be between -1 and +1. A value of 0 indicates no monotonic relationship is apparent. A positive value of Tau means that as one variable increases the other variable tends to increase. If Tau is negative, as one variable increases the other variable tends to decrease. The tendency increases in strength as the value approaches either 1 or -1. The probability that a sample would generate the observed value of Tau, if there were no relationship between the two variables, is denoted as the "p-value." The smaller the p-value, the more certain one can be that a relationship exists (the p-value for the scatter plots noted above is 0.0002 for ammonia and propanol and 0.0033 for ammonia and nitrous oxide. Therefore, it is concluded a relationship exists for both pairs). If any of a very broad collection of possible relationships exists, it can be detected by this method. The technique is quite robust against large measurement errors and can be useful on small data sets.

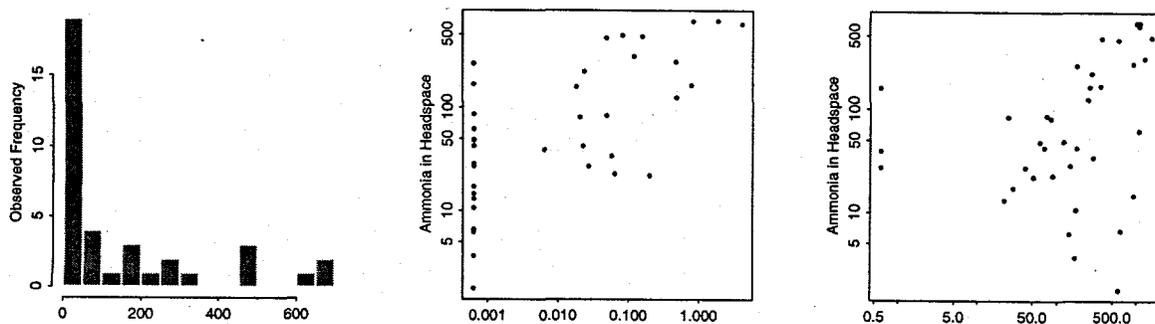


Figure 4.2. Selected Plots for Single-Shell Tanks

Kendall's Tau was applied to investigate the relationship between ammonia concentration in the head space of the SSTs and the other head space analytes. For the following analytes, the p-value was less than 1%, which indicates strong evidence of a relationship:

propanol	butanol	acetonitrile
decane	butanenitrile	hexane
pentanenitrile	propanenitrile	undecane
nitrous oxide	drainable liquid volume	hydrogen
pentanone		

The following analytes had p-values of less than 10%, indicating possible evidence of a relationship:

dodecane	carbon dioxide	tridecane
tetradecane		

For all analytes except carbon dioxide, the Tau correlation was positive.

Investigations were also conducted on the SST data to relate ammonia concentrations in the head space with the data on the waste. The following waste analytes had p-values less than 10% when compared to ammonia concentration levels in the head space: total organic carbon (TOC), aluminum, nitrate, pH, and zinc. The Tau values indicated the relationships have positive correlation, except for aluminum and zinc. More details on this investigation are included in Section 4.2.3.

For DSTs, the ammonia (and/or ammonium) concentration was compared with seven constituents. Only nitrite had a Kendall's Tau that was noteworthy (p-value of 2%), indicating that a relationship probably exists between dissolved ammonia and nitrite. The relationship shows a positive correlation; that is, if two tanks are considered together, the one with the lower nitrite concentration is likely to have the lower ammonia concentration as well.

4.2.2 Investigations of Specific Hypotheses

Several investigations of specific hypotheses were conducted. Seven proposed relationships were investigated to determine if the data supports the relationship, refutes the relationship or is inconclusive. Of the seven relationships investigated, two hypotheses received decisive support, three received partial support and two of the hypotheses received no support (To refute any hypothesis, very strong evidence would be needed).

The two hypotheses with decisive support are:

1. Investigation of the relationship between ammonia in the head space and drainable liquids in the waste showed indications of a positive correlation, with a Kendall's Tau p-value of 0.004.
2. Investigation into the relationship of ammonia, nitrous oxide and hydrogen (all in the head space) showed an association between ammonia concentration and the other constituents. (See Appendices B and D.)

4.2.3 Relationship Between Ammonia in the Head Space and Selected Waste Data

Sixteen SSTs had data for ammonia in the head space and some observations of concentrations in the waste data. The analysis showed likely relationships between concentrations of ammonia in the head space and TOC, aluminum, nitrate, pH, and zinc in the waste. The functional relationships between the natural logarithm of ammonia concentration and these variables was investigated using linear techniques. Three additional variables were formed from these three analytes by taking the natural logarithm of each of the analyte concentrations. These six variables were passed to a statistical package which selected the best regression candidates for using two variables of the six (regression 1 below) and three variables of the six (regression 2 below). Each explains much of the variation in ammonia. They both use the natural logarithm of ammonia concentration in the head space as the dependent variable and are regressed on:

1. the nitrate concentration and the natural logarithm of the aluminum concentration;
2. the aluminum concentration, the nitrate concentration and the natural logarithm of the aluminum concentration.

There were 10 tanks with data reported on these variables. Cross-validation of the regressions using that data is presented in Figure 4.3 below. The regressions clearly explain much of the variability, based on nitrate and aluminum.

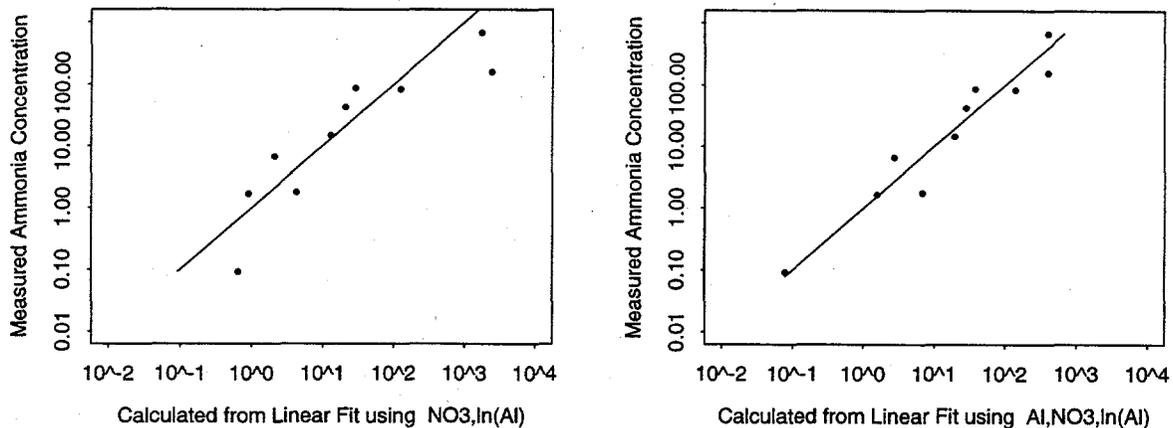


Figure 4.3. Cross-Validation Results of 2 Regressions (log-log scale)

4.2.4 Ammonia Discrimination Investigation

Multivariate discriminant analysis and principal component analysis are two “top-down” analysis methods used to look for relationships between ammonia concentrations and other constituent data. The tanks were grouped into categories of “high”, “medium”, or “low” ammonia concentrations as indicated below, with the number of tanks in each group in parentheses:

	Criteria for Grouping		
	"low"	"medium"	"high"
	less than	between	more than
SST: Ammonia in head space (ppm)	100 (20)	100-300 (8)	300 (9)
DST: Ammonia in waste (mg/L)	200 (7)	200-500 (3)	500 (3)

The multivariate discriminant analysis tool then determined the coefficients for all the constituents other than ammonia, that resulted in the "best" ability to group the tanks into the "high", "medium", or "low" groups. The result can be visualized in the following Figures 4.4 and 4.5.

In each plot the "high", "medium" and "low" tanks are well separated spatially, indicating a good ability to separate the groups; which in turn indicates that the other constituents can be associated with "high", "medium" and "low" ammonia concentrations. The algorithm for this discriminant analysis investigated various linear combinations of 22 constituents and ammonia concentrations in the head space (SSTs). The discriminant variables were formed from the original set by finding the linear combinations that maximize the separation of the three groups. The algorithm statistically focused on 15 constituents as the "optimum" set; that is the set of constituents most likely to have a relationship with ammonia concentrations. A graphical representation of the separation achieved by these 15 constituents and the discrimination process is displayed in Figure 4.4. The causal factors of this association have not yet been identified (see Table B-6 for a list of the 15 constituents).

Similarly for ammonia in the waste (DSTs), the data allowed consideration of 7 constituents and focused on 5 constituents as the "optimum" set. Again a graphical representation of this separation is presented in Figure 4.5. The conclusion drawn from the DST data is that low concentrations of strontium-90 and nitrate, and high concentrations of TOC, nitrite and aluminum were associated with the medium and high ammonia tanks.

The principal component analysis is a separate approach that does not use ammonia concentrations in its calculations; it uses only the concentrations of other constituents. By a different technique, principal component analysis separated the tanks into groups that when viewed as "low", "medium" or "high" ammonia tanks, confirmed the findings of the discriminant analysis.

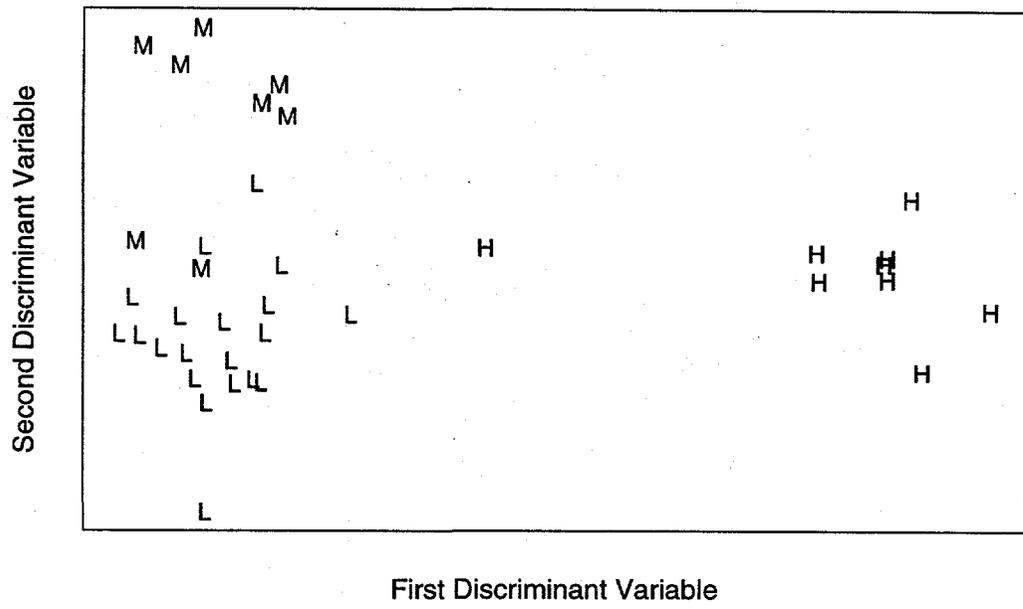


Figure 4.4. Discriminant Analysis for SST Head Space Data

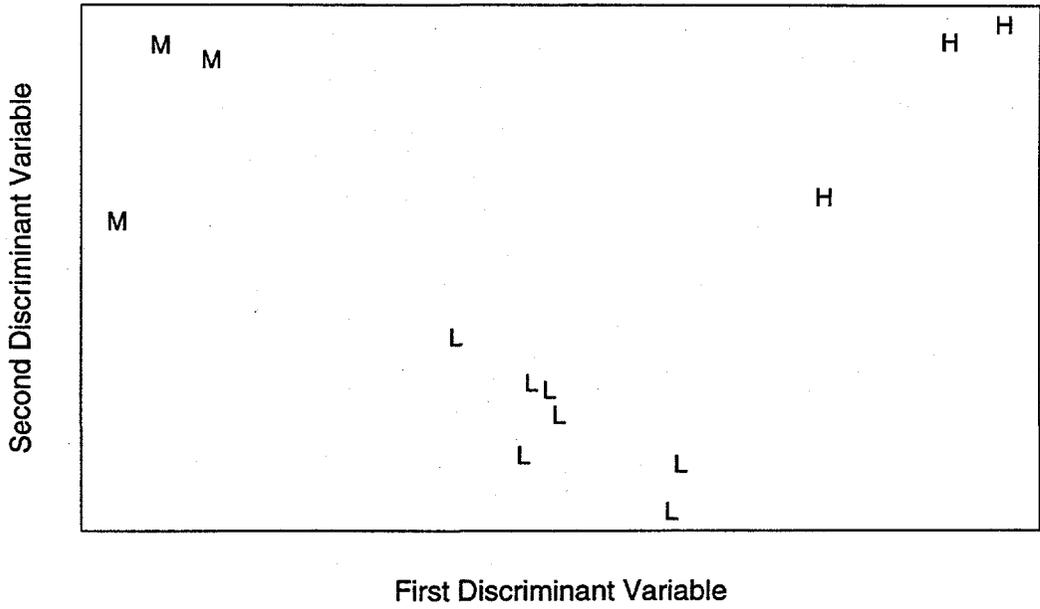


Figure 4.5. Discriminant Analysis for DST Liquid Waste Data

4.3 Conclusions

The data gathered for this task is specifically targeted on the ammonia generation, retention, and release issues at Hanford. This data set is composed of 63 variables and all the tanks that had the required data. The data set supported analysis of head space data from 37 single-shell tanks and waste data from 13 double-shell tanks, and limited exploratory analysis on the waste/head space data of 10 single-shell tanks.

The data were examined utilizing a variety of statistical techniques. Ammonia concentration level in the head space was found to correlate with 13 analyte concentration levels in the head space and 5 in the waste in the single shell tanks. Statistical analysis indicates the existence of relationships between ammonia concentration level in the head space and drainable liquid volume, and between ammonia concentration level and nitrous oxide, carbon dioxide, and hydrogen, all in the head space. The analysis also shows a relationship between ammonia concentration in the head space and aluminum and nitrate in the waste of single-shell tanks. Analysis of double shell tanks indicates tanks with high ammonia concentration levels are identifiable from concentration levels of aluminum, nitrate, total organic carbon, nitrite, and strontium, all in the waste.

4.4 Recommendations

The easiest recommendation to make, and probably the most difficult to implement, is to get more data of higher quality from more tanks.

But additional, less costly, recommendations can result in a fuller understanding of the generation, retention and release of ammonia. Some deal with focusing sampling activities that are already funded; others deal with more sophisticated statistical analysis that utilizes more robust data analysis techniques to work with data of limited quality and quantity and with new studies; and yet others deal with more specific investigations of chemical theories.

The recommendations for data sampling are:

1. Plan simultaneous sampling of waste and head space, when possible (the large amount of time between sampling events allows retention/release aspects to confound the analysis of generation);
2. If duplicate tests of the same segment of the same core sample result in distinctly different results, re-test or provide explanations of variance; and

3. Collect some data more often (Naturally, this assumes the more frequently collected data is less expensive to collect. This is especially useful if a correlation or association of the frequently collected data can be found with ammonia or with some other associated variable. Statistical techniques are available to exploit such relationships and to get more knowledge at less expense).

While concerns for data quality and quantity are significant, there are statistical techniques that can utilize data with varying degrees of measurement errors and provide significant findings. Specifically, the recommendations are:

1. Perform discrimination using chemical interactions, different transformations, and non-linear techniques to develop a better understanding of the generation process;
2. Use an "Errors in the Variables" regression technique to allow prudent use of regression to investigate the relationships, even though there are measurement errors in the regressor variables; and
3. Perform inter-tank investigation to see if ammonia/head space/waste relationships are affected by tank to tank cascades of head space or drainable liquid contents.

Also, specifically focused investigations of chemical hypotheses should be pursued:

1. Work with chemists to develop concepts for ammonia generation and to test them on existing and new data, to interpret the results and to evolve new understandings and new models to investigate;
2. Compare the ammonia generation aspects of the HDW (Agnew, 1995) model to existing and new data and relate them to the generation theories noted above;
3. Conduct sensitivity studies using the models to answer "what if" questions regarding changes in concentrations in tanks, relationships between variables, and fidelity of the models.

5.0 Summary

Modeling of ammonia generation, retention, and release suggests that the most important characteristics for determining the maximum ammonia concentrations in the head space are the concentration of ammonia in the waste and the Henry's Law constant for the waste. Given the upper bound on observed ammonia concentrations in the waste and estimates of the Henry's Law constant, it is possible to achieve ammonia head space concentrations which represent a significant fraction of the LFL for ammonia in dry air, and which therefore pose a potential threat to human health and safety. Because of transport limitations, ammonia concentrations in the head space will under-represent the concentration of ammonia in the waste in tanks that remain undisturbed for long periods of time. Only tanks with a significant concentration of ammonia in the waste can pose an ammonia safety hazard. Because transport is generally limited by diffusion, these tanks are likely to achieve high ammonia concentrations in the head space only if there is a large disturbance of the waste. This can occur naturally via a rollover or as a result of tank operations such as those involved in retrieval, dilution, or saltwell pumping.

The Lake Nyos effervescent release scenario (limnic eruption) was chosen for detailed modeling. This kind of release is possible if some or all of the waste becomes saturated with ammonia. Because a limnic eruption could potentially release an enormous amount of ammonia, establishing the likelihood of such an eruption is of special concern. A one-dimensional model was created to simulate the diffusive transport of ammonia in the sludge and convective transport of ammonia in the supernatant layer and the tank head space. The results indicate that in tanks with a crust or foam layer, moderate ammonia generation rates (comparable to or less than those estimated for Tank 241-SY-101) can produce ammonia concentrations in the supernatant layer that are comparable to those observed in double-shell waste tanks. However, the concentration profile in these tanks does not approach saturation at any point in the tank. For tanks with no crust or foam layer, very high ammonia generation rates are necessary to match the ammonia concentrations in the supernatant layer observed in the tanks. These generation rates are much higher than those estimated for Tank 241-SY-101. The probability of a limnic eruption appears to be low, based on the modeling and the observed behavior of both SSTs and DSTs.

Data on ammonia and related waste characteristics for the Hanford SSTs and DSTs were collected and analyzed for correlations between the presence of ammonia and other waste characteristics. Problems with the data set include the small number of tanks for which waste characterization, waste properties, and head space vapor characterization data are all simultaneously available; and the fact that determinations of the concentrations of ammonia/ammonium are frequently missing, even if other properties of the waste have been characterized.

The available data do indicate that ammonia is ubiquitous in the waste tanks and is present in at least a low concentration in nearly all of them. No major conclusions could be drawn about relationships between ammonia and other waste characteristics, but the statistical analysis did suggest the possibility of some correlations. These may become more firmly established as more data become available.

Statistical analysis of the data for single-shell tanks supported relationships between ammonia concentration in the head space and drainable liquid volume; and between ammonia and hydrogen, nitrous oxide, and carbon dioxide concentrations in the head space. The analysis also showed a relationship in the SSTs between ammonia concentration in the head space and nitrate concentrations in the waste. Analysis of the data for double-shell tanks indicates that tanks with high ammonia concentrations are identifiable from the concentrations of aluminum, nitrate, total organic carbon, nitrite, and strontium.

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Appendix A

Data Collection

Appendix A - Data Collection

This appendix outlines the steps taken to collect data and assemble it into a form appropriate for statistical analysis. The original proposed list of constituents and tank properties is presented in Table A.1. The list of variables actually available for analysis is presented in Table A.2. If a variable from the original list (Table A.1) is not present in the available list (Table A.2), it means that little or no data were found for that variable. It should be noted that because a variable is listed in Table A.2 does not necessarily mean that a measurement was found for that variable in all possible tanks. For example, measurements of ammonia/ammonium concentration in liquid were found for only seven of the single-shell tanks. The data sources used to compile the data in Table A.2 are described in Section 4.1.1. The issues that have been dealt with during the collecting process are presented in the following sections. The procedures are presented in four sections (headspace, single-shell tank waste, double-shell tank waste, and tank engineering information) corresponding to the four data categories listed in Table A.2. The statistical methods used for analysis are briefly described in Section A.5.

A.1 Head Space Data

Data on the head space chemical concentrations were gathered primarily from the Tank Waste Information Network System (TWINS). The headspace property data were gathered from several different sources, including the Surveillance Analysis Computer System (SACS), the database in which the tank waste level and temperature data are stored. See Tables A.8 and A.9 for the final head space data sets.

A.1.1 Head Space Chemical Constituents

The following issues were addressed while developing the final data set for chemical properties in the head space.

Data Gathering

TWINS was accessed and all of the head space data were downloaded. These data were converted to an Splus data frame. Using Table A.1 as a guide, the data set was reduced to only those variables that matched (or were possibly related to) those in the proposed list.

