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BIOLOGICAL DEGRADATION OF HYDRAZINE

MICHAEL G. MACNAUGHTON
JAY A. FARMWALD , et al
ENVIRONICS DIVISION
ENVIRONMENTAL SCIENCES BRANCH

OCTOBER 1979

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Due to the increased procurement, storage, and transportation of hydrazine (HZ) in support of the Titan and Minuteman operational missiles, the Space Shuttle, and F-16 combat fighter programs, the Air Force Engineering and Services Laboratory has been tasked with documenting the effects of fuel spills and low level continuous flow discharges on publicly owned treatment works (POTW). Using 12 bench scale continuous flow recycle reactors, it was shown that treatment efficiency (as measured by COD removal) is not seriously impaired for slug doses which increase aeration basin HZ concentrations up to 44 mg/l. Chemical oxygen

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Demand (COD) recovery times for slug doses of 243 mg/ℓ were approximately 4 to 5 days. Nitrification ceased at HZ concentrations above 23 mg/ℓ. The "no effect" concentration with respect to ammonia oxidation was determined to be between 1 to 23 mg/ℓ while nitrate recovery times for doses up to 243 mg/ℓ were on the order of 10 days. Continuous influent HZ concentrations above 10 mg/ℓ seriously degrade COD removal capabilities. Nitrification under continuous feed conditions was inhibited above 1 mg/ℓ. Conclusions of this study are as follows:

1. The use of activated sludge for continuous treatment of waste hydrazine fuel is not recommended. The rigid controls required to insure influent concentrations are maintained below the "no effect" level (1 mg/ℓ) would not be practical.

2. Discharges for pretreatment processes must be held to concentrations low enough to prevent values greater than 1 mg/ℓ in the influent to POTW using activated sludge treatment to insure they are not adversely affected and that final fuel discharges into receiving waters are below environmentally significant levels.

3. Treatment plant efficiency as measured by COD removal is not seriously impaired for slug doses which result in aeration basin fuel concentrations up to 44 mg/ℓ.

4. COD recovery times for slug doses up to 243 mg/ℓ are on the order of 4 to 5 days.

5. Nitrification ceased at slug doses above 23 mg/ℓ. The "no effect" concentration with respect to ammonia oxidation is between 1 to 23 mg/ℓ.

6. Ammonia recovery times for slug doses up to 243 mg/ℓ are on the order of 7 to 10 days.

PREFACE

This report was prepared by the Environmental Sciences Branch based on research performed from June 1977 to August 1978. This research was accomplished under Program Element 63723F, project 2103 and the project officers were Maj Michael G. MacNaughton and Capt Jay A. Farmwald. The research was performed in support of SAMSO/LV TN-1302-76-49.

This report has been reviewed by the Public Affairs (PA) and is releasable to the National Technical Information Services (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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SECTION I
INTRODUCTION

BACKGROUND

The Air Force (AF) procures amine-based hydrazine (N_2H_4) fuels for use in Titan II and III, Minuteman III, Bomarc, and F-16 systems and is also responsible for the procurement, storage, and transport of such fuels in support of the National Aeronautics and Space Administration (NASA) and AF Space Shuttle Programs. This results in an annual movement of approximately 2.4 million kilograms (mkg) (5.2×10^6 lb) of neat hydrazine (HZ), monomethylhydrazine (MMH), unsymmetrical dimethylhydrazine (UDMH), and Aerozine 50 (1:1 HZ:UDMH). Within private industry, significant quantities of neat hydrazine are used as plastic blowing agents, anti-corrosion agents for boiler waters, and growth inhibitors. MMH and UDMH are not widely used outside of NASA and the Department of Defense.

Hydrazine is not currently regulated under the Federal Water Pollution Control Act (PL 92-500) as amended by PL 95-217. However, in anticipation of specific guidelines and in an effort to more clearly define Best Available Treatment Technology (BAT) for hydrazine-laden effluents (scrubber liquors and tank washings), the Air Force is evaluating alternative chemical treatment methodologies (chlorination is state of the art). In addition, this laboratory has been tasked with documenting the effects of fuel spills and low level continuous flow discharges (resulting from incomplete pretreatment) on publicly owned treatment works (POTW). This report will summarize data on the effects portion of this research related to the activated sludge process. Within the Air Force, these data will serve as a basis for formulating contingency plans and will also be used in impact assessment exercises. These data should be of interest to POTWs along hydrazine transportation routes, near storage facilities, and those receiving discharges from industrial users of neat hydrazine.

