

HYDRAZINE CHEMISTRY IN AQUEOUS
AND SOIL ENVIRONMENTS

By

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The effects of several factors on the fate of hydrazine in aqueous and soil systems were studied. In aqueous systems the main mechanism of hydrazine degradation appears to be a four-electron oxidation by oxygen. The rate was very slow in distilled water but increased with the addition of catalysts such as copper(II) (Cu^{II}) and phosphate ions. Conditions that accelerated the formation of the hydrazil radical, the first step in hydrazine oxidation, increased the proportion of one-electron oxidation giving ammonia (NH_3) as one of the degradation products. Ammonia evolution was correlated with Cu^{II} and phosphate ion concentration as well as temperature. Hydrazine oxidation was primarily dependent on the rate of oxygen diffusion from the gas phase.

Experiments conducted with montmorillonite partially saturated with Cu^{II} and under aerobic conditions revealed

that hydrazine interacted with the clay suspension in several ways. Some hydrazine was initially adsorbed by the clay and remained adsorbed until most hydrazine in the supernatant had disappeared. Hydrazine was also degraded in the presence of the clay even in the absence of Cu^{II} . Free Cu^{II} in the supernatant was a more active catalyst for oxidation of hydrazine than Cu^{II} on the exchange sites.

The nature and extent of the interactions between hydrazine and the soil colloids was clearly dependent on the pH of the suspension.

Under acidic conditions hydrazine was primarily retained on the exchange sites in all systems studied. A large fraction of hydrazine retained by the clays was displaced by potassium ions (K^+). Hydrazine adsorbed on Arredondo soil horizons was not removed by K^+ . It is postulated that hydrazinium ions adsorbed on exchange sites reacted further with neighboring groups rendering, a nonexchangeable species.

Under alkaline conditions hydrazinium was the main species adsorbed by montmorillonite, although the extent of adsorption was lower than at pH 4. In studies with whole soils and kaolinite unprotonated hydrazine was the primary species adsorbed and the extent of adsorption was significantly higher than at pH 4.0. Hydrazine retained on the exchange sites of soil horizons was displaced by K^+ .

CHAPTER I INTRODUCTION

Hydrazine, $\text{NH}_2\text{-NH}_2$, was first prepared by T. Curtious in 1887. Many of its organic derivatives were known prior to the discovery of the parent material. Hydrazine and its derivatives are very versatile compounds that have found a wide variety of applications. They are readily oxidizable and exothermic, and for this reason have served as fuels, antioxidants, oxygen scavengers, and intermediates for the production of explosives and propellants. Hydrazines are basic, difunctional, polar molecules that find many applications in the manufacture of diverse organic compounds. The toxic nature of hydrazines is the basis for their use in the preparation of various pesticides.

Whereas more than half of all hydrazine was used as a rocket propellant in the 60s, in the meantime many other industrial applications are taking the major share of all hydrazine produced. Since the 60's the worldwide production of hydrazine has more than double (from 33 million lbs to 80 million lbs N_2H_4 in 1977) (Schmidt, 1987), the USA having the lead in the world market.

The widespread use of this material provides the opportunity for spills during transportation or leakage when

stored underground resulting in contamination of the environment. Hydrazine has a great affinity for water and is therefore extremely irritating to eyes and mucous membranes. Experiments with laboratory animals showed that exposure to hydrazine may produce either immediate toxicity or delayed kidney and liver injury in animals that survive the exposure (Clemens et al., 1988). It also has been shown that hydrazine can produce tumors in animals and the National Institute of Occupational Safety and Health has listed hydrazine fuels among the industrial substances suspected of being human carcinogens (Braun and Zirrolli, 1983). For this reason, understanding its fate in soils and water is of utmost importance.

Physical and Chemical Properties of Hydrazine

Hydrazine is the simplest diamine and has unique properties due to the N-N bond (Figure 1-1). The $2s^2$ shell of the nitrogen atoms is active in establishing a bond between the two nitrogen atoms. A $2sp^3$ hybridization is assumed to occur that it is similar to the tetrahedral arrangement in a saturated carbon atom (Schmidt, 1984). One of the $2sp^3$ orbitals in each N atoms is occupied by a pair of lone electrons with opposite spins. Bond lengths and angles of the hydrazine molecule have been measured using a variety of techniques and have been summarized by Schmidt (1984). Average values are presented in Table 1-1.

Table 1-1. Bond lengths and bond angles of hydrazine.

Bond	Length (10^{-10} m)	Angle	Angle ($^{\circ}$)
N-H	1.02	N-N-H	110
N-N	1.5	H-N-H	112

The dipole moment of hydrazine has been measured by Audrieth et al. (1933) and by Ulich et al. (1935). At 298°K it is 1.84 Db. It was originally assumed that there is free rotation around the N-N axis. However, further investigations revealed that rotation is restricted due to interaction of the two lone pairs of electrons. A rotational barrier of 25-41 kJ must be overcome (Schmidt, 1984). This increase in energy leads to decomposition before spectra of the freely rotating molecule can be obtained. Audrieth and Ogg (1951) reported that the high dipole moment can be explained only by assuming a cis-unsymmetrical configuration.

Hydrazine is a colorless liquid material at ambient temperatures (b.p. 114.5°C and m.p. 2.01°C). It is quite hygroscopic and tends to adsorb carbon dioxide and oxygen from the atmosphere.

The vapor pressure in the range of temperatures where

hydrazine is liquid can be represented by the equation (Scott et al., 1949):

$$\log p \text{ (mm Hg)} = \frac{1680.745}{t \text{ (}^\circ\text{C)} + 227.74}$$

The density of the hydrazine is higher in the solid state than in the liquid state; in this respect it is different from water. The density of the liquid at ambient temperature is 1.01 g cm^{-3} (Ahlert et al., 1962).

The use of hydrazine as a fuel is based on its endothermic nature [$(\delta H)^f (1) = +12.1 \text{ Kcal mole}^{-1}$]. However, anhydrous hydrazine is thermally very stable (250°C) in the range of ambient temperatures (Schiessel, 1980). The presence of certain metals and oxides can lower the decomposition temperature.

Since hydrazine is a highly polar substance, it is miscible only with polar solvents such as water, alcohols, ammonia, and the amines, and it is insoluble in nonpolar solvents such as the hydrocarbons and the halogenated hydrocarbons. Due to its polarity, hydrazine will most likely interact with polar groups on the solid surfaces of soils.

Hydrazine is a base slightly weaker than ammonia ($\text{pK}_a=7.95$) (Condon et al., 1974). Although it can act as a polyprotic base only the first protonation constant is relevant at the pH's found in natural environments.

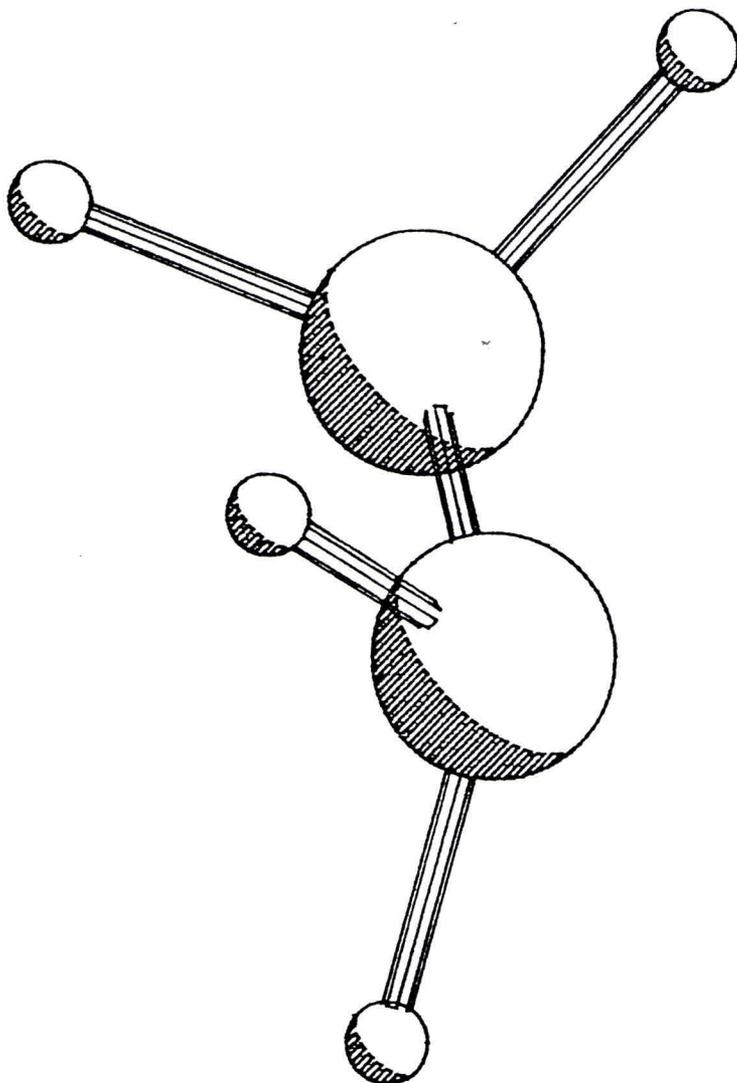
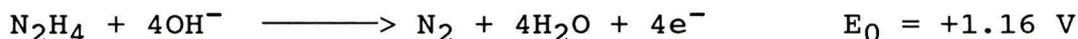


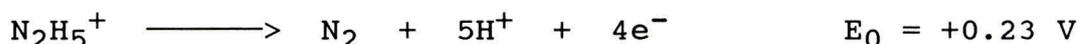
Figure 1-1. Computer-drawn figure of the hydrazine molecule structure (Courtesy of C. T. Johnston).

The two lone electron pairs on the N atoms impart a very strong nucleophilic character to the hydrazine molecule. Due to this property, hydrazine can form a large variety of complexes with metals. Several survey papers have been published on this subject, the most recent being the one published by Dilworth (1976). Schmidt (1984) stated that it is difficult to determine whether a true complex with hydrazine exists or whether hydrazine is simply included in the crystal lattice of some salts (e.g. calcium salts) as a solvate just like water of crystallization.

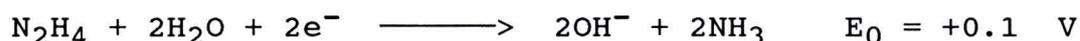
Hydrazine is a strong reducing agent and as such it reduces many metal ions to lower valence states or to the metal themselves depending on the reaction conditions. The standard redox potentials (Latimer, 1952) of hydrazine:

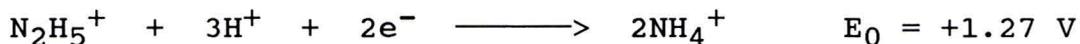


and of hydrazinium ion:



indicate that hydrazine is a better reducing agent in alkaline than in acidic solution. Hydrazine can also act as an oxidizer as indicated by the standard redox potentials:





Although they are thermodynamically favorable, especially in acidic solution, there are few examples of such reactions in the literature, indicating that they are perhaps very slow in the absence of an appropriate catalyst. All these redox reactions are closely related to the pathways of hydrazine degradation in solution and in the atmosphere; however, it should be noticed that other reactions may also be involved.

The gas-phase transformations and atmospheric fate of hydrazine fuels have been under intensive study during the past fifteen years (Pitts et al., 1980; Stone, 1980; Stone and Wiseman, 1988a; Stone and Wiseman, 1988b; Wiseman and Stone, 1988; Tuazon and Carter, 1988). Mainly the reactions of hydrazine with ozone, nitrogen gases and OH radicals have been considered. With respect to the air oxidation of hydrazine, Stone and Wiseman (1988a, 1988b) and Wiseman and Stone (1988) showed evidence that hydrazine does not react with oxygen in the gas phase at ambient conditions. They suggested that surface interactions often account for the major losses of hydrazine vapor in chambers. Since gas-phase reactions were not an objective of our study we will not go into more detail concerning this literature.

Autoxidation of hydrazine in solution has received considerable attention because of its implications

concerning hydrazine stability during storage. Although this reaction seems to be very slow in distilled water (MacNaughton et al., 1978), the presence of trace amounts of metals greatly increases the rate of reaction (Gaunt and Wetton, 1966). Of all the metals tested as possible catalysts, only Cu^{+2} and Mn^{+2} have an appreciable effect on the autoxidation rate of hydrazine.

Most of the research done since the discovery of hydrazine was based on the premise that hydrazine solutions are unstable and that precautionary measures should be taken during their storage to avoid losses. Experimental conditions such as high oxygen pressures and high concentrations of catalysts were conducive to hydrazine degradation. Our starting hypothesis as environmentalists concerned with pollution is that hydrazine does not always degrade and might be a hazard to the natural environment.

Since soils and natural waters contain an extensive variety of elements in solution and active surfaces there is a large potential for interaction. Some research has been conducted on the environmental fate of hydrazine and will be discussed in the following chapters. However, the heterogeneity of the results as well as the large variety of experimental soils and aquatic systems requires more specific answers.

Presentation

Three lines of study, related to the basic problem of hydrazine fate in the environment, will be presented in three separate chapters. First, investigations of the effect of environmental factors on hydrazine degradation in aquatic systems will be discussed. The effect of laboratory methods of incubation will also be evaluated.

The second line of study is devoted to the effect of Cu^{II} on hydrazine adsorption and degradation by a montmorillonitic clay (Saz-1) under aerobic conditions.

The third line of study is related to the extent of adsorption and mechanisms of interaction of hydrazine with several clays and soils at two different pH's under anaerobic conditions.

The results presented in the three chapters are summarized and discussed in the final chapter in terms of implications for the fate of hydrazine in the environment.

CHAPTER II
EFFECTS OF ENVIRONMENTAL FACTORS ON
HYDRAZINE DEGRADATION IN AQUATIC SYSTEMS

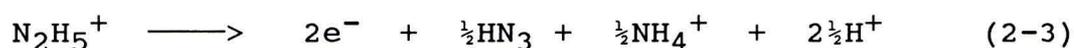
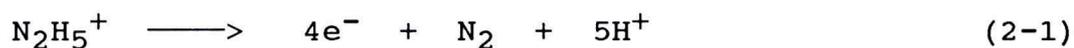
Literature Review

The stability of hydrazine solutions during manufacturing operations, handling, storage, and use has been a main concern to the industries that produce or that use them. Information from studies on the factors that influence hydrazine stability may also be useful to environmental scientists studying the decomposition of hydrazine in the environment.

Oxidation of Hydrazine in Solution

As it was previously stated, hydrazine is a strong reducing agent and as such can reduce many ions to lower oxidation states. The standard redox potentials indicate that hydrazine is a better reducing agent in alkaline than in acidic solutions. Although the two adjacent nitrogen atoms of hydrazine should favor the formation of nitrogen when the hydrogens are abstracted by oxidation, this simple reaction is not usually the only path followed (Schmidt, 1984). In addition to molecular nitrogen, the following compounds have been identified as reaction products: ammonia, hydrazoic acid, diazene, and hydrogen peroxide.

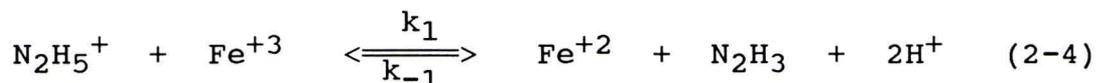
Early investigators had to rely on intuition to explain the mechanisms leading to different products. Browne and Shetterly (1907, 1908, 1909a, 1909b) were the first investigators that attempted to classify various oxidizing agents on the basis of their behavior towards hydrazine. A tremendous amount of work (Bray and Cuy, 1924; Cuy, 1924; Cuy and Bray, 1924; Cuy et al., 1924; Kirk and Browne, 1928) was done before three basic reactions were identified:



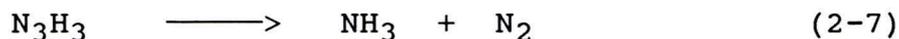
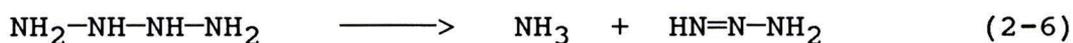
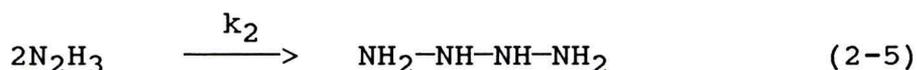
Most reaction schemes, such as the one proposed by Kirk and Browne (1928), assumed polynitrogen intermediates although none of them were actually identified at that time.

Higginson et al. (1953) grouped the oxidizing agents according to their ability to oxidize hydrazine by one-electron or four-electron reactions. They suggested that the ability of metal ions to adsorb hydrazine in their coordination sphere determined the path of reaction. Later Higginson and Sutton (1953), Cahn and Powell (1954) and Higginson and Wright (1955) used ^{15}N to verify the oxidation mechanisms that had been proposed. The reaction with oxidants which give exclusively four-electron oxidation (acid iodate, alkaline ferric cyanide, Tl^{III} , V^{V}), yielded N_2

which was unrandomized. Therefore, they stated that all four hydrogen atoms had to be removed from a single hydrazine molecule. Although they did not find any oxidation agent which gave exclusively one-electron oxidation of hydrazine, they found many which gave simultaneously four-electron and one-electron oxidation (Ce^{IV} , Fe^{III} , Mn^{III} , $\cdot\text{OH}$, KMnO_4 etc.). It was proven that the extent of isotopic randomization is proportional to the fraction of N_2 produced by one-electron oxidation. Hydrazoic acid was found as a by-product only when hydrazine was oxidized in hot, concentrated sulfuric with hydrogen peroxide. Their results are consistent with the following mechanism:



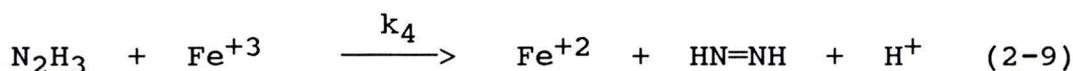
A dimerization step then leads to tetrazene:



Instead of dimerization of hydrazyl radicals, dismutation can occur:



The hydrazyl radical can be oxidized further:





Cahn and Powell (1954) stated that although the cupric ion does not react at any appreciable rate with hydrazine in acid solution, its presence greatly increases the proportion of four-electron oxidation. This observation suggests that oxidation of the hydrazil radical (Equation 2-9) is catalyzed by cupric ions. This mechanism has been confirmed by Rosseinsky (1957) and by Pollard and Nickless (1960).

In general, yields of ammonia, relative to hydrazine consumed, are very much smaller in alkaline, neutral, and weakly acid solutions than in strong acidic solution ($\text{pH} < 3$) (Higginson, 1957). It was suggested that the effect of the large change in proton concentration must therefore be to increase greatly the rate of oxidation of N_2H_3 (Equation 2-9) relatively to dimerization (Equation 2-5).

Recently, more direct evidence for the validity of the mechanism has been obtained by the pulse radiolysis technique. Pagsberg (Cited by Sutherland, 1979) identified the hydrazyl radical as a transient produced during the attack of hydrazine by OH radicals in basic media. At the same time, Hayon and Simic (1972) described the characteristics of a more stable transient which decayed by a first-order acid-base catalyzed reaction and which was formed by a first-order reaction in basic solution. They suggested the transient was triazene. In subsequent

experiments, Sutherland (1979) described triazene as an amphiprotic molecule. It was suggested that the rate of decomposition of the neutral form is negligible at any pH when compared to the rate of reaction of its conjugated acidic or basic form (Sutherland, 1979). Phosphate was found to be a catalyst for the decomposition of triazene.

Evidence of radical reaction intermediates has been presented by Adams and Thomas (1963), Smith et al. (1971), Francis and Jones (1971), and Atkinson and Bard (1971) using ESR techniques.

Autoxidation of Hydrazine in Solution

Autoxidation by atmospheric oxygen appears to be the most important factor contributing to the disappearance of hydrazine in the environment since oxygen is in great supply.

Cuy and Bray (1924) were the first investigators to study this reaction. It was found that hydrazine solutions in 1.0M sodium hydroxide were not stable; however, no decomposition took place when the solutions were kept under nitrogen. It was assumed that decomposition was due to oxidation by air. They stated that acid hydrazine solutions were perfectly stable. Later, Gilbert (1929) studied the autoxidation of hydrazine by the procedure of passing oxygen through a fritted glass disk into the solution. He proved that an increase in hydroxyl concentration first accelerates autoxidation and above certain concentration (between 0.01-

0.03M sodium hydroxide) a retardation effect occurs. Hydrogen peroxide was formed under all conditions when hydrazine in dilute alkaline solution was exposed to the action of oxygen. The optimum sodium hydroxide concentration corresponded to that for the maximum rate of decomposition of hydrogen peroxide.

Gilbert's observations (1929) were later verified by Brown (Cited by Audrieth and Ogg, 1951) who studied the hydrazine autoxidation at higher concentrations. He established the fact that traces of copper exert a marked catalytic effect on the autoxidation of hydrazine. Audrieth and Mohr (1951) tested several metallic ions, specifically those which are capable of existing in more than one valence state and that are known to be reducible by hydrazine. Dissolved copper was by far the most active catalyst, followed by vanadium (VO_3^-). Audrieth and Mohr (1951) used metal deactivators which form insoluble salts or stable complexes with copper to inhibit its catalytic effect. No inhibitors were found that would totally neutralize the effect of copper; the more effective stabilizers included sulfide, dithizone, thiocyanate, and potassium ethyl xanthate. They expressed some doubts about the direct reaction between molecular oxygen and the hydrazine molecule.

Several investigators have tried to develop a kinetic rate equation for the hydrazine-oxygen reaction. Ellis et

al. (1960) stated that it is very difficult to elucidate the kinetics of the hydrazine-oxygen reaction because of the hydrazine decomposition that occurs even in the absence of oxygen. Also, trace amounts of metals have a pronounced effect on the rate of either reaction. However, Cuy and Bray (1924) and later Gaunt and Wetton (1966) did not detect any hydrazine decomposition in the absence of oxygen. Ellis and coworkers (1960) found that the overall reaction approximated a second-order reaction, best expressed by an empirical rate equation

$$dc/dt = ac + bc^2 \quad (2-11)$$

where a and b change with pH and temperature. The rates of disappearance of oxygen and hydrazine were of the same order, but hydrazine disappeared somewhat faster than did oxygen. The rate of reaction increased by about 1.2 per 10° rise in temperature. Ammonia was detected when the hydrazine was in excess, but at no time was hydrogen peroxide detected.

There have been several reports about the effect of the container material on hydrazine autoxidation rate. These reports suggest that the reaction is heterogeneous. Gilbert's data (1929) suggested a reaction at a surface but the surface was not identified. The possibility of dust particles acting as the active surfaces was mentioned and the fritted glass used to pass oxygen was under suspicion. Gaunt and Wetton (1966) found that reaction rates in

polythene bottles were extremely slow. Rates were also very slow in glass flasks but could be considerably increased by a suitable "cleaning" of the glass with chromic acid mixture before use; however, the rate did not slow down if a reacting sample was transferred from glass to a polythene bottle. They concluded that the reaction was catalyzed not by the container wall itself but by contaminants that had leached from the wall prior to the addition of hydrazine. They identified the contaminant as copper (II). When copper (II) was added as a catalyst in caustic soda solutions, they found the maximum rate at about pH 12 from approximately zero at pH 11, whereas in ammonia solutions a larger peak rate was found at about pH 9.

On the other hand, Lim and Fagg (1984) stated that the manganese-catalyzed autoxidation of aqueous hydrazine was a chain reaction propagated by hydrogen peroxide, diimine (N_2H_2), hydrazyl ($N_2H_3\cdot$), peroxy ($O_2^{-\cdot}$) and hydroxy ($OH\cdot$) radicals. The reaction was sensitive to the nature of the reaction wall. Their kinetic results suggested that the termination reaction switches from the unimolecular adsorption of the perhydroxy radical at a low manganese concentration to the unimolecular adsorption of a manganese-hydrazyl radical complex at a high manganese concentration. In the mechanism they proposed the manganese-hydrazyl radical complex decomposed on the wall into N_2 and NH_3 without going through the intermediate tetrazene. The

overall reaction was much slower in a Teflon reactor than in a glass reactor with the same surface-to-volume ratio. They explained the pronounced effect of pH on the reaction by proposing the oxidation of Mn(II) by oxygen to Mn(III), which is strongly pH dependent, as the rate limiting step.

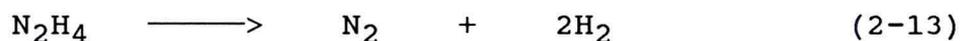
The effect of contact between hydrazine solutions and some polymer materials was studied by Bott and Rassoul (1970). Their results suggested that there is no decomposition of hydrazine in the absence of oxygen in contact with polyethylene, polypropylene or Pyrex glass. On the other hand polyvinyl chloride (PVC) interacted with hydrazine and was considered an unsuitable material for containing hydrazine solutions. In a later study Bott and Rassoul (1972) allowed air to leak into the space above an alkaline hydrazine solution contained in a Pyrex cell. Hydrazine concentration diminished with time; however, they did not discuss about how the Pyrex container affects hydrazine autoxidation.

Hydrazine Decomposition in Solution

Heterogeneous catalyzed decomposition of hydrazine has been widely studied because of its implications in the satellite industry. Schmidt (1984) mentioned a survey conducted by Eberstein and Glassman of metals that catalyzed hydrazine decomposition. They noted that transition metals having incomplete d subshells act as strong catalysts for hydrazine decomposition, whereas metals having no d

subshells or completely filled shells are not catalytic. It was theorized that electrons from the lone electron pairs in hydrazine interact with unfilled d orbitals in the early stages of adsorption and chemisorption of hydrazine. To our knowledge only metals with zero valence either in powdered state or supported by other solid have been studied.

At least two basic equations can be used to describe heterogeneous decomposition of hydrazine in solution:



Any possible combination of both reactions has been found to occur depending on the catalyst used and the experimental conditions (Contour and Pannetier, 1970; Maurel and Menezo, 1978; Oosawa, 1984). No report has been found in the literature of these reactions taking place under environmental conditions.

Hydrazine Degradation in Natural Waters

There are a few reports on the behavior of hydrazine in natural waters. Slonim and Gisclard (1976) studied the disappearance of hydrazine in waters of different origin that varied in hardness, organic matter content, oxygen content, pH, and temperature. Hydrazine at 5 mg l^{-1} was added to water samples and analyses were done every day for

five days. Within the first hours the most polluted water (solids in suspension) caused the greatest breakdown of hydrazine. Water from the same source but taken under calm weather conditions showed no hydrazine breakdown initially but hydrazine was not detectable after four days. A correlation was found between the degree of hardness and the rate of hydrazine decay. In city tap water, which was softened and chlorinated, concentration remained nearly the same after 4 days. Slonim and Gisclard stated that polluting material rich in organic matter was the leading contributor to hydrazine degradation; however, they did not mention the possibility of hydrazine's being adsorbed to the organic surfaces. In no case was biological activity considered as a possible factor in degradation.