Table A.1. Original List of Variables

<u>Headspace</u>	<u>Waste</u>	<u>Tank Engineering Information</u>
Volume	Liquid Volume	Volume
Temperature	Solid Volume	Ventilation Type
	Temperature	
<u>Chemical Constituents</u>	Crust Coverage	Ventilation Rate
Ammonia	Waste Type - SORWT	
Nitrous Oxide	Waste Type - HTCE	
Hydrogen	Layer Dimensions	
Water - Dewpoint	Liquid to Solids Fraction	
Water - Relative Humidity	Solid Density	
Carbon Dioxide	Liquid Density	
	pH	
<u>Organic Constituents</u>	Total Beta	
Methanol	Total Gamma	
Ethanol		
1-Propanol	<u>Chemical Constituents</u>	
1-Butanol	(for both solid and liquid)	
Butanal	Ammonia/Ammonium	
Decanal	Aluminum	
Acetonitrile	Total Organic Carbon	
Propanenitrile	Nitrate	
Butanenitrile	Nitrite	
Pentanenitrile	Chromium	
Hexane	Manganese	
Decane	Technetium	
Undecane	Iron	
Dodecane	Nickel	
Tridecane	Palladium	
Tetradecane	Platinum	
Pentadecane	Zinc	
Acetone	Cadmium	
2-Pentanone	HEDTA/EDTA	
Methylisobutyl Ketone	Total Inorganic Carbon	
Bicyclics		
Decahydronaphthalenes		
Nitric Acid Esters		

Table A.2. Variables Available for Use in Analysis

Headspace	SST Waste (Solid)	DST Waste (Liquid)	Tank Engineering
1-Butanol	Solid	Liquid	
1-Propanol	Aluminum	Aluminum	
2-Pentanone	Ammonia	Ammonia	
Acetonitrile	Cadmium	Cesium-137	
Ammonia	Carbonate *	Cyanide (CN)	
Butanal	Chromium	Density before centrifugation	
Butanenitrile	Density	Hydroxide	
Carbon Dioxide	Gross Beta *	Iron	
Decane	Hydroxide	Liquid density *	
Dodecane	Iron	Manganese	
Hexane	Manganese	Nickel	
Hydrogen	Nickel	Nitrate	
Nitrous Oxide (N2O)	Nitrate	Nitrite	
Pentanenitrile	Nitrite	Palladium *	
Propanenitrile	Palladium *	Solid density *	
Tetradecane	Technetium-99 *	Specific gravity	
Tridecane	Total Inorganic Carbon	Strontium-90	
Undecane	Total Organic Carbon	Technetium-99 *	
Water	Weight Percent Solids *	Total Alpha	
	Zinc	Total Beta	
	pH measurement	Total Inorganic Carbon	
	Total Alpha	Total Organic Carbon	
	Total Beta	Weigh percent solids *	
	Total Gamma	Zinc	
	Cyanide (CN)	pH measurements	
	Liquid	Chromium	
	Ammonia	Cadmium	
		Density	
Properties	Properties		Total volume
Temperature**	Temperature**		Vent status
Volume**	Volume**		Vent rate
Dew-Point**	Drainable liquid volume**		
Relative Humidity**	% liquid surface**		
	Waste type-SORWT**		
	Wast type-HTCE**		

*These variables were part of the data search but were not used in the final data set and subsequent analysis because they were determined not to be appropriate for data needs.

Only the latest head space sampling data were kept for this effort (earlier sampling events were often specialized and not aimed at a complete characterization). The only exceptions to this rule were Tanks 241-BY-105, 241-C-102, and 241-C-103.

- 241-BY-105 had only six values at the latest date, so it was combined with the more complete earlier set.
- 241-C-102 had a typographical error in the database. Two dates were shown, but the information in both, combined, represented one sampling event at one time.
- 241-C-103 was unusual because it had five sample dates, all within a two-week period. All of the other tanks had at least several months between the vapor samples. After reviewing the data contained in each sample data and talking to scientists involved in the sampling, we decided to combine all of the information for all of the dates for Tank 241-C-103.

A few small corrections were made as suggested by Mr. J. Huckaby (PNNL), a vapor program scientist familiar with the data.

- For Tank 241-C-103, an extraneous low result for hydrogen was dropped.
- For Tank 241-C-103, gas chromatograph/mass spectrometer results for dodecane and tridecane were dropped.
- For Tank 241-C-107, the extraneous result for butanol was dropped.
- Nitrogen monoxide (NO) and nitrogen dioxide (NO₂) variables were dropped.
- Ammonia and water average values for Tank 241-C-103 were taken from WHC-EP-0780, pages 4-4 and 4-5.

Convert Units

Head space chemical constituents were reported in units that ranged from ppm to ppb to mg/m³ to mg/L. It was decided to convert all constituents to the same units of mg/m³.

In addition, units reported from the laboratory are in dry air at standard temperature and pressure (STP).

To more closely represent the state of the head space at the time of sampling, the units were further converted to mg/m^3 , wet air at tank temperature and pressure.

Determine Appropriate Sampling Methods

TWINS data had designations for three sample methods: SUMMA for summa canisters, TST for triple sorbent tubes, and $\text{NH}_3/\text{NO}_2/\text{NO}/\text{H}_2\text{O}$, which is a sorbent tube specifically for these compounds.

Many of the chemical data had values from two of the sample methods, TST and SUMMA. Some had widely differing results. The database was edited to keep only the preferred sample method for each chemical constituent. Preferred sample methods were determined in one of two ways. First, experience and input about what worked best for which chemicals was sought from the chemists. If the chemists had no input, plots were consulted that compared the methods to determine which, if any, might be best. The results follow.

For 1-butanol and 1-propanol, SUMMA was the preferred method, and the data were used where possible. It was determined that TST data could be used if SUMMA data were missing for any given tank. For hydrogen and nitrous oxide (N_2O), SUMMA was the preferred method, and only SUMMA data were used.

For pentanenitrile, butanenitrile, acetonitrile, and propanenitrile, TST was the preferred method, and only TST data were used.

For all other constituents that had both TST and SUMMA data (2-pentanone, butanol, carbon dioxide, decane, dodecane, tetradecane, hexane, tridecane, and undecane), both methods were merged because no preference could be found.

For ammonia and water, the $\text{NH}_3/\text{NO}_2/\text{NO}/\text{H}_2\text{O}$ sample method was used.

Assess Missing Data and Less-Than Detections

It was necessary to "fill in" missing data and data that were represented as less than a detection limit to facilitate the multivariate statistical analyses. The multivariate techniques used do not allow a single missing value in the data set. If some data values are missing, either the whole data set must be discarded, or the missing values must be filled in. For data sets within only a few missing values, it is preferable to fill in the data set. For this effort, missing values were treated like "less-than-detection" (LTD) values. The argument for this is that in the laboratory analyses, even if the laboratory wasn't

looking for a given chemical, if the chemical was present and produced a significant spike in the spectrometer, it would be reported. Therefore, chemical constituents not reported were not present or were not present at high enough levels to be detected by the analyses.

Missing values and LTD values were addressed on an analyte-by-analyte basis. If missing or LTD values appeared, but real values were also observed, the missing and LTD values were omitted, and tank averages were computed with only the real data.

If a tank/analyte combination had all missing or LTD values, a different approach was needed. All of the values for the given analyte across all tanks were observed, as well as all the reported detection limits for that analyte across all tanks. The missing or LTD value was replaced by the minimum of 1) the smallest observed value across the tanks divided by 10; or 2) the smallest detection limit across tanks. To get the data set in final form (i.e., ready for analysis) a few more steps were taken.

First, only those variables with a significant amount of real data were kept in the final data set to reduce the uncertainties that would be introduced from estimating missing and LTD values. The variables included are shown in Table A.3.

Table A.3. Variables in Final Data Set for SST Head Space

1-butanol	tridecane
1-propanol	undecane
2-propanone	pentanenitrile
butanol	butanenitrile
carbon dioxide	acetonitrile
decane	propanenitrile
dodecane	hydrogen
tetradecane	nitrous oxide
hexane	ammonia
water	

Second, several of the tanks were excluded from the final data set.

- Tanks 241-C-104, 241-C-105, 241-C-106, 241-SX-101, 241-SX-102, 241-SX-103, and 241-SX-106 were excluded because they are actively ventilated. Active ventilation was determined to be too great a factor in head space concentrations to be considered simultaneously with passively ventilated tanks.

- Tank 241-C-103 was excluded because it was determined to be an outlier. Given the information about how the tank was sampled (early in the vapor program history and over several days) and by looking at scatter plots across tanks, it was determined that 241-C-103 should not be included in the analyses.
- Tanks 241-U-203 and 241-U-204 were excluded because most of their data were estimated, not actually observed. This was determined to add too much uncertainty to the analysis.

A.1.2 Head Space Property Data

Head space temperature and volume were determined by accessing the SACS database for surface levels and temperatures. The head space sampling date was used to locate the surface level and temperature measurement closest to that date. The surface level was used to determine the head space volume directly and to divide the temperature data into measurements that were taken above and below the surface of the waste. Those measurements that were taken above the waste level were averaged to get a head space temperature. These temperatures were compared with the head space vapor sampling program measurements and found to be generally equivalent.

Head space dew point and relative humidity data were provided by Mr. J. Huckaby of PNNL and the head space vapor sampling program.

Vent status was determined from information in the Hanlon Tank Surveillance Reports (Hanlon 1994).

A.2 Single-Shell Tank Waste Data

Data on single-shell tank waste were gathered primarily from the Tank Characterization Reports, with exceptions as noted below. (See Table A.10 for final data set).

A.2.1 Single-Shell Tank Waste (Solid and Liquid) Chemical Concentrations

These variables were taken directly from the Tank Characterization Reports for the relevant tanks. It is assumed that the TCRs have already addressed the data issues listed in Section 4.1.1, so no further adjustments were made to the data. The pH values were obtained from the report titled, *Summary of Single-Shell Waste Tank Stability* (Wodrich et al. 1992). To get the final data set for this category, the variables in Table A.4 were used.

Table A.4. Variables Used for Final Data Set for SST Waste

Aluminum	Total Alpha
Iron	Total Beta
Chromium	Total Gamma
Manganese	Nitrite
Nickel	Nitrate
Zinc	Cyanide
Palladium	Total Organic Carbon
Cadmium	Total Inorganic Carbon
Ammonia (liquid)	pH

There were 16 single-shell tanks that had head space data and TCRs. They are listed in Table A.5.

Table A.5. SSTs with Head Space Data and TCRs

241-BY-108	241-C-109
241-T-111	241-C-111
241-T-107	241-C-108
241-C-110	241-C-105
241-C-101	241-U-203
241-C-107	241-U-204
241-TY-104	241-B-103
241-AX-102	
241-C-112	

A.2.2 Single-Shell Tank Waste Property Data

- Waste temperature and volume were determined by accessing the SACS database (see the description in Section A.1.2.).
- Drainable liquid volume was estimated from tank surveillance reports (Hanlon 1994).
- Percent liquid surface (percent of the waste surface occupied by liquid) was estimated from tank photographs.

A.3 Double-Shell Tank Waste Data

Data on double-shell tank waste was gathered primarily from the Tank Characterization Reports. In the final data set for this category, the variables listed in Table A.6 were used.

Table A.6. Variables for Final Data Set for DST Waste

*Aluminum	Total Alpha	*Ammonia
Iron	Total Beta	pH
Chromium	*Nitrite	*Hydroxide
Manganese	*Nitrate	*Cesium-137
Nickel	Cyanide	*Strontium-90
Zinc	*Total organic carbon	Density
Cadmium	Total inorganic carbon	

* Only these variables were actually used in multivariate analyses for DST

It is assumed that TCRs have already addressed the data issues listed in Section 4.1.2, so no further adjustments were made. All data were converted to units of $\mu\text{g/L}$.

There were 17 DSTs that had TCRs and were included in this data set (see Table A.7).

Table A.7. DSTs with TCRs

241-AP-101	241-AW-102	241-AN-102
241-AP-102	241-AW-103	241-AW-101
241-AP-103	241-AW-104	241-SY-101
241-AP-105	241-AW-105	241-SY-103
241-AP-106	241-AW-106	241-AY-102
241-AP-107	241-AZ-102	

Note that the TCR for Tank 241-SY-101 was based on the tank's status before the mixing pump was installed and operating. The data no longer represent the true state of the tank.

A.4 Tank Engineering Information

- Total tank volume came from the report titled, *Evaluation of Hanford Tanks for Trapped Gas* (Hodgson et al. 1995).
- Vent status and rate came from information in the tank surveillance reports (Hanlon 1994).

A.5 Final Data Sets for Analysis

Sections A.1 through A.4 provide information on the variables that were available for analysis. All available data were not used for every analysis.

The variables used in the analysis for SST head space data are those listed in Table A.3 except water, plus five additional variables: temperatures in the head space, volume of waste, ventilation rate, volume of drainable liquids, and pH. Water was not used as a variable because it was used during the unit conversions to convert head space data from dry air to wet air. Thirty-seven tanks were used in these analyses, i.e., the 47 original tanks minus the exceptions listed in Section A.1.1.

The variables used in the head space and waste data analysis for SSTs are listed in Table A.4. Since only exploratory analyses were conducted on this category of data, all variables were used even though some of them were quite incomplete.

Only eight variables, including ammonia, were used in double-shell tank waste analyses. These variables are listed in Table A.6, marked with an asterisk. The rest of the variables were excluded from the analyses due to missing data. Among the 17 double-shell tanks listed in Table A.7, Tanks 241-AZ-102, 241-AN-102, 241-AW-103, and 241-AW-104 were excluded from the analyses because no ammonia data are available for these four tanks.

A.6 Statistical Analysis Methods

The statistical analyses conducted in this study include three methods: exploratory data analysis, principal component analysis (PCA), and discriminant analysis. This section provides a brief description of each method.

Table A.8. Single-Shell Tank Head Space Data (mg/m³)

Tank	1-Butanol	1-Propanol	2-Pentanone	Acetonitrile	Ammonia	Butanol	Butanenitrile	Carbon Dioxide	Decane	Dodecane	Hexane	Hydrogen Oxide(N ₂ O)	Pentanitrile	Propanenitrile	Tetraecane	Tridecane	Undecane	Water
A-101	1.14e+01	1.55e+01	6.42e-02	1.40e-01	4.79e+02	8.24e-01	4.71e-02	2.64e+01	1.41e-02	2.82e-01	2.82e-02	5.70e+01	2.22e-02	5.46e+02	4.32e-01	6.09e-01	7.58e-02	2.25e+04
AX-101	3.22e-01	2.68e-02	4.39e-02	2.09e-02	2.72e+01	4.30e-02	4.46e-03	5.32e+02	9.96e-04	8.15e-03	3.22e-03	7.93e+00	1.59e-03	4.77e-03	1.91e-02	3.98e-02	3.69e-03	1.16e+04
AX-102	3.51e-01	8.72e-02	2.51e-02	2.50e-01	2.30e+01	1.71e-01	2.40e-01	1.23e+03	1.17e-02	6.00e-02	1.61e-02	6.50e-02	5.32e-02	1.27e+01	9.41e-02	2.27e-01	2.43e-02	1.20e+04
AX-103	1.09e-02	6.16e-04	4.50e-04	8.90e-03	2.71e+01	1.37e-03	9.88e-04	7.39e+02	3.89e-05	3.41e-04	2.75e-04	6.50e-02	2.72e-04	1.51e-03	1.77e-03	1.40e-03	2.75e-04	1.31e+04
B-103	9.17e-01	6.18e-04	2.91e-04	6.22e+00	2.74e-01	3.18e-02	7.85e+02	7.85e+02	1.82e-02	4.54e-01	1.09e-01	6.50e-02	1.41e-02	1.24e+00	7.74e-01	1.24e+00	1.77e-01	9.99e-03
BX-104	5.24e+00	7.82e-01	3.48e-01	5.71e-01	1.62e+02	7.15e-01	1.65e-01	1.32e+02	1.76e-01	7.01e+00	5.77e-01	6.50e-02	7.82e-02	1.57e+01	1.98e+00	1.12e+01	1.57e+00	5.94e+03
BY-103	2.16e+00	6.18e-04	5.73e-02	4.08e-02	1.74e+01	1.31e-01	2.40e-01	2.16e+02	3.48e-03	1.48e-01	6.51e-03	6.50e-02	3.19e-03	2.92e-03	4.07e-01	3.25e-01	1.42e-02	1.16e+04
BY-104	5.95e-01	6.18e-04	4.39e-01	4.59e-01	1.65e+02	2.76e-01	4.59e-02	1.82e+01	1.79e-01	7.83e-01	8.17e-01	2.33e+01	3.92e-02	2.90e-02	6.88e-01	1.10e+00	4.44e-01	1.40e+04
BY-105	4.81e-01	6.18e-04	4.02e-02	1.29e-01	2.89e+01	1.30e-01	2.92e-03	1.60e+02	5.02e-02	6.28e-02	2.92e-01	6.89e+00	2.81e-03	3.48e-03	1.28e-01	8.62e-02	7.69e-02	1.49e+04
BY-106	9.55e-01	6.18e-04	7.07e-02	1.97e-01	4.87e+01	1.58e-01	4.10e-03	8.07e+01	4.21e-02	5.74e-02	3.61e-01	4.94e+00	3.02e-03	1.12e-02	3.90e-02	6.20e-02	5.95e-02	1.42e+04
BY-107	4.59e+00	4.96e+00	1.07e+00	3.41e+00	6.37e+02	2.15e-01	3.28e-01	1.59e+02	2.75e-01	1.95e+00	2.86e+00	2.07e+01	8.85e-02	1.00e-01	3.16e+00	2.62e+00	1.09e+00	1.29e+04
BY-108	1.08e+01	1.82e+00	1.46e+00	1.48e+00	6.79e+02	2.39e+00	8.25e-01	3.77e+02	8.05e-01	5.23e-00	6.14e+00	3.09e+01	1.09e-03	1.01e-01	4.51e+00	4.83e+00	2.85e+00	1.32e+04
BY-110	5.07e-01	6.18e-04	5.58e-01	1.27e+00	2.63e+02	1.07e-01	7.51e-02	3.88e+02	1.49e-01	4.93e-01	5.75e-01	6.50e-02	2.17e-02	5.20e-02	2.87e-01	6.87e-01	2.84e-01	8.38e+03
BY-111	1.52e-01	6.18e-04	1.39e-01	7.93e-02	3.93e+01	2.59e-02	6.42e-03	3.76e+02	3.89e-05	3.95e-02	3.95e-02	6.50e-02	1.36e-03	4.61e-03	1.05e-04	3.41e-02	4.34e-02	6.72e+03
BY-112	7.57e-02	6.18e-04	6.95e-02	1.61e-01	6.60e+01	6.60e-02	2.10e+02	2.10e+02	9.72e-03	6.50e-02	6.50e-02	6.50e-02	3.77e-03	5.25e-03	9.26e-03	1.45e-01	3.79e-02	1.10e+04
C-101	6.15e-01	6.18e-04	4.52e-01	9.29e-01	6.19e+01	9.56e-01	1.34e-01	2.51e+03	9.26e-01	1.82e+01	9.00e-01	3.24e+01	7.06e-02	1.47e-01	1.41e-01	1.01e+01	4.82e+00	3.00e+04
C-102	2.41e+01	4.80e-01	1.20e+00	1.06e+00	1.24e+02	7.54e+00	3.26e-01	1.39e+01	3.23e+00	1.13e+01	3.02e+00	1.13e+01	2.43e-02	1.81e-01	5.84e+00	1.10e+01	9.12e+00	2.03e+04
C-103	8.06e-01	6.18e-04	3.26e+00	1.23e+01	2.31e+02	2.98e+00	5.66e+00	1.84e-01	2.46e+00	2.10e+02	2.50e+00	5.71e+01	2.96e+00	6.34e+00	5.99e+01	2.92e+02	2.18e+01	4.22e+04
C-104	2.15e+00	6.18e-04	4.04e-02	2.16e-01	2.93e+01	4.03e-01	1.18e-01	2.15e+00	4.98e-01	3.07e+00	1.27e-01	5.50e+00	1.10e-02	8.93e-02	8.44e-01	3.01e+00	2.54e+00	1.29e+04
C-105	1.67e-01	6.18e-04	8.28e-03	4.27e-02	1.69e+00	1.04e-04	3.80e-02	2.63e+00	8.63e-02	1.85e-01	1.70e-02	1.80e+00	7.47e-03	1.77e-02	1.41e-01	1.97e-01	2.84e-01	6.83e+03
C-106	5.42e-02	6.18e-04	1.98e-04	3.68e-03	1.73e+00	1.04e-04	9.13e-04	3.90e+00	3.89e-05	2.44e-02	2.49e-05	7.86e-01	1.86e-04	2.03e-05	9.60e-02	9.45e-02	2.19e-03	1.77e+04
C-107	2.32e-01	6.18e-04	6.22e-03	3.41e-01	4.80e+01	4.20e-03	2.77e-02	9.63e+02	5.17e-03	1.12e-01	3.40e-03	7.45e+00	2.62e-04	1.17e-01	1.80e-01	4.69e-01	3.31e-02	5.80e+04
C-108	1.78e-03	6.18e-04	3.80e-06	8.29e-03	1.78e+00	1.04e-04	2.59e-05	2.80e+01	3.83e-05	9.48e-03	4.78e-03	1.21e+00	1.85e-05	2.03e-06	3.38e-03	7.89e-03	2.75e-05	1.75e+04
C-109	1.22e-02	6.18e-04	2.16e-03	4.09e-01	6.64e+00	5.29e-03	7.06e-04	5.10e+00	3.89e-05	1.69e-03	2.42e-05	9.71e+00	1.86e-05	3.66e-03	4.16e-03	3.34e-03	2.75e-05	1.93e+04
C-110	2.76e+00	4.73e-02	6.39e-02	2.66e-01	8.36e+01	1.29e+00	3.43e-02	1.18e+02	1.48e-01	5.96e-01	8.29e-03	9.52e-01	1.96e-02	7.47e-02	3.31e-01	7.98e-01	2.54e-01	1.26e+04
C-111	4.77e-03	6.18e-04	3.90e-06	1.47e-02	3.67e+00	3.47e-02	2.59e-05	3.35e+02	3.89e-05	3.48e-03	3.05e-04	9.62e-01	1.69e-02	2.03e-06	1.05e-04	8.71e-03	2.75e-05	2.23e+04
C-112	1.54e-02	6.18e-04	4.02e-03	4.63e+00	1.48e+01	1.04e-04	8.45e-03	1.72e+02	3.83e-05	2.81e-03	3.05e-04	1.59e+01	1.18e-03	4.72e-02	4.05e-03	4.18e-03	2.75e-05	2.24e+04
S-102	1.04e+00	4.85e-01	2.23e-02	1.30e-01	2.75e+02	1.66e-01	4.77e-02	1.84e-01	1.52e-02	2.15e-02	2.41e-02	5.29e+01	2.59e-03	1.37e-02	1.05e-04	4.75e-02	1.59e-02	1.41e+04
S-111	8.76e-02	1.99e-02	7.21e-03	3.52e-02	8.11e+01	4.11e-02	1.01e-02	1.39e+01	2.11e-03	1.37e-03	1.10e-02	3.09e+01	9.25e-04	3.26e-03	1.53e-03	2.55e-03	1.59e-03	1.10e+04
SX-101	5.76e-02	6.18e-04	3.80e-06	2.67e-04	2.45e+00	1.51e-01	2.59e-05	5.62e+02	3.89e-05	2.49e-05	2.43e-05	6.50e-02	1.86e-05	2.03e-06	1.05e-04	1.16e-04	2.75e-05	9.99e+03
SX-102	8.96e-02	2.69e-02	3.90e-06	2.67e-04	1.01e+01	1.04e-04	2.59e-05	5.63e+02	3.89e-05	2.49e-05	2.43e-05	6.50e-02	1.86e-05	2.03e-06	1.05e-04	1.16e-04	2.75e-05	6.79e+03
SX-103	4.21e-01	6.18e-04	1.64e-03	1.29e-02	5.19e+01	6.36e-02	3.54e-03	3.37e+02	1.76e-03	1.52e-03	2.91e-03	6.50e-02	1.02e-03	1.71e-03	1.05e-04	3.73e-03	1.81e-03	1.29e+04
SX-106	3.66e-01	9.59e-02	1.33e-03	2.81e-02	1.17e+02	6.10e-02	8.56e-03	1.82e+02	1.04e-03	2.95e-03	2.32e-03	6.50e-02	1.86e-05	2.08e-03	3.20e-03	4.36e-03	3.15e-03	1.43e+04
T-107	8.22e-02	6.18e-04	1.02e-02	8.00e-02	8.55e+01	3.19e-03	1.51e-02	1.33e+02	2.99e-03	1.42e-02	2.71e-03	6.50e-02	6.03e-03	9.03e-03	2.89e-02	4.19e-02	9.54e-03	1.21e+04
T-111	1.75e-02	1.81e-02	4.31e-02	8.50e-02	1.57e+02	3.04e-02	1.55e-02	9.30e+01	1.47e-01	1.99e+00	4.78e-03	6.50e-02	1.14e-02	9.41e-03	6.26e+00	9.26e+00	8.78e-02	1.18e+04
TX-105	2.80e-02	6.18e-04	1.11e-02	8.89e-03	1.31e+01	2.23e-02	4.12e-03	2.67e+02	4.99e-04	4.56e-03	2.09e-03	6.50e-02	9.00e-04	1.77e-03	1.40e-03	7.05e-03	4.99e-04	1.31e+04
TX-118	8.16e-01	1.97e-01	4.47e-02	7.59e-02	2.23e+01	1.93e-01	5.25e-02	1.71e+02	2.32e-02	4.70e-02	2.53e-02	6.50e-02	1.84e-02	3.93e-02	2.71e-02	1.55e-01	1.67e-02	7.91e+03
TY-101	8.12e-03	6.18e-04	2.21e-03	4.86e-02	1.07e+01	1.05e-02	3.23e-03	1.48e+02	8.65e-04	2.92e-02	5.03e-04	6.50e-02	1.19e-03	8.45e-03	4.70e-02	1.08e-01	2.28e-03	1.08e+04
TY-103	5.02e-01	5.66e-02	1.63e-02	6.76e-02	3.41e+01	1.02e-01	3.51e-02	2.17e+02	3.94e-02	6.00e+00	5.91e-01	6.50e-02	2.85e-02	1.98e-02	9.09e+00	2.25e+01	2.98e-01	1.16e+04
TY-104	9.29e-02	2.19e-02	8.37e-03	7.23e-02	4.22e+01	1.04e-01	1.70e-02	1.25e+01	1.65e-03	1.08e-01	2.42e-03	6.50e-02	4.64e-03	2.26e-02	2.76e-01	4.77e-01	7.33e-03	1.18e+04
U-103	6.66e-01	7.96e-02	6.44e-03	2.56e-01	4.89e+02	1.04e-04	4.36e-02	1.63e+02	6.27e-03	9.77e-03	2.39e-02	4.40e-01	1.52e-03	1.99e-02	1.02e-02	2.49e-02	6.19e-03	1.25e+04
U-105	9.78e-02	3.11e-02	2.90e-03	6.07e-02	2.20e+02	1.04e-04	8.90e-03	1.23e+01	1.61e-03	7.85e-03	7.42e-02	6.50e-02	2.69e-02	6.28e-03	1.05e-04	3.35e-02	3.93e-03	1.27e+04
U-106	1.04e+00	8.13e-01	1.08e-02	1.71e-01	6.74e+02	1.04e-04	9.94e-03	8.20e+01	5.25e-03	1.50e-02	2.59e-02	1.70e-01	9.86e+02	2.59e-02	2.57e-02	3.42e-02	1.01e-02	1.30e+04
U-107	1.01e-01	1.18e-01	3.80e-06	2.04e-01	3.06e+02	1.04e-04	1.70e-02	1.84e-01	1.71e-02	2.78e-02	2.63e-02	4.00e+01	1.22e+03	7.70e-03	1.47e-02	7.69e-02	1.57e-02	1.15e+04
U-111	7.74e-01	4.73e-02	7.58e-03	3.24e-01	4.64e+02	4.57e-02	5.51e+01	2.61e+02	7.20e-03	2.97e-02	1.47e-02	2.01e+01	5.81e+02	1.62e-02	4.67e-02	6.55e-02	8.44e-03	1.12e+04
U-203	2.56e-05	6.18e-04	3.90e-06	2.67e-04	5.94e+01	1.04e-04	2.59e-05	1.84e-01	3.89e-05	2.49e-05	2.43e-05	6.50e-02	1.86e-05	2.03e-06	1.05e-04	1.16e-04	2.75e-05	1.17e+04
U-204	3.42e-02	6.18e-04	3.80e-06	2.67e-04	9.28e-02	1.04e-04	2.59e-05	1.84e-01	3.89e-05	2.49e-05	2.43e-05	6.50e-02	1.86e-05	2.03e-06	1.05e-04	1.16e-04	2.75e-05	1.46e+04