Hydrazine As A Process Inhibitor

To date, very little research has been conducted on the effects of hydrazine on biological waste treatment systems. Tomlinson, Boon, and Tratman[1] conducted batch-screening tests on nitrifying activated sludge at various concentrations of neat hydrazine. They found that a concentration of 64 mg/ℓ caused a 75-percent inhibition of ammonia oxidation and 48 mg/ℓ resulted in 75-percent inhibition of nitrite oxidation. That hydrazine was more toxic to *Nitrobacter sp.* than *Nitrosomonas sp.* in activated sludge was in general agreement with Meyerhof[2] who studied pure cultures of *Nitrosomonas sp.* and found 20-percent inhibition of ammonia oxidation at 32 mg/ℓ.

Yoshida and Alexander[3] used neat hydrazine as a selective inhibitor in their studies with *Nitrosomonas europaea* to show that hydroxylamine is an intermediate in the conversion of ammonia to nitrite. They reported that pure cultures exposed to 32 mg/ℓ immediately ceased nitrite formation, but the rate of nitrite generation at 3.2 mg/ℓ was still appreciable. Ammonium oxidation seemed to proceed to some degree even in the presence of 320 mg/ℓ hydrazine, as evidenced by an accumulation of hydroxylamine. Verstraete and Alexander[4] in their work on heterotrophic nitrification found that the growth of Arthrobacter sp. was inhibited at 32 mg/ℓ hydrazine but observed negligible effects at 3.2 mg/ℓ. Tomlinson concluded that concentrations in this range may not actually cause problems in treatment plants because (1) the nitrifying bacteria may acclimate with time and (2) hydrazine may be destroyed, in part, by any heterotrophic population present. His recommendations included investigations into the feasibility of pretreating such industrial wastes in a high rate trickling filter or activated sludge process before attempting nitrification. To date, this assumption has not been verified, and no continuous flow experiments have been conducted.

SECTION II

METHODS AND MATERIALS

Using bench scale continuous flow recycle reactors a series of experiments were conducted to accomplish the following:

1. Establish control parameters favoring the oxidation of both carbonaceous matter and ammonia (nitrification) for a supplemented primary effluent.

2. Evaluate treatment efficiency under the selected operating conditions as a function of various continuous flow hydrazine concentrations.

3. Document the effects of shock hydrazine loadings under the selected conditions and monitor process recovery.

Substrate Base

Throughout this investigation primary effluent from the Tyndall AFB sewage treatment plant (STP) was used as the raw feed. The Tyndall facility, which treats $3.0\text{-}6.1 \times 10^6$ liters (0.8-1.6 MG) of predominately domestic wastewater per day, employs two single-stage trickling filters for secondary waste stabilization. Characterization of the raw feed solution was undertaken to aid in designing the experiment and in an effort to quantify supplemental requirements. Characteristics of the raw feed are summarized in Table 1. The values represent an average of numerous data points collected over several months during the early stages of the study when system familiarization and troubleshooting runs were being conducted. From these data it was decided to enrich the raw feed by elevating the chemical oxygen demand (COD) to 320 mg/ℓ with Carnation Slender®. Stoichmetric relationships as described by McCarty[5] were then developed which were used to predict relevant nitrogen/oxygen requirements and indirectly estimate phosphorous and alkalinity demands. Based on these results, the enriched feed could be supplemented to insure the final feed solution (Table 1) fits the experimental design.

TABLE 1. FEED CHARACTERISTICS

PARAMETERS	RAW FEED (mg/ℓ)	FINAL FEED (mg/ℓ) Theoretical*	Measured
COD	100	386	320
BOD_5	85		
Suspended Solids	60		110
Volatile Suspended Solids	50		100
NH_4-N	12.7		12.7
Organic-N	5	20.7	20.3
NO_3-N	ND		
NO_2-N	ND		
Total -N		33.4	29.8
PO_4-P	6	11.9	10
Alkalinity (Total	97	254 (as $CaCO_3$)	275
pH	7		

*Based on Stoichiometric Relationships

NOTE: All samples were unfiltered

Bench Scale System

Reactors were initially seeded with mixed liquor from the Panama City conventional activated sludge plant and subsequently maintained as summarized below.