MacNaughton et al. (1978) found that hydrazine degraded faster in natural waters. Addition of 4×10^{-6} moles l^{-1} of copper had a more dramatic effect in seawater than in pond water. They indicated that the higher dissolved organic content of the pond water would be expected to reduce the free copper concentration more than the seawater. Filtration of the pond water resulted in no change in oxidation rate, suggesting that suspended material was not important in catalyzing the hydrazine oxidation or complexing the added copper. The oxidation rate was unaffected by changes in oxygen concentration between 0.5 and 40 mg l^{-1} , as measured with a dissolved-oxygen meter. In another study, Lurker

(1976) showed that Fe^{+2} , Fe^{+3} , Zn^{+2} , Co^{+2} , or Ni^{+2} ions at typical environmental concentrations do not catalyze the rate of hydrazine oxidation in well-aerated water.

From the literature we can infer that the disappearance of hydrazine from solution is highly dependent on reaction conditions. At low pH, hydrazine can be oxidized mainly to N_2 and NH_3 by many metals and other oxidizing agents. At high pH, autoxidation can take place, the main product being molecular nitrogen. This reaction is pH dependent and metals, especially copper and manganese, can act as catalysts. Autoxidation is sensitive to the nature of the container, but it still is not clear if the wall surface plays an active part catalyzing the reaction.

Our objective in this part of the study was to gain more information on the parameters that affect degradation of hydrazine in aqueous systems.

Materials and Methods

Reagents

Hydrazine monohydrate was purchased from Aldrich Chemical Company, (Milwaukee, WI). All other chemicals were analytical grade or the highest grade available.

Natural Waters

Natural waters were collected in 20-gallon plastic carboys from the Saint Johns River and from Santa Fe Lake. River water samples were collected under the East Palatka

Bridge on U.S. highway 17. The lake samples were taken near Buddy's Landing on Lake Santa Fe in Melrose, Florida. After arrival at the laboratory the dissolved-oxygen concentration, pH, and total carbon content of the water samples were measured. Two liters of each type of water were autoclaved at 121°C for twenty minutes and two other liters were filtered through a 0.2 μm membrane to sterilize and eliminate suspended solids in the samples. They were stored in the dark in a refrigerator at 4°C until ready for use.

Analytical Methods

The laboratory method selected to determine hydrazine concentrations less than 12 mM was the colorimetric method developed by Watt and Chrisp (1952) in which p-dimethylaminobenzaldehyde (PDBA) was used to form a yellow-color dimeric azine which absorbs at 460 nm. The color reagent was prepared by dissolving 10 gm of PDBA in 1 liter of absolute ethanol and adding 50 ml of concentrated hydrochloric acid. A typical calibration curve for the determination of hydrazine was obtained in the following manner: ten milliliters of the color reagent were placed in a 25 ml volumetric flask and small aliquots (10-100 μl) of a standard hydrazine hydrate solution (103 mg l⁻¹) were added. A yellow color developed instantly and reached a maximum after approximately 15 minutes. Afterwards the volume was brought up to 25 ml with 1 M HCl. Solutions prepared in this manner were stable for at least 12 hours if stored covered,

to avoid ethanol evaporation, and in the dark. Standard hydrazine hydrate solutions (103 mg l^{-1}) were prepared every two weeks by adding $100 \mu\text{l}$ hydrazine hydrate to 1 liter of 1 M HCl to avoid autoxidation. The results were expressed in terms of hydrazine concentrations. The final hydrazine concentration in the volumetric flasks was between 0.05 and 0.6 mg l^{-1} .

When higher hydrazine concentrations ($> 12\text{mM}$) were to be analyzed, a direct iodate titration in 4 N HCl was used as described by Penneman and Audrieth (1948), using carbon tetrachloride to detect the end point. The initial reaction involves reduction of iodate to iodine, which is subsequently oxidized by additional iodate to iodine chloride. This results in disappearance of the iodine color. A few milliliters of carbon tetrachloride were added to dissolve the iodine; the end point is reached when the solvent layer is decolorized.

The concentration of oxygen in aqueous solutions in small vials was determined with a dissolved-oxygen electrode (Microelectrode, Inc.). For determination of dissolved oxygen concentration in water samples in Pyrex cells a dissolved-oxygen electrode, Orion model 97-08, was used. Total metals concentration was determined on an atomic absorption spectrophotometer (Perkin Elmer model 460). A specific gas-sensing electrode (Orion 951201) was used to detect ammonia in aqueous media in the degradation studies.

The concentration of total soluble organic carbon in water was determined on a Total Carbon System from Oceanography International Company, Model 0524B. A small aliquot was placed in a glass ampule along with a series of reagents to acidify and digest any organic forms present. Ampules were purged of inorganic carbon with purified oxygen. After the ampules were sealed, they were autoclaved to convert organic carbon to CO_2 , which was measured by a non-dispersive infrared analyzer equipped with a digital integrator. The integrated peak area was related to the weight of carbon by comparison with standards of known C content.

Experimental Procedures

Solutions of hydrazine ranging from 10 to 500 mg l^{-1} were prepared in 2-liter volumetric flasks that contained bi-distilled water at the desired temperature. After the desired chemical compositions were obtained, 10-ml aliquots were placed into small bottles and incubated in a constant temperature water bath at either $25(\pm 0.3)^\circ\text{C}$, $30(\pm 0.1)^\circ\text{C}$, or $45(\pm 0.1)^\circ\text{C}$. Experiments at 22°C (ambient temperature) were carried out either in a fume hood or in an anaerobic incubator without temperature control. Three bottles were opened for hydrazine analysis at various time intervals. In some cases pH, oxygen concentration, and ammonia concentration were also determined. The frequency of analysis depended on the rate of hydrazine degradation.

Various constant ionic strengths were maintained using CaCl_2 as the background electrolyte. Acidic pH values were obtained with HCl. Neutral pH values were obtained with phosphate buffers of various ionic strengths.

Three different types of bottles were used to investigate the effects of container material: scintillation vials made of borosilicate glass low in potassium content, serum vials made of borosilicate glass (with crimped aluminum tops and a teflon liner), and polyethylene bottles. All glassware was rinsed with water, soaked in 0.1 N HCl for at least 24 hours, then soaked in bi-distilled water for another 24 hours followed by extensive rinsing with deionized water. Initially the glassware was soaked in very dilute "household bleach" to destroy any hydrazine that might be adsorbed onto the walls from previous experiments; however, this practice had a strong effect on the rate of hydrazine degradation, probably due to some "bleach" remaining adsorbed even after repeated rinsing. This practice was therefore discontinued and data obtained using this washing procedure were discarded. Most of the experiments, unless otherwise specified, were carried out in serum vials because they proved more resistant and because we assumed they were impermeable to oxygen. New bottles were opened each time an analysis was needed and the rest of the solution was discarded. This procedure was subsequently modified in a study to determine the effect of container

size on autoxidation rate. In this study serum vials of 10, 50, and 100 ml size were used. Vials were opened periodically for analysis, shaken, and then put back in a constant temperature water bath (45°C) for future analysis.

In one of the later experiments, it was found that oxygen could diffuse slowly into the serum vials as well. After this finding, vials were kept in an anaerobic incubator under a nitrogen atmosphere whenever we wanted to minimize autoxidation over time.

One set of experiments was carried out in a 1.5-liter Pyrex cell that had a glass top to which a pH electrode and an oxygen electrode were attached. The cell also had an entrance for gas introduction and a syringe for withdrawing samples. The contents of the cell were continuously stirred with a teflon-coated magnetic stirring rod. Solutions of different Cu^{+2} concentration were equilibrated with gases of known oxygen content (0.27 mmol l^{-1} or less) prior to the addition of hydrazine. Under ambient air conditions, a trap was installed between the air pump and the cell, to remove CO_2 . The trap had a slight effect on pH of the experimental solution. After the addition of 2.1 mmol l^{-1} of hydrazine, electrode readings were monitored and samples were withdrawn periodically for hydrazine analysis.

Results and Discussion

System I--Degradation of Hydrazine in Distilled Water

Effect of reaction vessels

In order to study the effect of the reaction vessel on the degradation rate of hydrazine at 22°C, hydrazine concentration was monitored in solutions prepared with deionized-bidistilled water contained in three different types of reaction bottles: glass serum vials, polyethylene vials, and glass scintillation vials. For each type of container four treatments were prepared:

T1: under air atmosphere, with head space.

T2: under nitrogen atmosphere, with head space.

T3: under air atmosphere, no head space.

T4: under nitrogen atmosphere, no head space.

Upon addition of hydrazine the solution pH rose from 6.9 to 10.1 in the air treatments and to 10.2 in the nitrogen treatments (Table 2-1). The fact that the oxygen concentration increased slowly with time, in vials that originally contained only nitrogen, suggests that the seal was not completely impermeable to oxygen in any of this types of bottles. For this reason, hydrazine degradation data for the nitrogen treatments will not be reported.

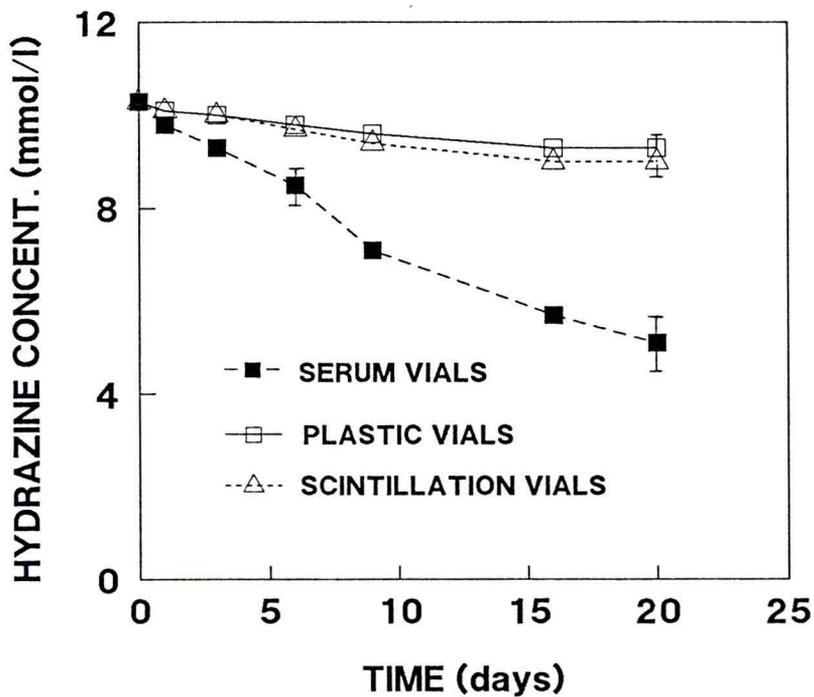
Degradation was very slow in both the polyethylene vials and the scintillation vials (Figure 2-1). After 24 days only 9.5% of the added hydrazine had degraded. This

suggests that these materials had little or no catalyzing effect on hydrazine degradation.

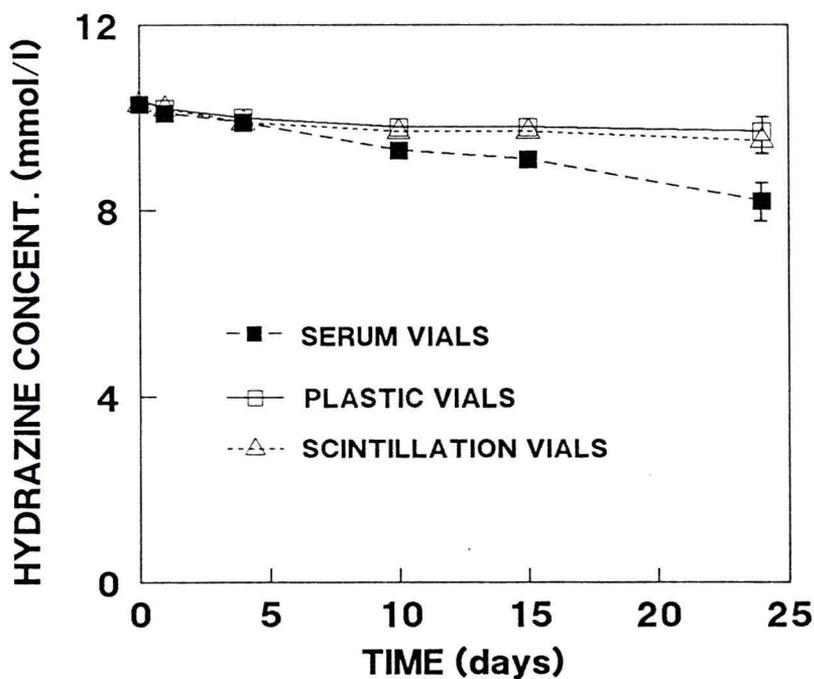
Table 2-1. Initial and final pH values and oxygen contents during hydrazine degradation.

Treatment	pH		O ₂ (mg l ⁻¹)	
	Initial	Final	Initial	Final
<u>Serum vials</u>				
T1	10.1	9.4	8.8 ^a	3.1
T2	10.2	9.5	0	1.5
T3	10.1	9.5	8.8 ^a	3.3
T4	10.2	10.1	0	1.1
<u>Plastic vials</u>				
T1	10.1	9.9	8.8 ^a	8.7
T2	10.2	10.0	0	8.3
T3	10.1	9.9	8.8 ^a	8.6
T4	10.2	10.1	0	8.2
<u>Scintillation vials</u>				
T1	10.1	9.9	8.8 ^a	8.1
T2	10.2	10.0	0	7.6
T3	10.1	9.7	8.8 ^a	7.2
T4	10.2	10.1	0	6.0

^a in equilibrium with air at 22°C.



(a)



(b)

Figure 2-1. Effect of container materials on hydrazine autoxidation at 22°C: (a) head space filled with air (T1), (b) bottles filled completely with solution (T3).

On the other hand, the serum vials had a significant effect on hydrazine autoxidation rate. Degradation was also faster in vials that had air in the head space because oxygen diffused freely into the solution from this source. For the treatments without head space, oxygen had to diffuse first through the seal; consequently, hydrazine degraded more slowly. Final oxygen content in Table 2-1 reflects the balance between oxygen diffusing into the solution and oxygen consumed.

Diffusion of oxygen can be assumed to follow Fick's first law:

$$dn = - D A (dc/dx)_t dt$$

where D is the diffusion coefficient expressed in $\text{cm}^2 \text{sec}^{-1}$. The diffusion coefficient is a property of the medium and the gas and is affected by temperature (Grable, 1966). The diffusive transfer of O_2 is approximately 10,000 times faster in air [$D=0.226$ (Willey and Tanner, 1964)] than in water [$D=2.6 \times 10^{-5}$ (Lemon and Wiegand, 1962)] with equal gradients and cross-sectional areas for diffusion. In the present study, the entrance of oxygen to the bottle was supposed to be physically prevented by the seal, but apparently the seal leaked slowly.

Since Gaunt and Wetton (1966) had suggested that catalysis was due to copper that had leached from the wall of the container, the solutions were analyzed for copper at the end of the experiment using anodic-stripping voltametry

at pH 3.0 along with atomic absorption. These results were negative. This suggests that the reaction intermediates themselves had some interaction with the surface of the container.

It is interesting to note that two types of glass, both made of borosilicate, differ in their behavior towards catalysis of hydrazine autoxidation. According to the manufacturers, the main difference between them is in their potassium and calcium contents, with potassium content being lower for the scintillation vials. When both types of glass were examined under the electron microscope using an X-ray probe, each revealed the presence, among other constituents, of copper and titanium but the amounts could not be quantified.

In another set of experiments at 25°C and in the presence of Cu^{+2} , hydrazine degraded faster in polyethylene bottles than in glass serum vials (Figure 2-2). Initially this was attributed to faster leakage of oxygen into the polyethylene bottles; however, when the experiment was repeated and the concentration of oxygen was measured during the course of the reaction, it was observed that the rate of oxygen replenishment in both types of bottles was similar after hydrazine had disappeared (Figure 2-4).

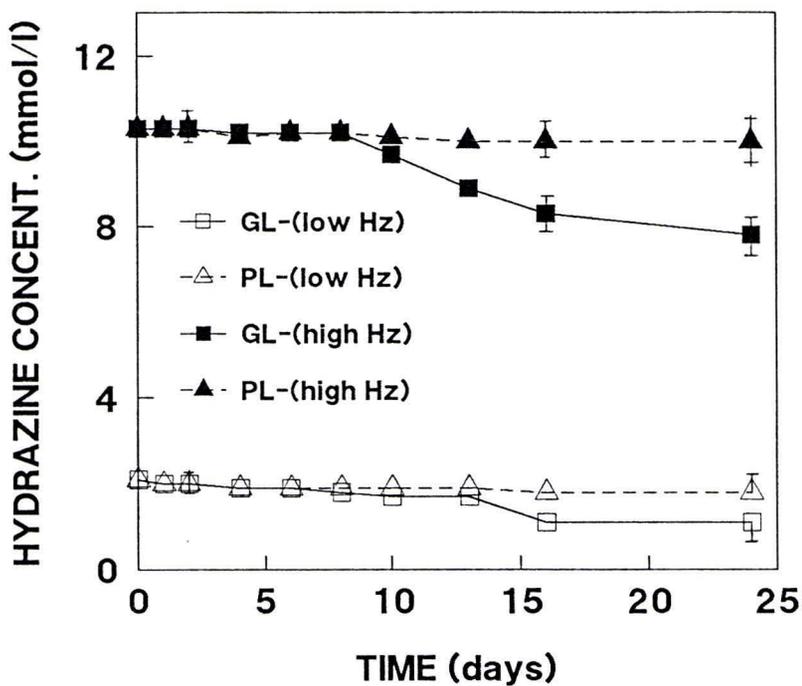
In order to further test the hypothesis that the container wall in the serum vials was catalyzing autoxidation, an experiment was set up using three different

sizes of the same type of serum vial, with exactly the same sealing system. Hydrazine solutions were prepared in five different treatments: distilled water, $0.001 \text{ mg l}^{-1} \text{ Cu}^{\text{II}}$, $0.01 \text{ mg l}^{-1} \text{ Cu}^{\text{II}}$, $0.1 \text{ mg l}^{-1} \text{ Cu}^{\text{II}}$, and $1.0 \text{ mg l}^{-1} \text{ Cu}^{\text{II}}$. All were incubated at 45°C . This set of vials was opened for analysis and sealed again after air had filled the head space and saturated the solution. Measurements for each size of serum vial are shown in Table 2-2.

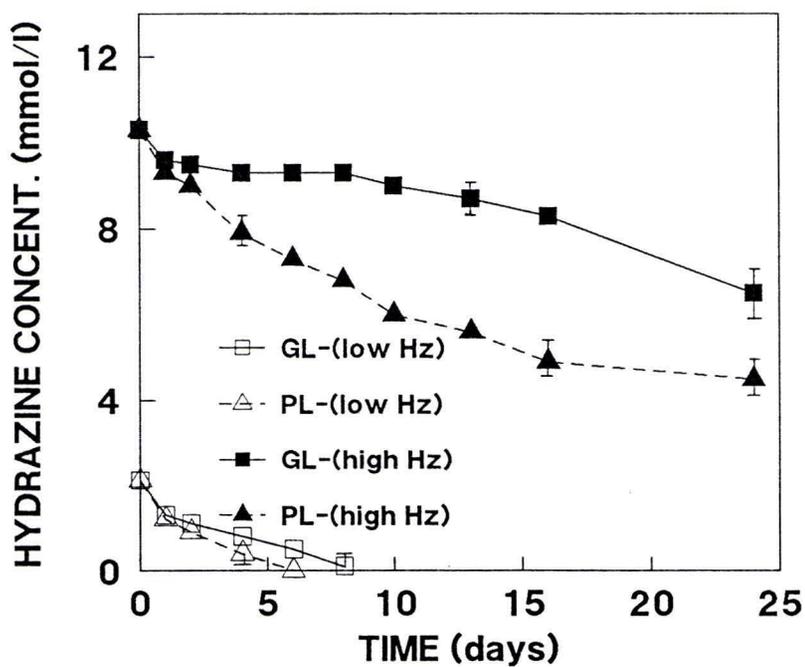
Container size had no effect on the degradation of hydrazine in distilled water (Figure 2-5a). However, in the presence of copper, hydrazine degraded faster in the 10-ml

Table 2-2. Average measurements for the serum vials.

	10 ml	50 ml	100 ml
Head space (ml)	4.4	10.2	20.6
Height of solution (cm)	2.90	4.40	6.00
Internal radius (cm)	1.05	1.90	2.30
Gas-liquid interphase (cm^2)	3.46	11.3	16.6
Head space/solution (ml/ml)	0.44	0.20	0.20
Contact surface/volume (cm^2/ml)	2.25	1.28	1.03



(a)



(b)

Figure 2-2. Effect of container materials on hydrazine degradation at 25°C; GL-serum vial, PL-polyethylene vial, (low)-hydrazine 2.0 mM, (high)-hydrazine 10.3 mM: (a) distilled water, (b) 1 mg l⁻¹ Cu²⁺ solution.

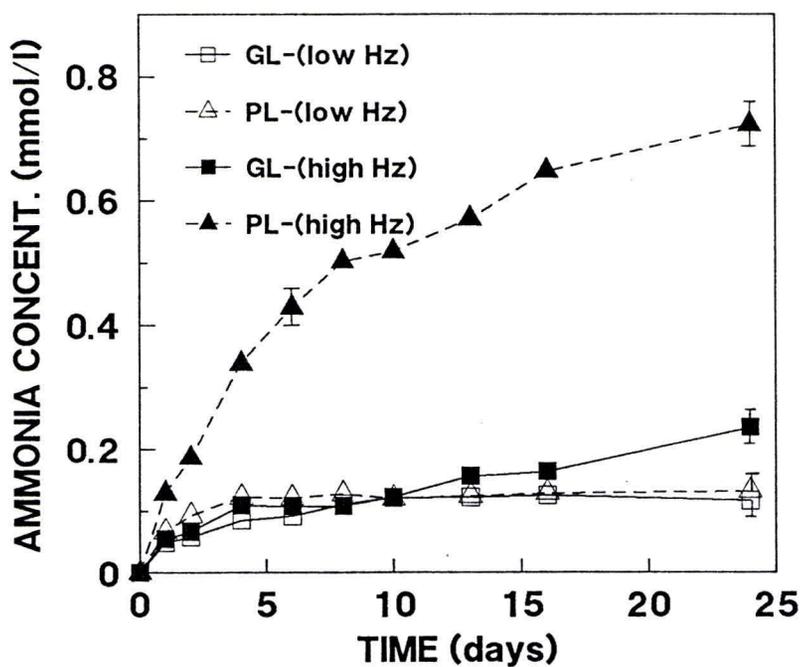
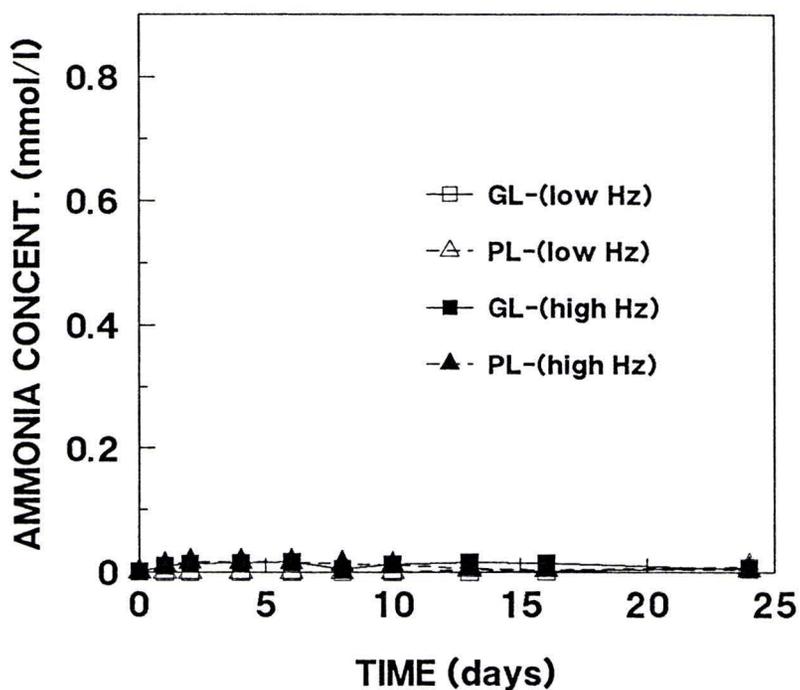


Figure 2-3. Effect of container materials on ammonia evolution at 25°C; GL-serum vial, PL-polyethylene vial, (low)-hydrazine 2.0 mM, (high)- hydrazine 10.3 mM: (a) distilled water, (b) 1 mg l⁻¹ Cu²⁺ solution.