Table A.9. Single-Shell Tank Property Data

Tank	Temperature of Waste (C°)	Temperature of Head Space (C°)	Total Tank Volume (gal)	Volume of Waste (gal)	Volume of Head Space (gal)	Dew Point (C°)	Relative Humidity (%)	Ventilation Status	FIC present	Ventilation Rate (CFM)	Drainable Liquid Volume (kgal)	pH
A-101	69.5	35.6	1263826.3	941523.75	322302.5	25.1	NA	Pass	N	0.135	413	14.0
AX-101	57.0	30.3	1263826.3	754596.00	509230.3	NA	NA	Pass	Y	1.210	320	14.0
AX-102	NA	23.4	1263826.3	25818.75	1238007.5	14.4	57	Pass	N	0.517	17	11.3
AX-103	40.5	32.2	1263826.3	112914.00	1150912.3	NA	NA	Pass	Y	1.480	36	14.0
B-103	14.9	14.1	855771.4	87959.60	767811.8	11.1	82	Pass	Y	1.320	0	12.4
BX-104	30.6	22.8	855771.4	100352.60	755418.8	4	29	Pass	Y	1.320	33	14.0
BY-103	27.2	25.4	1051761.0	384634.25	667126.8	14	49	Pass	N	0.279	160	13.5
BY-104	52.5	26.8	1051761.0	333685.25	718075.8	17	55	Pass	N	0.300	18	14.0
BY-105	48.6	28.6	1051761.0	437993.00	613768.0	18	53	Pass	N	0.256	192	13.3
BY-106	53.3	29.0	1051761.0	653264.00	398497.0	17.8	51	Pass	N	0.166	235	13.5
BY-107	35.8	28.0	1051761.0	264491.00	787270.0	16.1	48	Pass	N	0.329	25	14.0
BY-108	42.7	30.5	1051761.0	203903.00	847858.0	16.3	42	Pass	N	0.354	9	9.6
BY-110	47.6	31.3	1051761.0	253130.75	798630.3	8.5	24	Pass	N	0.334	9	14.0
BY-111	28.5	25.0	1051761.0	426977.00	624784.0	6.4	30	Pass	N	0.261	0	9.6
BY-112	32.4	27.6	1051761.0	135397.25	916363.8	13.3	48	Pass	N	0.383	8	14.0
C-101	34.9	35.1	855771.4	56629.50	797141.9	30.1	75	Pass	N	0.333	3	10.7
C-102	29.1	26.5	855771.4	425600.00	430171.4	23	78	Pass	Y	1.180	37	13.3
C-103	47.9	39.0	855771.4	194264.00	661507.4	36.3	88	Pass	Y	1.280	133	9.5
C-104	35.5	28.9	855771.4	253199.60	602571.8	15.7	45	Act	Y	100.000	11	11.5
C-105	26.2	16.6	855771.4	139908.60	716662.8	5.5	48	Act	Y	1360.000	11	9.7
C-106	65.0	19.3	855771.4	221528.60	634242.8	20.4	107	Act	Y	1550.000	48	9.2
C-107	48.0	49.7	855771.4	140974.10	714797.3	43	81	Pass	Y	1.300	25	9.6
C-108	25.0	25.0	855771.4	75153.50	780617.9	20.5	76	Pass	N	0.326	0	10.6
C-109	28.2	27.2	855771.4	49449.50	806321.9	23.1	78	Pass	N	0.337	4	10.1
C-110	21.2	22.7	855771.4	192887.00	662884.4	14.8	61	Pass	N	0.277	7	11.0
C-111	NA	26.2	855771.4	57252.50	798518.9	24.5	90	Pass	N	0.334	0	13.9
C-112	29.2	28.1	855771.4	100972.25	754799.2	24.6	81	Pass	N	0.315	32	11.9
S-102	42.1	24.2	1051761.0	544297.40	507463.6	16.9	64	Pass	Y	1.210	280	14.0
S-111	33.8	21.4	1051761.0	540249.02	511512.0	13	59	Pass	N	0.214	205	14.0
SX-101	57.0	35.5	1276326.2	444158.24	832168.0	NA	NA	Act	N	NA	146	13.3
SX-102	64.4	34.8	1276326.2	519934.55	756391.7	NA	NA	Act	N	NA	183	14.0
SX-103	78.1	18.0	1276326.2	649166.00	627160.2	14.9	82	Act	N	NA	233	13.2
SX-106	46.1	30.0	1276326.2	536554.94	739771.3	17.5	47	Act	N	NA	255	13.2
T-107	18.9	17.4	855771.4	181905.42	673866.0	14.2	81	Pass	N	0.282	22	11.4
T-111	18.6	16.1	855771.4	447632.00	408139.4	13.7	85	Pass	Y	1.170	49	12.9
TX-105	36.7	26.7	1051761.0	567890.00	483871.0	15.9	52	Pass	N	0.202	20	14.0

Table A.9. (Contd)

Tank	Temperature of Waste (C°)	Temperature of Head Space (C°)	Total Tank Volume (gal)	Volume of Waste (gal)	Volume of Head Space (gal)	Dew Point (C°)	Relative Humidity (%)	Ventilation Status	FIC present	Ventilation Rate (CFM)	Drainable Liquid Volume (kgal)	pH
TX-118	24.9	22.0	1051761.0	287900.00	763861.0	8.1	41	Pass	Y	1.320	27	12.3
TY-101	17.6	16.6	1051761.0	117978.20	933782.8	11.7	73	Pass	Y	1.390	0	8.2
TY-103	19.6	16.3	1051761.0	157360.40	894400.6	13.5	83	Pass	Y	1.370	5	10.1
TY-104	16.4	16.4	1051761.0	44446.40	1007314.6	13.7	84	Pass	Y	1.420	15	11.9
U-107	25.6	20.4	855771.4	409186.16	446585.3	13.5	65	Pass	N	0.187	178	11.4
U-111	26.7	21.8	855771.4	12500.00	843271.4	13.2	58	Pass	Y	1.350	122	11.2
U-203	18.1	17.9	855771.4	65170.25	790601.2	11.1	64	Pass	N	0.330	1	13.1
U-204	17.5	13.6	855771.4	60695.00	795076.4	16.9	123	Pass	N	0.332	1	12.6

Table A.10. Single-Shell Tank Waste Data

Tank	Aluminum ($\mu\text{g/g}$)	Iron ($\mu\text{g/g}$)	Chromium ($\mu\text{g/g}$)	Manganese ($\mu\text{g/g}$)	Nickel ($\mu\text{g/g}$)	Zinc ($\mu\text{g/g}$)	Palladium ($\mu\text{g/g}$)	Cadmium ($\mu\text{g/g}$)	Total Alpha ($\mu\text{Ci/L}$)	Total Beta ($\mu\text{Ci/L}$)	Total Gamma ($\mu\text{Ci/L}$)	Nitrite ($\mu\text{g/g}$)	Nitrate ($\mu\text{g/g}$)	Cyanide ($\mu\text{g/g}$)	Total Organic Carbon ($\mu\text{g/g}$)	Total Inorganic Carbon ($\mu\text{g/g}$)	pH	Ammonia (Liquid) ($\mu\text{g/mL}$)	w% H ₂ O
BY-108	39800	7190	255	209.00	2510.0	83.50	413	16.30	0.06180	549.0	NA	23700	201000	362.0	4480	5340	NA	NA	27.2
T-111	570	18500	1980	6330.00	132.0	106.00	NA	5.80	0.36800	15.1	NA	793	41300	NA	2995	812	NA	400.0	76.5
T-107	16300	29200	360	213.00	267.0	NA	NA	6.94	0.43400	330.0	NA	11700	74500	69.0	1500	NA	11.4	122.0	56.0
C-110	14500	11000	470	56.30	23.9	224.00	NA	5.36	0.12500	42.4	NA	6890	110000	5.0	802	2030	11.0	86.4	59.8
C-101	NA	NA	NA	NA	NA	NA	NA	NA	1.09000	NA	NA	NA	NA	NA	1260	3990	10.7	NA	33.8
C-107	NA	NA	NA	NA	NA	NA	NA	NA	3.90000	NA	NA	NA	NA	NA	NA	NA	NA	NA	53.7
TY-104	9080	32600	1410	1730.00	1490.0	NA	NA	16.20	0.31900	728.0	47.2	12200	46600	NA	1930	18700	11.9	NA	51.8
AX-102	NA	NA	NA	NA	NA	NA	NA	NA	1.20000	NA	NA	40700	172000	26.3	56600	NA	NA	NA	30.5
C-112	26540	27900	NA	NA	13100.0	NA	NA	NA	0.76700	5260.0	NA	47200	62000	8400.0	2470	5830	NA	5.0	41.5
C-109	67400	18700	250	128.00	14100.0	362.00	NA	22.20	0.39500	2120.0	NA	40700	40300	882.0	2850	5450	10.1	53.0	20.7
C-111	128000	54700	222	307.00	20700.0	151.00	NA	NA	0.88400	NA	NA	NA	NA	37.6	1250	NA	NA	NA	21.1
C-108	52100	7170	NA	NA	8410.0	NA	NA	NA	0.05110	200.0	NA	24700	44600	1980.0	945	2380	NA	NA	38.8
C-105	61800	10600	943	2470.00	2150.0	154.00	NA	158.00	1.33000	NA	182.0	NA	10500	46.8	999	NA	NA	NA	40.7
U-203	NA	NA	NA	NA	NA	NA	NA	NA	0.00151	NA	NA	NA	NA	NA	80	NA	NA	NA	47.7
U-204	221000	2722	176	82.16	3940.0	902.33	NA	15.68	0.09670	NA	NA	3000	12000	NA	470	1025	NA	NA	26.3
B-103	NA	NA	NA	NA	NA	NA	NA	NA	0.18600	NA	NA	NA	NA	NA	678	1845	NA	NA	44.8
T-105	95100	33100	505	11600.00	81.3	NA	NA	15.40	0.27800	866.0	NA	29800	21200	11.4	4130	7660	10.9	400.0	25.9

Table A.11. Double-Shell Tank Waste Data

Tank	Aluminum (µg/L)	Iron (µg/L)	Chromium (µg/L)	Manganese (µg/L)	Nickel (µg/L)	Zinc (µg/L)	Cadmium (µg/L)	Total Alpha (µCi/L)	Total Beta (µCi/L)	Nitrite (µg/L)
AP-101	667	281	39.3	NA	NA	494	143	0.00594	5.48	13400000
AP-102	11600000	3810	618000	NA	26600	NA	1470	0.003996	NA	380000000
AP-103	246000	1230	4390	43.1	NA	441	111	NA	NA	1300000
AP-105	11700000	6600	187000	NA	11000	NA	1770	NA	NA	483000000
AP-106	211000	6890	4740	NA	408	NA	5920	NA	NA	1190000
AP-107	1060	NA	NA	77.3	NA	990	NA	NA	0.211	235000000
AW-102	346000	NA	NA	NA	NA	NA	NA	NA	NA	1820000
AW-103	41600	NA	NA	NA	NA	NA	NA	NA	NA	1220000
AW-104	98800	NA	NA	NA	NA	NA	NA	NA	NA	2174000
AW-105	907000	1070	64800	66.7	90600	3090	170	1.44	60000	118000000
AW-106	1080000	NA	NA	NA	NA	NA	NA	NA	NA	6070000
AZ-102	1540000	NA	966900	NA	NA	NA	NA	NA	NA	276000000
AN-102	15000000	NA	NA	NA	400000	NA	NA	167	NA	834000000
AW-101	27900000	NA	161000	26100	NA	NA	NA	NA	NA	1020000000
SY-101	44700000	160500	1950000	NA	119800	69450	NA	122.9	807000	1800000000
SY-102	635500	NA	NA	NA	NA	NA	NA	6.17	8230	3224000
AY-102	13700	NA	NA	NA	NA	NA	NA	NA	NA	884000

Table A.11. (Contd)

Tank	Total Beta ($\mu\text{Ci/L}$)	Nitrite ($\mu\text{g/L}$)	Total Organic Carbon ($\mu\text{g/L}$)	Total Inorganic Carbon ($\mu\text{g/L}$)	Ammonia ($\mu\text{g/L}$)	pH	Hydroxide ($\mu\text{Cg/L}$)	Cesium-137 ($\mu\text{g/L}$)	Strontium-90 ($\mu\text{g/L}$)	Sensitivity ($\mu\text{g/L}$)
AP-101	1580000	340	23700	190000	1960000	13	1820000	3.26	0.563	0.986
AP-102	78200000	24600	3280000	5350000	273000	13.7	9150000	228000	1440	1.2
AP-103	4040000	551	112000	514000	38200	13	1690000	6540	2.62	1.003
AP-105	165000000	18300	2750000	4490000	40000	14.5	53900000	227000	208	1.333
AP-106	4900000	503	435000	503000	17730	12.9	1430000	5360	0.698	0.996
AP-107	1020000	579	52000	295000	1038000	12.2	2660000	0.123	0.118	0.989
AW-102	10200000	NA	339000	580000	127000	NA	2040000	15300	45.2	NA
AW-103	3510000	NA	935000	921000	NA	13	3200000	20600	0.22	1
AW-104	10770000	NA	460400	417900	NA	12.4	1759000	4545	7.785	0.988
AW-105	36700000	NA	2470000	NA	475000	13.1	13100000	66300	6.04	1.08
AW-106	24600000	NA	728000	308000	89600	NA	6340000	50700	29.5	NA
AZ-102	23800000	NA	1503000	5843000	NA	12.9	1880000	1040000	1760	1.1
AN-102	221000000	NA	26100000	13500000	NA	13.1	4100000	382000	73700	1.4
AW-101	214000000	26800	2460000	NA	247000	NA	86200000	520000	1090	1.56
SY-101	202500000	NA	17550000	7650000	1650000	NA	33300000	552000	11670	1.5
SY-102	23480000	1040	250300	NA	9140	12.8	3471000	6767	1.164	1.03
AY-102	526000	NA	82100	483000	16970	11.1	307000	3366	198	0.99

Exploratory Data Analysis

This phase of the study examines the distributions of each variable under consideration and explores pairwise correlations between ammonia measurements and other measurements, as well as other pairwise correlations of interest. A strong correlation between ammonia and a specific variable indicates that ammonia concentration might be well predicted by that variable. The statistical tools for this exploration include histograms, pairwise scatter plots and Kendall's Tau statistics (Randles and Wolfe 1991, p. 108).

Histograms display the empirical distribution of each variable and show the center, range and skewness of the distribution. The scatter plots illustrate the relationships between ammonia and the other variables.

Kendall's Tau statistic calculates a numerical value to show a relationship between two variables. It is similar to the most common measure of correlation, Pearson's Product Moment Correlation, often denoted r . Pearson's r measures linear relationships between variables; Kendall's Tau measures less restrictive associations. Values of Tau are always between -1 and 1. Positive values indicate that as one variable increases the other tends to increase. Negative values indicate an inverse relationship. A value of 1 indicates a perfect monotonic relationship, that is, higher values of one variable correspond to higher values for the other. A value of -1 indicates the opposite, higher values of one variable indicate lower values of the other. A value near 0 indicates no apparent relationship.

The p-value reported in many areas of statistics denotes the probability that the result would happen by chance if the two variables were completely independent of each other. Its value is restricted between 0 and 1. A low p-value indicates a result is unlikely to have occurred by chance.

In this report, Kendall's Tau is used to assess the chance of a relationship between the ammonia concentration and the values of other data items. If the p-value is low, say 0.1 or less, it is likely that ammonia and the other variable have some kind of relationship. If the p-value is very low, less than 0.01, then it is more likely that some kind of relationship exists. As to what kind of relationship, all that can be said is: if Kendall's Tau is positive, if the ammonia concentration and the other variable in two tanks are compared, both will tend to be either higher or lower in the second tank than in the first tank. If Kendall's Tau is negative, and the p-value indicates a likely relationship, the two variables will tend to have opposite natures; that is, if one increases, the other tends to decrease.

Principal Component Analysis (PCA)

PCA is a multivariate statistical analysis tool (Rencher 1995). When the ammonia concentration in a tank cannot be well characterized by any single variable, which appears to be the case in this study, PCA offers a method to discover the combined effect of all variables of interest.