Several afternoons each week 200 gallons of primary effluent were withdrawn just upstream from the Tyndall sewage treatment plant (STP) trickling filters and immediately transported to the Environics Laboratory located approximately one mile from the plant. At this point the wastewater was transferred to five 150 ℓ containers inside a refrigeration unit (4.4°C) adjacent to the laboratory. All raw feed was stored in this configuration until used as substrate base, but, in no case did the storage time exceed four days.

The raw feed, having been enriched and supplemented in the feed tank, was pumped through a heat exchanger (20°C) and then into a mixing chamber which was designed such that two continuous feed toxicant concentrations and a control could be evaluated simultaneously in the 12 reactors. The 6-liter Plexiglas® aeration basins detailed in Figure 1 were supplied with 4ℓ/min humidified air passed through an activated carbon filter to provide excess dissolved oxygen and complete mixing. Based on 5 percent O_2 transfer, this represents a 30-percent excess over stoichmetric requirements. Sludge return from the 2-liter Pyrex® clarifiers was maintained using gravity draw-off and an in-line air pump.

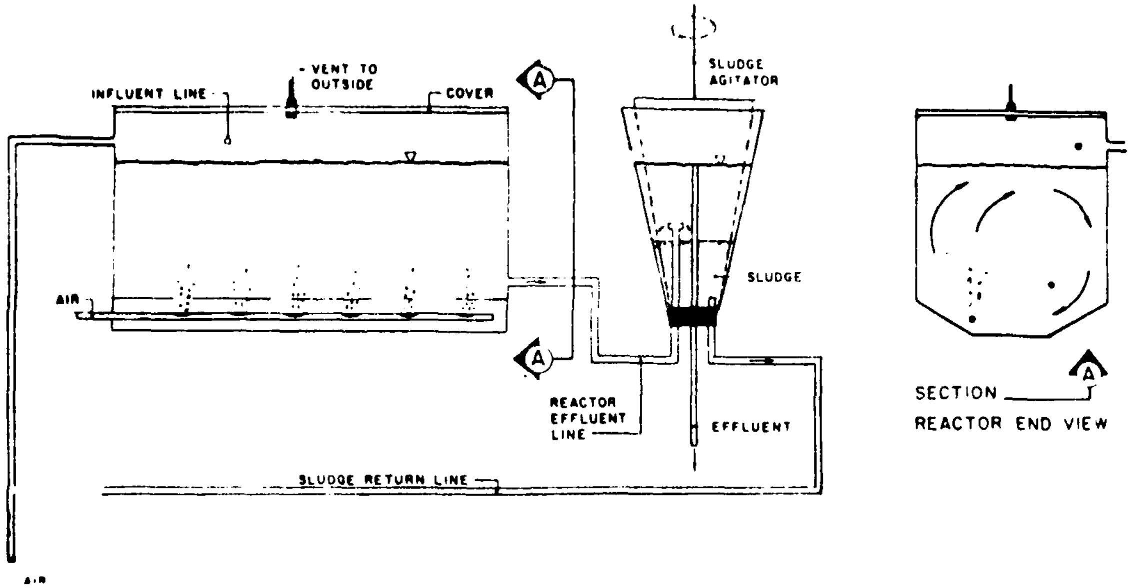

Figure 1. Aeration Basin and Clarifier

Experimental Matrix

Fuel Loadings: The continuous feed studies were conducted over a wide range of fuel concentrations, specifically 20, 10, 6, 3, 1.0, and 0.5 mg/ℓ. Four reactors were evaluated at each concentration in addition to four controls operated throughout the study. Because two concentrations could be evaluated simultaneously, a total of three runs were performed. These have been designated 20/10, 6/3, and 1/.5 with the numbers referring to the target fuel concentrations. Slug loading experiments were performed at concentrations of 250, 125, 50, and 25 mg/ℓ (based on a 6ℓ volume) on duplicate continuous flow reactors. These concentrations were achieved by adding 1 to 12 mℓ of stock fuel solutions directly to the aeration basin. In the slug studies, effluent characteristics are monitored for sufficient time to make inferences about process recovery. All reactors were allowed to achieve steady state, as indicated by effluent COD and NO_3^--N concentrations, prior to starting hydrazine feeds for any one particular evaluation.