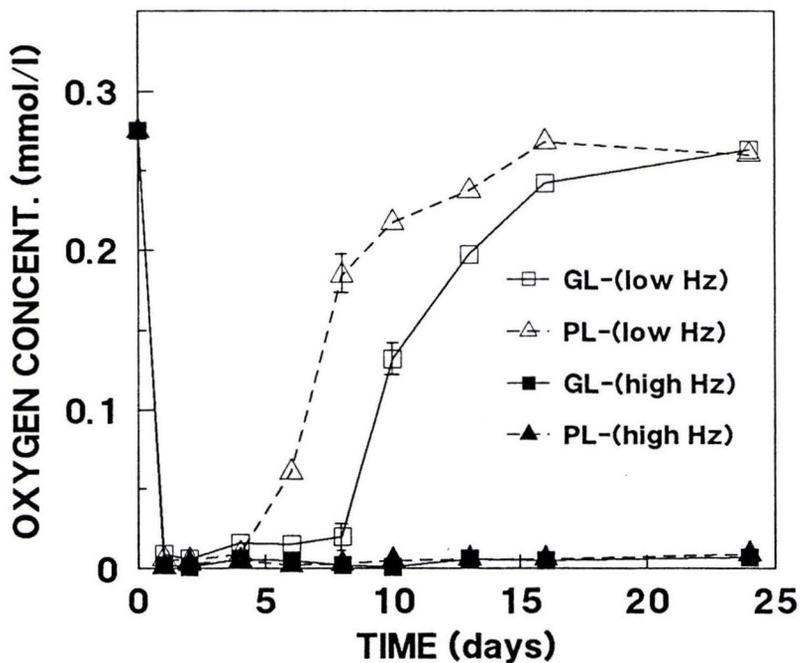
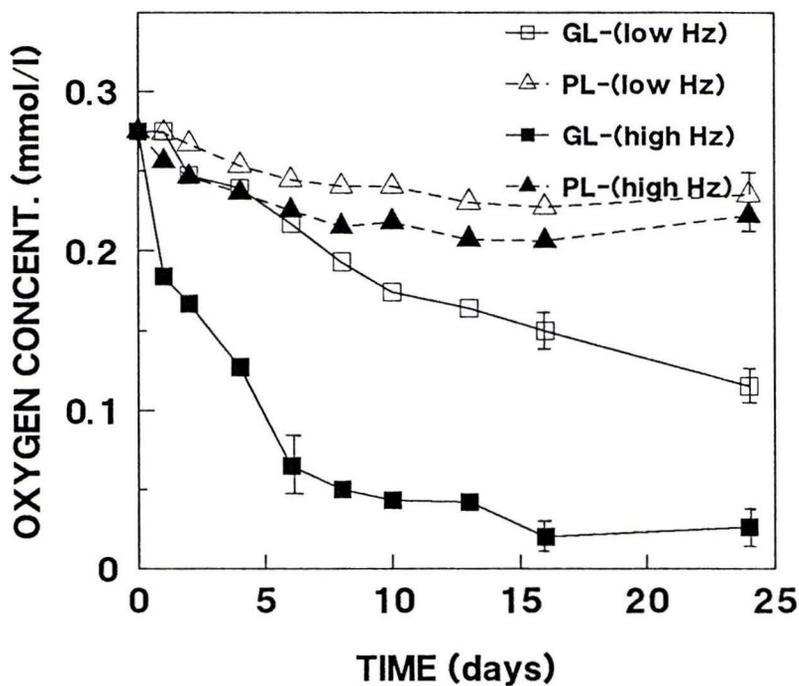


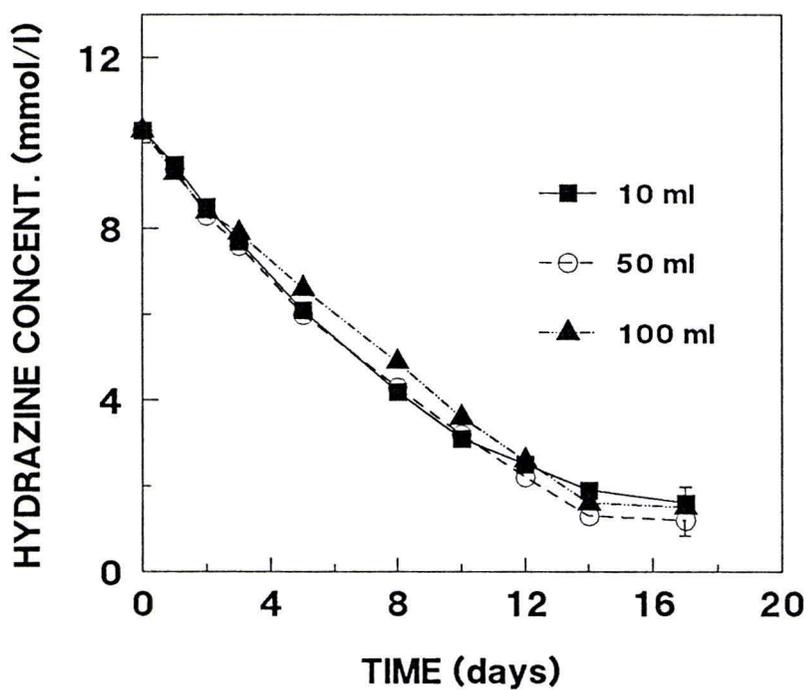
Figure 2-4. Effect of container materials on changes in oxygen concentration at 25°C; GL-serum vial, PL-polyethylene vial, (low)-hydrazine 2.0 mM, (high)- hydrazine 10.3 mM: (a) distilled water, (b) 1 mg l⁻¹ Cu²⁺ solution.

vials that had much larger head space volume/solution volume ratios and contact surface/solution volume ratios than in the 50- or 100-ml vials (Figures 2-6c, d, and e).

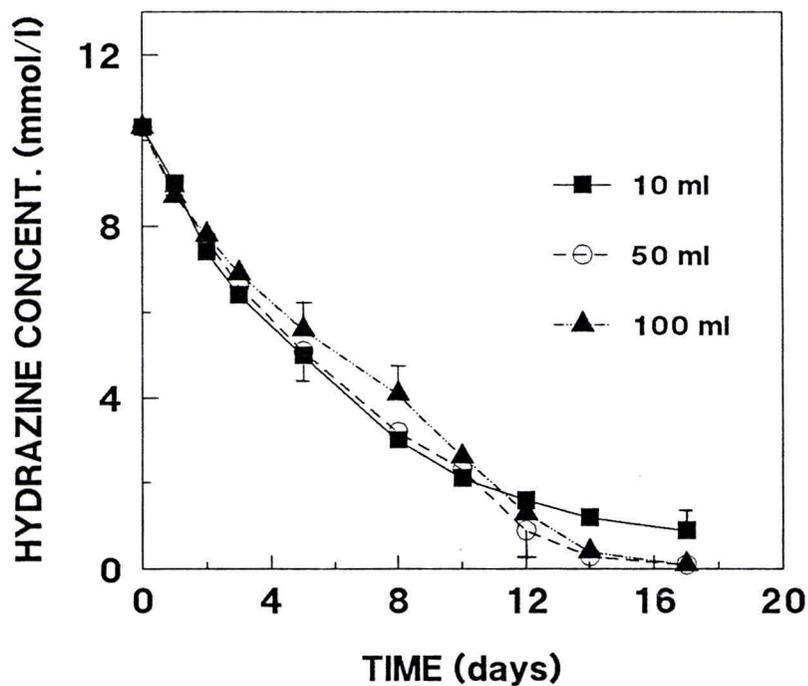
In the presence of these relatively high concentrations of copper compared to what could realistically leach from the container walls, most likely any differences in hydrazine autoxidation rate would arise from differences in the amount of oxygen diffusing into the solution or from the amount of surface exposed to the hydrazine solution.

Both the 50-ml and 100-ml vials had the same head space to solution ratio. It could be assumed that the oxygen status during the course of the reaction would be similar for both sizes of vials. The amount of solution in contact with the wall of the container was 25% higher for the 50-ml vials. Since the presence of catalyst is not a controlling factor at high copper concentrations, the differences in autoxidation rate can be attributed to increased amounts of surface exposed to the solution. This fact confirms the hypothesis that surface area plays an active role with respect to hydrazine autoxidation in solution.

In spite of the fact that serum vials have a catalytic effect on hydrazine autoxidation, we continued to use them in many of our experiments because their sealing system was better at higher temperatures, and because they were more resistant to fracture.

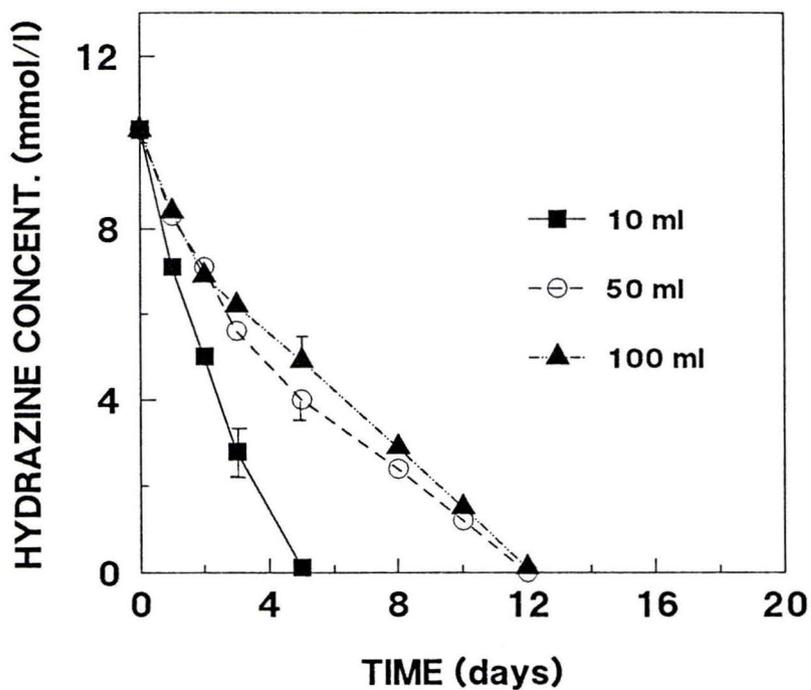


(a)

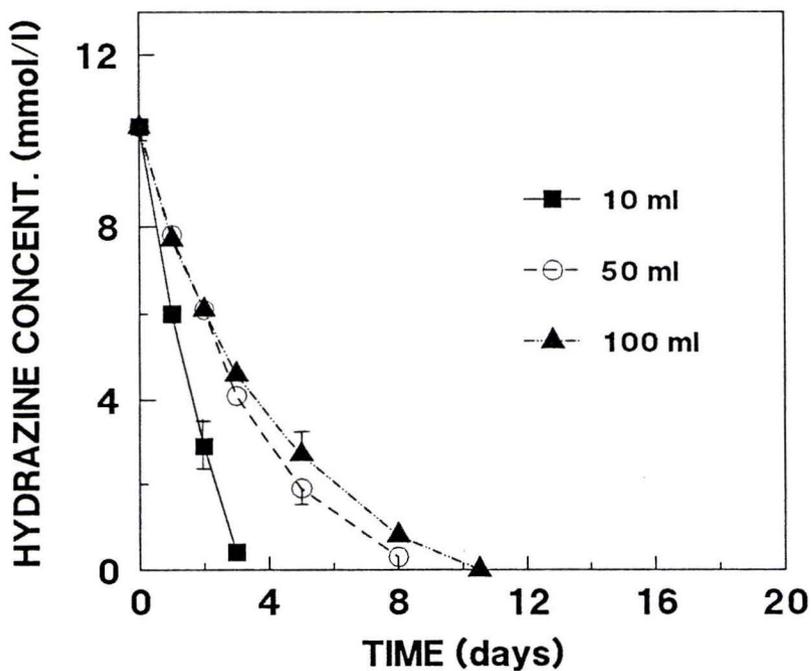


(b)

Figure 2-5. Effect of container size on hydrazine degradation at 45°C: (a) in distilled water, (b) in 0.001 mg l⁻¹ Cu²⁺ solution.

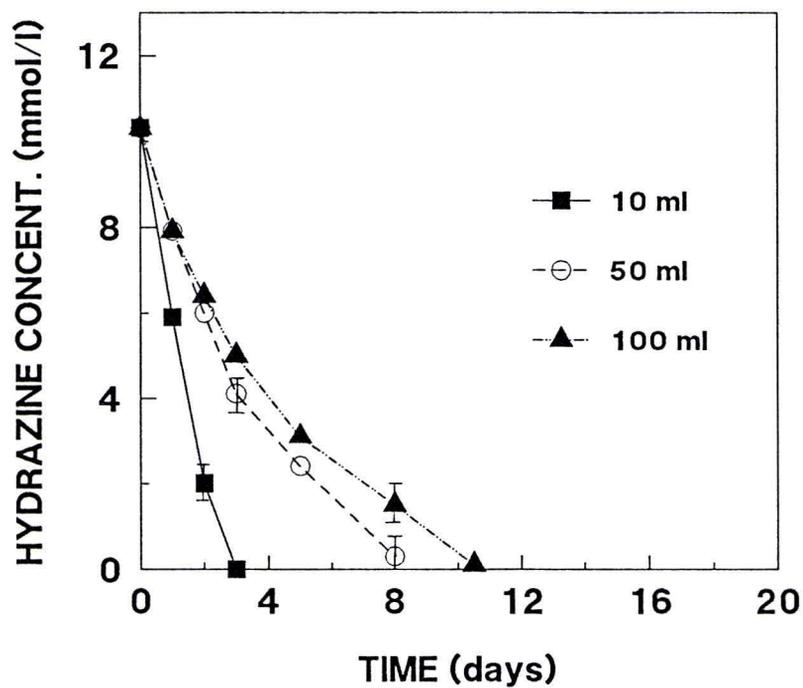


(c)



(d)

Figure 2-5 (cont.). Effect of container size on hydrazine degradation at 45°C: (c) in 0.01 mg l⁻¹ Cu²⁺ solution, (d) in 0.1 mg l⁻¹ Cu²⁺ solution.



(e)

Figure 2-5 (cont.). Effect of container size on hydrazine degradation at 45°C: (e) in $1.0 \text{ mg l}^{-1} \text{ Cu}^{+2}$ solution.

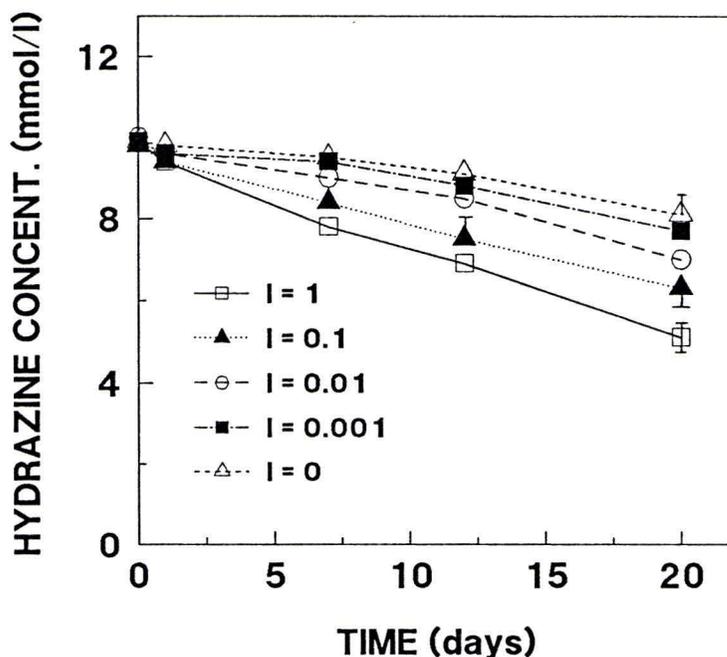


Figure 2-6. Effect of solution ionic strength (I) on hydrazine autoxidation at 22°C.

Effect of solution ionic strength

The experiment to evaluate the effect of ionic strength on hydrazine degradation was carried out in scintillation vials at 22°C. The ionic strength was adjusted using CaCl_2 solutions. After mixing of the solutions with hydrazine the pH rose to 9.9. As is evident in Figures 2-6 and 2-7, ionic strength had a significant effect on the degradation rate. The effect of water hardness on hydrazine autoxidation has been previously reported (Slonim and Gisclard, 1976; MacNaughton et al., 1978). MacNaughton et al. (1978) reported that there was a significant increase in the oxidation rate of hydrazine with increasing chloride or

nitrate concentration; however, a similar increase was not observed in seawater collected from the Gulf of Mexico of approximately the same salinity.

Weston and Schwarz (1972) stated that reaction-rate constants for reactions between ions vary with ionic strength in a manner resembling the dependence of equilibrium constants on ionic strength. Rate constants will increase with ionic strength for reactions between ions of the same sign, decrease with ionic strength for reactions between ions of opposite sign, and be unaffected by ionic strength for reactions in which one of the two species is uncharged (Weston and Schwarz, 1972).

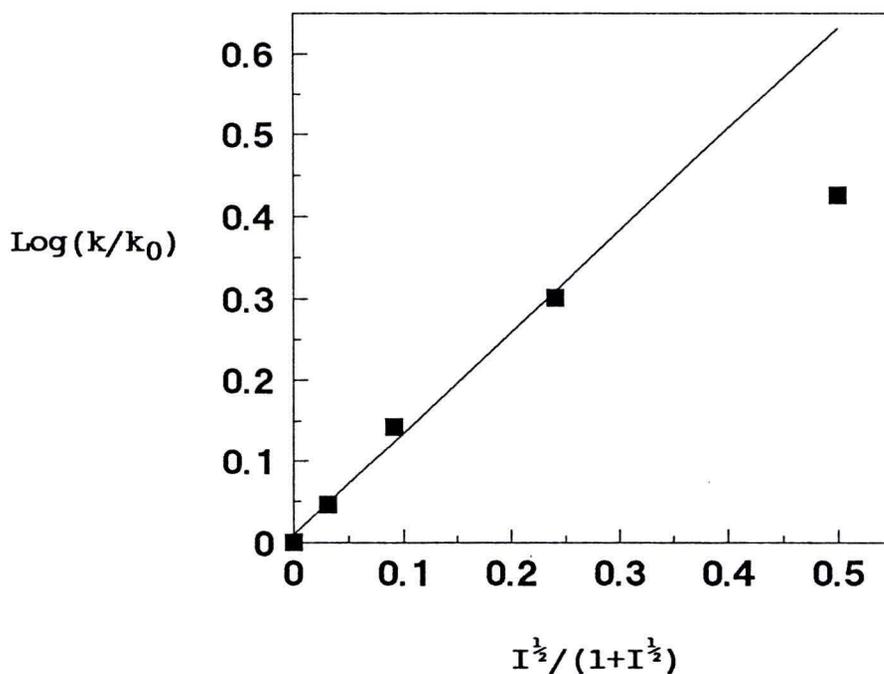


Figure 2-7. Effect of ionic strength on the rate constant at 22°C (k_0 - rate constant at infinite dilution).

The oxidation mechanisms described in the literature section do not give any information about the charge on the various reaction intermediates: however, each reaction intermediate has the ability to coordinate a H^+ and its charge thus a function of the pH. The fact that the rate of hydrazine autoxidation increases with ionic strength suggests that some step in the mechanism involves a reaction between two ionic intermediates that have the same charge sign.

Effect of pH

In preliminary studies, conducted at 45°C over a wide range of pH values in serum vials, it was found that the fastest rate of hydrazine autoxidation occurred at pH 7.0 (Figure 2-8). These results contradict a previously published report (Gaunt and Wetton, 1966) that the autoxidation rate rises from zero at pH 7.0 to a plateau value at about pH 12. For this reason, a study was set up at pH 7.0 using phosphate buffers of different ionic strengths (I) (Figure 2-9). These results showed that hydrazine autoxidation rate is first-order with respect to phosphate concentration (Figure 2-10). Extrapolating the line to zero phosphate concentration, predicted zero autoxidation rate as well at pH 7. To check if the reaction taking place was a) direct oxidation by the phosphate ion or b) autoxidation catalyzed by the phosphate ion, an experiment was carried out in scintillation vials completely filled with solution

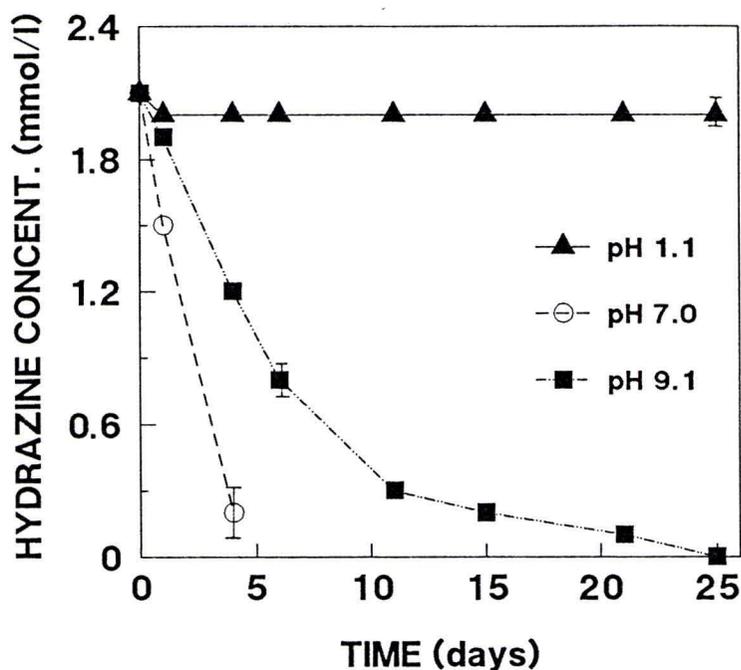


Figure 2-8. Effect of pH on hydrazine degradation in serum vials at 45°C.

in order to retard the entrance of oxygen. The reaction was very slow and of the same order in both the phosphate buffer at pH 7.2 and in the unbuffered solution at pH 9.5 (Figure 2-11). This suggests that the reaction was controlled by the diffusion of oxygen into the bottles, and that the reaction involved was hydrazine autoxidation catalyzed by the phosphate ion. After hydrazine had degraded completely, the solutions were analyzed for ammonia (Table 2-3).

Table 2-3. Effect of phosphate ionic strength (I) on ammonia produced during the catalyzed autoxidation of hydrazine at 45°C.

Ionic Strength (I)	NH ₃ (mmol l ⁻¹)
0.1	0.8
0.05	0.5
0.01	0.1

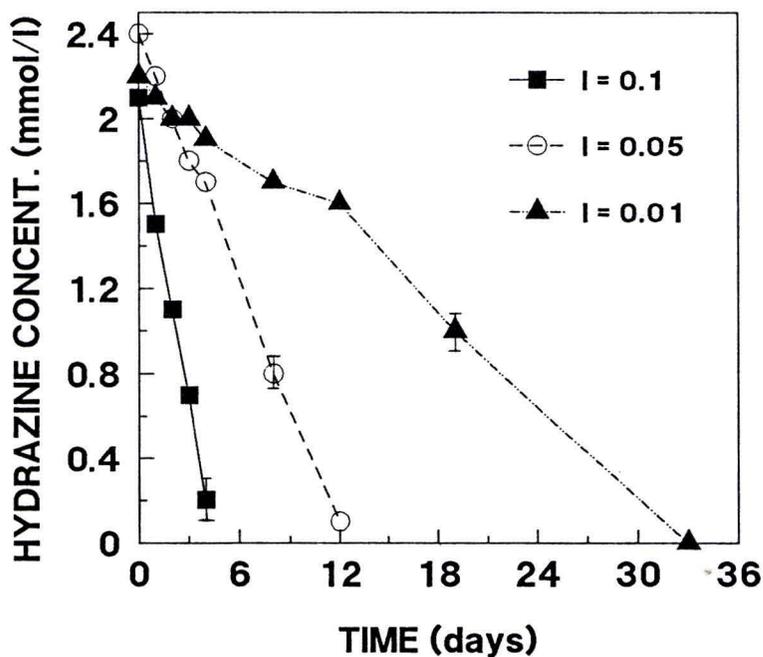


Figure 2-9. Effect of ionic strength of phosphate buffer at pH 7 on hydrazine degradation at 45°C.

It has been previously reported by Sutherland (1979) that the phosphate ion is a specific catalyst for the decomposition of triazene, and that the catalytic mechanism does not involve simple proton transfer. The fact that the amount of ammonia produced increased with phosphate concentration suggests that triazene was one of the intermediate species in the reaction.

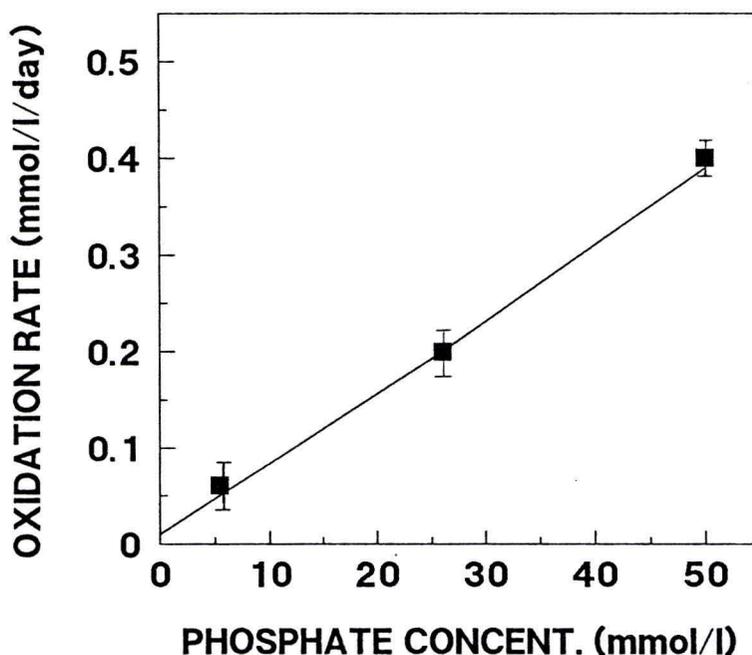


Figure 2-10. Relationship between hydrazine autoxidation rate at pH 7.0 and phosphate concentration at 45°C.

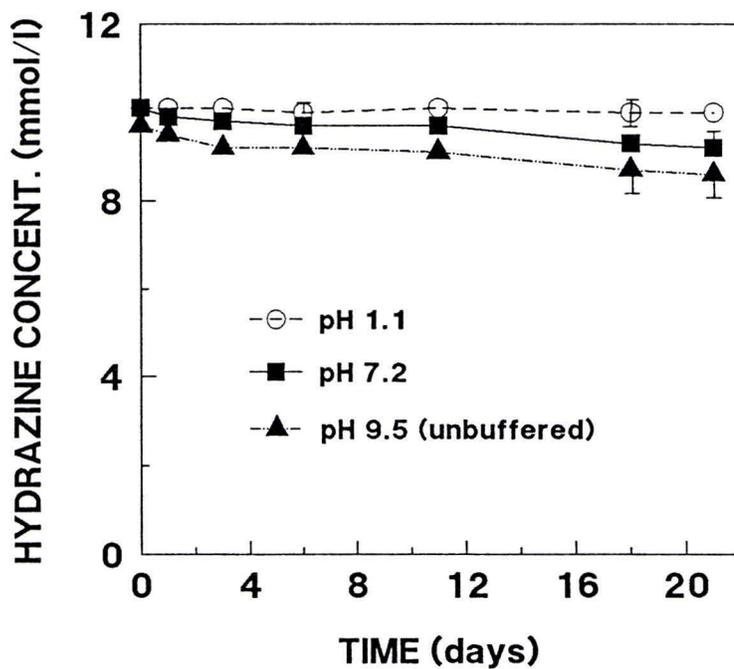
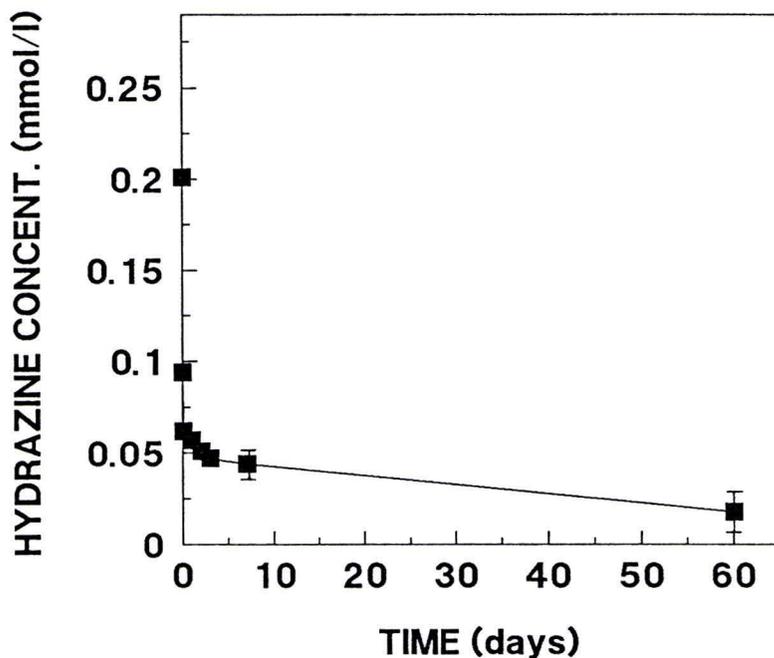


Figure 2-11. Effect of pH on hydrazine autoxidation at 22°C in completely-filled scintillation vials.