PCA creates a new set of uncorrelated variables called principal components, each of which is a linear combination of the original variables. These principal components are formed in such a manner that the variation contained in the original data set is retained to the maximum extent possible. Normally, the number of principal components needed to retain more than 90% of the information in the original data set is much smaller than the number of variables under study. Consequently, the original data set can be examined in a data space of much lower dimension (e.g., two or three dimensions instead of 22).

The major objective of the PCA approach in this study is to discover the similarities in the tanks, independently of their ammonia concentrations. If certain tanks that share similar chemical or physical characteristics also share similar features relating to ammonia, there is a possibility that the ammonia concentration in a tank can be predicted based on its concentrations of other constituents or the physical properties of its waste contents. The similarity between two tanks is measured by the distance between the tanks when their characteristics are plotted in a multi-dimensional space defined by all the variables under consideration. Each tank is represented as a single point in this multi-dimensional space.

Discriminant Analysis

Discriminant analysis is also a multivariate statistical tool (Rencher 1995). Assuming that all tanks fall into one of three categories in terms of ammonia concentration (high, medium, and low), this approach develops a discriminant rule to classify each tank into one of the three ammonia groups. The discriminant rule is based on a set of chemical and/or physical measurements on the tank. The rule could then be used to classify the ammonia concentration for other tanks in which ammonia was not measured, but which have the other data necessary to support this classification technique.

Another objective of discriminant analysis is to aid in understanding the underlying relationships between ammonia and other discriminating variables. This may be achieved by generating two new variables, called discriminant variables, that maximize the between-group distances. Similar to principal components, these discriminant variables are also linear combinations of the original variables. However, these linear combinations are driven by the distances between groups instead of by the overall variability, as in PCA. The coefficients on the two discriminant variables sometimes provide insight into the relative contributions of the corresponding original variables. However, the interpretation of the contributions is often difficult. In many cases, further investigation is required.

Appendix B

SST Data Analysis

Appendix B - SST Data Analysis

B.1 Exploratory Data Analysis for SST Data

This section provides a brief look at the variables in the data. The data for each variable are displayed in a histogram in Figure B.1. The histograms show that

- For most variables, the majority of the observations are at the low end of the scale, with a few readings distributed over higher levels.
- The temperature of the headspace has a distribution ranging from 13 to 50°C, with the majority of observations in the 20 to 30°C range.
- The vent rate measurements fall into two distinct groups, one less than 0.6 cfm and one between 1.1 and 1.5 cfm. Tanks with very high vent rates were eliminated from this study.
- The pH reading was 14.0 for 13 tanks and above 11.8 for 24 of the 37 tanks.
- Nitrogen oxide (N₂O) concentration was less than 786 mg/m³ (400 ppm) for 26 tanks, between 982 and 1280 mg/m³ (500-650 ppm) for three tanks, and more than 1670 mg/m³ (850 ppm) for eight tanks.

To display the relationship between ammonia and each data item, Figure B.2 shows scatter plots with the concentration of ammonia on the vertical axis and the other variables on the horizontal axis. The scatter plots show that

- No variables exhibit an obvious relationship; i.e., none are tightly grouped about a line or curve.
- Some variables, such as hydrogen, nitrogen oxide, and propanol, hint at a very diffuse tendency to increase as ammonia increases.
- The carbon dioxide and vent rate variables hint at inverse relationships with ammonia concentration.

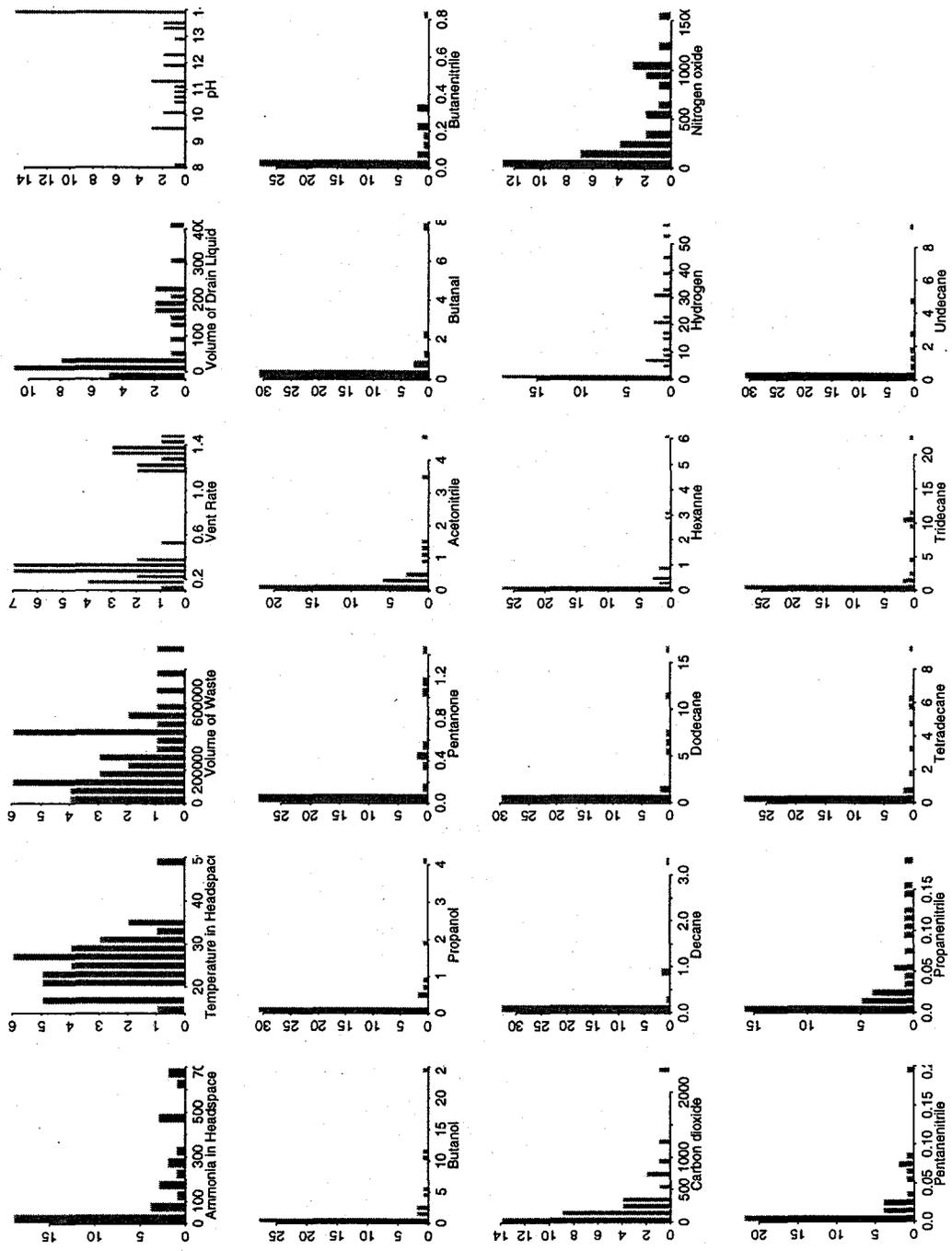


Figure B.1. Histograms of SST Data for Ammonia in the Head Space Analysis

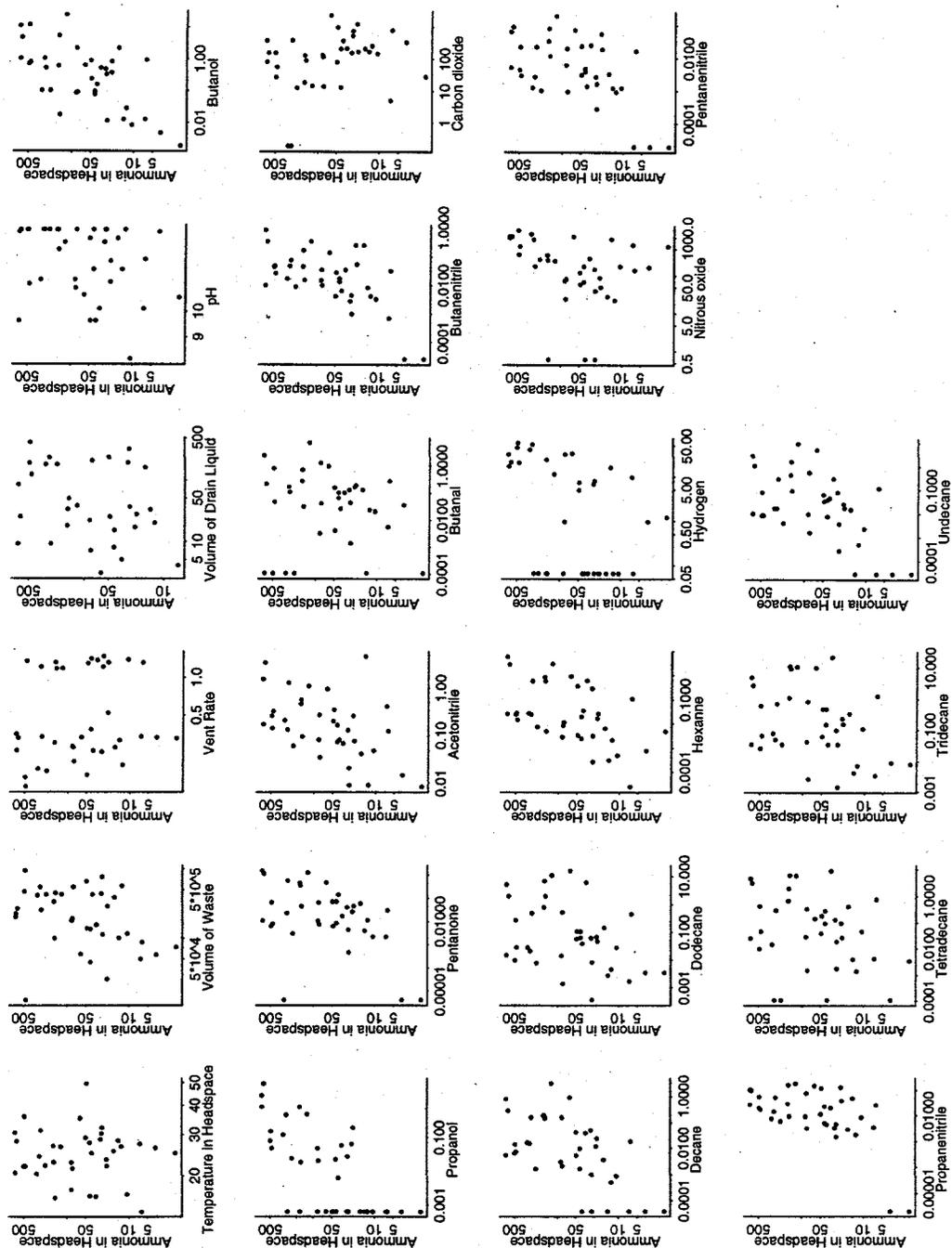


Figure B.2. Scatter Plots of SST Data for Ammonia in the Head Space Analysis

Table B.1 shows the values of Kendall's Tau for the data collected.

Table B.1. Kendall's Tau Values for Ammonia and Available Data

Variable	p-value	Tau
temperature in head space	0.88	0.0180
volume of waste	0.041	0.23(a)
vent rate	0.13	-0.17
volume of drainable liquids	0.0044	0.33(b)
pH	0.10	0.19
1-Butanol	0.0003	0.42 (b)
1-Propanol	0.0002	0.43 (b)
2-Pentanone	0.0063	0.31 (b)
Acetonitrile	0.0006	0.40 (b)
Butanal	0.25	0.13
Butanenitrile	0.0007	0.39 (b)
Carbon dioxide	0.05	-0.22 (a)
Decane	0.0006	0.39 (b)
Dodecane	0.04	0.23 (a)
Hexane	0.0008	0.38 (b)
Hydrogen	0.0062	0.31 (b)
Nitrogen oxide	0.0033	0.34 (b)
Pentanenitrile	0.0021	0.35 (b)
Propanenitrile	0.0021	0.35 (b)
Tetradecane	0.089	0.20 (a)
Tridecane	0.067	0.21 (a)
Undecane	0.0029	0.34 (b)

(a) p-value less than 10%, which indicates the likely existence of some kind of relationship.

(b) p-value less than 1%, which indicates the high probability of some kind of relationship.

Clearly, the values of Kendall's Tau show that

- Only vent rate and carbon dioxide have negative Tau values.
- There are 18 variables with p-values less than 10%, and 13 variables with p-values less than 1%, indicating the existence of probable relationships.

- Even though the p-values are impressive, the values of Tau are all between -0.2207 and 0.4324, which are not viewed as being highly explanatory of the ammonia concentrations found in the head space.

While the data do not appear to exhibit any strong relationships between the individual variable values and the concentration of ammonia, additional studies presented in Sections B.2 and B.3 show that more sophisticated techniques can produce more meaningful results.

B.2 Principal Component Analyses for SST Head Space Data

Twenty two variables were used in the PCA analyses (see Section A.5). The PCA analysis is based on the normality assumption that the variables used in the analysis have a joint multivariate normal distribution. However, as shown in Figure B.3, the distributions of several variables are quite skewed. To ensure that the distribution of each individual variable would not be too different from a normal distribution, several transformation formats were investigated. A log₁₀ transformation showed the best result and was applied on each of the variables. The PCA analysis was then applied on the transformed data.

The PCA analysis was conducted with an Splus procedure, PRCOMP (Splus 1991). Figure B.4 shows the cumulative percent of variance addressed by the principal components. The figure shows that the first six principal components are needed to retain 90% of the variance in the original data set. This number of principal components is relatively high, an indication that the head space data set truly has a high dimensional structure.

These six principal components make it possible to explore the high (22) dimensional data structure in a low (2 or 3) dimensional plot, since each of the new variables includes multi-dimensional information. The pairwise scatter plots of the six principal components were studied. It was found that the plot of the second versus the third principal components, shown in Figure B.5, displayed an interesting structure.

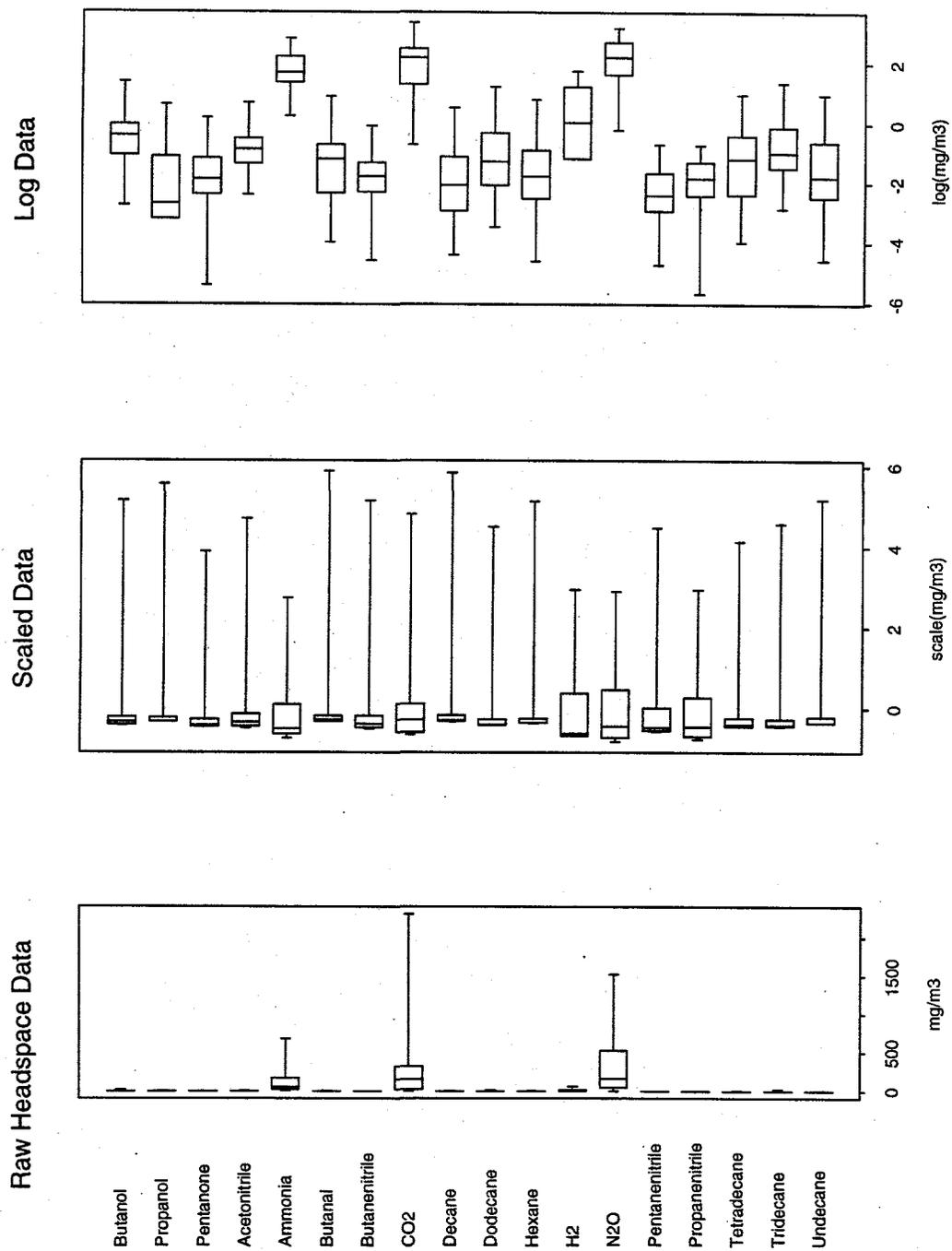


Figure B.3. Distributions of SST Head Space Data

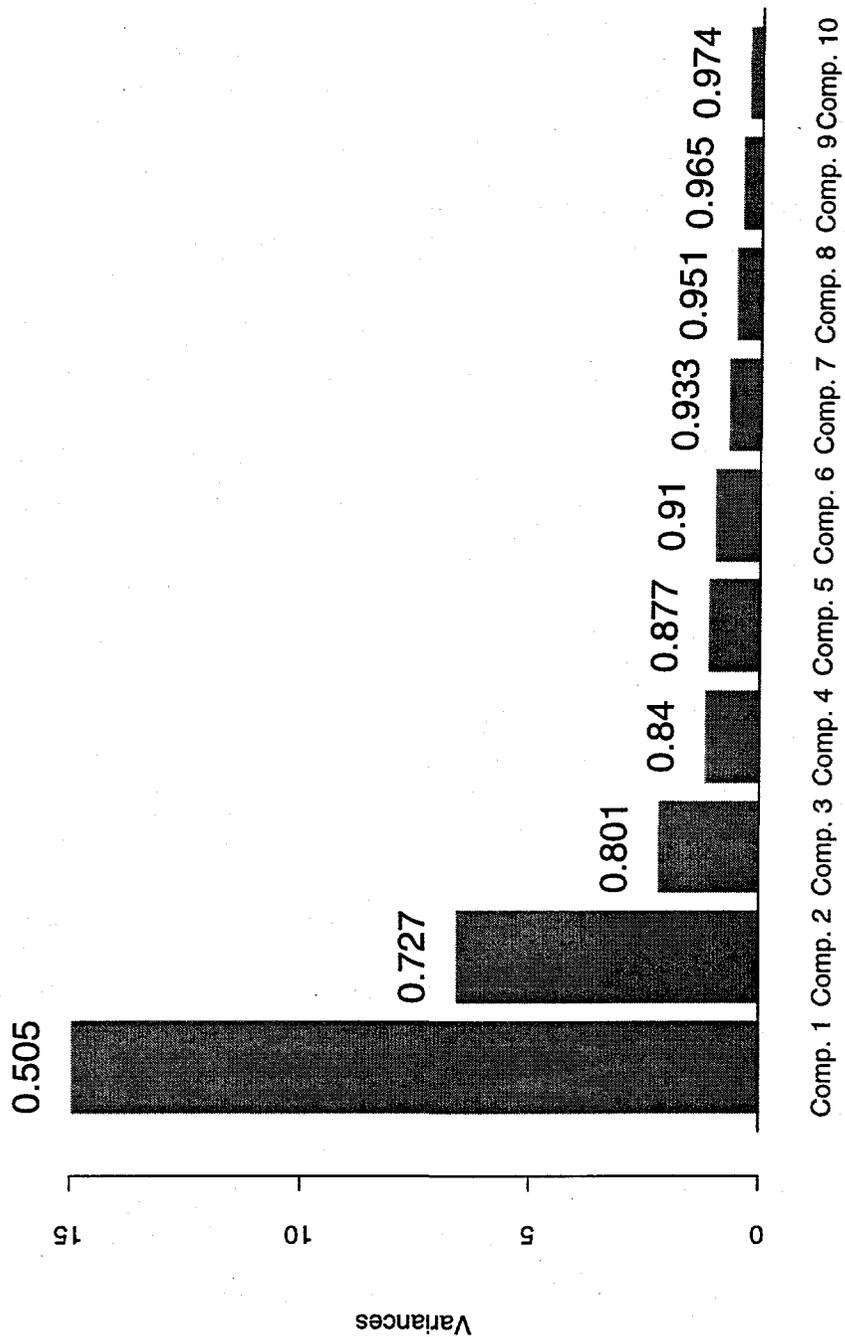


Figure B.4. Fractions of Variance Explained by Principal Components for SST Head Space Data

The seven tanks located at the upper right corner of the plot all have high ammonia head space concentrations (more than 228 mg/m³), except Tank 241-S-111 (It is worth noting that Tank 241-S-111 is on the watch list for flammable gas). Although not all high ammonia tanks were captured in this corner (three of them, 241-BY-107, 241-BY-108, and 241-BY-110, were not captured), the plots suggest that a high ammonia concentration in the head space might be characterized by the linear concentrations of the variables under study.