Operating Parameters:

Knowing the bacterial growth and substrate utlization coefficients for a particular waste under specified environmental conditions, Equation (1) may be used to relate effluent soluble substrate concentration to mean cell residence time.

$$S = \frac{K_s\ (1+b\Theta_c)}{\Theta_c\ (yk-b)-1} \qquad (1)$$

where: S = substrate concentration in reactor and effluent (mass/volume)

K_s = half velocity coefficient (mass/volume)

b = organism death coefficient ($time^{-1}$)

Θ_c = mean cell residence time (time)

y = maximum cell yield coefficient (mass/mass)

k = maximum rate of substrate utilization per unit of organisms ($time^{-1}$)

Using the coefficient data summarized in Table 2, the relationship in Figure 2 results. In order to insure viable heterotrophic and autotrophic populations during this laboratory investigation, a cell residence time of at least six days should be maintained. As described by Christenson[6] Mixed Liquor Volatile Suspended Solids (MLVSS) can be described by Equation (2) as a function of Θ_c.

TABLE 2. BACTERIAL GROWTH AND SUBSTRATE UTILIZATION COEFFICIENTS

TREATMENT OBJECTIVE	COEFFICIENT	DOMESTIC SEWAGE VALUE	DOMESTIC SEWAGE REFERENCE	SKIM MILK VALUE	SKIM MILK REFERENCE	BASIS
COD Removal	Y	0.45	7	0.48	10	mg Cells/mg COD
	b	0.05	7	0.05	10	Day^{-1}
	k	20.9*	8	6.0*	9	mg COD/mg Cells-Day
	K_s	60	8	110	9	mg/ℓ COD
Nitrification	Y	0.36	7	-	-	mg Cells/mg NH_4^+-N
	b	0.05	7	-	-	Day^{-1}
	k	1.8	7	-	-	mg NH_4^+-N/mg Cells-Day
	K_s	3.6	7	-	-	mg/ℓ NH_4^+-N

* The references for these values reported $\mu_m = Yk$
k was calculated based on the Y value given in this table.

NOTE: Values calculated for cell yield, Y, based on the developed stoichiometry are:

Heterotrophic: 0.46 mg/cells/mg COD
Autotrophic: 0.36 mg/cells/mg NH_4^+-N

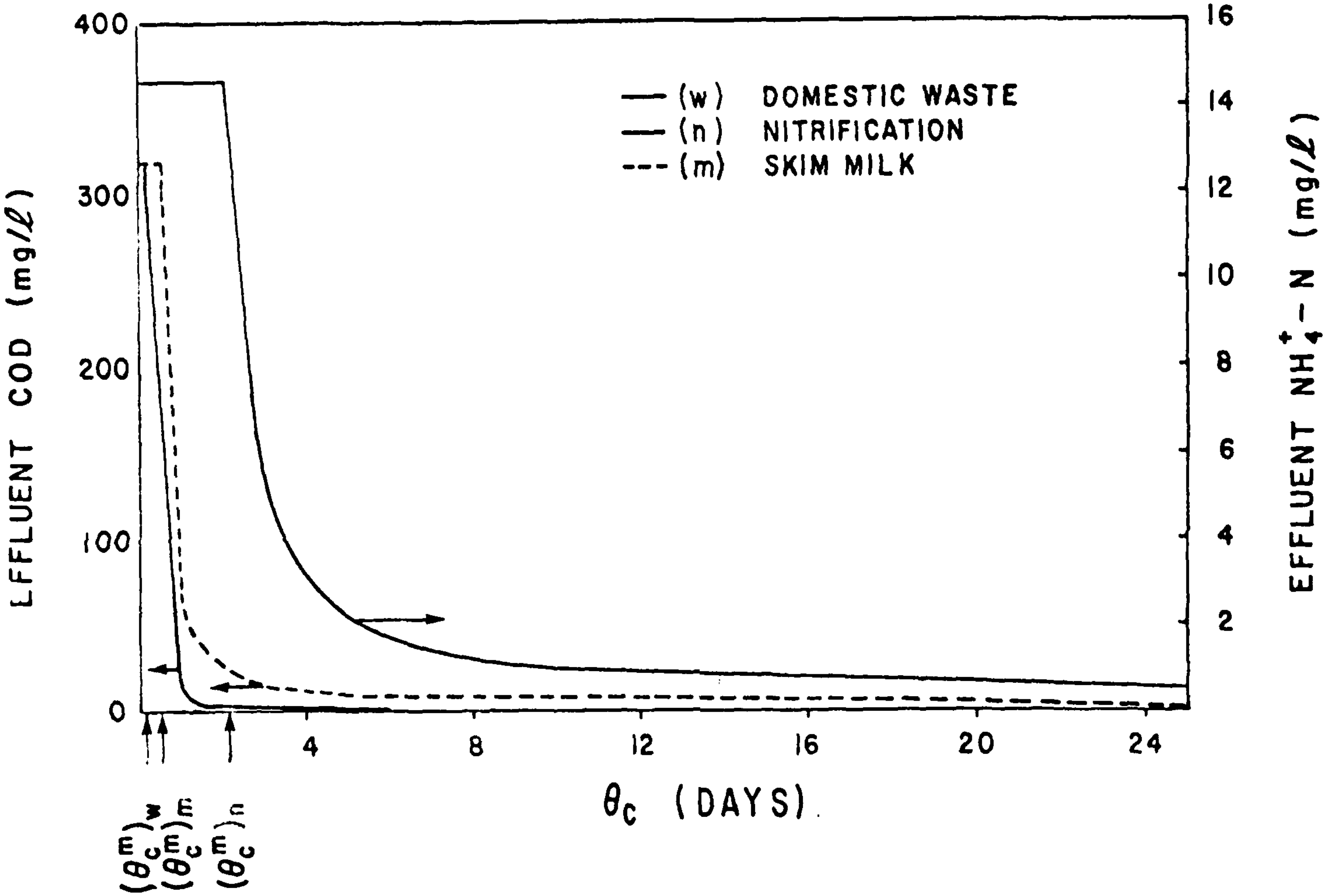

Figure 2. Theoretical Effluent COD and Ammonia Nitrogen as a Function of Mean Cell Residence Time

$$\text{MLVSS*} = \frac{\Theta_c}{\Theta} X_r^o + \frac{S}{S^o} X_d^o + \frac{Y\ (S^o - S)}{1+b\ \Theta_c} (1=(1-f_d)\ b\ \Theta_c \tag{2}$$

*The autotrophic biomass is only 4 percent of the heterotrophic; therefore, only COD removal coefficients were used in establishing MLVSS.

where: Θ = hydraulic detention time (time)

x_r^o = influent refractory volatile suspended solids (mass/volume)

x_d^o = influent degradable volatile suspended solids (mass/volume)

S^o = influent substrate concentration (mass/volume)

f_d = fraction of organism decomposed during decay (usually assumed to be 0.8).

and

$$\text{MLSS} = \frac{\Theta_c}{\Theta} X_{in}^o + \text{MLVSS} \tag{3}$$

where x_{in}^o = influent inorganic suspended solids (mass/volume). Using the skim milk coefficients (conservative) and Equations (1) and (2). The target solids levels summarized in Table 3 were developed.

TABLE 3. DESIGN OPERATING PARAMETERS

RUN	Θ(hr)	MLSS (mg/ℓ)	CALCULATED Θ_c (days)
20 mg/ℓ	6.7	5600	10
10 mg/ℓ	6.7	4000	6.5
6 mg/ℓ	6.7	5600	10
3 mg/ℓ	6.7	4000	6.5
1 mg/ℓ	6.7	4500	7.5
0.5 mg/ℓ	6.7	4500	7.5

NOTE: During the 20/10 and 6/3 runs, two controls were operated at each MLSS. Four controls were maintained at 4500 mg/ℓ MLSS for all subsequent studies.

Analytical Procedures

General: Those parameters of interest included the major forms of nitrogen (NH_3, organic, NO_3^-). COD, total and volatile suspended solids, hydrazine, and pH. Orthophosphate and alkalinity were monitored less frequently. All analyses were performed in accordance with Standard Methods for the Examination of Water and Wastewater, 14th edition. Notable exceptions and comments are summarized below.