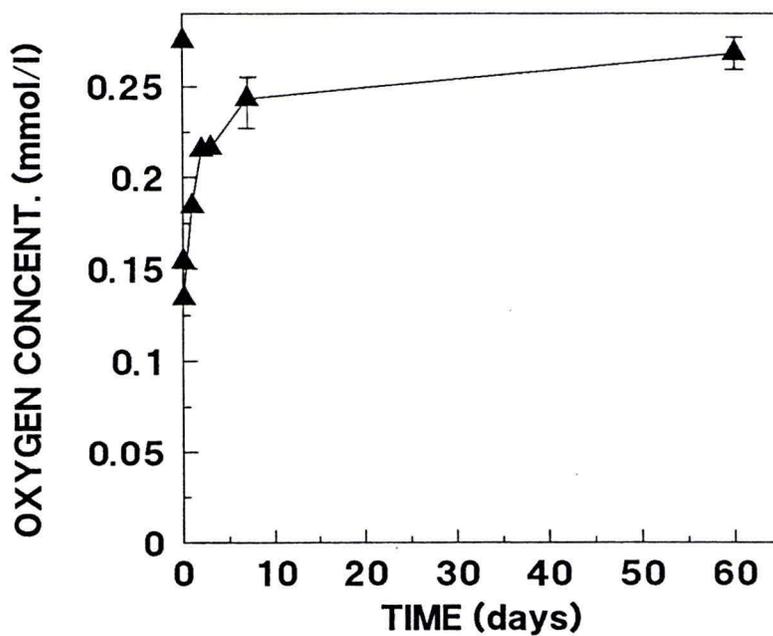
Effect of copper

The catalytic effect of Cu^{+2} on hydrazine autoxidation has been previously reported (Audrieth and Mohr, 1951; Gaunt and Wetton, 1966; McNaughton et al., 1978). However, most of the studies were carried out at pH 12 where the hydrazine degradation rate is maximum (Gaunt and Wetton, 1966). Since the objective of this study was to simulate what occurs in natural environments, it was found necessary to conduct the experiments at the pH values obtained by adding hydrazine without further adjustments, and at copper concentrations similar to those found in soils and natural waters. In each case, the results were compared with those obtained in deionized-bidistilled water.

The first experiment was conducted at 25°C, and compared hydrazine degradation in polyethylene bottles with that in serum vials (Figure 2-2). Visual observation of the experimental solutions containing Cu^{+2} revealed the presence of a reddish precipitate in solutions of low initial hydrazine concentration (2.1 mM) and a dark precipitate in solutions of high initial hydrazine concentration (10.3 mM). Due to the instability of the precipitates in the presence of air, they could not be isolated. Hydrazine concentration in the absence of copper remained almost constant in the polyethylene bottles after 24 days (Figure 2-2a); however, in the serum vials autoxidation occurred after an induction period.



(a)



(b)

Figure 2-12. Hydrazine autoxidation in 1 mg l^{-1} copper solution at 25°C in serum vials, when initial oxygen concent. is in slight excess over hydrazine concentration; (a) hydrazine concentration, (b) oxygen concentration.

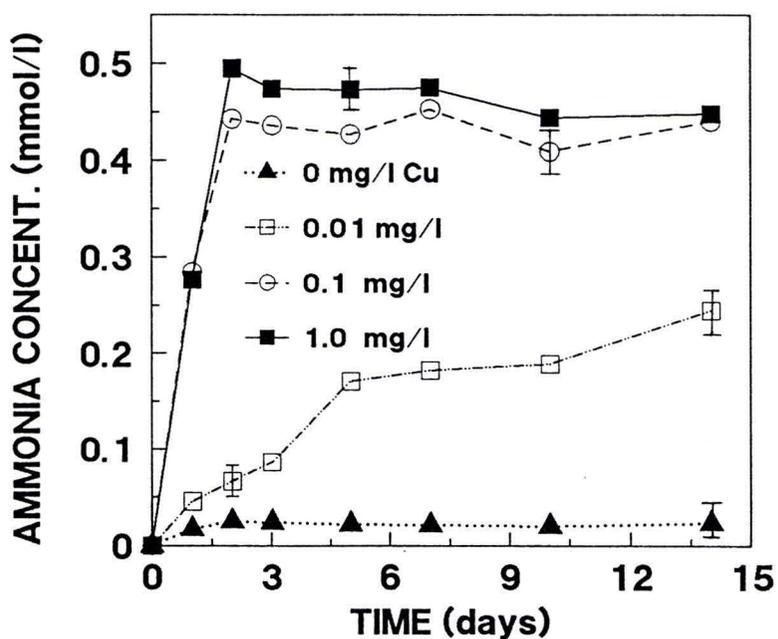
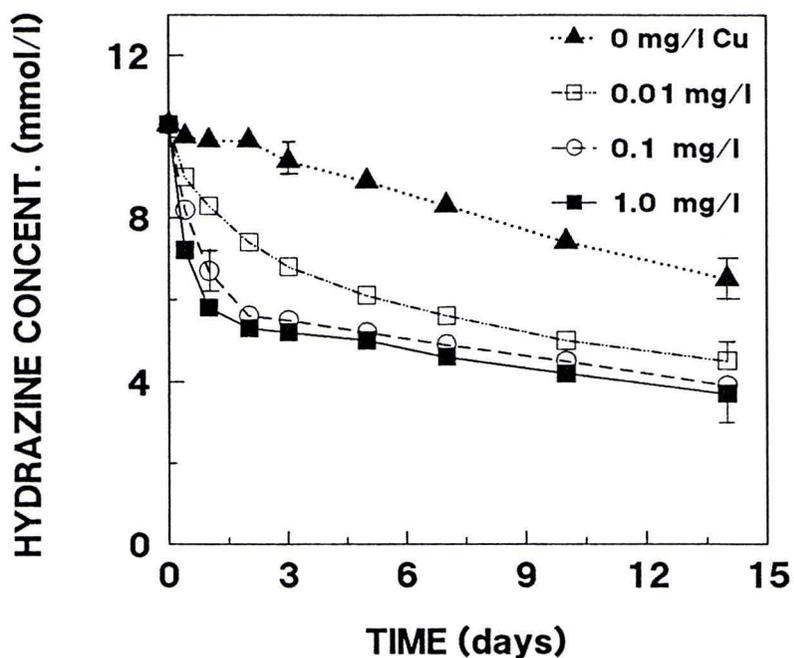
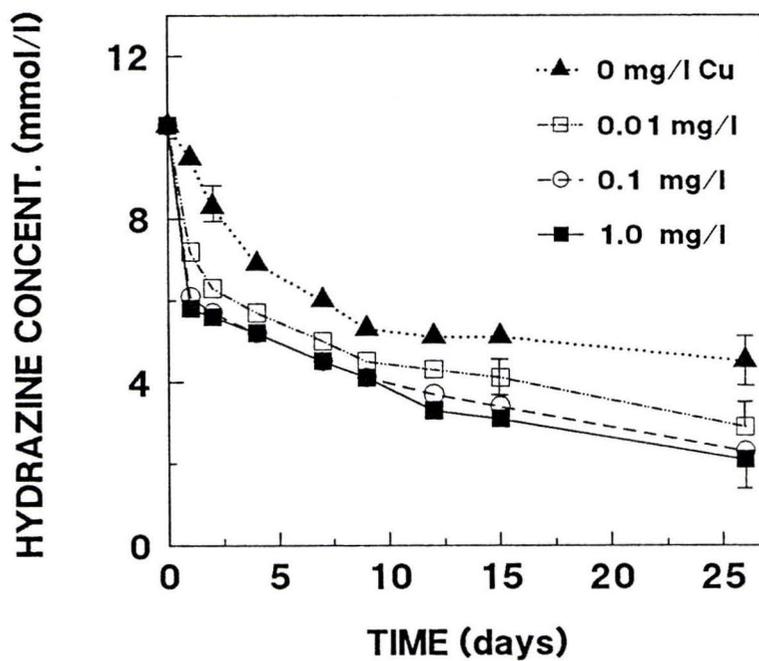
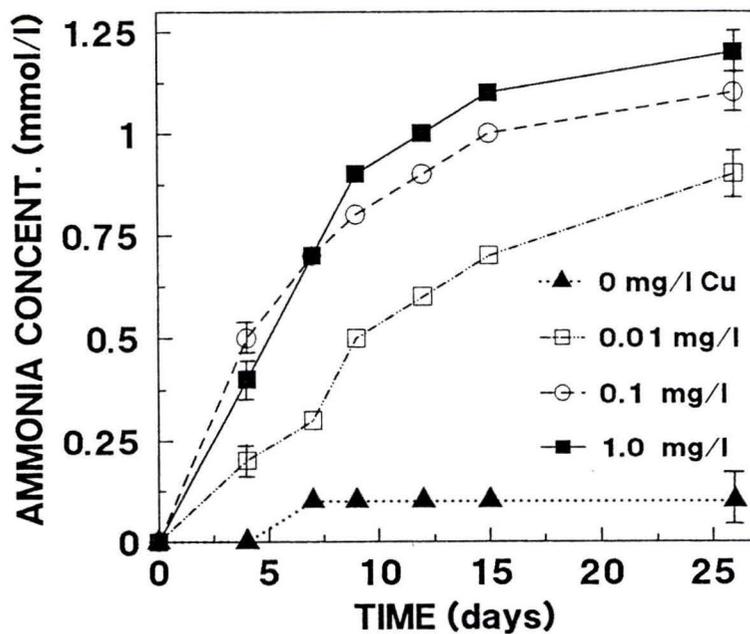


Figure 2-13. Hydrazine degradation at 30°C in serum vials; effect of copper concentration on (a) hydrazine degradation, (b) ammonia evolution following hydrazine degradation.



(a)



(b)

Figure 2-14. Hydrazine degradation at 45°C in serum vials; effect of copper concentration on (a) hydrazine degradation, (b) ammonia evolution following hydrazine degradation.

On the other hand, when copper was present hydrazine degraded faster in the polyethylene bottles than in the serum vials (Figure 2-2b). Ammonia was present as a degradation product only in the solutions containing copper (Figure 2-3), with a linear relationship being found between hydrazine degraded and ammonia produced at 25°C. Oxygen concentration in solutions containing copper stayed below 0.01 mmol l⁻¹ as long as some hydrazine remained (Figure 2-4). Once hydrazine had degraded completely, however, the oxygen levels in solution increased once more until reaching equilibrium with the air. The rate of oxygen replenishment was similar in the two types of containers.

When oxygen was in slight excess over hydrazine, degradation was initially fast and the stoichiometry of the reaction was 1:1 (Figure 2-12). Ammonia, if produced, was below detection limits. After the initial degradation, hydrazine concentration changed only slowly even though the solution was saturated with air. Ten per cent of the initial hydrazine concentration remained after 60 days.

Increasing the temperature to 30°C and 45°C had a marked effect on the rate of hydrazine autoxidation in distilled water. The effect of temperature was not so dramatic in solutions containing copper, however, probably because oxygen diffusion was limiting the autoxidation rate. After all the oxygen from the solution and the head space had disappeared the reaction slowed considerably (Figures 2-

13a and 2-14a). The initial autoxidation rate was a function of the logarithm of copper concentration, and at elevated temperatures, the relation between hydrazine degraded and ammonia produced was not linear. For example, at 30°C and 1 mg l⁻¹ copper (Figure 2-13a), hydrazine autoxidation rate decreased sharply after one day but ammonia was produced at the same initial rate during the second day as well (Figure 2-13b). This suggests that some reaction intermediate preceding the formation of ammonia was more stable than hydrazine. The ratio of mmols of ammonia produced to mmols of hydrazine degraded increased with temperature and with copper concentration (Table 2-4).

Table 2-4. Effect of temperature and copper concentration on the ratio: NH₃ produced (mmol l⁻¹)/N₂H₄ degraded (mmol l⁻¹).

Temperature (°C)	NH ₃ produced /N ₂ H ₄ degraded				
	Copper conc. (mg l ⁻¹)				
	0	.001	.01	.1	1.0
25	.002	ND ^a	ND	ND	.062
30	.007	ND	.046	.076	.078
45	.014	.084	.146	.173	.173

^a Not determined

Experiments carried out in a 1.5-liter Pyrex cell allowed for control of the gas atmosphere and for monitoring changes in pH throughout the degradation. Nitrogen, and a mixture of nitrogen and oxygen (88 and 12%), were bubbled directly from commercial tanks. However, in the case of air, a dilute NaOH trap had to be installed in order to remove CO₂. The trap had a small effect on the pH of the solution. This in turn had an effect on the hydrazine autoxidation rate. The effect was more evident at low copper concentrations. For this reason several traps were tested at low copper concentrations (Figure 2-18).

When purified nitrogen was bubbled through the cell containing hydrazine solution in either distilled water or 1 mg l⁻¹ Cu⁺² solution, no degradation had taken place after 20 days. This observation confirmed that no decomposition occurred in the absence of oxygen. When a stream of a mixture of nitrogen gas and oxygen (88 and 12%) was bubbled through a hydrazine solution in distilled water, half the amount of hydrazine had disappeared after 15 days (Figure 2-15); however, after the pH decreased below 7.5 the rate of degradation slowed considerably. Seventeen percent of the initial hydrazine remained after 50 days.

In the case of hydrazine solutions containing 1 mg l⁻¹ copper, most hydrazine had degraded after 80 minutes when either air or the mixture of nitrogen and oxygen were bubbled through the solution (Figure 2-16).

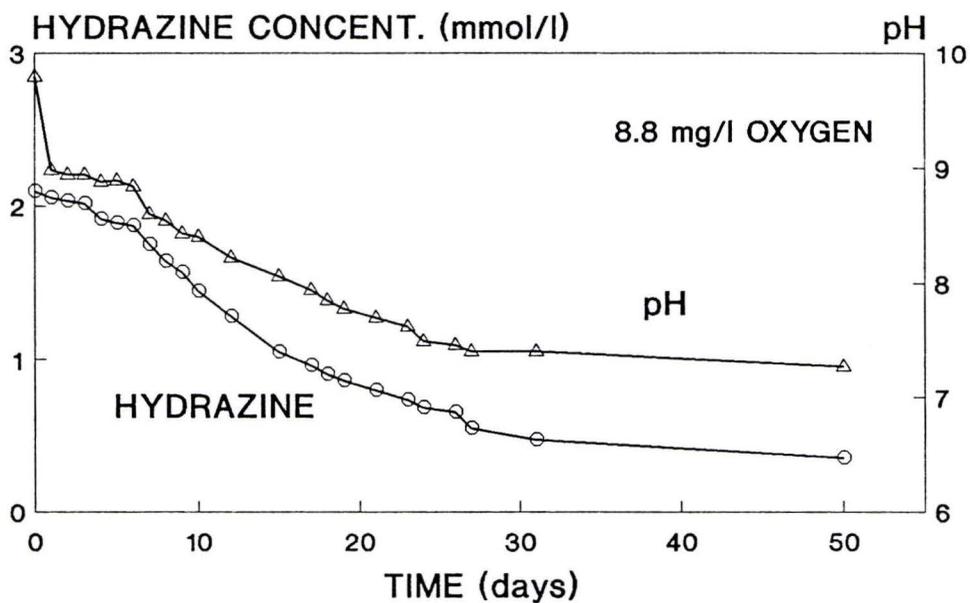


Figure 2-15. Hydrazine degradation in distilled water, at 22°C, in a 1.5-l Pyrex cell, maintained at constant O₂ tension.

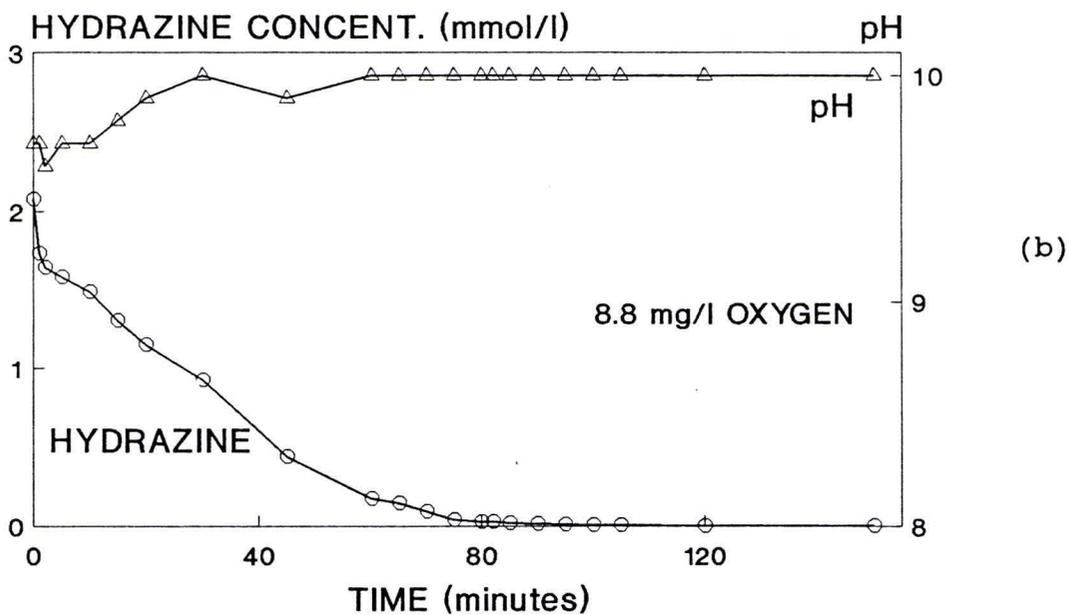
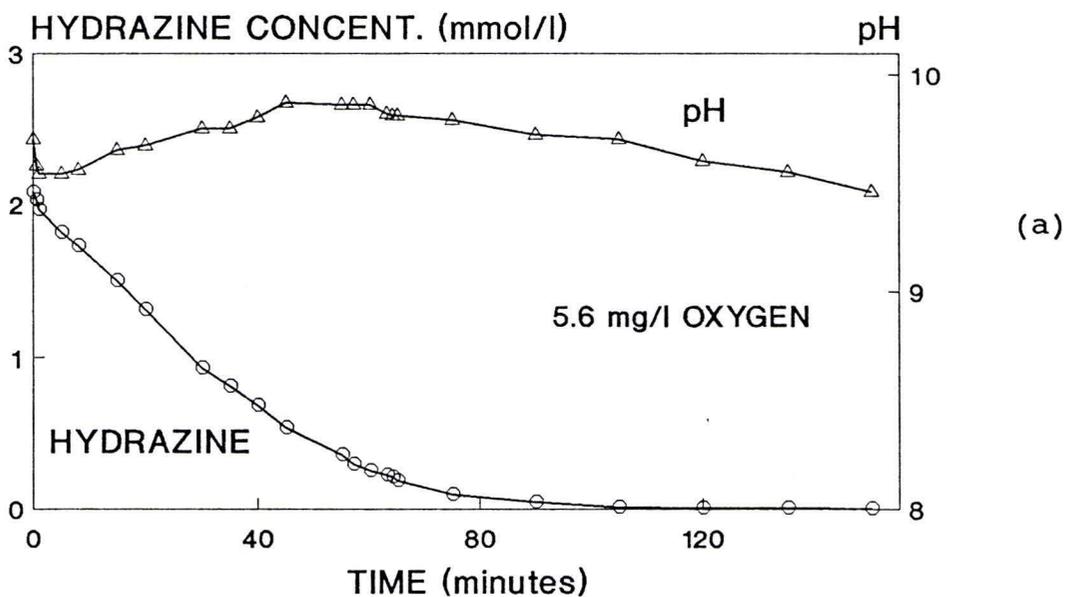


Figure 2-16. Hydrazine degradation in 1 mg l⁻¹ copper solution, at 22°C, in a 1.5-l Pyrex cell, maintained at constant O₂ tension: (a) no CO₂ trap, (b) dilute NaOH trap.

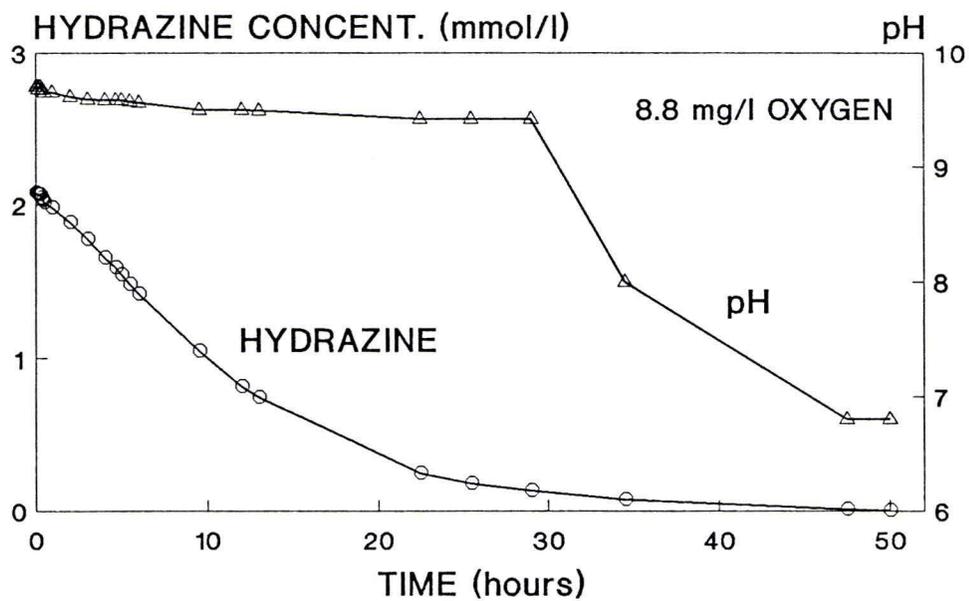


Figure 2-17. Hydrazine degradation in 0.01 mg l^{-1} copper solution, at 22°C , in a 1.5-l Pyrex cell, maintained at constant oxygen tension (CO_2 trap was dilute NaOH).

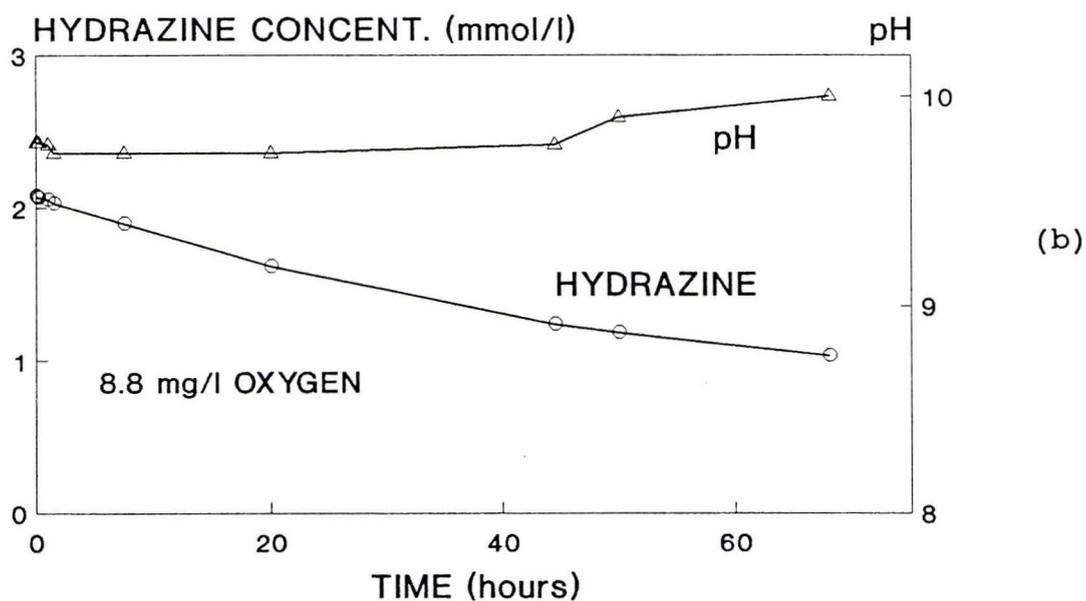
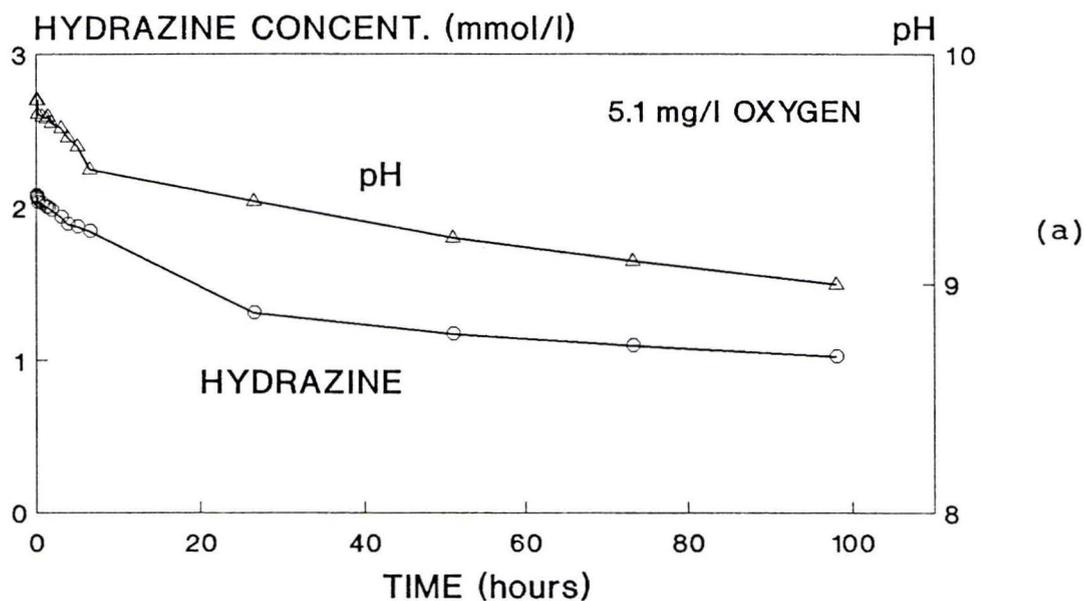


Figure 2-18. Hydrazine degradation in 0.001 mg l^{-1} copper solution, at 22°C , in a 1.5-l Pyrex cell, maintained at constant oxygen tension: (a) no trap, (b) dilute NaOH trap.