The loadings of the original variables on the first four principal components are given in Figure B.6. The loadings, listed in decreasing order, indicate the levels of effects of the original variables on the principal components. The figure shows that the liquid volume in a tank tends to have a strong positive relationship with the second principal component. A set of decanes as well as butanal and hexane tend to have almost equally negative relationships with this principal component. For the third principal component, hydrogen, propanol, and nitrogen oxide tend to have strong positive impact, while carbon dioxide tends to have a strong negative impact.

B.3 Discriminant Analyses for SST Head Space Data

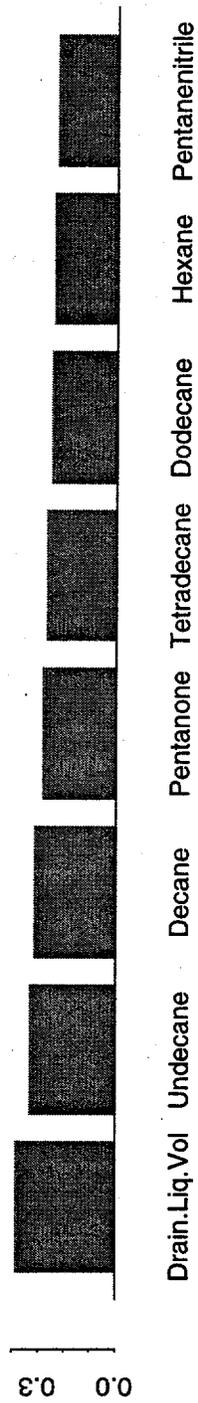
As described in Appendix A, there are two major objectives for discriminant analysis: to develop a classification rule to predict the ammonia level for other tanks, and to identify the relative contributions of the variables used for ammonia group separation. An analysis was conducted on the SST head space data to meet both of these objectives; this section summarizes the results.

The tanks were grouped into three classes based on the concentration of ammonia in the head space. The different levels of ammonia concentration and the number of tanks in each class are shown in Table B.2.

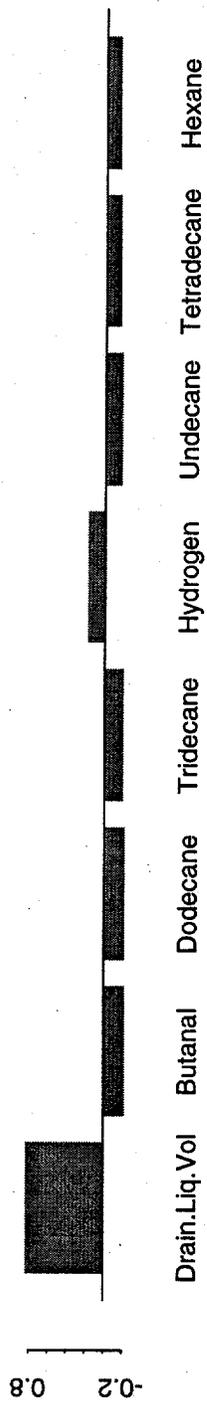
Table B.2. SST Tank Grouping, Head Space Data

Class	NH ₃ Range (mg/m ³)	NH ₃ Range (ppmv)	No. of Tanks
High	> 228	>300	9
Medium	76 - 228	100-300	8
Low	< 76	<100	20

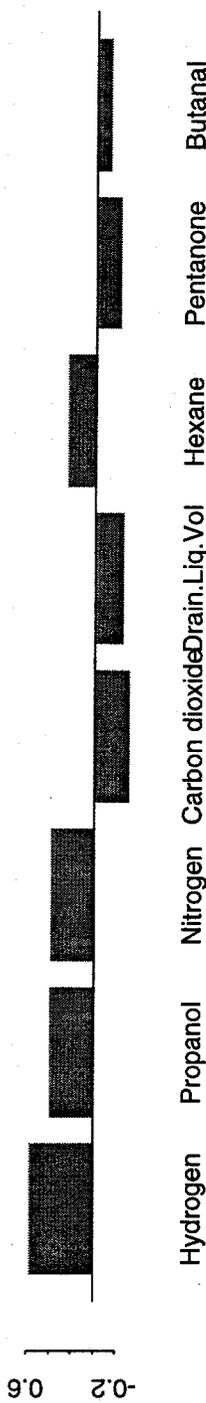
Comp. 1



Comp. 2



Comp. 3



Comp. 4

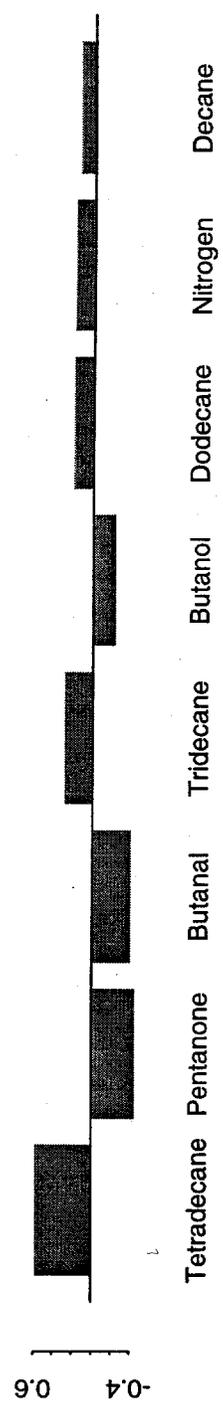


Figure B.6. Principal Component Loadings for SST Head Space Data

The first step in the analysis is to search for the smallest possible subset of variables that can separate the groups nearly as well as all variables under study. This step is necessary especially when the number of tanks is relatively small and the number of variables under consideration is relatively large, which was the case in this study. The SAS (SAS 1989) procedure, STEPDISC, was used for this process. From the 22 variables of interest the procedure selected 15 that significantly contribute to group separation. The selected variables are listed in Table B.5.

The discriminant analysis was then conducted using the SAS procedure DISCRIM. Figure B.7 shows the scatter plots of the first and second discriminant variables for the 37 tanks, labeled by tank number and ammonia concentration level. The high ammonia group was clearly separated from the other two groups, except for Tank 241-U-111, which was located closer to the low group. However, there are some overlaps between the medium and low ammonia groups. The high ammonia group tanks are located in an area with high values of the first discriminant variable; both medium and low ammonia groups have relatively low values of the first discriminant variable and are separated by the second discriminant variable.

A classification rule for prediction was also developed by this procedure. The developed rule was re-applied to the same data, and 33 out of 37 tanks were correctly classified. One high ammonia tank was classified into the low ammonia group, and other misclassifications occurred within the medium and low groups. These results are summarized in Table B.3.

Table B.3. Resubstitution Results on SST Head Space Data

Actual	Classified		
	L	M	H
L	19 95.00%	1 5.00%	0 0.00%
M	2 25.00%	6 75.00%	0 0.00%
H	1 11.11%	0 0.00%	8 88.89%

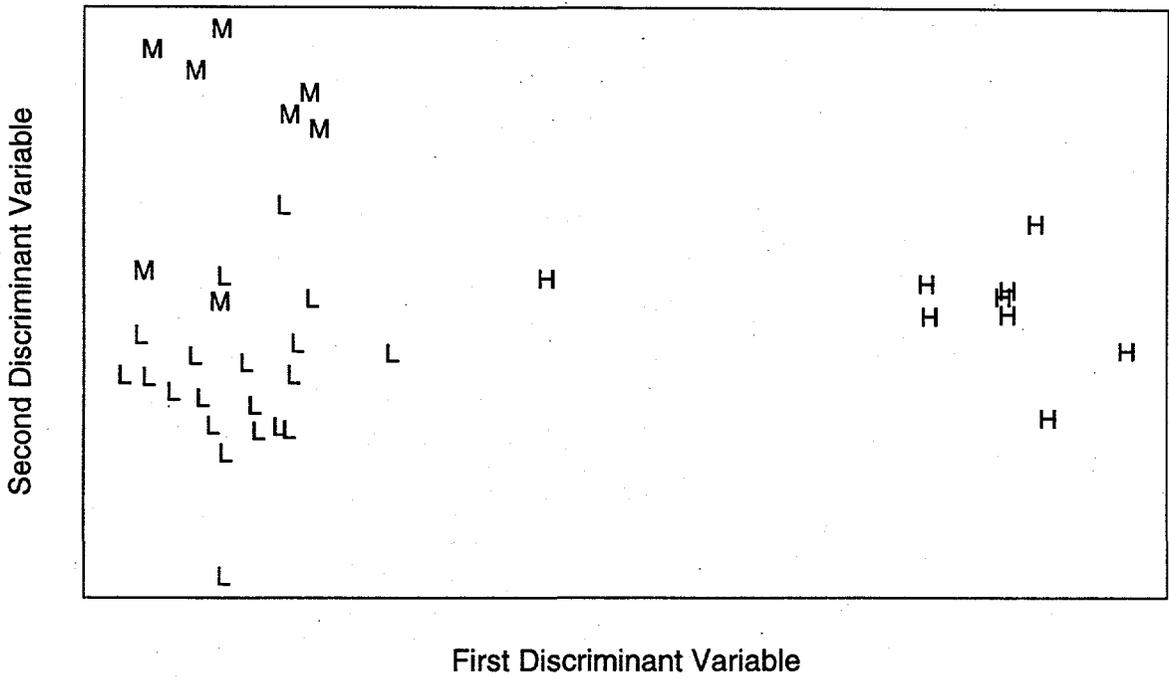
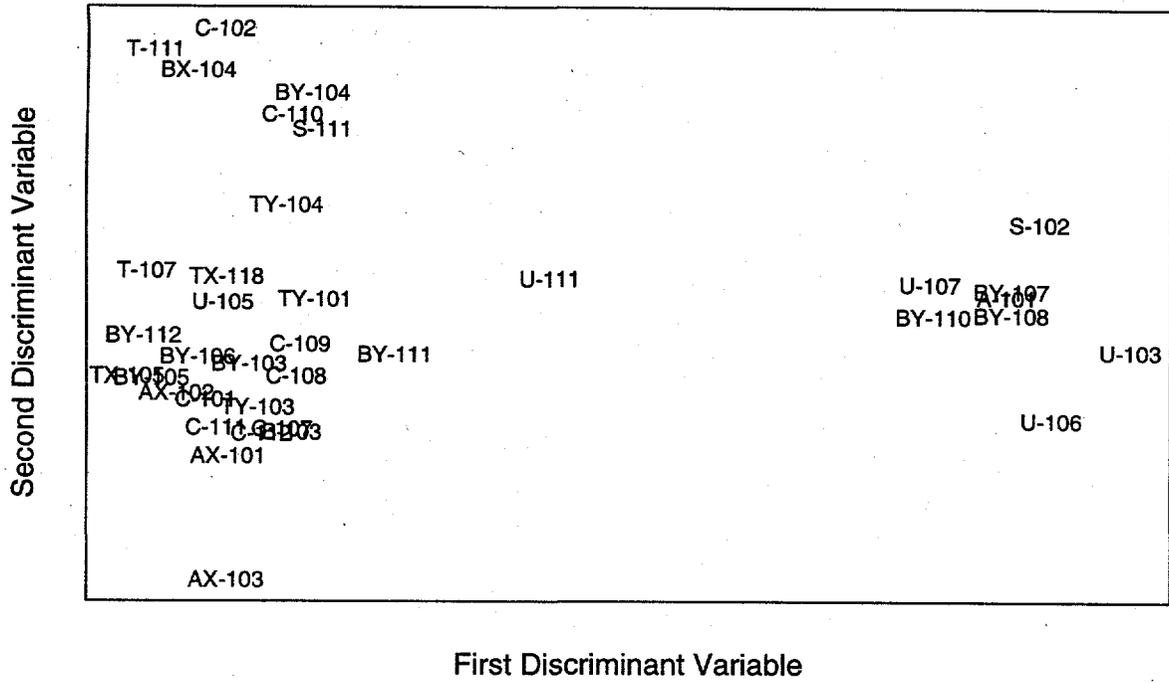


Figure B.7. Discriminant Analysis for SST Head Space Data

The misclassification rate shown in the table above represents the discrimination performance too optimistically, because the rule was "tuned" to that exact data set. A more appropriate way to investigate the level of performance is with a cross-validation technique. This technique removes one tank at a time, generates a new classification rule using the rest of the data, and then applies the rule to the removed tank for classification. The process is repeated for each of the 37 tanks. Table B.4 shows the results of this investigation, in which 29 out of 37 tanks were correctly classified. The percentages of correct classifications for high, medium, and low groups are 77%, 62%, and 85%, respectively. Two high ammonia tanks were classified into the low group, Tanks 241-U-111 and 241-BY-110. The medium and low ammonia tanks that were misclassified into the high group are 241-C-102 and 241-C-112. These results of cross-validation offer evidence that the ammonia level in headspace of a passively ventilated tank could be classified by the 15 variables selected by the STEPDISC procedure.

Table B.4. Cross-Validation Results on SST Head Space Data

Actual	Classified		
	L	M	H
L	17 85.00%	2 10.00%	1 5.00%
M	2 25.00%	5 62.50%	1 12.50%
H	2 22.22%	0 0.00%	7 77.78%

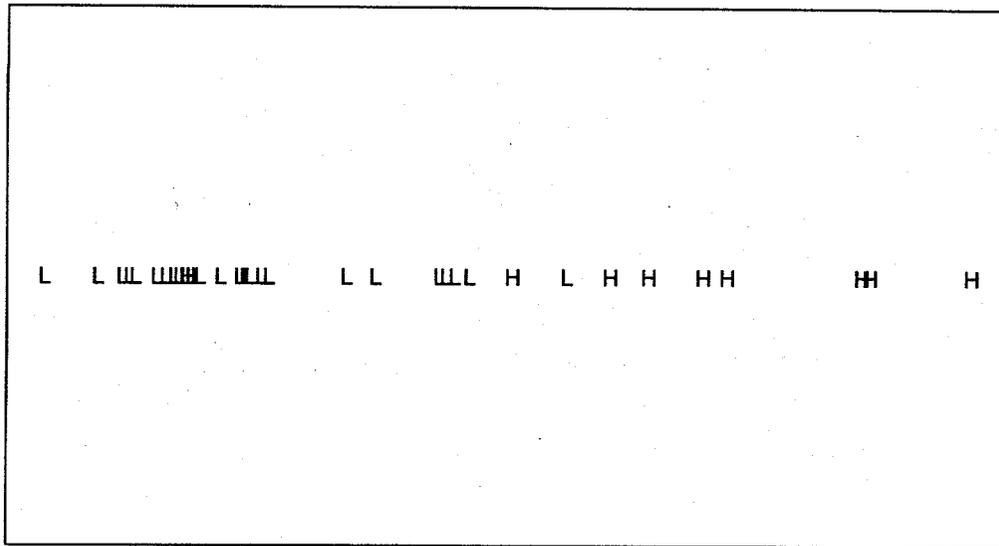
Table B.5 lists the raw and standardized coefficients on the two discriminant variables. The raw coefficients were used to calculate the discriminant variables plotted in the figures above, while the standardized coefficients reflect the relative impact of each variable. The standardized coefficients are those that result if the original variables were centered by group mean and scaled by the standard deviation within the group. Therefore, these coefficients are free of the effect due to different scales of the original variables. According to the table, undecane, decane, pentanenitrile, pentanone, tridecane and tetradecane seem to rank highest in terms of their relative contributions to the group separation. Notice that five out of these six variables (all except pentanone) have oppositely signed coefficients on the two discriminant variables. However, the "high" group was not located at the right lower corner of the plot. This indicates that these variables probably contribute to the group separation in a complex and joint manner. To obtain more insight into the behaviors of these variables, further investigations were conducted.

Table B.5. Coefficients for the Two Discriminant Variables

Variable	DV1 (Raw)	DV2 (Raw)	DV1 (Standard)	DV1 (Standard)
HS Temperature	-0.15	-0.058	-1.02	-0.39
1-Butanol	0.65	-0.41	2.99	-1.90
1-Propanol	3.64	-1.29	2.67	-0.94
2-Pentanone	19.76	3.84	7.00	1.36
Acetonitrile	1.23	-0.32	-1.16	-0.30
Carbon dioxide	0.0039	-0.0048	1.75	-2.11
Decane	31.27	-13.81	17.36	-7.66
Hexane	-3.30	-1.37	-3.90	-1.62
Hydrogen	0.058	0.061	0.95	1.00
Nitrogen oxide	0.0043	-0.0021	1.82	-0.89
Pentanenitrile	-250.82	19.62	-9.33	0.73
Propanenitrile	67.66	28.72	3.41	1.45
Tetradecane	-2.20	1.77	-4.63	3.73
Tridecane	1.20	-0.79	5.69	-3.73
Undecane	-10.45	5.22	-17.94	8.96

The first question to be addressed was, "Are the variables with large absolute coefficient values truly influential to the group separation?" A series of discriminant analyses were carried out, starting with only undecane and decane as the discriminators with the largest absolute values of the standardized coefficients. More variables were then added into the analysis one at a time, in the order of their coefficient values. A fairly good separation did not appear until 12 variables were included in this process. The misclassification rate of cross-validation with the 12 variables is 11 out of 37, which is not as low as it was using 15 variables. A reasonable conclusion, therefore, is that the good classification result obtained at first is truly a joint effort of the 15 variables. The three group separations cannot be characterized by only the smaller number of variables with large absolute standardized coefficients.

Since the tanks in the high ammonia group are the biggest concern, the next effort was to identify the most influential variables for separating the high ammonia group. Recall that the scatter plots of ammonia versus hydrogen and nitrous oxide showed some patterns of correlation. The search started with three inorganic gases: hydrogen, nitrous oxide, and carbon dioxide. The 37 tanks were further merged into two classes by combining the medium and low groups. The discriminant analysis procedure was then applied to the two-group data, and the results were quite promising. The plot of the single discriminant variable generated for the two groups is displayed in Figure B.8. The majority of high



Discriminant Variable

Figure B.8. Discriminant Analysis on Two Group Setting Using CO₂, H₂, and N₂O

group tanks lie on the right end of the line. The misclassification rate from the cross-validation calculation is 6 out of 37 tanks (see Table B.6). Only one high ammonia tank, U-111, was misclassified into the low group, the same tank that was misclassified based on 15 variables.

Table B.6. Cross-Validation Results on Two Group Discriminant Analysis

Actual	Classified	
	L&M	H
L&M	23 82.14%	5 17.86%
H	1 11.11%	8 88.89%

The results provide evidence that tanks with high ammonia in the head space can be identified by using only these three inorganic measurements in the head space. However, the three variables could not effectively separate the medium and low groups. This phenomenon indicates that hydrogen, nitrous oxide, and carbon dioxide have a fairly strong correlation with ammonia when the ammonia concentration is above a certain level, i.e., 228 mg/m³, but the correlation fails to hold at lower ammonia concentrations.

B.4 Head Space and Waste Exploratory Data Analysis for SST Data

This section presents observations regarding relationships between the ammonia concentration in the head space and other data variables in the waste. Figures B.9 through B.12 contain histograms for each variable of interest and scatter plots of each variable versus the ammonia concentrations. Table B.7 provides several statistics for the various analyte measurement data. The following conclusions are drawn from these figures and calculations of Kendall's Tau:

- Data on ammonia concentration in the head space is available, along with some other data items, for 16 tanks for which TCRs are available. The ammonia concentrations include one high value (679 mg/m³), one medium value (157 mg/m³), and 14 low values (less than 100 mg/m³).

The variables with the largest correlation values (for Kendall's Tau statistic) are:

Constituent	Tau	p-value
TOC	0.49	0.01
Aluminum	-0.56	0.02
Nitrate	0.53	0.02
pH	0.62	0.05
Zinc	-0.62	0.05

- These variables show a noteworthy relationship, based on the non-parametric Kendall's Tau test, but did not show a significant relationship based on Pearson's correlation coefficient for TOC, aluminum, water, and zinc. This may indicate that a nonlinear relationship exists.
- Ammonia in the head space and ammonia in the liquid show a tendency to increase together, but with only six tanks having data for both variables, this result is not conclusive.

Additional investigations were conducted. Out of the 16 tanks, only four records contain data on ammonia plus the five constituents listed above. Ten records contain data on ammonia, as well as TOC, aluminum and nitrate. These ten records formed the mini-database for the following investigation. Inspection of the plots shown in Figures B.9 through B.12, suggests that a log transformation of the variables should be considered.