Hydrazine: Neat hydrazine is a colorless liquid with a density of 1.004 gm/ml at 20°C. It is very soluble in water. Duplicate analyses of a 125-mg/ℓ stock solution resulted in 0.23 mg COD/mg HZ, with no detectable ammonia or organic nitrogen. The colorimetric method described by Watt and Chrisp[11] was used for all HZ analyses. This procedure is based on a stable yellow color which develops upon addition of p-dimethylaminobenzaldehyde to dilute solutions of hydrazine. Absorbance was measured at 460 nm using a Coleman Model 55 UV-visible spectrophotometer.

Schedule: Five days each week mixed liquor samples were collected and immediately analyzed for total and volatile suspended solids. Filtered effluent samples (Whatman #40) were used in the determination of NO_3^--N, COD, and pH. Unfiltered aliquots of these same samples were analyzed for NH_4^+-N and organic nitrogen. Unfiltered influent samples were analyzed for all of the above parameters. Both influent and effluent were intermittently checked for orthosphosphate, alkalinity, and suspended solids. Qualitative microscopic examinations of the mixed liquor were also conducted on an irregular basis throughout the investigation. Wasting was accomplished once daily directly from the aeration basin to realize the desired MLSS. During continuous flow hydrazine studies, influent fuel concentrations were assayed at least once daily from each reactor.

SECTION III

RESULTS

Continuous Feed Studies

HZ Degradation: The theoretical and measured average influent and effluent hydrazine concentrations for the continuous feed studies are summarized in Table 4. It is apparent that degradation of HZ occurs at all influent concentrations investigated. Because degradation by atmospheric oxidation was not observed in control studies where tap water was substituted for the activated sludge (Figure 8), the documented reductions in HZ are assumed to be the result of microbial metabolism or catalytic action by some cellular component released into solution. Although it was the objective of this study to maintain stable hydrazine concentrations during each run, actual analyses showed that there was some variation. As can be seen, the percent variation was greater in the lower concentration studies. Experiments attempted at 1 mg/ℓ actually represent exposure between 0.6 mg/ℓ and 0.9 mg/ℓ. Those designed for 0.5 mg/ℓ were measured to be between 0.2 mg/ℓ and 0.4 mg/ℓ.

COD: Table 5 summarizes the influent and control reactor effluent data for the continuous feed studies. While the mean influent values were very close to the target of 320 mg/ℓ for all runs, the standard deviations suggest a wider than optimal range for individual values. However, effluent quality remained very stable in the controls despite influent COD fluctuations. These findings agree with data presented by Saleh and Gaudy[12] who have reported that recycle systems can handle a 200-percent step change in influent organic substrate concentration with only a small, shortlived disturbance in effluent quality. They have further stated that when a constant recycle rate is employed, as was the case in the present study, such step increases can be accommodated with little or no change in effluent quality. Note also that the data presented are for unfiltered samples. The standard deviations on filtered influent CODs were consistently smaller.

Remaining COD in the clarifier effluent as a function of influent HZ concentration and time is shown in Figure 3. For the operating parameters in this study, an HZ concentration of approximately 3 mg/ℓ causes no reduction in treatment efficiency. Concentrations above 10 mg/ℓ result in the complete loss of COD removal capabilities within a few days.

Effluent organic nitrogen is related to effluent COD, as shown in Figure 4. Microscopic examinations of exposed activated sludge samples verified that significant cell lysis was affected by HZ, releasing soluble organic nitrogen and other organics which contributed to soluble effluent COD as well.