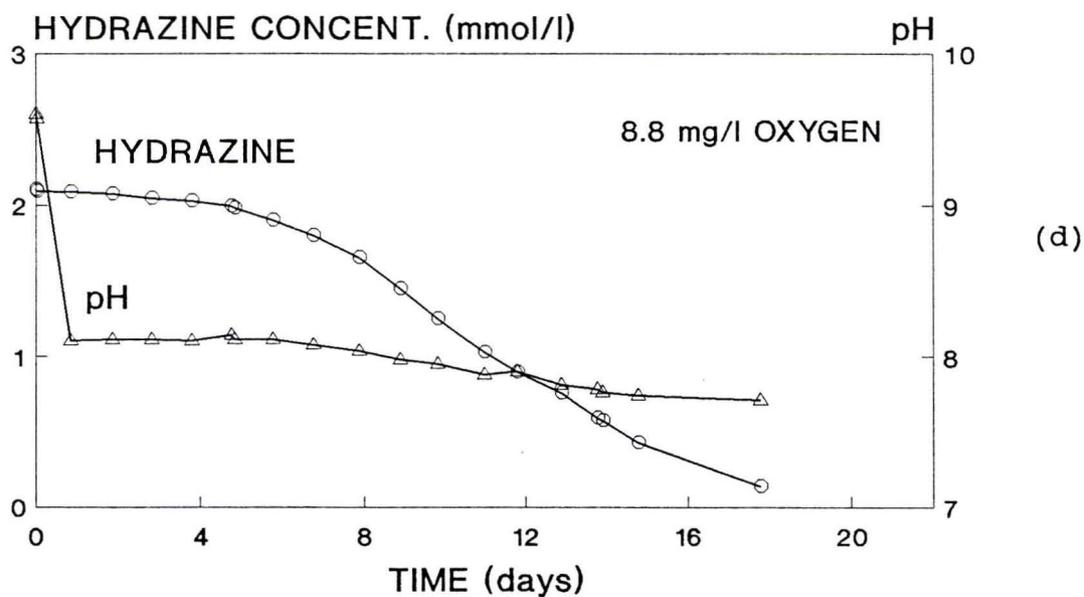
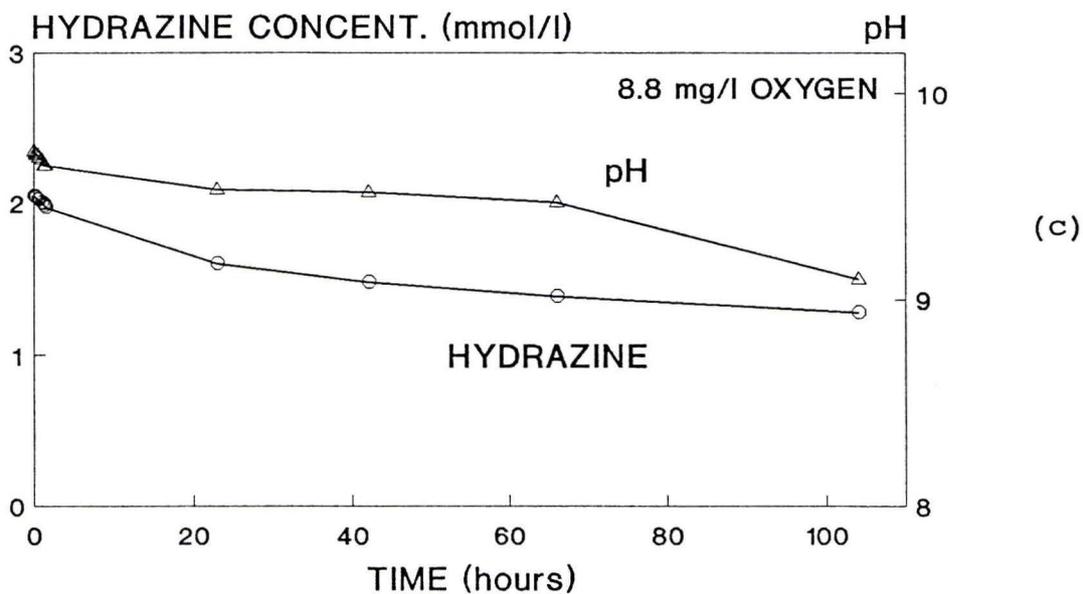


Figure 2-18 (cont). Hydrazine degradation in 0.001 mg l^{-1} copper solution. CO₂ Trap: (c) dilute NaOH followed by HCl and drierite, (d) dilute NaOH followed by dilute HCl.

The autoxidation rate was independent of oxygen concentration. The fact that the pH of the solution increased above its initial value when the hydrazine degradation rate was the highest suggests that ammonia was formed as a reaction product (Figure 2-16b).

When the hydrazine solution contained 0.01 mg l^{-1} copper it took 50 hours for all of the hydrazine to degrade (Figure 2-17). The pH then dropped once more to its value prior to the addition of hydrazine.

Hydrazine in the presence of $0.001 \text{ mg Cu}^{\text{II}} \text{ l}^{-1}$ was sensitive to the nature of the trap and to the pH of the solution. When the pH increased above its initial value, 50% of the added hydrazine had degraded after 60 hours. When the pH was subsequently decreased to 8 almost no hydrazine was oxidized during the first four days; however, only 6% remained after 18 days.

From the data obtained in the Pyrex cell it can be concluded that

- hydrazine autoxidation rate was first-order with respect to catalyst concentration.
- no decomposition occurred in the absence of oxygen.
- the reaction rate was independent of oxygen concentration in the range $0.05\text{-}0.275 \text{ mmol O}_2 \text{ l}^{-1}$.
- the solution pH had a strong effect on autoxidation rate, with the rate being higher at higher pH.

- the solution pH had a significant effect on length of the induction period and especially at low Cu^{II} concentrations.

System II--Degradation of Hydrazine in Natural Waters

Selected chemical properties of the two natural waters, Saint Johns River water and Santa Fe Lake water are presented in Table 2-5. The primary differences between these two waters were a higher pH and a higher salt content in the Saint Johns river water. It should be noted that the concentrations of Cu or Mn, the most active catalysts for hydrazine autoxidation, were below detection limits.

Upon addition of 10.3 mmol l^{-1} of hydrazine the pH of the solutions increased to 10.2. This experiment was conducted in serum vials, with the oxygen content remaining nearly in equilibrium with air throughout the study. This was due to large amount of head space coupled with air leaking through the caps. Differences in hydrazine disappearance observed in the untreated and autoclaved water (Figure 2-19a and 2-19b) were not significant due to the large scatter of the data; however, degradation in the control treatment of distilled water was always slower. Replicates in filtered samples were somewhat more homogeneous suggesting that solids in suspension had a small effect on the activity of the catalysts present.

Sterilization did not have a significant effect on the autoxidation rate (Figures 2-19b, and 2-19c), indicating

Table 2-5. Chemical properties of natural waters

Properties	Concentrations (mg l ⁻¹)	
	Santa Fe Lake	St. Johns River
pH (s.u.)*	6.2	8.0
O ₂	6.7	7.0
Organic C	6.23	7.16
K	0.4	5.7
Na	5.9	142
Ca	2.5	59
Mg	1.4	23
Cu	0.00	0.00
Fe	0.0	0.0
Mn	0.00	0.00
Zn	0.01	0.01
NH ₄ ⁺	0.2	0.1
NO ₃ ⁻	0.01	0.1
P	T**	T
Cl ⁻	12	320

* (s.u.) standard units

** T trace

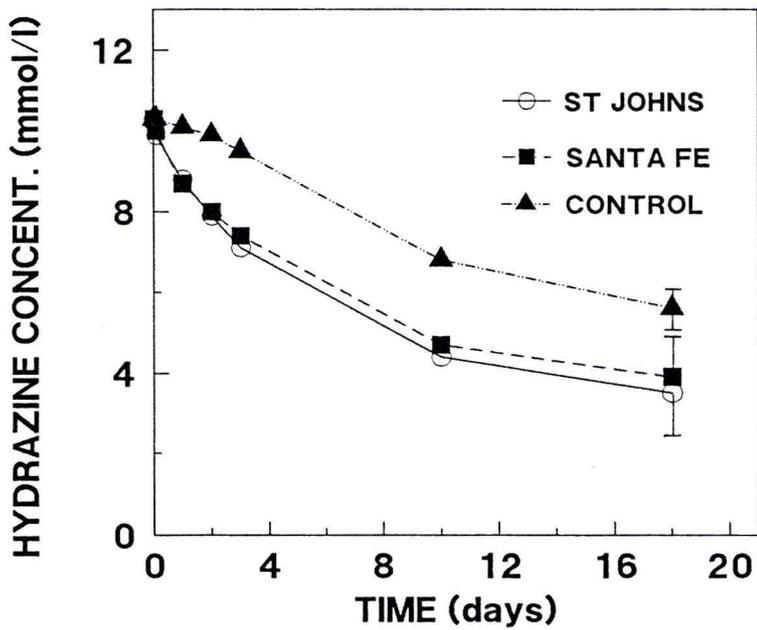
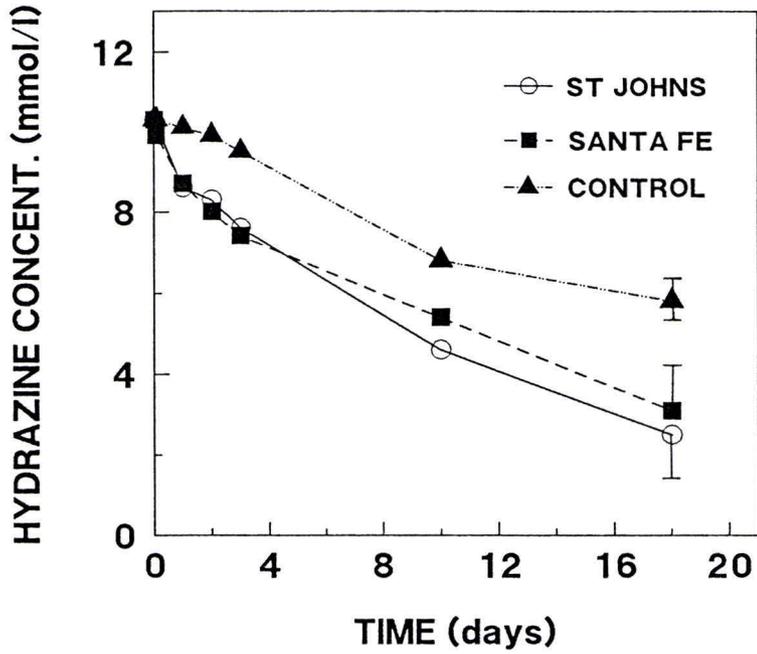
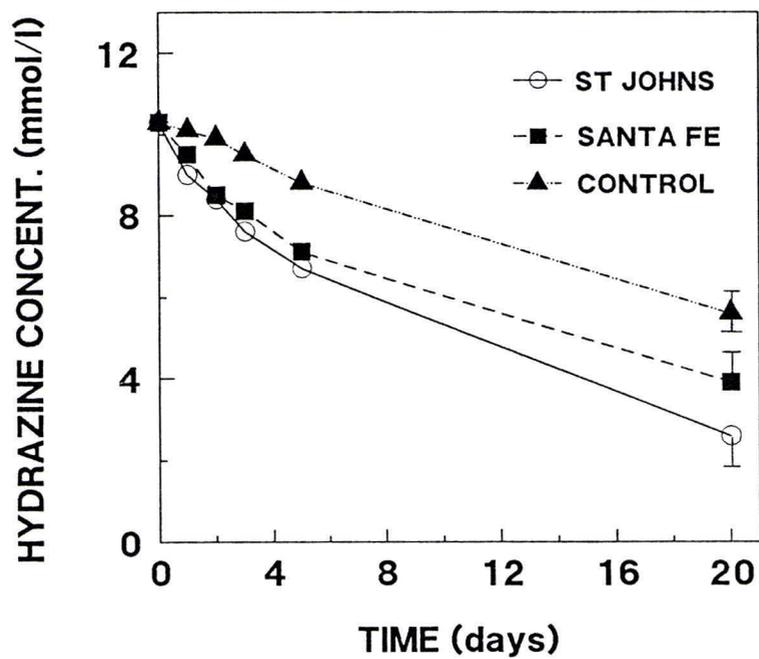


Figure 2-19. Degradation of hydrazine in natural waters at 22°C. Effect of sterilization: (a) untreated, (b) autoclaved.



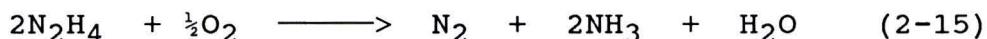
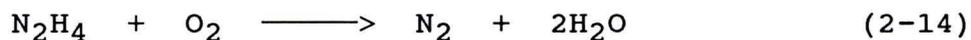
(c)

Figure 2-19 (cont.). Degradation of hydrazine in natural waters at 22°C. Effect of sterilization: (c) filtered.

that the mechanism was mainly chemical and not microbiological. This is in agreement with the findings of Ou and Street (1987), who reported that hydrazine concentrations above 5 mmol l⁻¹ might be toxic to microbial populations.

Conclusions

Hydrazine autoxidation in solution appeared to follow the mechanism proposed by Cahn and Powell (1954) and Higginson and Wright (1955) for the oxidation of hydrazine by Fe^{III} in acid solutions with the two basic reactions being:



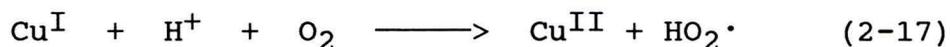
Hydrazine autoxidation occurred only at pH values above 4. Autoxidation did not occur when the pH value of the solution was below 4 even in the presence of a catalyst. In the absence of a catalyst the reaction was quite slow and followed only Equation 2-14. The rate of hydrazine autoxidation was affected by the nature of the reaction-vessel wall. This contradicts the results of Gaunt and Wetton (1966), who proposed that the active catalyst was Cu^{II} which had leached from the glass walls. In the studies

described above a wall effect was observed even when large amounts of catalyst were added.

Addition of copper even in concentrations as low as 0.001 mg l⁻¹ had a marked effect on the rate of hydrazine autoxidation. The rate of reaction was shown to be first-order with respect to catalyst concentration. The presence of copper also had an effect on the nature of the degradation path. Even though the main degradation product was probably N₂, NH₃ was detected when copper was present but it was not detected when the reaction took place in distilled water. Ammonia also was not detected when oxygen was present in excess of hydrazine. The fact that the amount of NH₃ produced was related to the amount of copper present (as well as to temperature) led us to believe that the first step of the reaction was the formation of the hydrazyl radical:



Cu^I was probably recycled back to Cu^{II} through the reaction:



Under conditions that could produce accumulation of N₂H₃· (for example, an excess of hydrazine over oxygen) dimerization of the hydrazyl radicals (Equation 2-5) had a

better chance to occur. This could give rise to the production of ammonia through the steps described previously (Equation 2-5 through 2-7). At high temperatures a time gap was found between hydrazine degradation and ammonia formation. No logical explanation was found for the fact that, in the presence of Cu^{II} , the reaction was faster in polyethylene bottles and involved a larger production of ammonia than in glass serum vials.

Results indicated that hydrazine autoxidation was catalyzed by the phosphate ion and that the degradation rate was first-order with respect to phosphate concentration. Extrapolation to zero phosphate concentration resulted in zero autoxidation rate at pH 7.

Autoxidation rate was also affected by the ionic strength of the solution, indicating that some step in the reaction involved the reaction of two ions having the same charge.

Since hydrazine autoxidation in bottles appeared to be controlled by the diffusion of oxygen into the solution, the effect of temperature on the degradation rate in the presence of copper was not as striking as the effect in the absence of copper.

There are so many factors affecting the rate of hydrazine autoxidation that it would be meaningless to propose at this time a half-life for hydrazine in natural waters. For the waters we studied the half-life was between

8 and 12 days. These values are comparable to the half-lives found by Braun and Zirrolli (1983) for monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) in pond and seawaters. More research is needed with natural waters of different chemical compositions. Conditions favorable for hydrazine disappearance include high pH, fast rate of oxygen diffusion, high temperature, and the presence of copper and/or manganese ions.

CHAPTER III
INTERACTIONS OF HYDRAZINE WITH
SAZ-1 MONTMORILLONITE

Literature Review

The degradation of hydrazine in aqueous solution has been widely studied. Most of the published information relevant to this subject was already cited in the aqueous-studies chapter. Reference was made to the importance of Cu^{+2} as a catalyst in the autoxidative degradation of hydrazine. It was also stated that the reaction was sensitive to the nature of the reaction-vessel wall, implying surface participation in the reaction.

Soils contain a large variety of active surfaces that have the potential to interact with hydrazine in a variety of ways. Furthermore, the ionic environment surrounding soil colloidal particles is quite different from that in the bulk of the solution. It is anticipated that the reactions taking place near particle surfaces will be affected by this environment.

Several authors have investigated the effect of added solids on the autoxidation rate of hydrazine. Ellis and Moreland (Cited by MacNaughton et al., 1978) found that the reaction was dramatically accelerated by the addition of activated carbon, copper sulfate, brick, or electrode

carbon. In contrast, MacNaughton et al. (1978) reported that the addition of excess surface area in the form of α -quartz, alumina, or kaolinite did not increase the oxidation rate and, if anything, actually caused a small reduction in the rate. The presence of small chips of concrete, however, caused significant oxidation of the hydrazine. This result is in agreement with the findings of rapid loss of hydrazine spilled on concrete pavement during spill clean-up studies (Stauffer and Eyl, 1978).

Hayes et al. (1981, 1984, 1988), in an extensive study of the interactions of hydrazine with soil constituents, found that degradation of hydrazine in the presence of homoionic Na^+ -, K^+ -, Mg^{+2} -, and Ca^{+2} -montmorillonite occurred to a greater extent than in the corresponding metal-chloride solutions (320 ppm). They suggested that the higher pH value of the clay suspensions contributed to the enhanced degradation observed in these systems. In the case of copper, cupric ions in both CuCl_2 solution (320 ppm) and Cu-montmorillonite suspension actively degraded hydrazine. The reaction more rapid in the suspension than in the chloride solution. The explanation given for this result was the increase in effective Cu^{+2} concentration on the clay compared to that in cupric chloride solution. Hydrazine would thus be brought into closer contact with exchangeable Cu^{+2} ions on the surfaces of the montmorillonite, resulting in a rapid degradation of hydrazine in the supernatant of

the clay suspension. However, after the hydrazine in the supernatant had apparently been degraded completely, hydrazine was still detected in the Cu^{+2} -montmorillonite suspension. Hydrolysis or reduction of exchangeable Cu^{+2} would cause an imbalance in the negative charge of the clay. Subsequently, this could be balanced by the adsorption of hydrazinium ions, which should be surface-stabilized against rapid degradation (Hayes et al., 1984).

In a series of studies on the autoxidation of hydrazine catalyzed by manganese, Lim and Fagg (1984) found that the reaction showed variable reaction orders over a narrow catalyst concentration range. With Mn concentrations above 1.6×10^{-4} M, the reaction rate dropped with respect to the rate at lower Mn concentrations. They postulated that the underlying cause of catalyst-inhibitor conversion in any liquid-phase autoxidation reaction is the ability of the metal ion to tie up and deactivate a radical-chain carrier through the reversible formation of a metal-radical complex. This complex is unreactive in the propagation chain but active in the termination-reaction sequence. The slow degradation rates of hydrazine in 320 ppm Cu^{+2} solutions as reported by Hayes et al. (1984) could be due to similar deactivation of free-radical chain carriers through complexation with Cu^{+1} .

It is generally assumed that cation-exchange reactions affect only the composition of the interlayer space, along

with some possible indirect effects on the clay surfaces themselves. The chemical composition of the phyllosilicate layers is assumed to remain unchanged. However, Rozenson and Heller-Kallai (1978), using Mössbauer spectroscopy, demonstrated that any chemical treatment of montmorillonite can cause changes in the oxidation state of structural iron. Oxidation of the structural iron during CEC determinations can lead either to a reduction in the exchange capacity or may be associated with deprotonation of some hydroxyl groups. Using the same technique, Griffith et al. (1980) found that hydrazine affected the oxidation state of iron in the structure of montmorillonite, with hydrazine not only reducing Fe^{+3} but also complexing with it. Their data showed that not all of the Fe^{+3} in montmorillonite was available for ready attack by hydrazine, but they did not report any quantitative data or conditions of the reaction. Therefore, the extent to which iron was reduced or the amount of hydrazine consumed in the process cannot be estimated.

From the data in the literature, several conclusions can be drawn:

- hydrazine can be oxidized in the presence of clay independently of the cation on the exchange complex. In the case of ions that are not easily reduced (K^+ , Na^+ , Mg^{+2} , Ca^{+2}), the amount of hydrazine degraded in the suspension was identical for all cations.

- hydrazine can also be oxidized by the cation on the exchange complex.
- hydrazine can be adsorbed directly by the clay by exchanging with cations on the surface. The amount of sorbate held by montmorillonite saturated with cations not in the transition series was similar for all except K^+ which did not adsorb any hydrazine at all.
- hydrazine can also be adsorbed by the clay by complexing with the cation on the exchange complex, with the reduced iron in the clay structure or with electronegative groups on the surface of the clay.
- the pH of the suspension has a significant effect on the degradation of hydrazine in the supernatant.

According to previously-discussed results from this study, hydrazine autoxidation appears to be unaffected by increasing Cu^{+2} concentrations above 10 mg l^{-1} . Taking this into account, the explanation given by Hayes et al. (1981, 1984) of increased decomposition at the Cu-clay surface due to increased concentrations may not be valid.

Clays that are completely saturated with a single cation, and especially copper, are not usually found in natural environments. For this reason it was decided to study the effect of Na-montmorillonite, partially saturated with Cu, on hydrazine adsorption and degradation. These

results were then compared with the degradation of hydrazine in Cu^{+2} solutions having the same amount of Cu added per unit volume. The objective was to determine the extent to which exchangeable metals can participate as active catalysts in the autoxidation of hydrazine.

Materials and Methods

Montmorillonite (SAz-1) fractions smaller than $0.5 \mu\text{m}$ were selected for the adsorption/degradation studies. This was accomplished by first washing the clay three times with 0.1N NaCl in order to obtain readily dispersed particles and saturated with a single cation. Samples were then dispersed by washing with deionized water until a negative test for chloride resulted. The smaller fractions were separated using an ultraspeed centrifuge. To minimize hydrolysis and dissolution of the clays, the suspension was stored in 0.1 N NaCl solution until ready for use. Just before use, the suspension was washed again with deionized water to remove excess NaCl from the supernatant. One-milliliter aliquots of different Cu^{+2} stock solutions were added to serum vials containing 9 ml of Na-saturated montmorillonite suspension (3 mg ml^{-1}). The same amount of Cu^{II} was added to vials containing 9 ml of distilled water. All vials were equilibrated and the Cu concentration in the supernatant was measured by differential-pulse stripping voltametry. The supporting electrolyte was NH_4^+ -citrate at pH 3.0.

Measurements were done with an EG&G Princeton Applied Research polarographic analyzer, model 384B.

Hydrazine was then added to the vials to give a final concentration of 2 mmol l⁻¹ or 4 mmol l⁻¹, and the contents were mixed using a vortex stirrer and covered with parafilm to minimize evaporation. Hydrazine in the suspension was measured at various time intervals using the PDBA method already described. A standard curve was developed by adding the same amount of clay to the standard volumetric flasks as was added to the volumetrics containing the samples. After centrifugation of the serum vials, hydrazine was measured in the supernatant. The amount of hydrazine that disappeared from the supernatant was considered to be degraded or adsorbed on the clay surface. The amount of hydrazine that disappeared from the suspension was considered to be degraded. This assumes that the difference between the amount of hydrazine in suspension and that in the supernatant represented that adsorbed onto the surface of the clay. This procedure was also used by Hayes et al. (1984).

Results and Discussion

Upon addition of Cu⁺² to the Na-montmorillonite suspension, the copper was distributed between the two phases. The results are presented in Table 3-1.

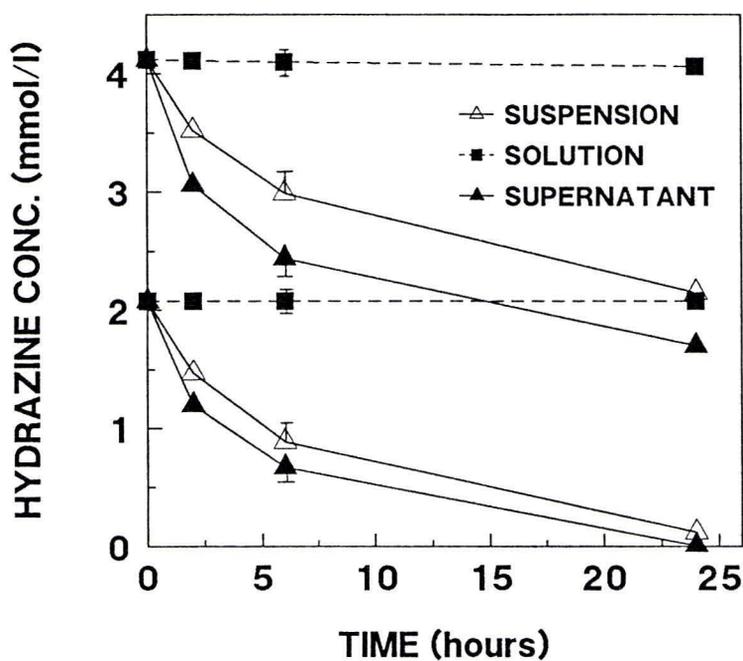
Table 3-1. Distribution of added Cu^{+2} between the supernatant and the surface of the clay.

Cu^{+2} added (mg/l)	Cu^{+2} supernatant (mg/l)	Cu^{+2} exchange ($\mu\text{eq/g}$ clay)	% of CEC with Cu^{+2}
0	0	0	0
0.01	b.d.l.*	-	-
0.1	0.015	0.98	0.12
1.0	0.19	9.4	1.2
10.0	1.31	100.0	12.5

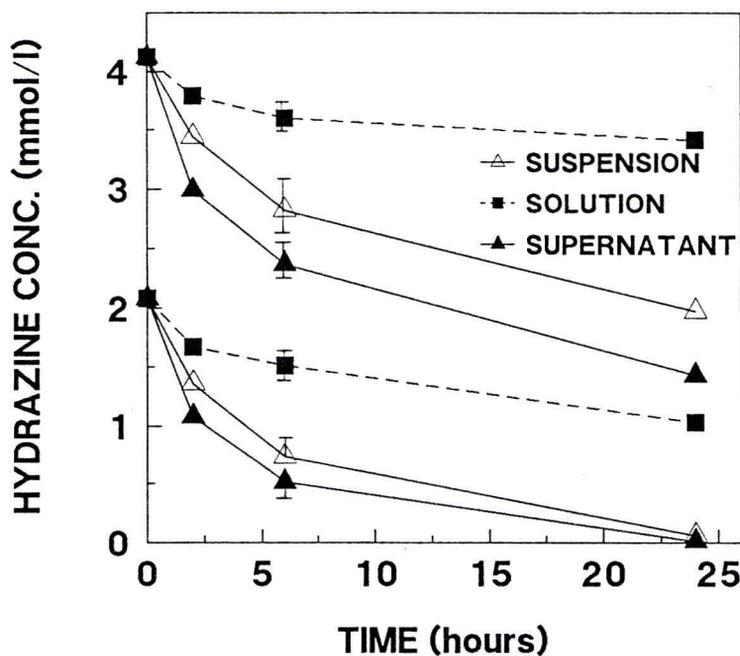
* b.d.l. below detection limits

About 85% of the Cu^{+2} was adsorbed by the clay and 15% remained in the supernatant.