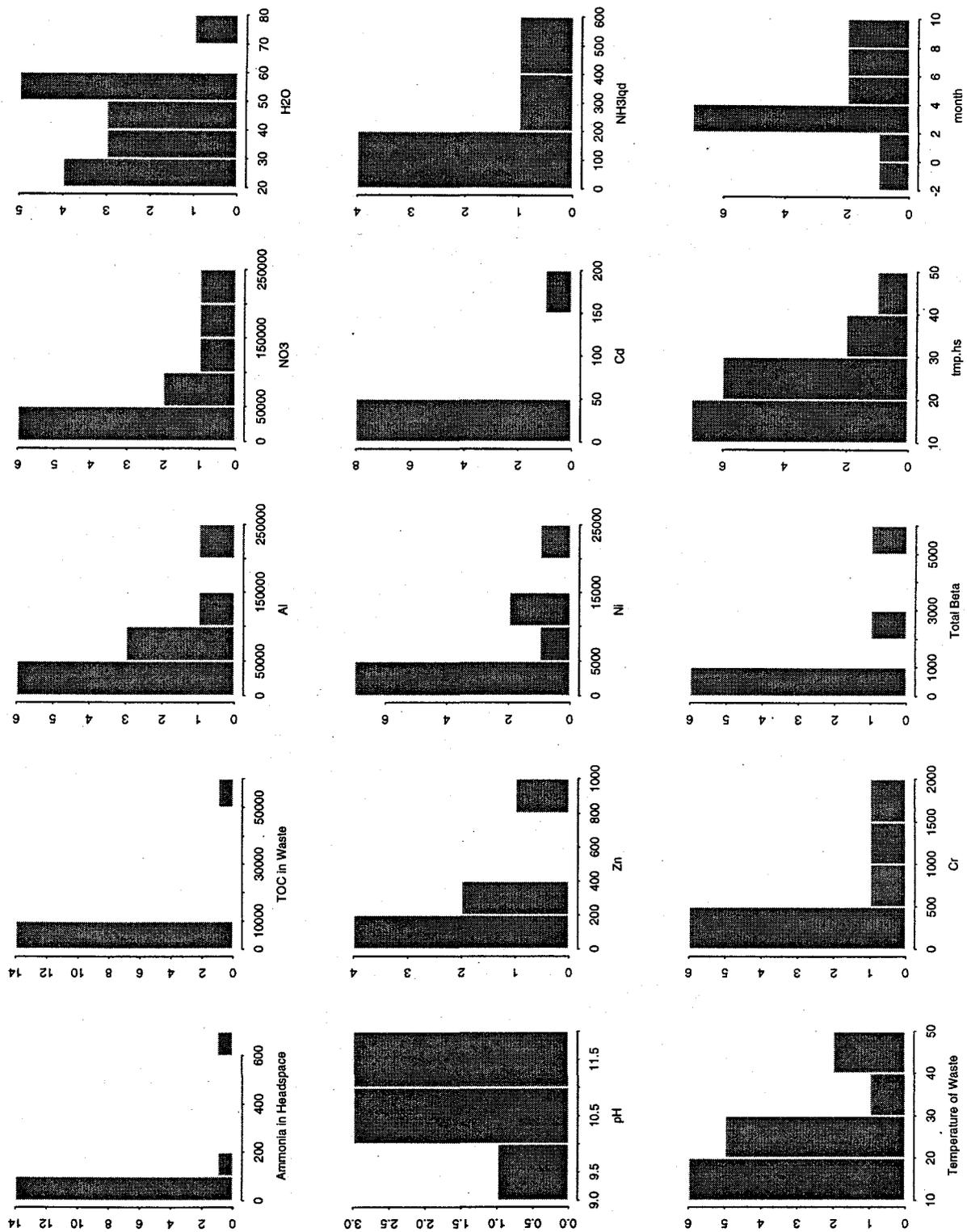


Figure B.9. Histograms of SST Data for Analysis of Ammonia Concentration in Head Space

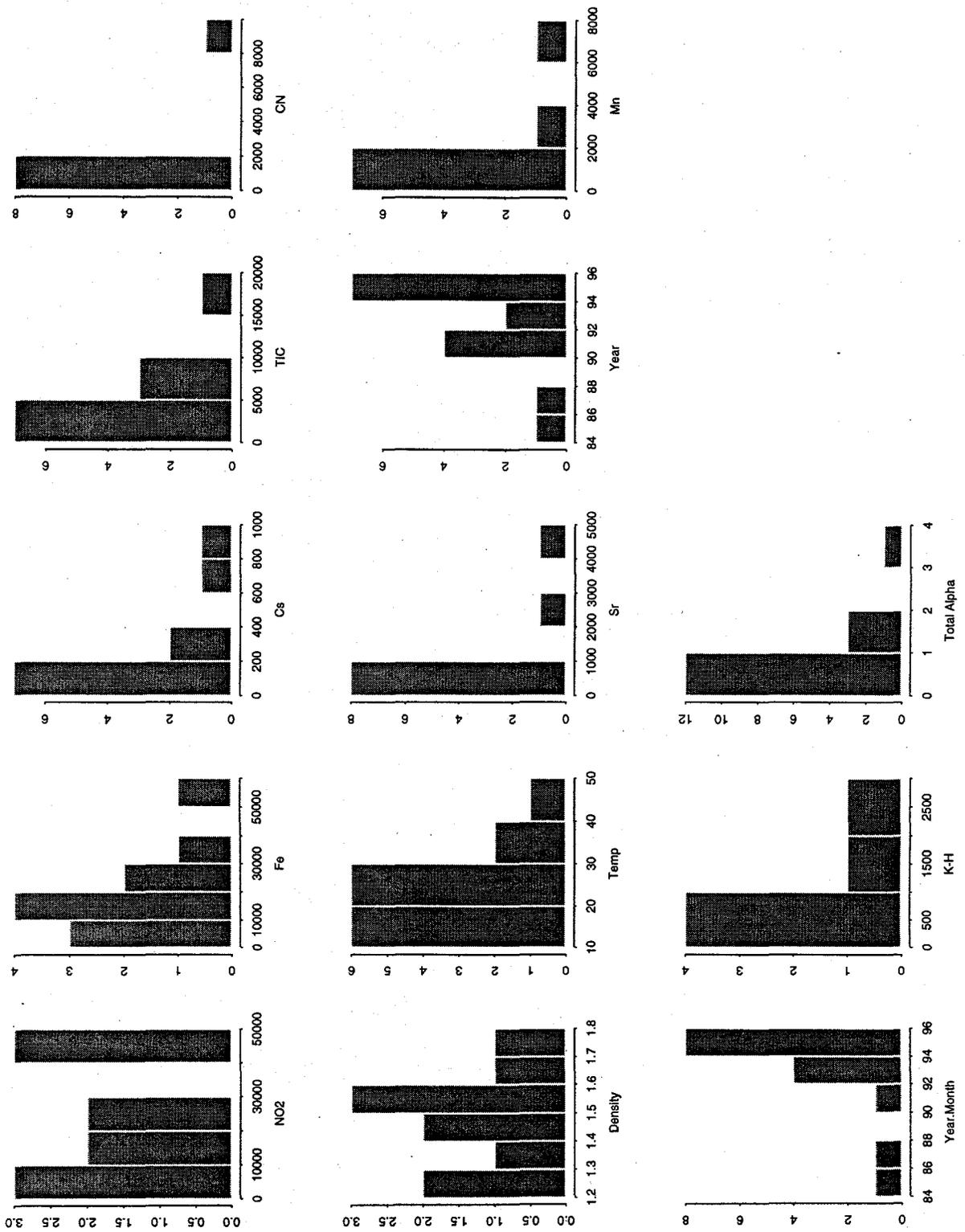


Figure B.10. Histograms of SST Data for Analysis of Ammonia Concentration in Head Space

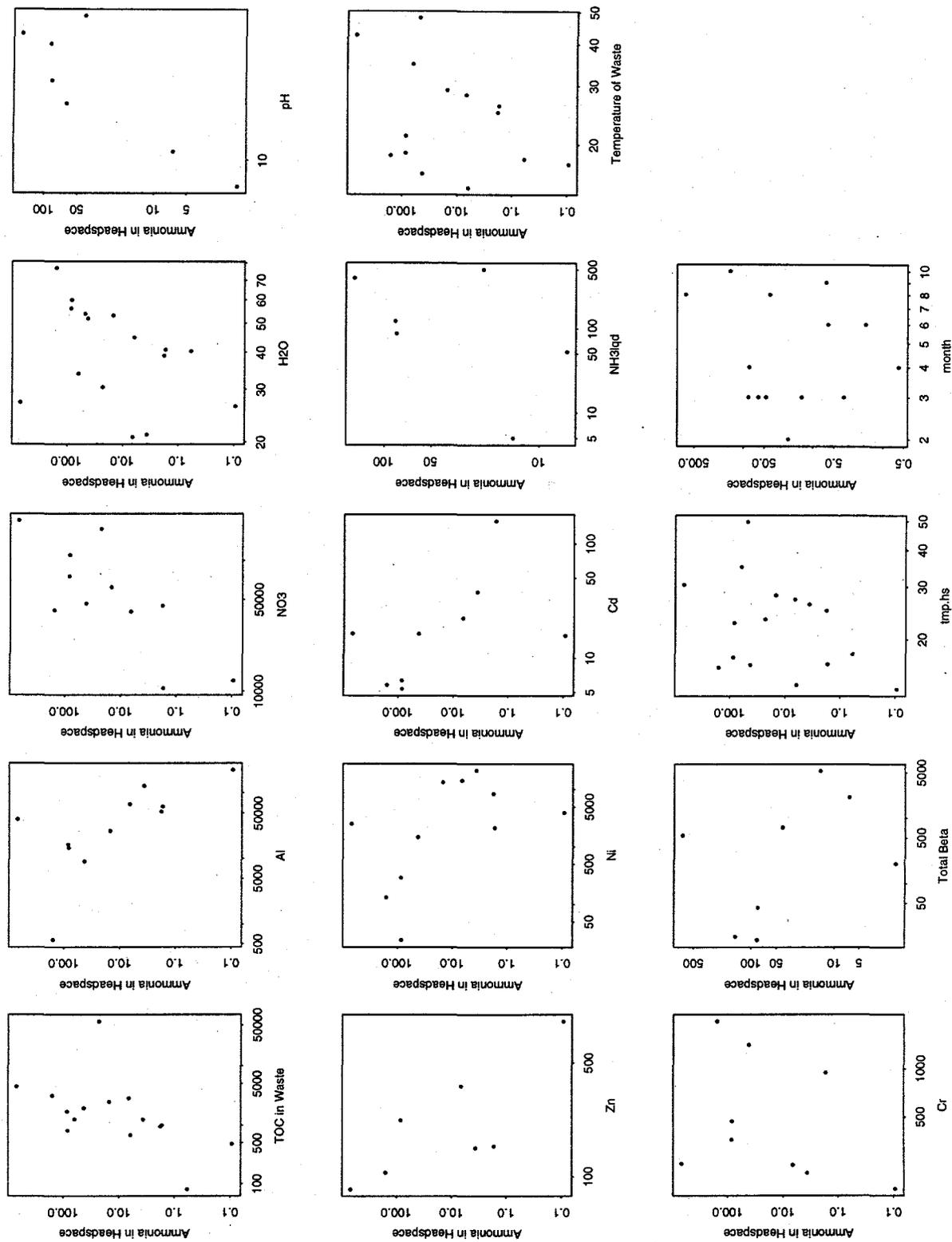


Figure B.11. Scatter Plots of SST Data for Analysis of Ammonia Concentration in Head Space

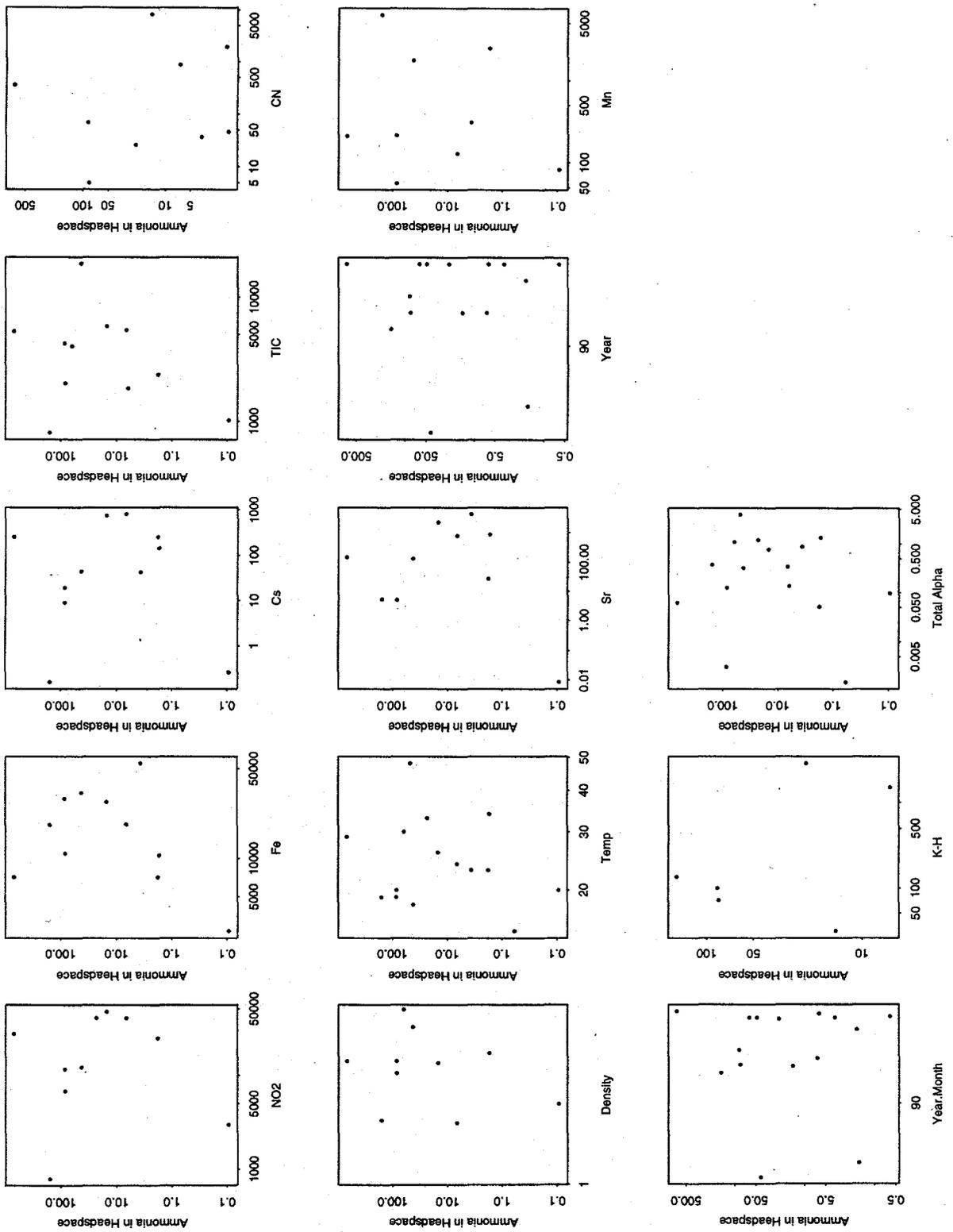


Figure B.12. Scatter Plots of SST Data for Analysis of Ammonia Concentration in Head Space

Table B.7. Selected Statistics for Ammonia in Head Space and Analytes in SST Waste

DATA	MIN	1 Q	MEDIAN	MEAN	3 Q	MAX	STD DEV	Pearson's		Spearman's		Kendall's	
								p-VAL	Rho	p-VAL	Rho	p-VAL	Rho
Ammonia in head space	0.1	4.875	28.5	115.5	104.5	1043	255.4	NA	NA	NA	NA	NA	NA
TOC	80	873.5	1260	5309	2660	56600	14240	0.9241	0.0269	0.0127	0.6679	0.0116	0.4857
Al	570	15400	39800	57920	64600	221000	65000	0.4833	-0.2368	0.0164	-0.7545	0.0158	-0.5636
NO3	10500	40800	46600	74070	92250	201000	62350	0.0202	0.6842	0.0279	0.7	0.024	0.5273
H2O	20.7	29.68	40.45	42.18	53.17	76.5	15.57	0.8478	-0.0522	0.0765	0.4588	0.0476	0.3667
pH	9.69	10.4	11	10.93	11.57	11.9	0.8234	0.0794	0.7008	0.1258	0.6429	0.0509	0.619
Zn	83.5	128.5	154	283.3	293	902.3	288.2	0.3832	-0.3929	0.0729	-0.7143	0.0509	-0.619
Ni	23.9	891	2510	6077	10760	20700	7015	0.3528	-0.3105	0.0926	-0.5273	0.1391	-0.3455
Cd	5.36	6.4	16.2	31.5	22.2	158	48.5	0.5563	-0.2274	0.1643	-0.4833	0.1444	-0.3889
Ammonia in liquid	5	61.35	104.2	194.4	330.5	500	204.2	0.5062	0.3426	0.2013	0.6	0.1885	0.4667
tmp.waste	14.94	18.23	23.1	25.7	28.95	48	10.13	0.0982	0.4597	0.1937	0.3626	0.208	0.2527
Cr	176	250	360	674	943	1980	639.1	0.8231	-0.0874	0.2116	0.45	0.2109	0.3333
TotalBeta	13.4	35.57	374.5	1116	1076	5260	1815	0.5665	-0.2403	0.1756	-0.5	0.216	-0.3571
tmp.hs	13.58	16.54	23.04	23.75	27.44	49.67	9.388	0.4857	0.188	0.243	0.3029	0.2418	0.2167
month	0	3	4	4.8	7	10	2.883	0.1608	0.3813	0.3325	0.2608	0.3201	0.1905
NO2	793	8092	18450	21520	37350	47200	17030	0.9433	-0.026	0.4883	-0.2249	0.4743	-0.1778
Fe	2722	8895	18500	20030	28550	54700	15200	0.4206	-0.2708	0.3964	0.2727	0.4835	0.1636
Cs	0.166	14.38	45.4	213.5	258.5	820	298.1	0.8721	-0.0551	0.5751	-0.1727	0.4835	-0.1636
TIC	812	1938	3990	4694	5395	18700	4983	0.9724	0.0119	0.7409	0.1091	0.5858	0.1273
CN	5	37.6	69	1312	882	8400	2736	0.6714	-0.165	0.6206	-0.1667	0.6767	-0.1111
Density	1.23	1.345	1.505	1.478	1.54	1.79	0.1817	0.9226	0.0354	0.7984	0.0912	0.7205	0.0889

Table B.7. (Contd)

DATA	MIN	1 Q	MEDIAN	MEAN	3 Q	MAX	STD DEV	Pearson's		Spearman's		Kendall's	
								p-VAL	Rho	p-VAL	Rho	p-VAL	Tau
Temp	15	19.5	23	25.4	29.5	48	8.424	0.7697	0.0826	0.8934	0.0376	0.7662	0.0571
Sr	0.0086	10.81	137.5	829.2	839.8	4160	1358	0.4711	-0.2583	0.7991	-0.0788	0.7884	-0.0667
year	85	92	94	92.7	95	95	3.172	0.5601	0.1636	0.8048	-0.0643	0.8023	-0.0476
Mn	56.3	128	213	1281	1730	6330	2080	0.9317	-0.0336	0.7593	0.1167	0.8348	0.0556
Year.Mon	85.67	92.29	94.5	93.1	95.25	95.67	3.154	0.4893	0.1936	0.8774	-0.0394	0.8431	-0.0381
K-H	31	78.25	117.5	772.8	1159	2800	1144	0.2793	-0.5301	0.7983	-0.0857	0.851	0.0667
Total Alpha	0.00151	0.088	0.33	0.6673	0.9355	3.9	0.975	0.5599	-0.1576	0.8331	0.0559	0.8571	0.0333

Note: Column headings are necessarily abbreviated. "1Q" stands for first quartile, "3Q" stands for third quartile, and "p-VAL" stands for p-value.

The next investigation that seemed appropriate was to perform multiple regressions to see if they explained the variations in ammonia concentrations based on values of the three independent variables. This would normally be done by rating the ammonia concentrations to a linear function of the other variables. However, there is a mathematical complication associated with this procedure. Investigations of the data quality lead to some concern that the quantities of TOC, aluminum and nitrate, may have been measured with significant error. This concern is based on evidence of spatial variation, measurement variance, and time separations between the samplings of the head space and the waste. The complication arises because most kinds of regressions are based on the assumption that the independent variables, the regressors, are measured with minimal (nil) error.

Figure B.13 presents a series of regressions using the measured ammonia concentration as the dependent variable plotted along the vertical axis, and the calculated estimate of the ammonia concentration fit obtained from the linear fit to the indicated regressors, plotted on the horizontal axis. This series of regression was based on three analyte concentrations: TOC, aluminum and nitrate; and the natural logarithm with each. A statistical program selected the best single variable regressor (NO_3), the best two-variable regression (NO_3 and $\ln [\text{Al}]$), the best three-variables regression (Al , NO_3 and $\ln [\text{Al}]$) and the best regression using all three analytes (NO_3 , $\ln [\text{Al}]$, $\ln [\text{TOC}]$). Since there were ten sets of data associated with the regressors, ten predictions were made on each regression chart. The calculated values of ammonia concentration are based on the values of the regressors identified under each subfigure, and on coefficients calculated from the fits derived from the remaining nine data sets (cross validation). Each prediction is plotted as a dot on the chart. The straight line with a 45-degree slope corresponds to a "perfect prediction" (calculated value = observed value). The regression plots do show evidence of a relationship.

This apparent relationship must be interpreted very carefully. Only ten data sets were available. The magnitude of the errors in measurements of the regressor variables is also of great concern. The apparent relationship of the six constituents with "high" association values should be investigated further, as well as the relationships hinted at by the exploratory regressions just discussed. Statistical analysis should be conducted to investigate the uncertainty in the data values for the regressor variables (as well as the uncertainty in the ammonia concentration values). A follow-on data analysis should be conducted, using an "Errors in the Variables" approach to regression and other more robust techniques.

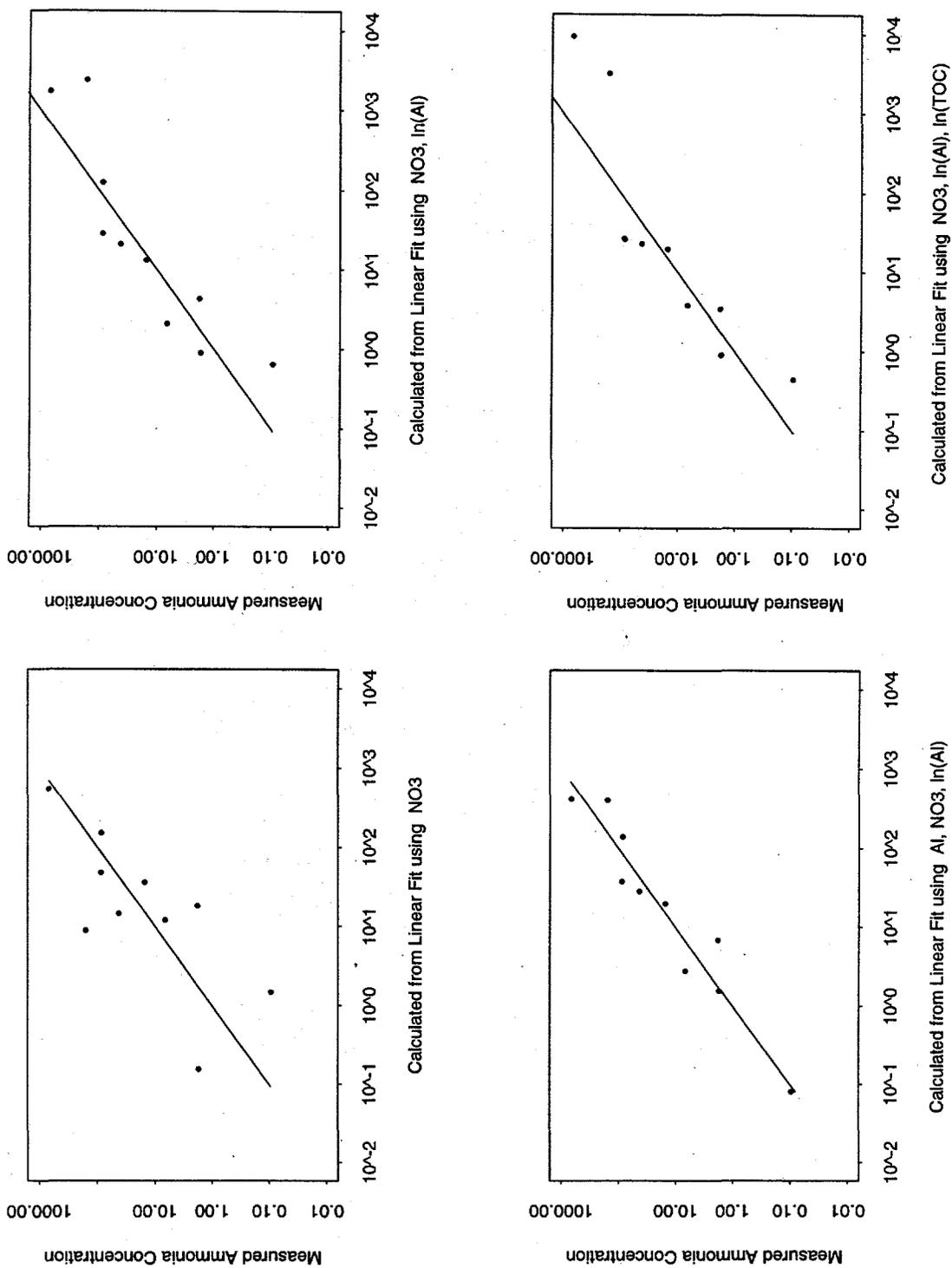


Figure B.13. Cross-Validation Regression Results of Ammonia Concentrations in Head Space and Nitrate and Aluminum in Waste for SSTs

Appendix C

DST Data Analysis

Appendix C - DST Data Analysis

C.1 Exploratory Data Analysis for DST Data

This section provides a brief look at the variables in the DST data. The data for each variable are displayed in a histogram in Figure C.1. The histograms show that, for most variables, the majority of the observations are at the low end of the scale, with a few readings distributed over higher levels.

To display the relationship between ammonia and each data item, Figure C.2 shows scatter plots with the concentration of ammonia on the vertical axis and the other variables on the horizontal axes. The scatter plots show that no variables exhibit an obvious relationship; i.e., none are tightly grouped about a line or curve.

Table C.1 shows the values of Kendall's Tau for the data collected.

Table C.1. Kendall's Tau Values for Ammonia and Available Data

<u>Variable</u>	<u>p-value</u>	<u>Tau</u>
Aluminum	0.63	0.10
Nitrite	0.020	0.49*
Nitrate	0.46	0.15
TOC	0.39	0.18
Hydroxide	0.33	0.21
Cesium-137	0.33	0.21
Strontium-90	0.54	0.13

* p-value less than 10%, indicating the existence of a probable relationship.

While the data do not appear to exhibit any strong relationships between the individual variable values and the concentration of ammonia, additional studies presented below show that more sophisticated techniques can produce more meaningful results.

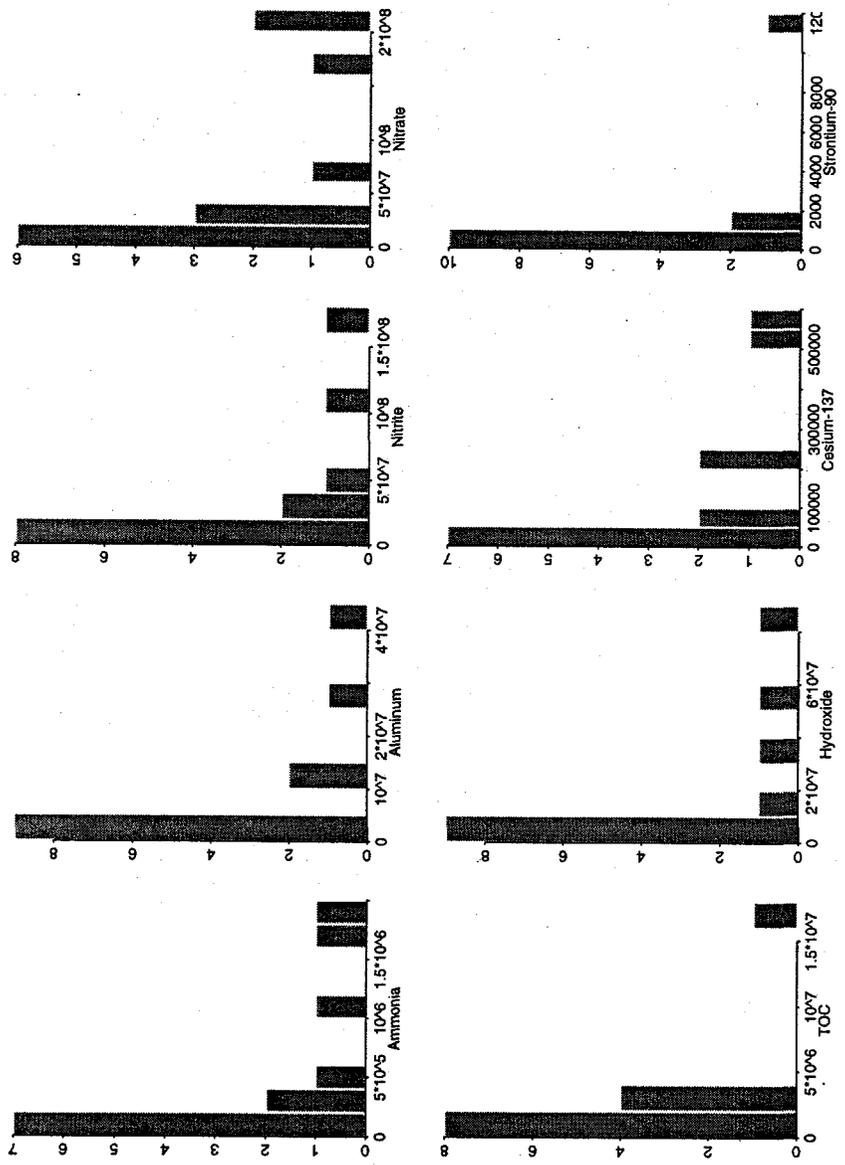


Figure C.1. Histogram of DST Data for Analysis of Ammonia in Waste

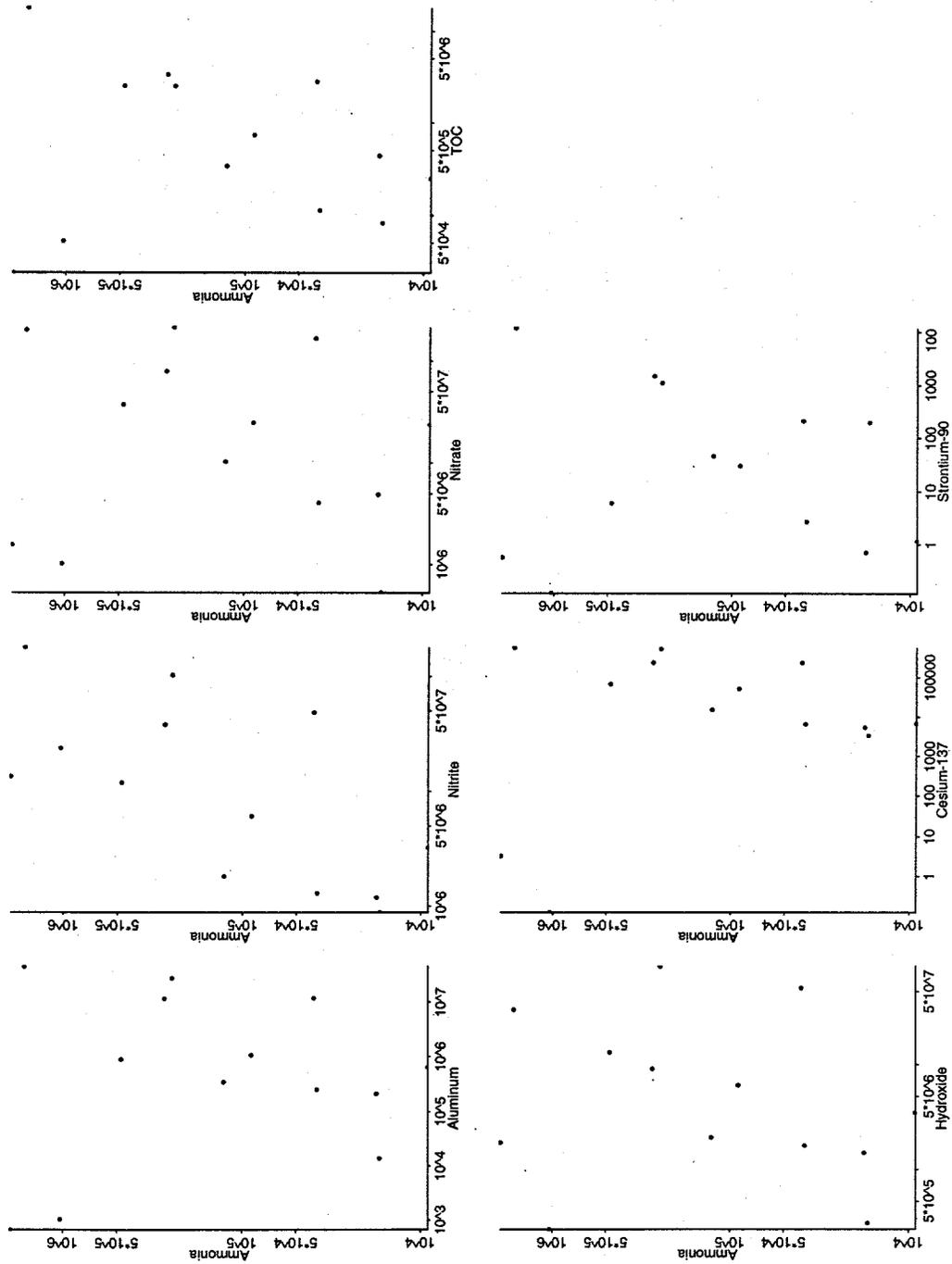


Figure C.2. Scatter Plots of DST Data for Analysis of Ammonia in Waste

C.2 Principal Component Analyses for DST Supernatant Data

The PCA technique was applied to the DST supernatant data to explore the data structure in multidimensional space. Similar steps were taken as for the SST head space data (see Appendix Section B.2). For the seven variables under consideration (see Appendix Section A.5), a Log10 transformation was applied to reduce the skewness and the effect of variable scales. The results are displayed in Figures C.3 through C.5.

Figure C.3 indicates that the first two principal components account for more than 90% of the variation contained in the original data set. Therefore, these two principal components were used to explore the data structure. Figure C.4 shows the scatter plot of the two principal components. The 13 tanks were separated into three clusters. The cluster in the left upper corner of the plot captured two of the three tanks with high ammonia level (more than 500,000 $\mu\text{g/L}$). Six of the seven tanks located close to the bottom of the plot have ammonia concentrations below 200,000 $\mu\text{g/L}$. This result encouraged further multivariate analysis on the DST supernatant data. The loadings of the original variables on the first and second principal components are shown in Figure C.5, which reflects the relative contributions of these variables to the principal components.

C.3 Discriminant Analyses for DST Supernatant Data

The discriminant analysis approach was also applied to the DST supernatant data. The 13 DSTs were grouped into three classes according to their ammonium concentrations. The cutoff values and number of tanks in each class are displayed in Table C.2.

Table C.2. DST Tank Groupings, Supernatant Data

Class	NH_4^+ Range ($\mu\text{g/L}$)	No. of Tanks
High	$\geq 500,000$	3
Medium	200,000-500,000	3
Low	$\leq 200,000$	7

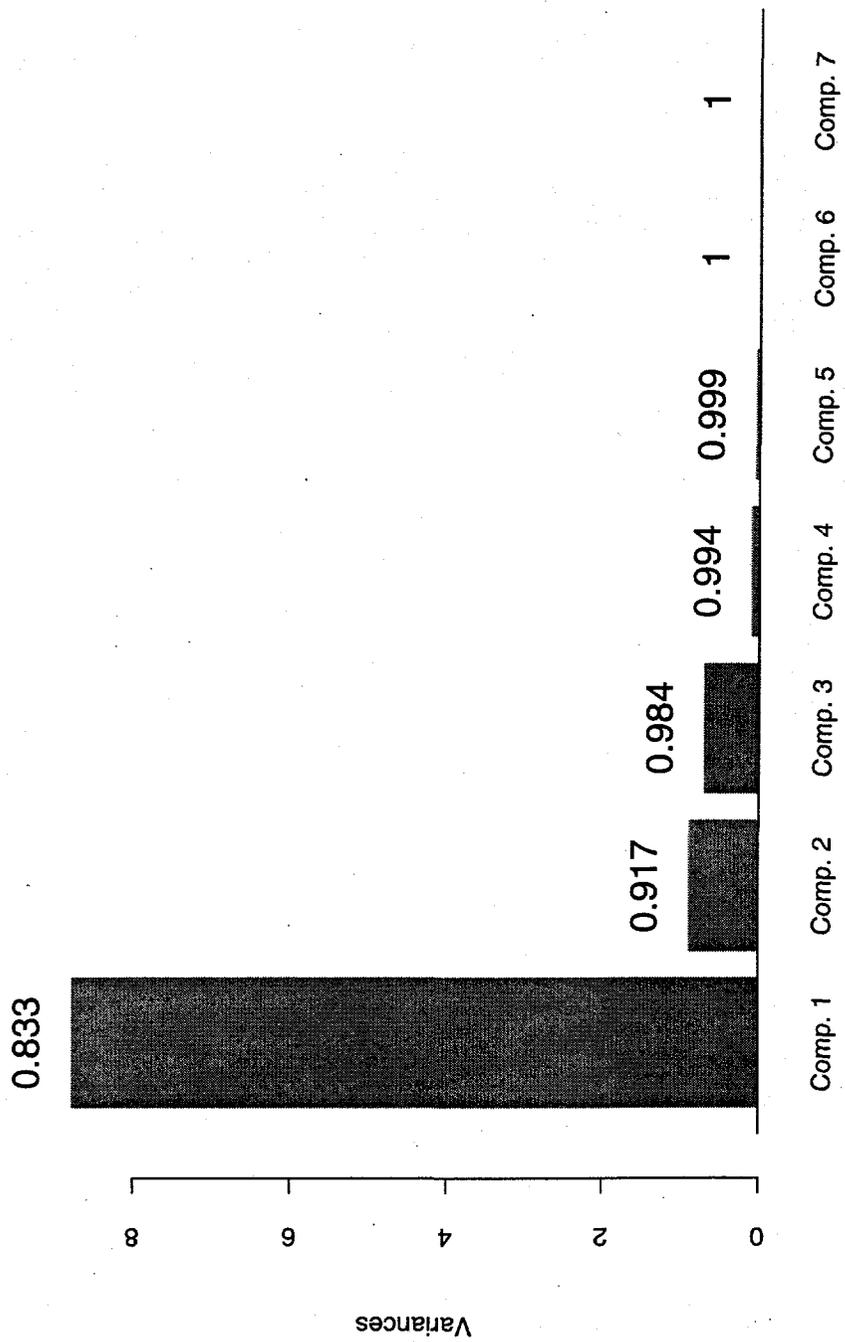


Figure C.3. Fractions of Variance Explained by PCs for DST

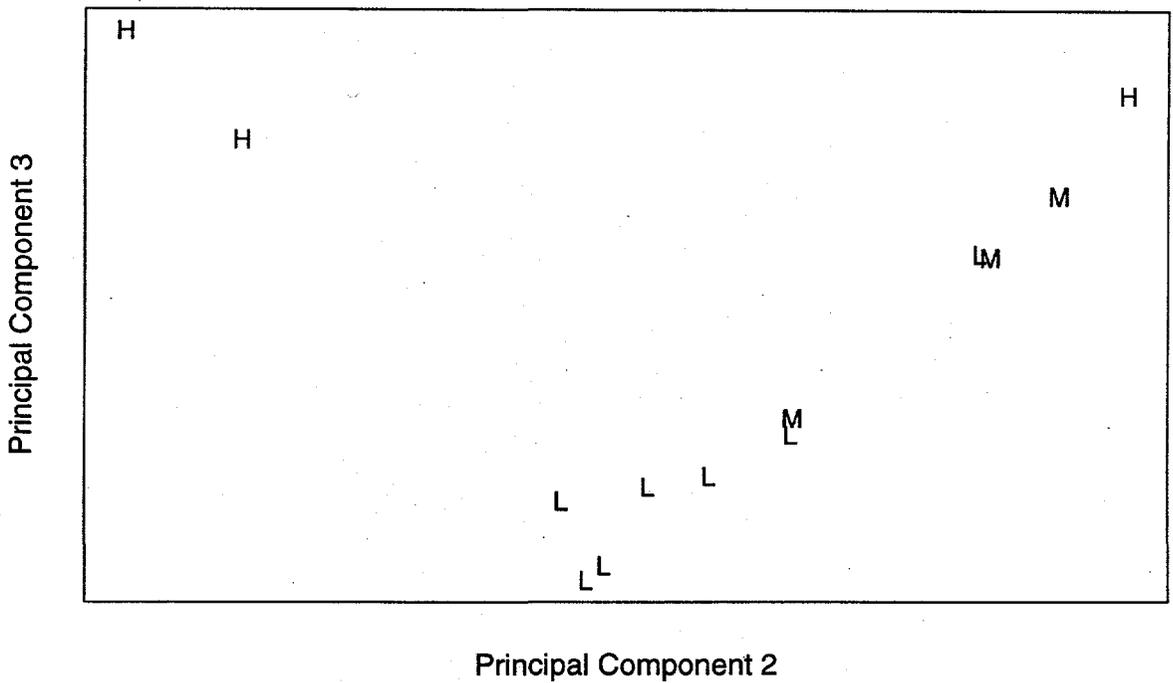
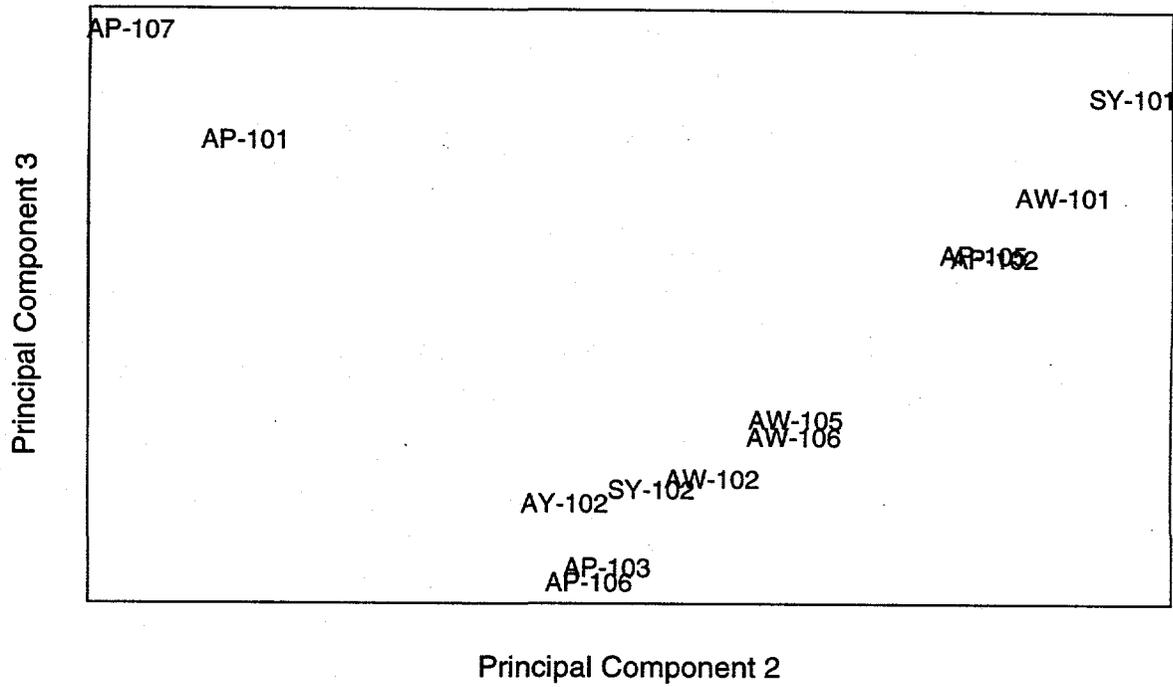