Results from the degradation/adsorption studies are presented in Figures 3-1a, b, c, and d. Hydrazine did not degrade in solution during the first 24 hours in the absence of Cu^{+2} (Figure 3-1a), but the presence of the clay had a strong catalyzing effect on hydrazine degradation even when Cu was not present. It is evident from the slope of the suspension curves in Figure 3-1a that the rate of hydrazine degradation in suspension was independent of hydrazine concentration. The amount of hydrazine adsorbed by the clay in the absence of copper remained nearly constant until



(a)



(b)

Figure 3-1. Effect of Cu^{2+} on hydrazine degradation in solution and in the presence of a Na-Montmorillonite suspension: (a) absence of Cu , (b) $0.1 \text{ mg l}^{-1} \text{ Cu}$.

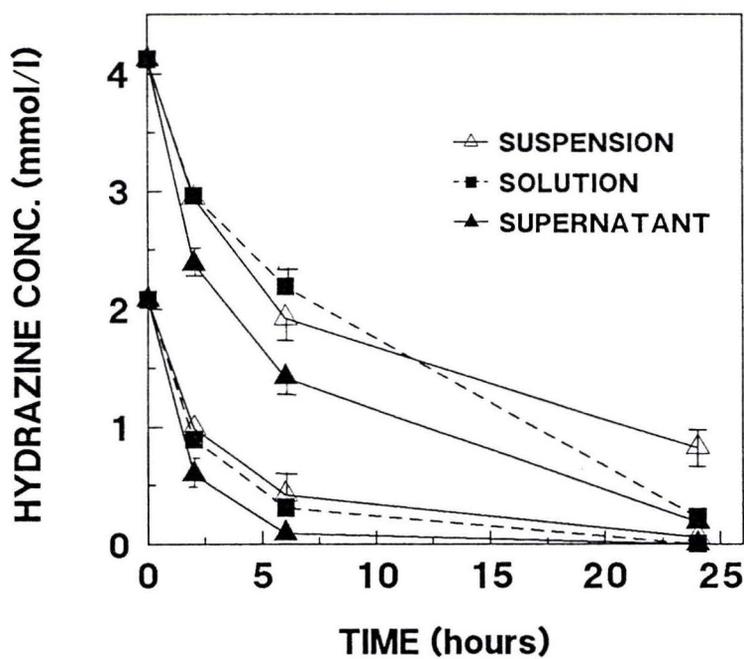
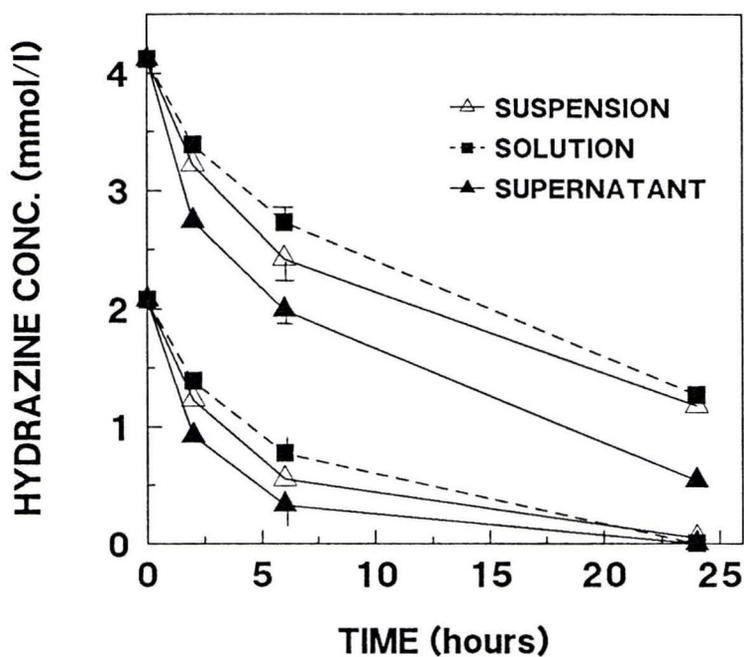


Figure 3-1 (cont.). Effect of Cu^{+2} on hydrazine degradation in solution and in the presence of a Na-Montmorillonite (Saz-1) suspension: (c) 1.0 mg l^{-1} Cu, (d) 10.0 mg l^{-1} Cu.

hydrazine was almost depleted from the suspension, and was higher for the higher initial hydrazine concentration.

In the presence of Cu^{+2} , hydrazine degradation was also faster in the suspension (Figures 3-1b, c, d); however, it should be noted that the clay itself had a catalytic effect, addition of Cu^{+2} had a stronger effect on the hydrazine degradation rate in solution than in suspensions having the same total Cu concentration. The amount of hydrazine adsorbed by the Na/Cu-montmorillonite complex was only slightly affected by the concentration of Cu and, similar to the case with Na-montmorillonite, remained nearly constant until hydrazine in the suspension was almost depleted. Higher initial hydrazine concentrations resulted in a larger amount of hydrazine being adsorbed by the clay.

In order to evaluate the effect of each of the individual components of the suspension on hydrazine adsorption and degradation, it was that the effects of the clay, the Cu in the supernatant and the Cu adsorbed on the clay were independent and additive.

There are several facts supporting this conclusion. Hayes et al. (1984) reported that degradation of hydrazine by homoionic clays was independent of the exchangeable cation as long as the cation was not easily reducible. This suggests that the clay itself was the active component in the oxidation or catalytic autoxidation of hydrazine.

It is probable that, even in the presence of a reducible cation on the clay surface, this type of interaction could take place. Due to the fact that the fraction of exchange sites saturated with Cu is small (Table 3-1), it is assumed that the extent of hydrazine degradation due to the clay itself is constant and independent of the exchangeable Cu concentration.

Using this assumption, the amount of hydrazine affected (degraded and/or adsorbed) by Cu^{+2} was calculated as the difference in hydrazine concentration of the supernatants for the Na/Cu-montmorillonite and the Na-montmorillonite suspensions (Tables 3-2 and 3-3) at each Cu concentration.

The amount of hydrazine degraded by Cu in suspension was calculated by subtracting the amount of hydrazine removed from suspension in the absence of Cu (degraded by the clay itself) from the amount of hydrazine removed from suspension in the presence of Cu (degraded by the clay and by the Cu) at each Cu concentration (Tables 3-2 and 3-3).

Degradation due to Cu was similar at both hydrazine concentrations. Comparing the extent of oxidation due exclusively to Cu in the suspensions and in the Cu solutions we observed that Cu had a stronger effect in solution (Table 3-2 and 3-3). A closer look at the data reveals that degradation due to Cu in the suspensions is of the same magnitude as degradation in solution at only one-tenth the amount of Cu added (values followed by superscripts a and

Table 3-2. Hydrazine balance after two hours of interaction (initial hydrazine concentration 2.08 mM).

Status of hydrazine	Cu ²⁺ added (mg l ⁻¹)			
	0	.1	1.0	10.0
Autoxidized in Cu solution (mmol/l/2h)	.00	.36 ^a	.70 ^b	1.18
Degraded by clay (mmol/l/2h)	.60			
Adsorbed by clay (mmol/l)	.28			
Adsorbed by clay or Cu (mmol/l)		.28	.32	.38
Autoxidized in suspension due to Cu (mmol/l/2h)		.12	.24 ^a	.50 ^b
Adsorbed by Cu (mmol/l)		.00	.04	.10

a, b See text, pages 75 and 78.

Table 3-3. Hydrazine balance after two hours of interaction (initial hydrazine concentration 4.12 mM).

Status of hydrazine	Cu ²⁺ added (mg l ⁻¹)			
	0	.1	1.0	10.0
Autoxidized in Cu solution (mmol/l/2h)	.00	.32 ^a	.72 ^b	1.16
Degraded by clay (mmol/l/2h)	.60			
Adsorbed by clay (mmol/l)	.46			
Adsorbed by clay or Cu (mmol/l)		.46	.48	.56
Autoxidized in suspension due to Cu (mmol/l/2h)		.08	.30 ^a	.58 ^b
Adsorbed by Cu (mmol/l)		.00	.02	.10

a, b See text, pages 75 and 78.

b). Keeping in mind that only 15% of the added copper remained in the supernatant, these data suggest that degradation takes place primarily in the supernatant and that exchangeable Cu was less active than Cu in the supernatant in catalyzing hydrazine degradation.

On the other hand, the amount of hydrazine adsorbed by Cu on the exchange complex was in the order of 1.2 to 1.5 moles of hydrazine per mole of exchangeable Cu. This hydrazine either could be complexed with Cu or could be neutralizing negative charge sites on the clay surface after Cu^{+2} was reduced to Cu^{+1} .

Conclusions

Hydrazine degraded faster in the presence of clay than it did in solution even in the absence of copper; however, if part of the hydrazine degradation in suspension is attributed to the effect of the clay itself and part to the effect of copper, either in the supernatant or on the exchange complex, copper had a stronger effect on the rate of hydrazine degradation in solution than in suspension. Comparing the extent of hydrazine degradation due to copper in solution and in suspension it appears evident that most of the autoxidation was taking place in the supernatant (i.e. involving free Cu^{II}). It is possible that Cu^{II} on the exchange complex was initially reduced to Cu^{I} and complexed by the hydrazyl radical or by hydrazine, making it inactive

towards the transfer of oxygen. It is also possible that the redox potential of exchangeable copper is lower than that of free copper making the reduction of oxygen more difficult.

The amount of hydrazine adsorbed by the clay was related to the initial hydrazine concentration; however, after initial adsorption it remained unchanged, even though hydrazine in the supernatant continued to disappear.

The amount of hydrazine degradation that can be attributed to catalysis by the clay was identical for both initial hydrazine concentrations. It is not clear if this fraction of hydrazine was autoxidized, or if it was consumed by reaction with Fe^{III} in the clay structure.

CHAPTER IV
INTERACTIONS OF HYDRAZINE WITH CLAY AND SOIL
SUSPENSIONS UNDER ANAEROBIC CONDITIONS

Introduction

Determination of the extent of hydrazine adsorption by soil components, and the stability of the complexes thus formed, is critical to the study of the compound's environmental fate. Adsorption depends on the reactivity of the surface functional groups present on soil colloids, and also on the chemical properties of hydrazine.

In order to understand the nature of hydrazine-soil interactions it would be useful to first consider the main functional groups on the surface of soil solids. Since the clay fraction (diameter $< 2\mu\text{m}$) presents the highest amount of surface exposed for adsorption, the constituents commonly found in this fraction need to be examined in greater detail. These include mainly silicate clays, oxyhydroxides, and humic colloids.

For the phyllosilicate-type minerals, the functional group associated with the siloxane surface is the ditrigonal cavity. Its reactivity depends on the origin of the charge imbalance in the clay structure itself. If there is no cation isomorphic substitution (kaolinite would be an

example), the cavity acts like a very soft Lewis base (Sposito, 1984), and is likely to complex only neutral dipolar molecules like water or unprotonated hydrazine. If the isomorphic substitution is located in the octahedral layer (as in the case of montmorillonite), the charge on the siloxane surface can distribute itself over 10 surface oxygen atoms associated with a single octahedron (Sposito, 1984). This type of cavity is able to form complexes with cations as well as with dipolar molecules.

On the other hand, when the substitution occurs in the tetrahedral layer, the surface charge is more localized and distributes itself over the 3 surface oxygen atoms associated with one tetrahedron. This makes possible the establishment of much stronger bonds with dipolar molecules and cations and also the formation of inner-sphere complexes between the siloxane surface and some cations.

Another type of surface functional group present in most inorganic colloids is the hydroxyl group. In silicate clays, the hydroxyl group may be coordinated to one, or two, cations. The charge arises predominantly at the edges from broken bonds and is pH-dependent. Both aluminol and silanol groups can form inner-sphere and outer-sphere complexes with cations.

A variety of functional groups, including COOH, phenolic OH, enolic OH, lactone, quinone, hydroxyquinone, ether, alcoholic OH, amino, and sulfonic, have been reported

in humic substances (Stevenson, 1982). The ability of these groups to complex metals and polar molecules is a function of the pH of the suspension and depends largely on the stereochemical configuration of the molecule.

Hydrazine is a base, slightly weaker than ammonia ($pK_a=7.96$). At pH values below the pK_a , hydrazine exists mainly as the protonated form and can take part in cation exchange reactions. Hayes et al. (1988) reported that, at pH 4, hydrazine sorption from solution was greatest for Na^{+1} -clays because the process involved simple exchange of Na^{+1} for hydrazinium ($N_2H_5^{+}$) ions. They suggested that cation exchange was less important than hydrolysis of and coordination to the cation in a Ca^{+2} -montmorillonite system. In a study with humic acid preparations at pH 4, Isaacson and Hayes (1984) found that hydrated hydrazine was more extensively held by H^{+} - than by Ca^{+2} - or Al^{+3} -saturated humic substances. This reflected the greater ability of the hydrazinium ion to exchange with H^{+} , and to disrupt hydrogen bonding rather than divalent- and polyvalent-cation bridges between polymer strands.

Due to the polarity of the N-H, bond hydrazine can form hydrogen bonds with electronegative groups on the surfaces of the clays and organic matter. Davis et al. (1988) using diffuse-reflectance spectroscopy, found that the primary surface-hydrazine interaction with silica, silica-alumina and alumina surfaces was hydrogen bonding. On the other

hand, Johnston et al. (1988) studied the interaction of hydrazine with kaolinite using non-invasive Raman, X-ray diffraction, and transmission FT-IR of kaolinite samples deposited on a ZnSe window. X-ray diffraction data showed expansion of the kaolinite lattice upon intercalation by hydrazine. FT-IR spectra indicated that strong hydrogen bonds were formed between the intercalated hydrazine species and inner-surface hydroxyl groups on the kaolinite interlamellar surface.

Unprotonated hydrazine is a strong nucleophile that can take part in condensation reactions with carbonyl groups in humic substances to form hydrazone. This is the basis of the procedure used by Schnitzer and Skinner (1965) to determine the concentration of carbonyl groups in soil organic matter. Isaacson and Hayes (1984) showed that this reaction took place even at pH 4.0. They also pointed out that the maximum rates should occur when the pH of the media is close to the pKa of hydrazine. The condensation complex is subject to hydrolysis. Hydrazine can also take part in substitution reactions at positions activated by carbonyl groups (Szabo et al. 1978; Isaacson and Hayes, 1984).

Aside from the direct adsorption of hydrazine to the surface of soil colloids, hydrazine can also be adsorbed through complexation with cations on the exchange complex (Griffith et al., 1980) or through replacement of water by hydrazine in the hydration shell (Hayes et al., 1984).

An assumption inherent in determining adsorption isotherms is that loss of the sorbate from solution is a valid measure of adsorption. The assumption is valid for most sorbates, but not so for the highly reactive hydrazine species. Earlier studies indicated that, in aqueous systems with O_2 present, hydrazine undergoes autoxidation that can be mainly represented by Equation 4-1:



As was seen in a preceding chapter, other side reactions are also possible (Equation 4-2). This is especially true when Cu^{+2} is present as a catalyst:



In order to avoid autoxidation, the following studies were conducted in an anaerobic incubator.

Besides oxygen, there are other oxidants present in the soil solution and in soil particles that may consume hydrazine and cannot be adequately accounted for. For example, metals such as Fe^{+3} , Cu^{+2} , Mn^{+3} , are widely present in soils and can be reduced by hydrazine to lower valence states. Griffith et al. (1980), using Mössbauer spectroscopy, showed that hydrazine not only reduces Fe^{+3} in

montmorillonitic clay and humic acids but also complexes with it.

As discussed in Chapter II hydrazine decomposes into N_2 , NH_3 , and/or H_2 in the presence of metals in a powdered form or supported by alumina or other solids. To our knowledge there is no mention in the literature of hydrazine decomposition taking place under conditions that can occur in natural environments; however, the possibility of such mechanism contributing to the total loss of hydrazine from soils cannot be ignored.

Exclusive of reactions that degrade hydrazine, the remaining possibilities for hydrazine disappearance from the supernatant would be as follows:



or



where X- represents the ion-exchange sites on clays or soils and Na^+ and H^+ represent potential counter ions. Such exchange reactions are reversible and non-destructive. Another type of retention mechanism is a sorptive reaction that may or may not be reversible:



where X-] are surface functional groups on mineral or organic surfaces that are able to retain the hydrazine molecule.

The adsorption isotherms of these studies were obtained under conditions that minimize reactions 4-1 and 4-2 and therefore partition the retention of hydrazine into reactions 4-3, 4-4, and 4-5, except for some hydrazine that might decompose or react with oxidants other than O₂ if present in clays and soils. Subsequent desorption experiments shed light on the magnitude of reversible adsorption of hydrazine in the systems studied.

Materials and Methods

Clays

The montmorillonite (SAz-1) and kaolinite (KGa-1) samples used in these studies were obtained from the Clay Minerals Repository, Department of Geology, University of Missouri.

Soils

The three upper horizons of an Arredondo fine sand (grossarenic paleudult, loamy, siliceous, hyperthermic): Ap (0-20 cm), E1 (20-80), and E2 (80-150), were collected from NW Alachua County, Florida. Samples were air dried and sieved through a 2 mm sieve before use.

Analytical Methods

Hydrazine was analyzed using the PDBA method described in Chapter II. Sodium, Fe, and Si in the clay and soil supernatants were measured by atomic absorption spectroscopy.

Experimental Procedures

Clay studies

Cation exchange capacity determination. In a preliminary experiment to compare the ability of hydrazine to engage in exchange reactions, the cation exchange capacity of kaolinite and montmorillonite saturated with N_2H_5^+ , Na^+ , and Ca^{+2} was measured at various pH values (4, 5, 6, and 7). Two grams of air-dried clay were placed in a preweighed centrifuge tube. They were washed three times with X-Acetate (where X represents Na^+ , Ca^{+2} , or N_2H_5^+) buffered at different pH values. Afterwards they were washed three times with 0.1 N X-Cl at the same suspension pH with the last supernatant being kept for analysis of X, Cl^- , and pH. The volume of occluded solution was calculated by weight difference. The cations in the exchange complex were extracted 5 times with $\text{Mg}(\text{NO}_3)_2$, and the supernatants were collected and brought to volume. X and Cl^- were analyzed in the collected extracts. The CEC was calculated by subtracting the amount of Cl^- from the amount of X in the final solution.

Adsorption isotherms. Initially an isotherm was calculated for a Na-montmorillonite suspension prepared in the same way as the suspension for the degradation studies described in Chapter III. Ten-milliliter aliquots containing 3 mg ml^{-1} of clay ($< 0.5 \mu\text{m}$) were placed in serum vials under anaerobic conditions. Increasing amounts of hydrazine solution were added to the vials. Afterwards the vials were stoppered, shaken and allowed to equilibrate in the absence of oxygen for 24 hours. The pH of the suspension was not controlled, and thus increased depending on the extent of hydrazine adsorption. Hydrazine concentration left in the supernatant was measured, and adsorption was calculated as the difference between the amount of hydrazine added and the amount remaining in the supernatant.

Adsorption isotherms of kaolinite and montmorillonite clays were measured at pH 4.0 and pH 8.0. Four grams of air-dried kaolinite and 1.0 gm of air dried montmorillonite without any pretreatment were placed in preweighed polyethylene centrifuge bottles. The contents were washed five times with 0.1 N NaCl (previously adjusted to the pH of the experiment either with HCl or NaOH) in order to saturate the exchange complex with Na^+ . All of the steps except centrifugation were carried out in an anaerobic incubator to minimize autoxidation. Afterwards, the excess of NaCl was removed by repeated washing with distilled water adjusted to the pH of the experiment. The supernatants from the last

wash were kept for analysis of Fe, Si, and Na. The volumes were brought to 20 ml with distilled water and increasing amounts of hydrazine solution were added to the centrifuge tubes. Samples were shaken and left to equilibrate for 24 hours. After centrifugation hydrazine, Na, Fe, Si, and pH in the supernatant were measured. Hydrazine adsorbed was calculated as the difference between the amount of hydrazine added and the amount left after equilibration with the suspension. The difference between the amount of sodium in the supernatant after equilibration with the suspension and before adding hydrazine is an indication of the amount of hydrazine exchanged with Na^+ on the exchange complex. All samples were also analyzed for Fe and Si in solution, after preliminary analyses indicated that excessive Na in solution was probably due to clay decomposition. After the determination of the isotherms, the samples with the highest hydrazine concentration were exhaustively washed with 0.1 N KCl to remove hydrazine from the clays.

Soil studies

Two different sets of isotherms were measured. In the first set, at pH 4.8 and 8.0, a constant ionic strength of 0.01 was maintained with CaCl_2 . The pH of the hydrazine stock solutions was lowered with HCl. Because $\text{N}_2\text{H}_5^+\cdot\text{Cl}^-$ contributes to the solution salt content as well, its concentration was taken into account when preparing the solutions of constant ionic strength. The isotherms were

obtained over a wide concentration range. Five gram samples of each Arredondo soil horizon were placed in glass serum vials and 10 ml of constant-ionic-strength solutions with increasing hydrazine concentration were added. After incubation for 48 hours under anaerobic conditions, samples were centrifuged and hydrazine was measured in the supernatant.

The second set of isotherms was conducted at pH 4.0 and pH 8.0. Twenty grams of soil were washed five times with 0.1 N NaCl at the desired pH, to saturate the exchange complex with a single cation. The procedure followed afterwards was identical to that for the clays already described above. After the last hydrazine extraction with KCl, the soils were also extracted with 0.1 N HCl.

Results and Discussion

Cation Exchange Capacity

The objective of the cation exchange capacity (CEC) determinations was to study the possibility of measuring selectivity coefficients for the exchange between ($\text{Na}^+/\text{N}_2\text{H}_5^+$) and ($\text{Ca}^{+2}/\text{N}_2\text{H}_5^+$). The values obtained using our technique are considerably lower than those reported by van Olphen and Fripiat (1979) (2.0 meq/100g for kaolinite and 120 meq/100g for montmorillonite). Kaolinite (KGa-1) had a very low CEC at the pH values selected in this study. The fact that the measured CEC for kaolinite using hydrazinium

Table 4-1. Cation exchange capacity of kaolinite and montmorillonite.

X-Clay	pH	CEC
		meq/100 g
Na-kaolinite	4.4	0.6 (± 0.1)
	5.2	0.6 (± 0.1)
	5.8	0.7 (± 0.1)
	6.1	0.9 (± 0.2)
Ca-kaolinite	4.2	0.5 (± 0.1)
	5.2	0.7 (± 0.2)
	6.1	0.9 (± 0.1)
	6.9	1.0 (± 0.1)
N ₂ H ₅ -kaolinite	3.3	0.7 (± 0.2)
	4.0	1.0 (± 0.2)
	4.9	2.4 (± 0.3)
	6.9	3.3 (± 0.2)
Na-montmorillonite	4.2	58 (± 1)
	5.1	59 (± 2)
	6.0	56 (± 3)
	6.6	57 (± 1)
Ca-montmorillonite	4.3	86 (± 1)
	5.2	87 (± 1)
	6.3	87 (± 1)
	7.1	88 (± 1)
N ₂ H ₅ -montmorillonite	4.3	53 (± 4)
	4.4	51 (± 3)
	4.5	48 (± 4)
	6.0	44 (± 5)

ion (Table 4-1) was higher than that for Na^+ or Ca^{+2} suggests that hydrazine was also adsorbed in non-exchangeable form and that the extent of this type of adsorption increased with pH. It would be difficult to measure the ability of hydrazinium ions to compete with other cations in this system because of the inability to distinguish between "exchangeable" and "adsorbed" hydrazine.

In the case of montmorillonite the values for CEC obtained with hydrazinium ion were comparable to those obtained with Na^+ but lower than those for Ca^{+2} . Increasing the pH resulted in a lower CEC. This could be the result of inability of the hydrazinium ion to compete with the Ca^{+2} that was originally on the clay. It also could be the result of some hydrazine being degraded by autoxidation during the extraction procedure.

Adsorption of Hydrazine on Na-kaolinite

Under acidic conditions (pH=4.0) and low hydrazine concentrations, the primary mechanism of retention was on exchange sites (Figure 4-1). This was evident because of the concurrent appearance and disappearance of equal amounts of Na^+ and hydrazine, respectively, in the supernatant. A slight rise in the pH of the clay suspension (Table 4-2) confirms that N_2H_5^+ was the main species disappearing from solution, because unprotonated hydrazine would have to react with protons to maintain the appropriate protonation deprotonation equilibrium. At higher concentrations some

hydrazine was adsorbed onto sites that had not been formerly occupied by Na^+ . Iron or silicon were not detected in the supernatant before or after the addition of hydrazine. This would indicate that kaolinite was stable in suspension even in the presence of hydrazine, and that no iron coatings were reduced by hydrazine. Exhaustive washing of the clay samples with 0.1 N KCl resulted in a 90% recovery of initially-adsorbed hydrazine from the highest hydrazine additions (Figure 4-9).

Under alkaline conditions (pH=8.0), the pattern was different. The amount of hydrazine adsorbed at any given solution concentration was much higher than at pH 4.0. However, the amount of sodium displaced by hydrazine was similar to that at pH 4.0 (Figure 4-1). Most of the adsorbed hydrazine was apparently in unprotonated form. This resulted in a lower clay suspension pH upon addition of the hydrazine (Table 4-3). Only 80% of the hydrazine adsorbed was recovered after washing with KCl (Figure 4-9).

Adsorption of hydrazine on Na-montmorillonite

The initial adsorption isotherm for Na-montmorillonite was conducted without controlling the pH (Figure 4-2). The fact that adsorption decreased at high hydrazine concentrations led us to believe that hydrazinium ion was preferentially adsorbed. At low hydrazine concentrations the pH value of the suspension was lower and a higher percentage of the hydrazine added was in protonated form. At

Table 4-2. Analysis of kaolinite supernatants at pH 4.

Before adding hydrazine		After adding hydrazine			
Fe mmol/l	Si mmol/l	Hydrazine mmol/l	pH	Fe mmol/l	Si mmol/l
0.00	0.0	0.30	5.6	0.00	0.0
0.00	0.0	0.91	5.2	0.00	0.0
0.00	0.0	1.54	4.9	0.00	0.0
0.00	0.0	2.19	4.8	0.00	0.0
0.00	0.0	2.68	4.7	0.00	0.0
0.00	0.0	3.31	4.8	0.00	0.0

Table 4-3. Analysis of kaolinite supernatants at pH 8.