Figure C.4. Principal Component Analysis for DST Liquid Waste

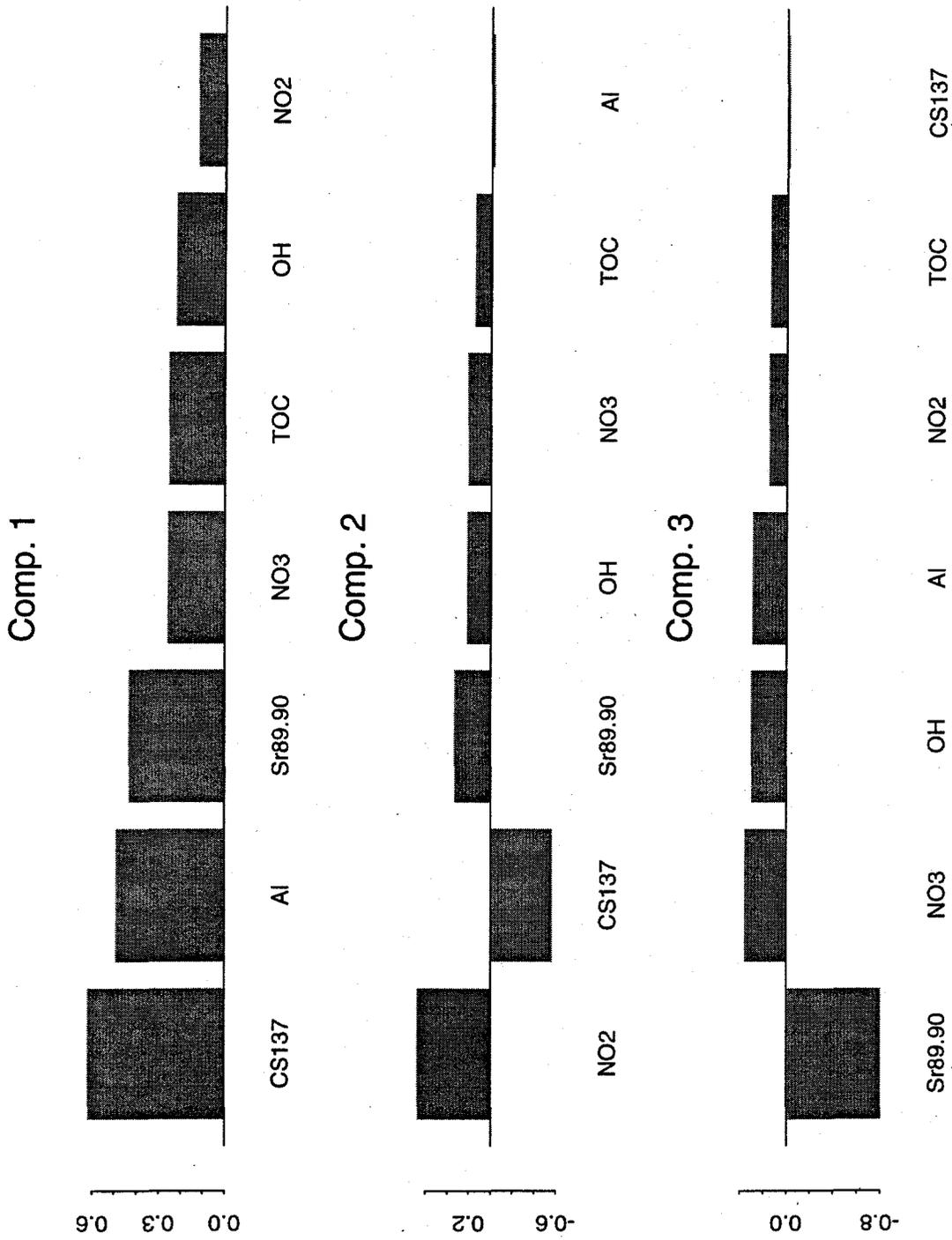


Figure C.5. PC Loadings for DST Liquid Waste Data

Seven variables were used in the analysis. The results of the variable selection process showed that hydroxide and cesium-137 did not contribute significantly to the group classification; consequently, these two variables were removed from consideration. Two discriminant variables were generated to identify the order of importance of the remaining five data variables. The scatter plot of the first and second discriminant variables is displayed in Figure C.6. The figure shows that the three groups were clearly separated by the two linear combinations. The second discriminant variable isolated the low group, while the first discriminant variable separated the high and medium groups.

The raw and standardized coefficients of the five parameters composing the two discriminant variables are given in Table C.3. The standardized coefficients of the five discriminators exhibited a pattern similar to that for the SST head space data; that is, the coefficients of four out of five variables have opposite signs on the two discriminant variables. The "high" group, however, was not located at the right lower or left upper corner of the scatter plot (see Figure 2.8). An appropriate interpretation requires further investigation. Because of the very limited number of tanks available, however, no further study was conducted on DST supernatant data.

Table C.3. Coefficients for the Two Discriminant Variables

Variable	Raw Coefficients		Standardized Coefficients	
	DV1	DV2	DV1	DV2
Al	-2.02E-06	4.11E-07	-27.12	5.52
NO ₂	2.46E-07	2.09E-07	11.97	10.13
NO ₃	1.26E-07	-1.31E-07	10.19	-10.52
TOC	-4.13E-06	2.61E-06	-18.95	11.95
89/90 Sr	8.37E-03	-6.05E-03	25.38	-18.33

The classification rules based on the five variables performed well. A 100% correct classification rate was achieved when these rules were applied to the same data set. The cross validation calculation yielded an 85% correct classification rate. Tank AW-105, which is in the medium group, was misclassified into the high group, while Tank AP-105, in the low group, was misclassified into the medium group. Cross-validation results are shown in Table C.4.

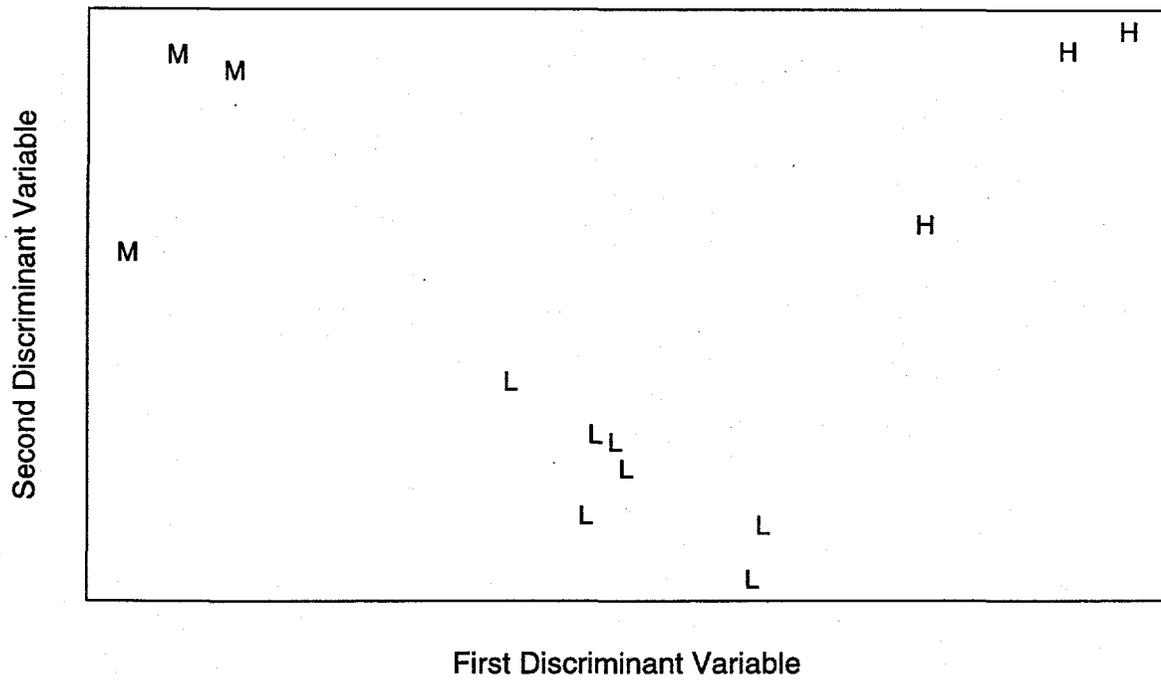
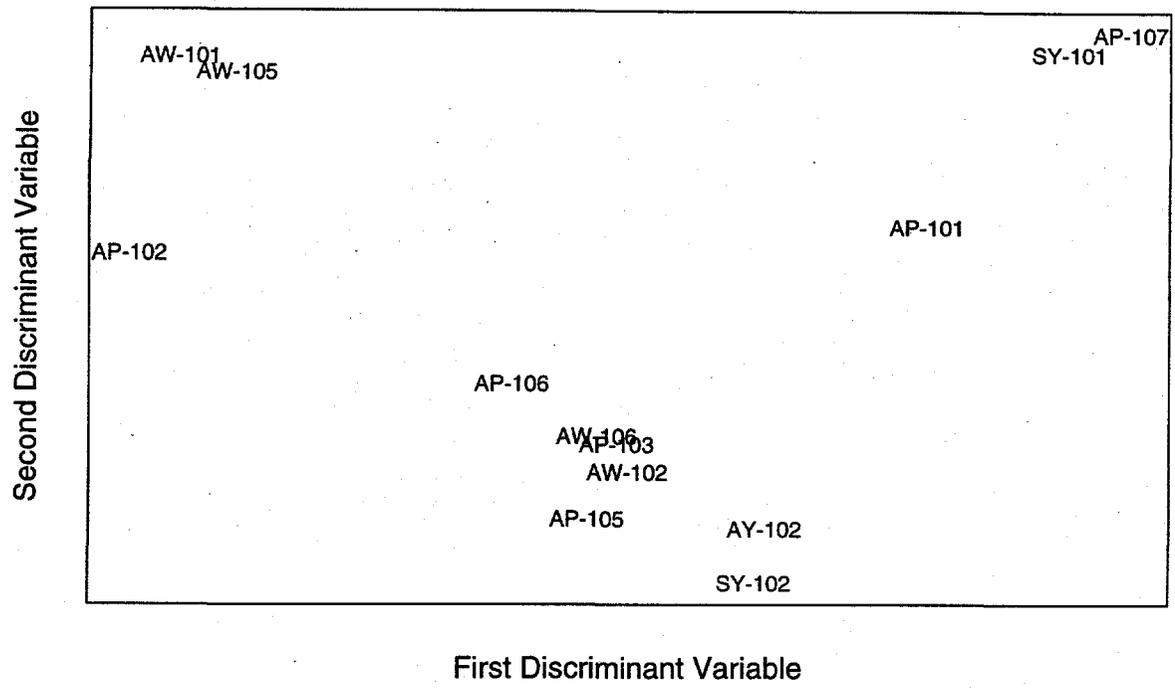


Figure C.6. Discriminant Analysis for DST Liquid Waste Data

Table C.4: Cross-Validation Results on DST Supernatant Data

Actual	Classified		
	H	L	M
H	3 100.00%	0 0.00%	0 0.00%
L	0 0.00%	6 85.71%	1 14.29%
M	1 33.33%	0 0.00%	2 66.67%

Appendix D

Ammonia Generation Hypotheses and Evidence

Appendix D - Ammonia Generation Hypotheses and Evidence

In this appendix, several groupings of variables are presented and discussed as representative of current hypotheses about how ammonia is generated, retained, or released. The underlying relationships are clearly more complicated and involved than can be represented by a group of two, three, or four variables. However, the investigation is worthwhile and the data may provide some basis for either casting doubt upon or adding strength to the hypotheses. The expectation is that the data will not be strong enough to prove or refute any hypotheses but may lead investigators to some clearer understanding of the underlying relationships among the variables. For presentation purposes, each group of variables is listed first, followed by a brief outline of the associated hypotheses and a summary of the limitations of using that group of variables to represent the possible underlying relationship. A statistical determination is then made to assess whether the available data support the hypotheses, refute it, or are insufficient to make a determination one way or the other.

D.1 Carbon Dioxide (head space), Ammonia (head space), pH

Hypotheses: Carbon Dioxide and ammonia concentrations should be inversely correlated. At high pH (greater than 10), the head space will contain more ammonia and less carbon dioxide. Tanks containing caustic wastes that are slowly ventilated will have low concentrations of carbon dioxide (because it is absorbed by the wastes and converted to carbonate) and higher concentrations of ammonia.

Limitations: The amount of liquid waste, the Henry's Law constant for the waste, its temperature, and its ventilation rate also affect this relationship. This correlation, if it exists, will not be apparent in well-ventilated tanks. Such tanks will have carbon dioxide concentrations approaching that of air, while ammonia (and other product gases) will be diluted. The upper limit of ammonia concentration in the head space will be determined by the concentration of aqueous ammonia, temperature, and the Henry's Law constant of the particular waste.

Observations: A three-way scatter plot of carbon dioxide in the head space, ammonia in the head space, and pH values in 37 passively ventilated SSTs is shown in Figure D.1. No apparent trend was observed to support the hypotheses. However, only four (out of 37) tanks had pH values less than 10.

Observations: The exploratory analysis on DST liquid waste data revealed no obvious relationship between ammonia and any one of the other four variables except nitrite (see Appendix C). However, nitrite, nitrate, and strontium-90 were identified by the discriminant analysis as influential variables in ammonia group separation.

D.3 Ammonia, Nitrite, Nitrate, Cesium-137, Strontium-90, Total Organic Carbon in Liquid Waste

Hypotheses: This hypotheses stems from the limitations of the previous one, but includes TOC.

Limitations: TOC (liquid) is too broad a classification, and should be subdivided into organic components that age and those that do not age. Production of N_2 and N_2O correlates with the aging of organics (Camaioni et al. 1995) The postulated pathway leading to N_2 and N_2O also leads to ammonia, although this correlation has not been demonstrated by direct experiment.

Observations: No significant pairwise correlation was found between ammonia and TOC in the liquid waste (Kendall's Tau value is 0.18; see Table C.1). The fact that aluminum, nitrite, nitrate, strontium-90, and TOC could effectively separate the three ammonia groups of the DST liquid waste data indicates that these variables do impact ammonia generation in the liquid phase, but in a complex and interactive manner (see Section C.3).

D.4 Ammonia (liquid), Ammonia (head space)

Hypotheses: Ammonia concentration in the liquid waste affects head space ammonia concentration.

Limitations: This correlation for passively ventilated tanks is temperature dependent. It may also depend on the exact value of the ventilation rate, the volume of the head space in the tank, and the presence or absence of liquid layers (see Section 3 of the main report).

Observations: There are only six tanks that have ammonia measurements in both head space and liquid waste. The scatter plot of these two concentrations (Figure D.2) does not show any apparent correlation. Kendall's Tau calculation results in a value of 0.47 and a p-value of 0.19. However, based on only six tanks, one cannot refute the hypotheses even though the data do not support it.

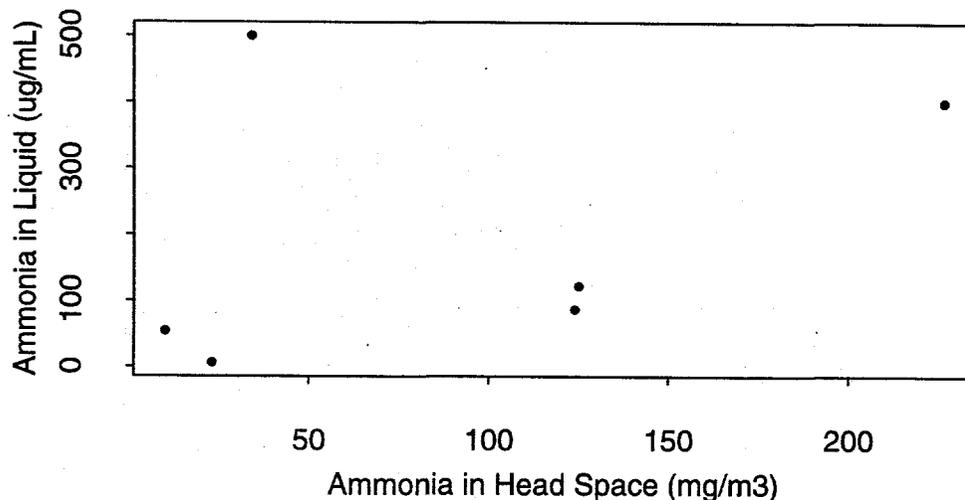


Figure D.2. Scatter Plot, Ammonia in Liquid vs. Ammonia in Head Space

D.5 Ammonia (head space), Volume of Drainable Liquids/Supernatant

Hypotheses: The major influence on the concentration of ammonia in the head space is the amount of drainable liquid/supernatant that exists in the tank.

Limitations: If there is adsorbed ammonia on the surface of particulates this correlation may also depend on the ratio of particulate surface area to volume. There may also be some dependence on the ventilation rate. If nearly all of the liquids are drained from a particular tank, most of the ammonia is expected to disappear as well.

Observations: Figure D.3 displays the scatter plot of the two variables. The plot does not demonstrate a monotonic trend between the two variables. However, Kendall's Tau statistic indicates a significant relationship between the two variables ($p\text{-value}=0.004$; see Table B.1). PCA also shows that drainable liquid volume tends to have a positive effect on ammonia concentrations in the head space (see Appendix C). However, this effect has to be considered with other factors.

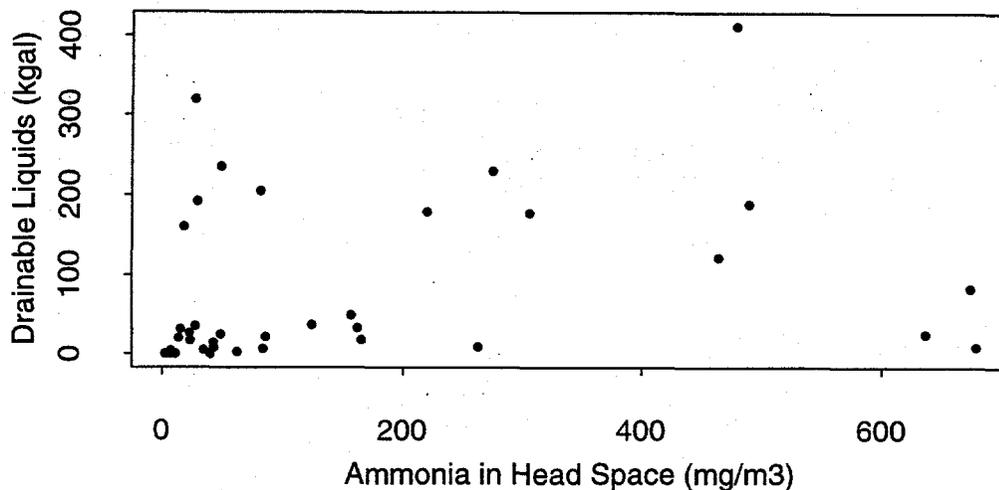


Figure D.3. Scatter Plot of Head Space Ammonia and Volume of Drainable Supernatant Liquid

D.6 Total Organic Carbon (liquid), Total Organic Carbon (head space)

Note: The TOC variable for the head space was not measured. An estimate was generated using a weighted average of the volatile organics. The weighting was based on the number of carbon atoms in each organic material.

Hypotheses: TOC concentration in liquid waste affects the TOC concentration in the head space.

Limitations: Non-chelator TOC (liquid) is more likely than chelator TOC to correlate with TOC (head space), with a strong temperature dependence. Chelators and chelator fragments dissolved in the liquid are unlikely to produce organic vapors. Lighter compounds, such as butanol from TBP (tri-butyl phosphate), will be well represented in the head space.

Observations: The scatter plot of the TOC concentrations in the two phases, Figure D.4, does not support the hypotheses. Calculations of Kendall's Tau result in a value of 0.33, with a p-value of 0.083. This shows a weak relationship and may support the hypotheses.

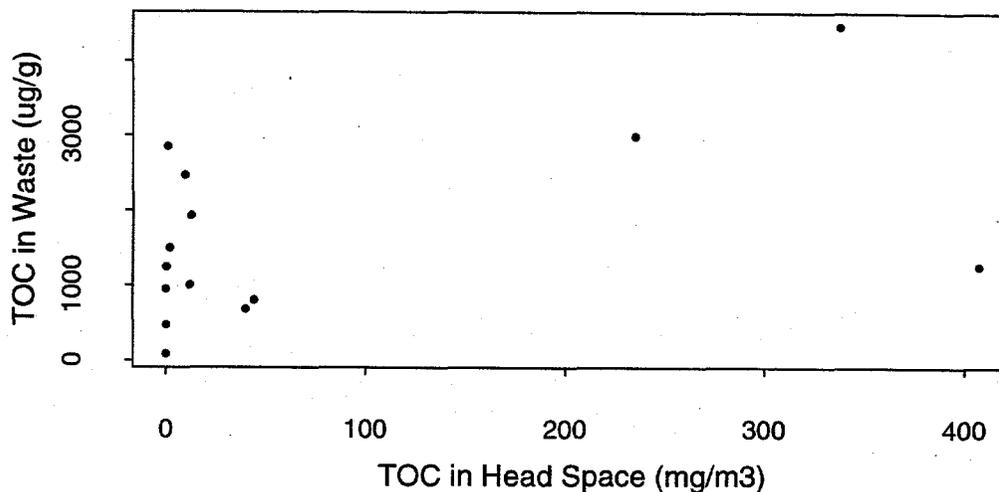


Figure D.4. TOC Concentrations in the Liquid and in the Head Space

D.7 Ammonia, Nitrous Oxide, Hydrogen in the Head Space

Theory: Hydrogen and nitrous oxide are released to the head space via bubbles rising to the surface of the liquid waste. Ammonia will also be contained in the rising gas bubbles. However, because most ammonia is dissolved in the liquid (ammonia is much more soluble than either nitrous oxide or hydrogen), ammonia can also enter the head space directly by evaporation from the surface of the waste.

Limitations: The ratio of hydrogen to nitrous oxide in product gases remains of interest. Early work with simulants containing chelators (HEDTA, EDTA) generated 10 to 25 times more nitrous oxide than hydrogen (Delagard 1980). The gases evolved from Tank 241-SY-101 during gas release events contained about equal concentrations of hydrogen and nitrous oxide (DOE 1994). Recent gas generation studies with actual wastes (from Tanks 241-SY-101 and 241-SY-103) produced similar quantities of nitrous oxide and hydrogen.

Observations: This relationship was examined by means of a three-way scatter plot of ammonia versus hydrogen and nitrous oxide. The plot, Figure D.5, does demonstrate a positive correlation among the three variables. The discriminant analysis on the head space data further indicates that this correlation is strong when the ammonia concentration in the head space is above 228 mg/m³ (see Section B.3).

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