Before adding hydrazine		After adding hydrazine			
Fe mmol/l	Si mmol/l	Hydrazine mmol/l	pH	Fe mmol/l	Si mmol/l
0.00	0.0	0.12	6.8	0.00	0.0
0.00	0.0	0.45	6.4	0.00	0.0
0.00	0.0	0.92	6.4	0.00	0.0
0.00	0.0	1.41	6.8	0.00	0.0
0.00	0.0	2.20	7.4	0.00	0.0
0.00	0.0	3.04	7.5	0.00	0.0

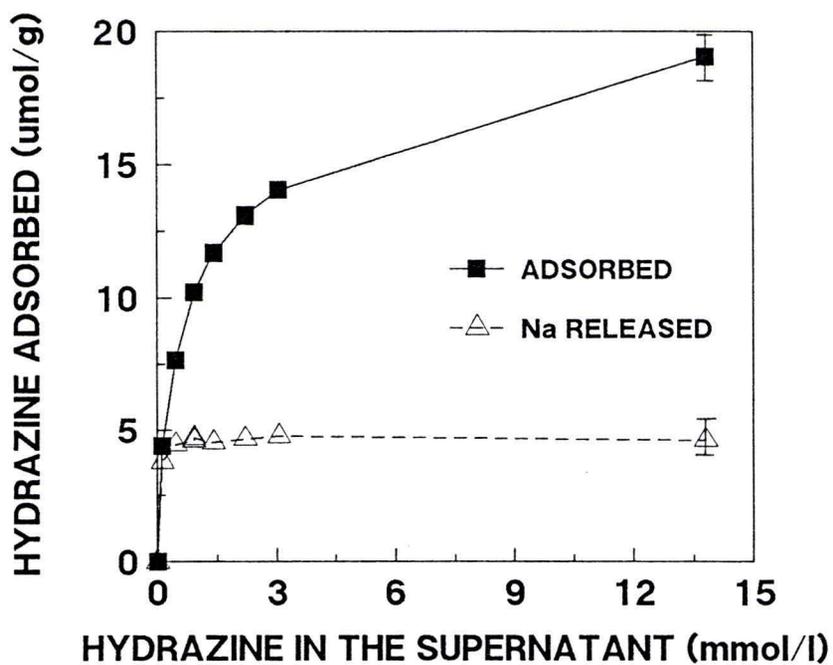
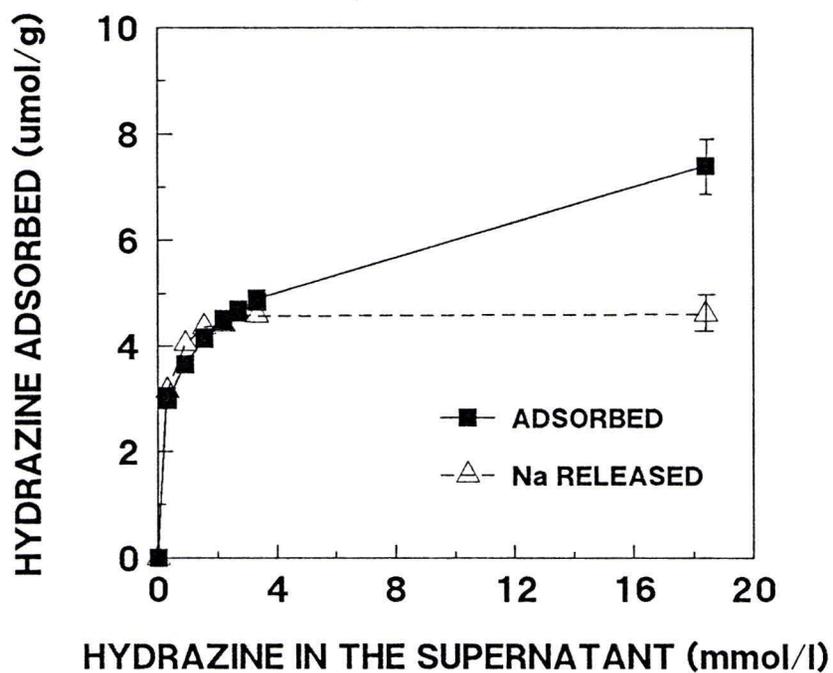


Figure 4-1. Adsorption isotherms of hydrazine on Na-kaolinite in the absence of O_2 : (a) pH 4, (b) pH 8.

higher hydrazine concentrations the pH of the suspension should be higher and less hydrazinium ion would be available for adsorption, thus resulting in less hydrazinium adsorption at higher hydrazine concentrations.

A subsequent set of isotherms at controlled pH confirmed that the primary mechanism of adsorption for this clay suspension was cation exchange, both at pH 4 and 8 (Figure 4-3). In both cases the pH of the suspension increased up to 2 units (Tables 4-4 and 4-5). At pH 8, the amount of Na released by the clay was higher than the amount of hydrazine being adsorbed. After analyzing for silicon and iron, it was found that small amounts of montmorillonite had dissolved. The excess sodium in the supernatant was probably associated with the dissolved clay. Adsorption of hydrazine was lower in the montmorillonite suspension at pH 8. This rationale is logical, because the pKa of hydrazine indicates that the majority of the hydrazine at this pH is in neutral form rather than the $N_2H_5^+$ form.

Extensive washing of the clay with KCl removed 60% of the adsorbed hydrazine at pH 4.0 and the same percentage was recovered at pH 8.0 (Figure 4-9).

Adsorption of Hydrazine on Arredondo Soil.

Selected chemical properties of the upper Arredondo soil horizons are presented in Table 4-6. The most striking differences among them with respect to potential for hydrazine adsorption are a higher clay and organic matter

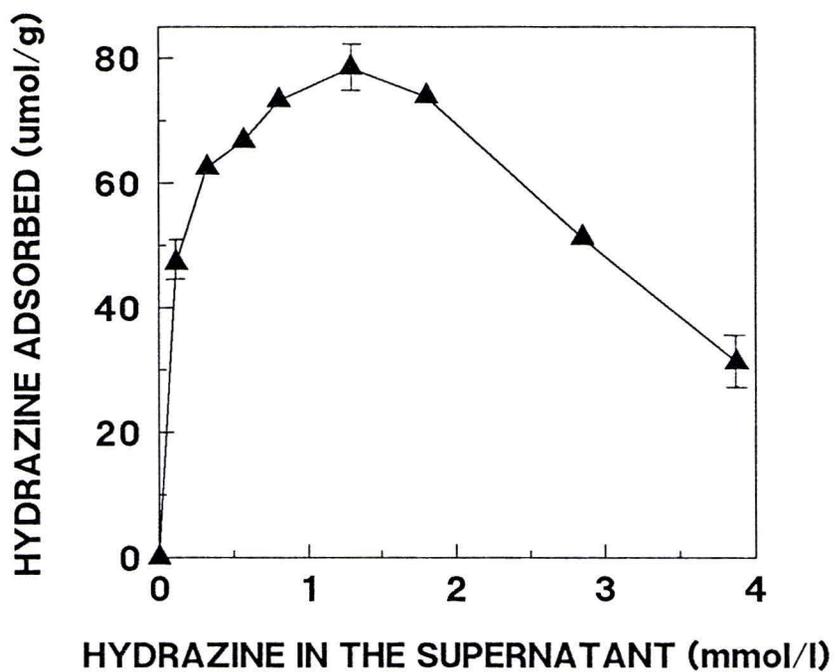


Figure 4-2. Adsorption isotherm of hydrazine on Na-montmorillonite in the absence of O_2 without pH control.

Table 4-4. Analysis of montmorillonite supernatants at pH 4.

Before adding hydrazine		After adding hydrazine			
Fe mmol/l	Si mmol/l	Hydrazine mmol/l	pH	Fe mmol/l	Si mmol/l
0.03	6.3	0.01	6.6	0.06	16.8
0.03	6.3	0.02	6.4	0.06	11.9
0.03	8.3	0.07	6.2	0.04	6.0
0.03	8.3	0.18	6.2	0.00	0.9
0.03	4.3	0.33	6.0	0.00	0.4
0.03	3.6	0.53	5.8	0.00	0.4

Table 4-5. Analysis of montmorillonite supernatants at pH 8.

Before adding hydrazine		After adding hydrazine			
Fe mmol/l	Si mmol/l	Hydrazine mmol/l	pH	Fe mmol/l	Si mmol/l
0.06	9.4	0.13	9.5	0.04	8.8
0.07	13.2	0.49	9.8	0.05	11.2
0.04	4.3	0.98	9.4	0.04	8.1
0.04	3.7	1.57	9.4	0.03	5.7
0.04	6.1	1.72	9.5	0.06	16.1
0.03	3.6	2.29	9.2	0.05	10.3

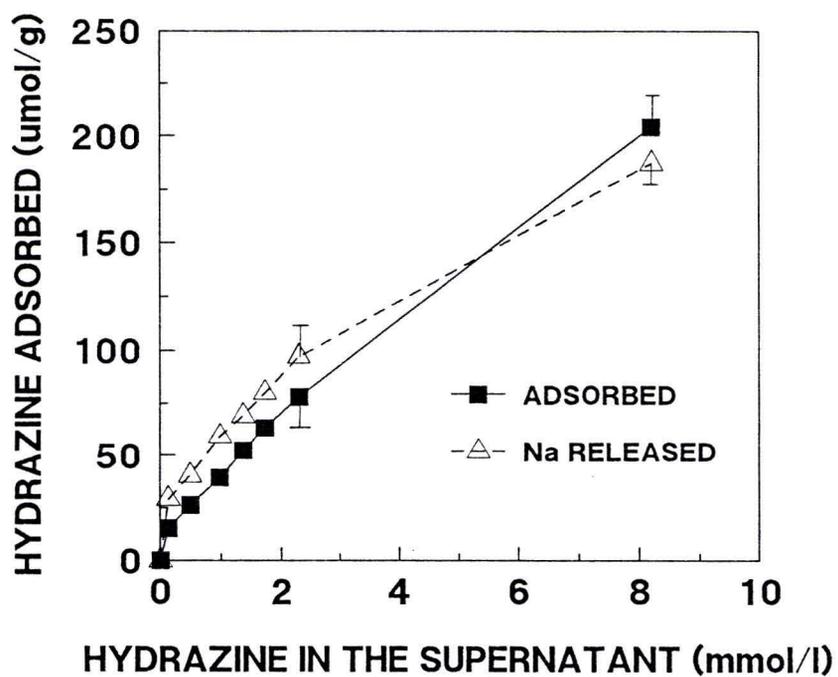
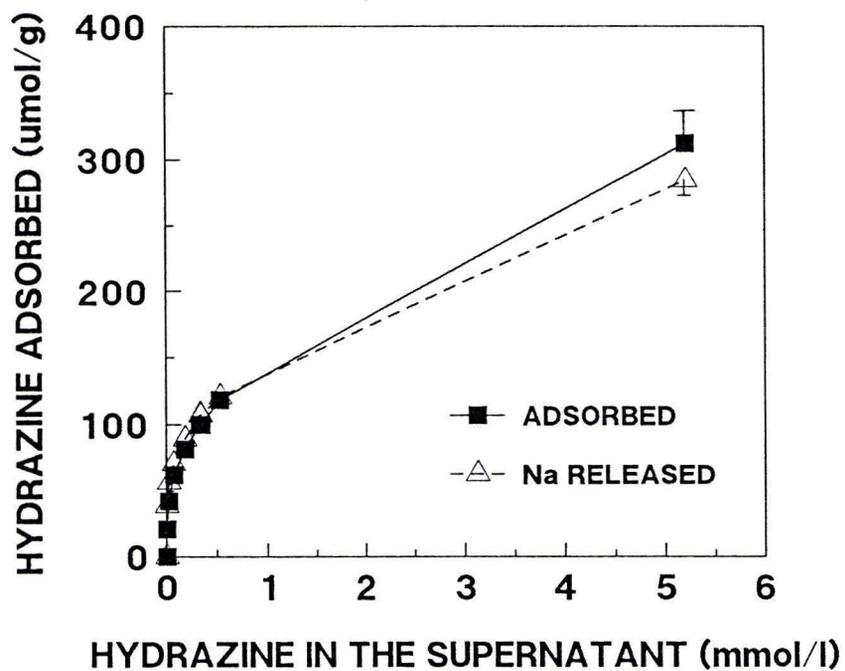


Figure 4-3. Adsorption isotherms of hydrazine on Na-montmorillonite in the absence of O_2 : (a) pH 4, (b) pH 8.

content for the Ap horizon and a lower concentration of metals in the E₂ horizon.

Table 4-6. Properties of upper Arredondo soil horizons

Horizon	Clay	O.M.	pH	Cu	Mn	Al	Fe
	%	%		mg / Kg soil			
Ap	2.6	1.84	6.0	0.04	9.6	221	17.6
E ₁	1.7	0.34	5.9	0.20	2.5	250	17.6
E ₂	1.8	0.14	5.4	0.16	1.2	86	10.4

The first set of adsorption isotherms for the Arredondo horizons are presented in Figures 4-4, 4-5, and 4-6. The isotherms were measured in an anaerobic incubator, maintaining a constant ionic strength. Hydrazine adsorption was well correlated with organic matter content. Adsorption was higher at pH 8.0 in all three horizons, indicating that both species, the neutral hydrazine and the charged hydrazinium were adsorbed. Comparing these isotherms with counterparts measured without the addition of CaCl₂ (Figures 4-7, 4-8) reveals that the amount of hydrazine adsorbed was smaller when CaCl₂ was present. This is likely due to the monovalent hydrazinium ion (N₂H₅⁺) having to compete with the divalent Ca⁺² for exchange sites.

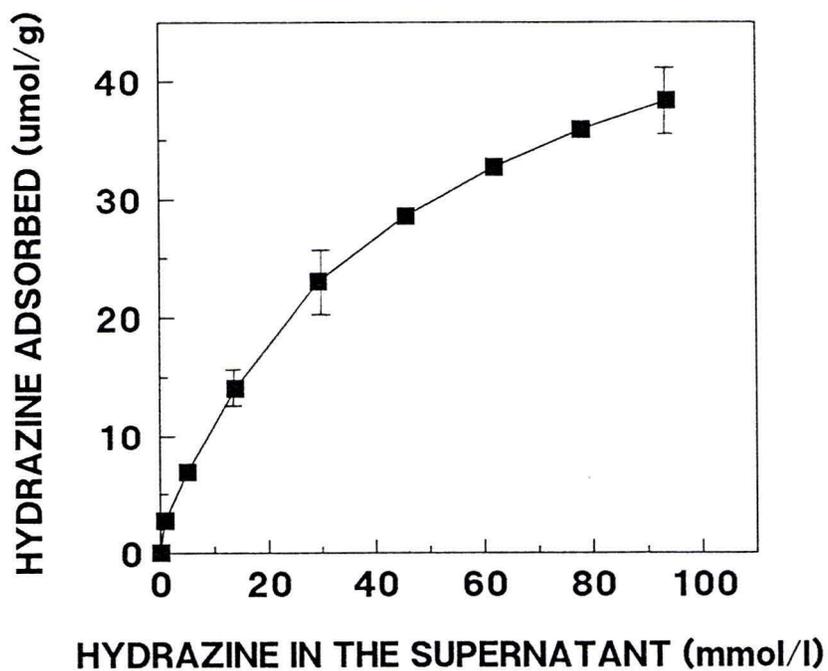
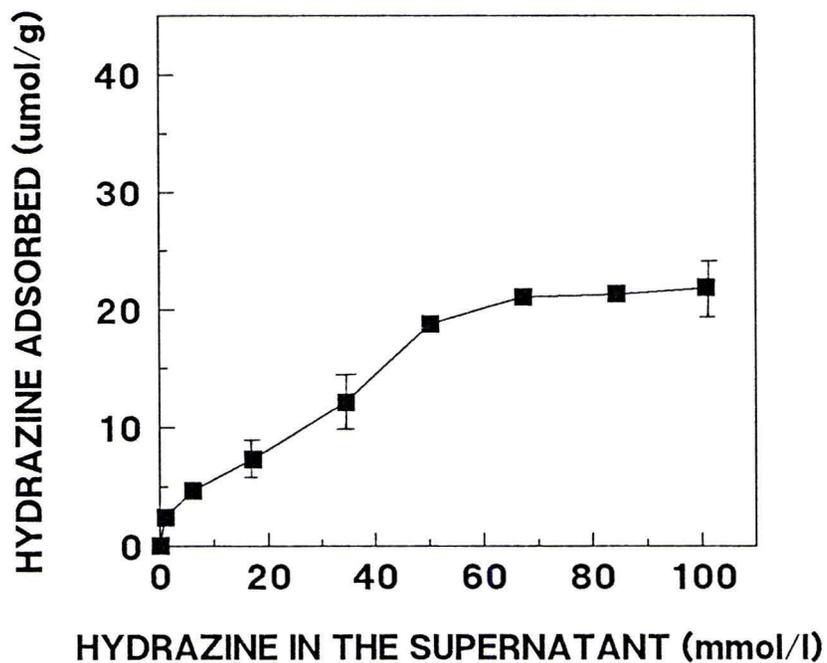


Figure 4-4. Adsorption isotherms of hydrazine on Arredondo-Ap in the absence of O_2 (ionic strength 0.01 N): a) pH 4.8, b) pH 8.0.

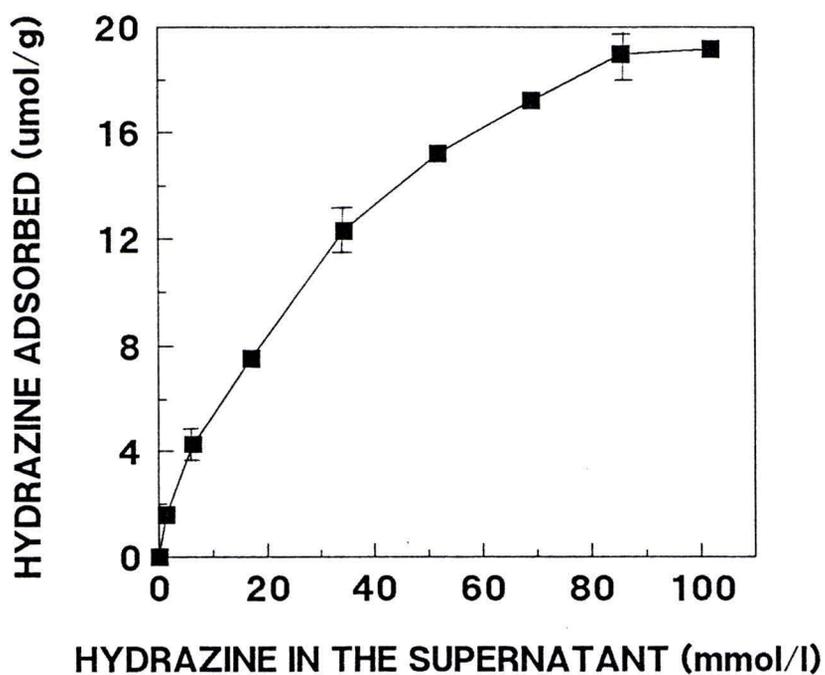
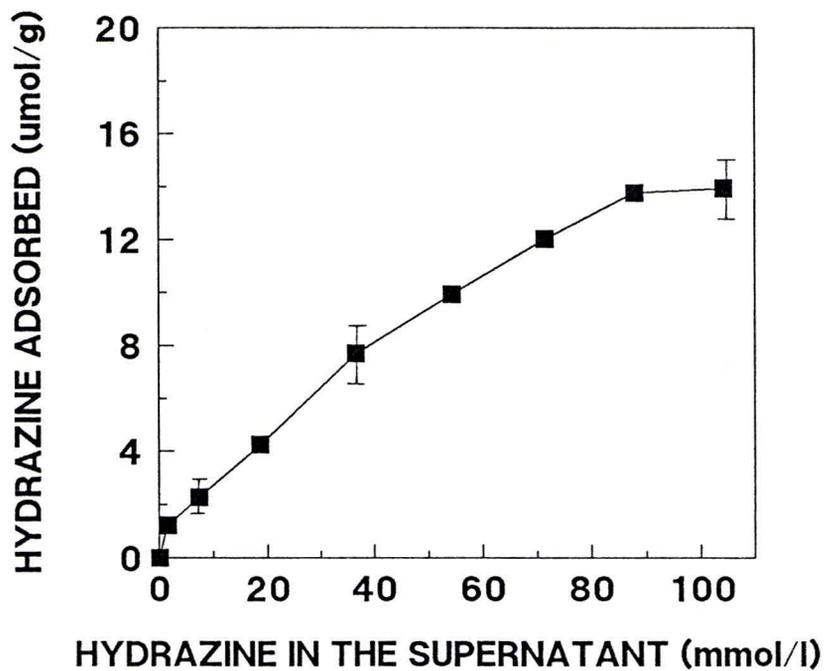


Figure 4-5. Adsorption isotherms of hydrazine on Arredondo-E₁ in the absence of O₂ (ionic strength 0.01 N): a) pH 4.8, b) pH 8.0.

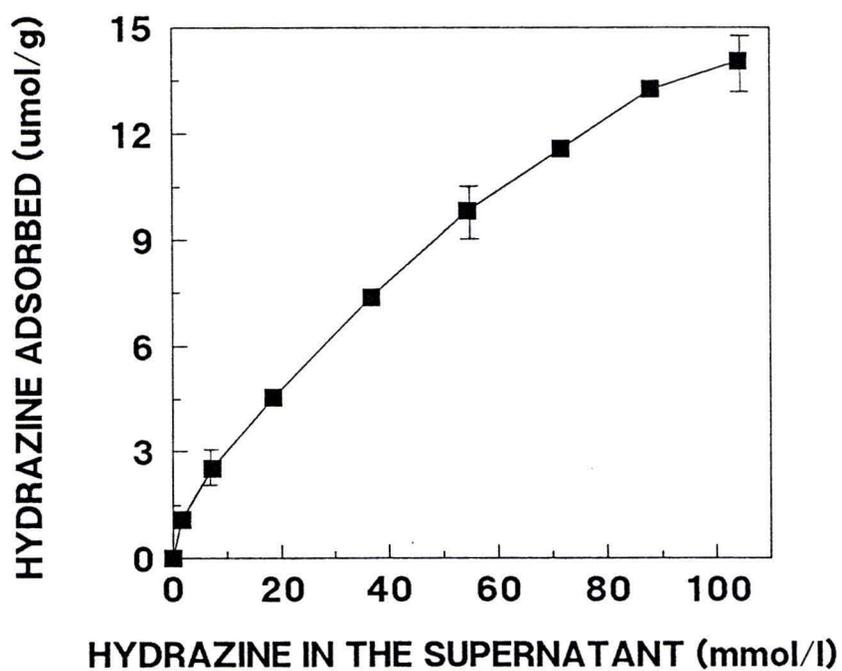
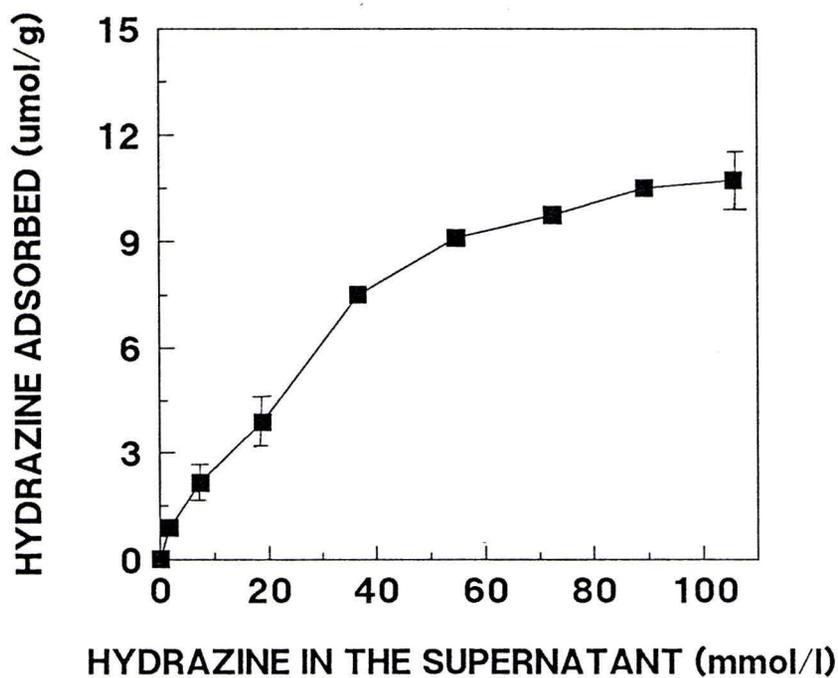


Figure 4-6. Adsorption isotherms of hydrazine on Arredondo-E₂ in the absence of O₂ (ionic strength 0.01 N): a) pH 4.8, b) pH 8.0.

Measuring a second set of isotherms for the Arredondo soil horizons also allowed us to distinguish the amount of hydrazine adsorbed from the amount of hydrazine retained on exchange sites, by measuring Na^+ displaced from the surface of the colloids (Figures 4-7 and 4-8).

The main mechanism for hydrazine retention at pH 4 and low hydrazine concentrations in the Arredondo Ap horizon was cation exchange. However, at higher concentrations more than 60% of the hydrazine interacted with a different type of binding site. Because the Ap horizon had almost 2% organic matter, we believe hydrazine was adsorbed on organic surface functional groups such as carbonyl groups. No hydrazine was recovered during the desorption process with 0.1 N KCl. The results were similar at pH 8.0 except for a greater amount of adsorption at high concentrations in non-exchangeable form. At this pH we were able to extract with KCl 20% of the hydrazine initially adsorbed (Figure 4-9). A subsequent extraction with 0.1N HCl removed 5% of the adsorbed hydrazine at pH 4.0 and 7% at pH 8.0.

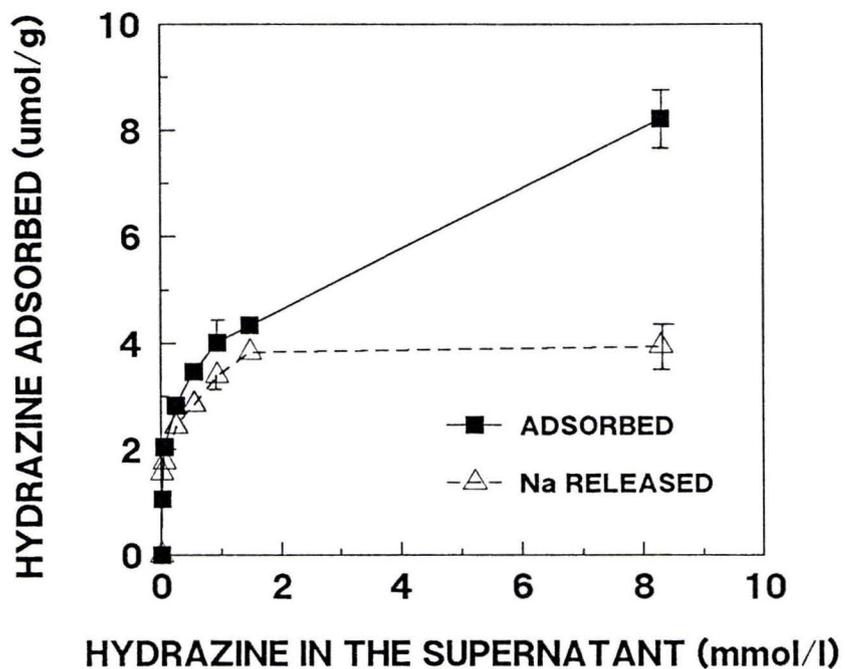
The Arredondo E₂ horizon contained significantly less clay and organic matter than the Ap horizon. Consequently, it adsorbed less hydrazine. Under acidic conditions (pH 4.0) the primary mechanism of adsorption was cation exchange, especially at low hydrazine concentrations. This is supported by the fact that the amount of Na^+ released by the

Table 4-7. Analysis of Arredondo-Ap supernatants at pH 4.

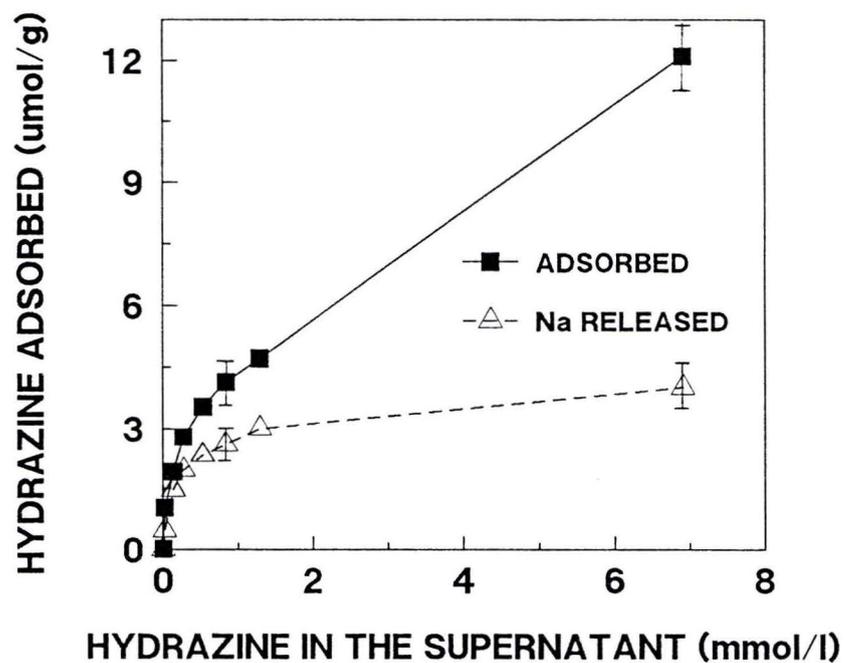
Before adding hydrazine		After adding hydrazine			
Fe mmol/l	Si mmol/l	Hydrazine mmol/l	pH	Fe mmol/l	Si mmol/l
0.14	1.3	0.01	6.4	0.15	1.3
0.12	1.1	0.05	6.0	0.12	1.0
0.12	1.2	0.25	5.7	0.00	0.2
0.15	1.5	0.54	5.4	0.00	0.5
0.13	1.3	0.93	5.3	0.01	0.5
0.16	1.5	1.47	5.0	0.02	0.4

Table 4-8. Analysis of Arredondo-Ap supernatants at pH 8.

Before adding hydrazine		After adding hydrazine			
Fe mmol/l	Si mmol/l	Hydrazine mmol/l	pH	Fe mmol/l	Si mmol/l
0.08	0.5	0.02	6.6	0.16	1.7
0.08	0.4	0.14	6.4	0.16	1.8
0.08	0.4	0.27	6.5	0.19	1.7
0.08	0.5	0.52	6.5	0.16	1.2
0.07	0.6	0.83	6.6	0.20	1.7
0.09	0.6	1.28	6.7	0.20	1.7



(a)



(b)

Figure 4-7. Adsorption isotherms of hydrazine on Arredondo-Ap in the absence of O_2 : a) pH 4, b) pH 8.

Table 4-9. Analysis of Arredondo-E₂ supernatants at pH 4.

Before adding hydrazine		After adding hydrazine			
Fe mmol/l	Si mmol/l	Hydrazine mmol/l	pH	Fe mmol/l	Si mmol/l
0.00	0.0	0.25	5.8	0.00	0.3
0.00	0.0	0.90	5.5	0.00	0.2
0.00	0.0	1.57	5.3	0.00	0.5
0.00	0.2	2.28	5.1	0.00	0.5
0.00	0.1	3.04	4.9	0.00	0.5
0.00	0.1	3.77	4.8	0.00	0.5

Table 4-10. Analysis of Arredondo-E₂ supernatants at pH 8.

Before adding hydrazine		After adding hydrazine			
Fe mmol/l	Si mmol/l	Hydrazine mmol/l	pH	Fe mmol/l	Si mmol/l
0.04	0.8	0.18	7.0	0.16	1.5
0.07	0.8	1.18	7.0	0.01	0.4
0.08	0.8	1.87	7.0	0.01	0.5
0.07	0.8	2.76	7.0	0.01	1.2
0.05	0.5	3.17	7.3	0.01	0.6
0.04	0.4	11.9	7.7	0.01	0.6

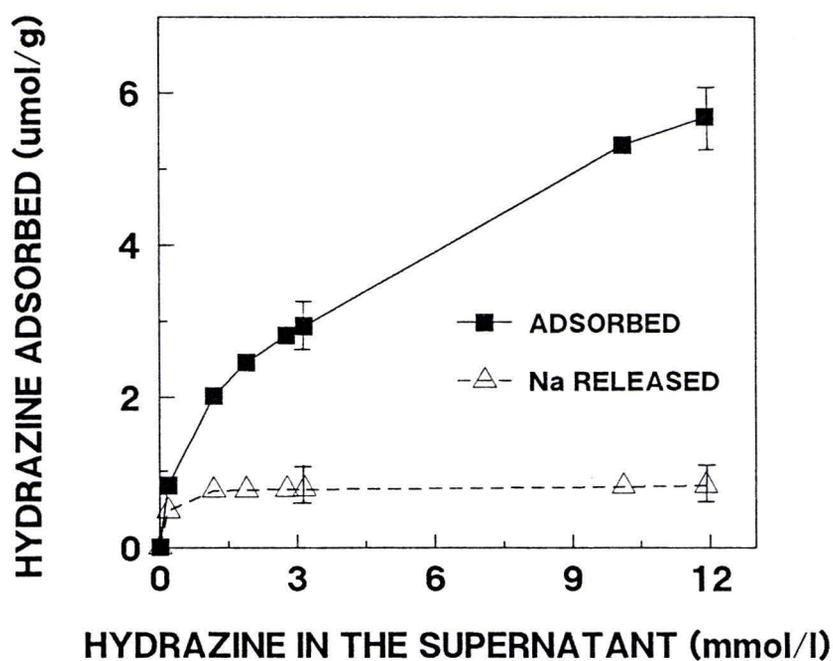
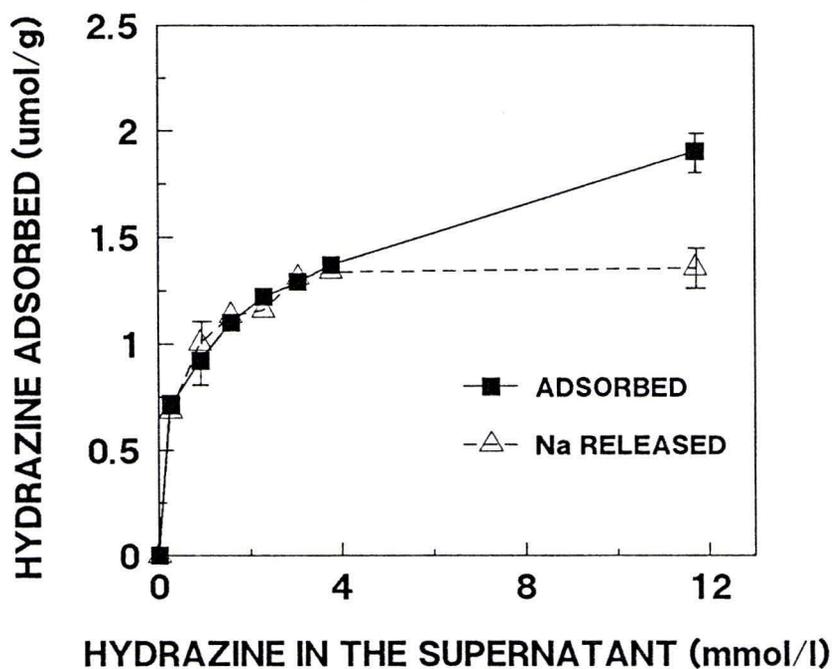


Figure 4-8. Adsorption isotherms of hydrazine on Arredondo-E₂ in the absence of O₂: a) pH 4, b) pH 8.

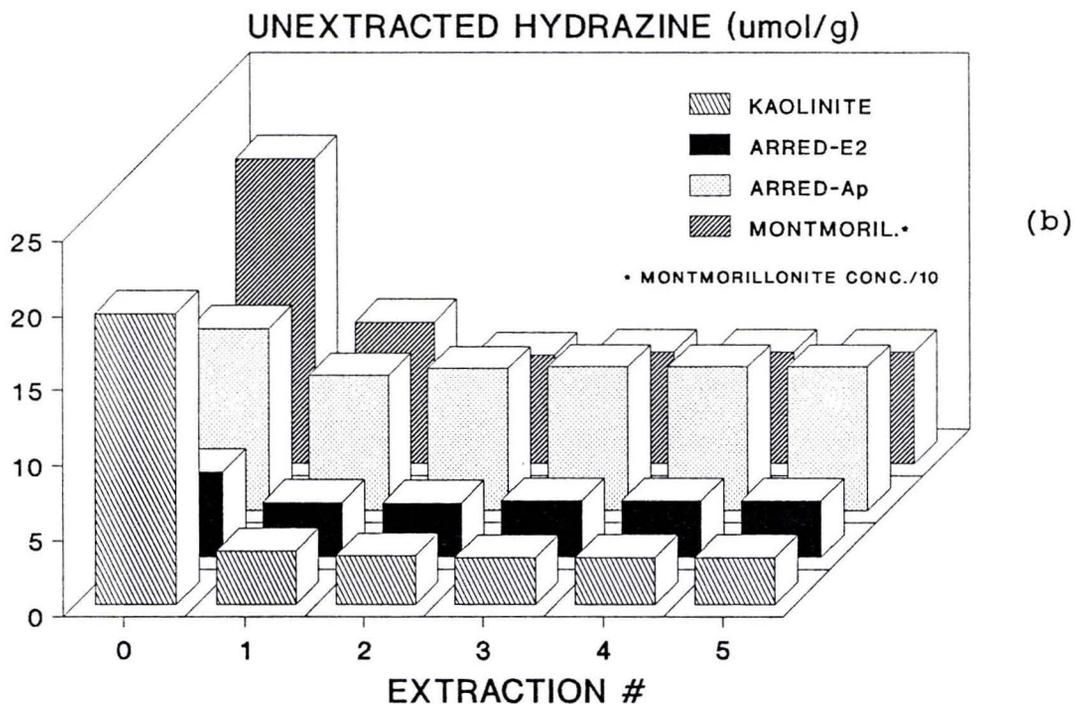
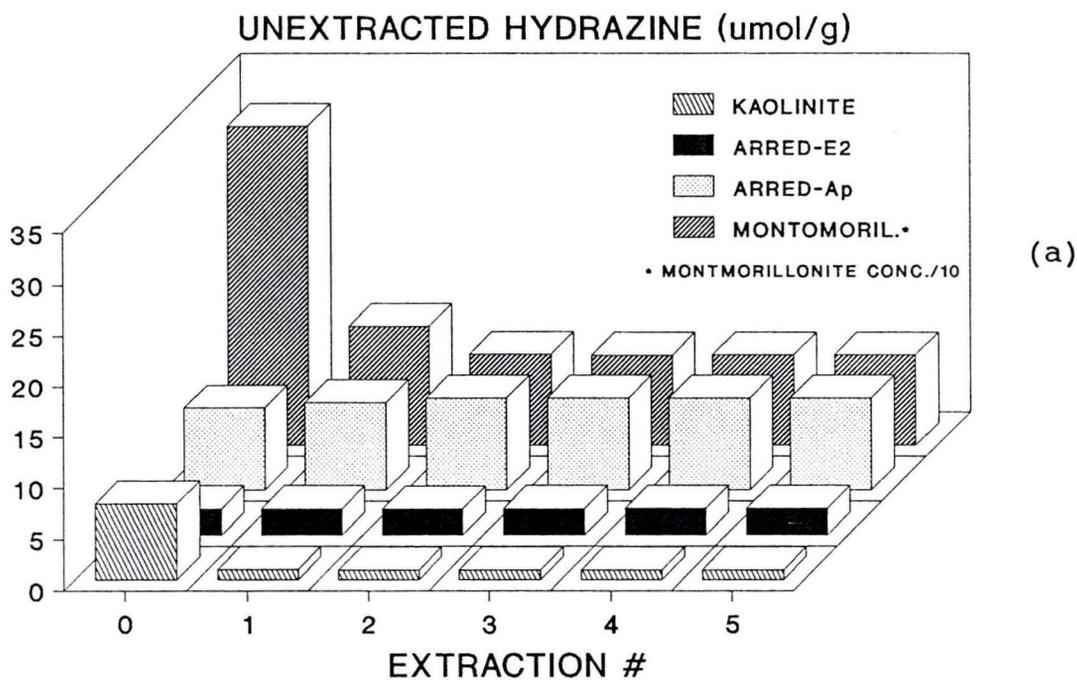


Figure 4-9. Hydrazine extraction from clays and soil horizons at: (a) pH 4, (b) pH 8.

soil was equivalent to the amount of hydrazine retained (Figure 4-8). None of the hydrazine adsorbed at pH 4.0 could be removed by repeated washings with KCl (Figure 4-9); however, 8% was removed by a single washing with HCl. It is our hypothesis that, once hydrazine replaces Na^+ on an organic matter exchange site, it further interacts through hydrogen bonding with neighboring groups. This makes its position more stable and prevents its removal by a salt solution. Addition of acid may reverse some of the bonding with neighboring groups, thus making some of the hydrazine available for extraction once more. Under alkaline conditions (pH 8.0) the amount of Na^+ released from the soil was less than at pH 4.0 and independent of hydrazine concentration. Most of the hydrazine adsorbed was retained on sites that had not been previously occupied by Na^+ . Hydrazine that replaced Na^+ ($\approx 30\%$) was easily removed by KCl in the first washing (Figure 4-9). Further extraction with KCl did not remove additional hydrazine. A subsequent washing with 0.1 N HCl extracted 5% of the hydrazine initially adsorbed.

Conclusions

The nature and extent of hydrazine adsorption by clays and soils is highly dependent on the suspension pH and on the types of surface functional groups present on the solid surfaces.

Under acidic conditions (pH 4.0) 99.9% of the hydrazine occurred as the protonated species ($N_2H_5^+$) and should have been able to readily replace Na^+ from the exchange sites. Under alkaline conditions (pH 8.0), 50% of the hydrazine was protonated and 50% was in neutral form.

In the case of kaolinite, where most of the surface functional groups consist of the inorganic OH groups exposed on broken edges, hydrazine primarily replaced Na^+ from exchange sites under acidic conditions. Under alkaline conditions, the same amount of Na^+ was displaced by hydrazine as at pH 4.0; however, most of the adsorbed hydrazine was retained on sites that had not previously been occupied by Na^+ . The most likely mechanism would be H bonding to the siloxane ditrigonal cavity on the outer surface of the clay particles. Ninety percent of the hydrazine adsorbed at pH 4 was removed by KCl washing, whereas 80% was removed at pH 8.0.

Montmorillonite has a much larger CEC due to isomorphic substitution in its octahedral layer. It primarily retained hydrazinium ion on exchange sites, both under acidic and alkaline conditions. Hydrazine adsorption was lower at pH 8.0 due to the reduced amounts of hydrazinium ion under alkaline conditions. Adsorption of small amounts of $N_2H_5^+$ at pH values near the pKa resulted in an equilibrium shift favoring the N_2H_4 species, in an increase in pH, and in a subsequent reduction in the $N_2H_5^+$ available for exchange.

Only 60% of the hydrazine adsorbed at both pH values could be removed with KCl. The remaining 40% was either irreversibly adsorbed or could have been degraded. A possible mechanism for irreversible adsorption could be through complexation with iron in the structure of the clay.

Even though the clay content (primarily kaolinite) in the upper horizons of the Arredondo soil was higher than the organic matter content, hydrazine adsorption was better correlated to organic matter content. This reflects its higher CEC and affinity of the organic reactive groups for hydrazine. Under acidic conditions and at low hydrazine concentrations, hydrazine primarily replaced Na^+ from exchange sites; however, none of the hydrazine adsorbed at pH 4 was removed from any of the two horizons by repeated washings with KCl, and only a small fraction was extracted by 0.1 N HCl. We believe that, after hydrazine was retained on the exchange sites of organic matter, hydrazine reacted further with other neighboring groups in the organic structure, thus preventing its extraction with KCl. Under alkaline conditions (pH 8) hydrazine was adsorbed more readily than at pH 4; however, the amounts of sodium released were slightly smaller. This indicates a preference for N_2H_4 at this pH. Most of the hydrazine that had replaced Na^+ was removed by a single washing with KCl.

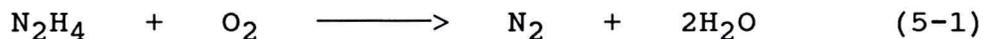
CHAPTER V
SUMMARY AND CONCLUSIONS

The effects of several environmental factors on the fate of hydrazine have been evaluated under laboratory conditions. The conclusions from each study will be presented separately in this chapter, and discussed in terms of their implications on the fate of hydrazine in natural environments.

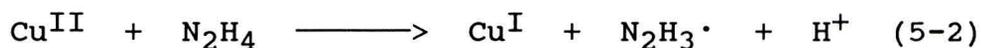
Hydrazine Degradation in Aqueous Systems

It has been shown that, at the relatively high concentrations used in this study, hydrazine degraded primarily through chemical mechanisms; however, microbial degradation should be taken into consideration when hydrazine is present in concentrations below 10 mg l⁻¹. Hydrazine was found to be susceptible to autoxidation at pH values above 4.0 and the rate of autoxidation increased with pH. Copper(II) at concentrations as low as 0.001 mg l⁻¹ was an effective catalyst for the reaction. Phosphate buffers at pH 7.0 were also effective catalysts.

The primary pathway of hydrazine degradation appeared to be



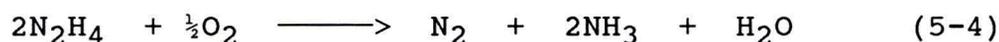
These reaction products do not present any environmental hazard. The mechanism by which Cu^{II} and phosphate ions catalyzed autoxidation appeared to be through the abstraction of a H^+ from the hydrazine molecule:



Cu^{I} is presumably recycled back to Cu^{II} through the reaction with oxygen:



Under conditions that favor the accumulation of $\text{N}_2\text{H}_3\cdot$ (such as the presence of a catalyst along with oxygen deficiency) dimerization of hydrazyl radicals occurs to some extent, producing NH_3 as one of the degradation products. The overall stoichiometry for this side reaction would be



The ratio of ammonia produced to hydrazine degraded increased with catalyst concentration and with temperature. At high temperatures (30°C and 45°C), there was a time lapse between hydrazine degradation and ammonia formation.

The rate of hydrazine degradation followed first-order kinetics with respect to Cu^{II} concentration when air was

bubbled through the reaction cell; however, it was a function of the logarithm of Cu^{II} when oxygen had to diffuse from the head space to the solution in a closed system, suggesting that the reaction was controlled by the rate of oxygen diffusion.

Hydrazine autoxidation rates increased with an increase in ionic strength of the solution. This indicates that some intermediate step in the degradation mechanism involves the reaction of two ionic species having charge of the same sign.

It was shown that the materials used to manufacture the reaction bottles had a significant effect on the rate of hydrazine autoxidation. Serum vials had a stronger effect than scintillation vials or polyethylene vials.

Results obtained under laboratory conditions are applicable to natural environments only if a number of considerations are kept in mind. In a natural environment, diffusion of oxygen from the atmosphere into surface waters and from the surface to lower depths is controlled by ambient conditions; this is likely to be the most important single factor affecting hydrazine degradation in natural environments.

Hydrazine Adsorption and Degradation in the Presence of Montmorillonite Partially Saturated with Cu^{II}

Several interactions occurred when hydrazine was in the presence of montmorillonite partially saturated with Cu^{II} .

The amount of hydrazine initially adsorbed was proportional to the amount of hydrazine added, and it remained adsorbed even when hydrazine in the supernatant was almost depleted. Copper on the exchange sites had only a slight effect on the total amount of hydrazine adsorbed equivalent to 1.2 to 1.5 moles of hydrazine per mole of exchangeable copper. It is not known if this hydrazine was either complexing Cu^{II} or Cu^{I} on the exchange sites, or just neutralizing negative charge on the surface of the clay after Cu^{II} had been reduced to Cu^{I} by hydrazine.

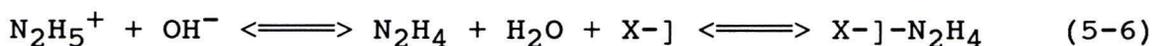
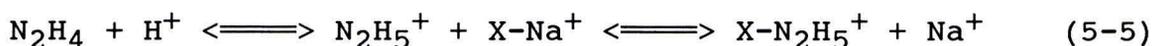
It was shown that hydrazine did not degrade in distilled water for the first 24 hours; however, it did degrade in clay suspensions even in the absence of Cu^{II} . Hydrazine degraded faster in the suspensions than in a solution containing the same amount of Cu^{II} . The amount of hydrazine degraded by the clay during the first two hours in the absence of Cu was independent of the amount of hydrazine added initially. It is believed that montmorillonite itself was one of the active components degrading hydrazine, presumably through the reduction of transition metals in the structure of the clay.

After comparing the amount of hydrazine degraded in suspension with the amount of hydrazine degraded in solution at the same concentration of copper, we hypothesize that the remaining hydrazine degradation was catalyzed by Cu^{II} in the

supernatant. Copper on the exchange sites appeared to be less active in the hydrazine autoxidation reaction.

Interactions of Hydrazine with Clay and Soil Suspensions

The nature and extent of the interactions between hydrazine and soil colloids was clearly dependent on the pH of the suspension. Suspension pH controlled hydrazine speciation as well as the availability of pH-dependent exchange sites. On the other hand, selective adsorption of one hydrazine species over another also had an effect on the pH of the suspension. This can be better explained by the following reactions:



In the case of kaolinitic clay under acidic conditions, the hydrazinium ion readily replaced Na^+ from exchange sites, with consequent rise in pH. At higher concentrations a small fraction of hydrazine was also adsorbed on a different kind of location. Ninety percent of the adsorbed hydrazine was removed by washing the clay with KCl. It is very likely that hydrazine desorbed by the salt was occupying exchange sites. Under alkaline conditions the extent of hydrazine adsorption was much higher; however, the amount of Na^+ displaced by hydrazine was similar to that at

pH 4.0. Only 80% of the adsorbed hydrazine was extracted by KCl.

Montmorillonite selectively retained hydrazinium ions on the exchange complex both at pH 4.0 and 8.0. Due to the extremely high final suspension pH (9.8) and the consequent decrease in hydrazinium-ion activity, the extent of adsorption was significantly lower at pH 8.0. After extraction with KCl, 40% of the adsorbed hydrazine remained unaccounted for. Based on literature findings we can hypothesize that some hydrazine was consumed during the reduction of iron(III) in the structure of the clay. Some was also probably complexing the reduced iron.

The three upper horizons of the Arredondo soil were characterized by a high content of inactive sand particles. The organic matter content decreased with horizon depth, and was correlated to the amount of hydrazine adsorbed. Under acidic conditions hydrazine mainly replaced Na^+ on from exchange sites; however, none of the hydrazine retained could be removed from any of the soil horizons by exhaustive washing with KCl. It is believed that the hydrazinium ions adsorbed on the exchange sites reacted further with neighboring organic groups, producing a non-exchangeable form. A subsequent extraction with dilute HCl reversed some of the bonds formed with the organic groups, so part of the hydrazinium was released from the colloidal organic surfaces. Hydrazine was adsorbed more readily under alkaline

conditions than at pH 4; however, most of this hydrazine was retained on sites that had not been previously occupied by Na^+ . The hydrazinium fraction that replaced Na^+ from exchange sites was readily available for extraction with KCl . The fact that exchangeable hydrazinium was readily exchanged by K^+ at pH 8.0 but not at pH 4.0 indicated that the interaction with neighboring groups was H^+ catalyzed. There was still a large portion of the adsorbed hydrazine that could not be accounted for. In future research it would be interesting to use labeled material to find out if hydrazine was irreversibly adsorbed or if it had partially degraded during the processes of adsorption and extraction.

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BIOGRAPHICAL SKETCH

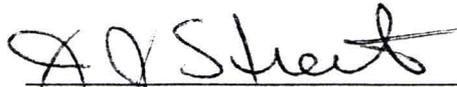
Ana Maria Moliner was born in Madrid, Spain, May 19, 1956. She spent most of her early years in Madrid and later moved to Burgos where she graduated from Bachillerato in 1972. The following fall she enrolled in the Colegio Universitario de Burgos to start the first cycle of the degree of chemistry. She continued her chemistry studies at the University of Valladolid where she obtained the degree of Licenciado en Ciencias Químicas in 1978.

After a summer of training in a paper industry she went back to school to do research in soil biochemistry under the direction of Salvador Carcedo at the Colegio Universitario de Burgos. That year of research made her realize that "soil" was different from "dirt".

In June of 1980 she started her M.S. in soil chemistry at the University of Florida from which she graduated in the summer of 1982. She came back in 1983 to work towards a Ph. D. in soil chemistry.

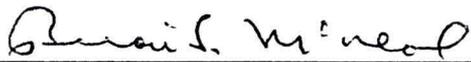
She is married to Garnet Jex.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



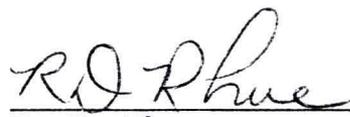
J. J. Street, Chairman
Associate Professor of Soil Science

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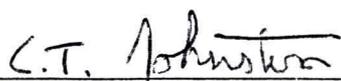
B. McNeal, Co-Chairman
Professor of Soil Science

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D. R. Rhue
Associate Professor of Soil Science

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C. T. Johnston
Assistant Professor of Soil Science

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L. T. Ou
Associate Research Scientist

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E. E. Muschlitz
Professor Emeritus of Chemistry

This dissertation was submitted to the Graduate Faculty of the College of Agriculture and to the Graduate School, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.



August 1988

Dean, College of Agriculture

Dean, Graduate School