TABLE 4. HYDRAZINE CONCENTRATIONS DURING CONTINUOUS FEED STUDIES (mg/ℓ)

	Study	Influent			Effluent			Reduction
Theoretical	Designation	Mean	σ	n	Mean	σ	n	Percent
20	20/10	19.7	0.9	22	6.1	2.0	26	69
10	20/10	9.6	0.8	22	2.1	0.9	26	78
6.0	6/3	5.4	0.7	44	0.4	0.3	56	93
3.0	6/3	2.7	0.6	43	0.1	0.1	52	96
1.0	1/.5	0.7	0.1	52	ND	0.0	46	∿100
0.5	1/.5	0.3	0.1	52	ND	0.0	36	∿100

NOTE: ND = None Detected

σ = Standard deviation about mean

n = Number of independent samples

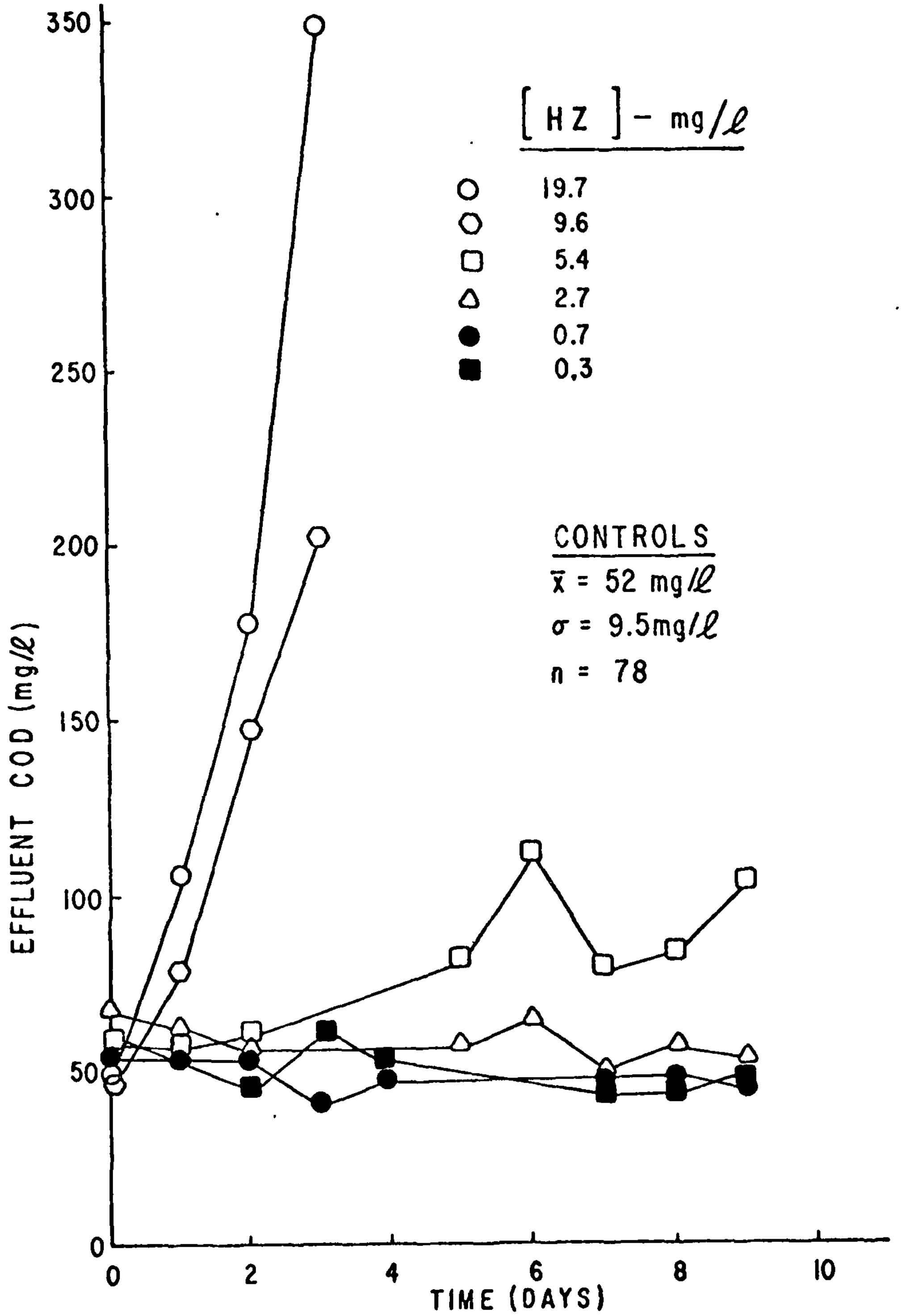

Figure 3. Effluent COD as a Function of Time and Continuous Feed HZ Concentration (Mean of 4 Replicates)

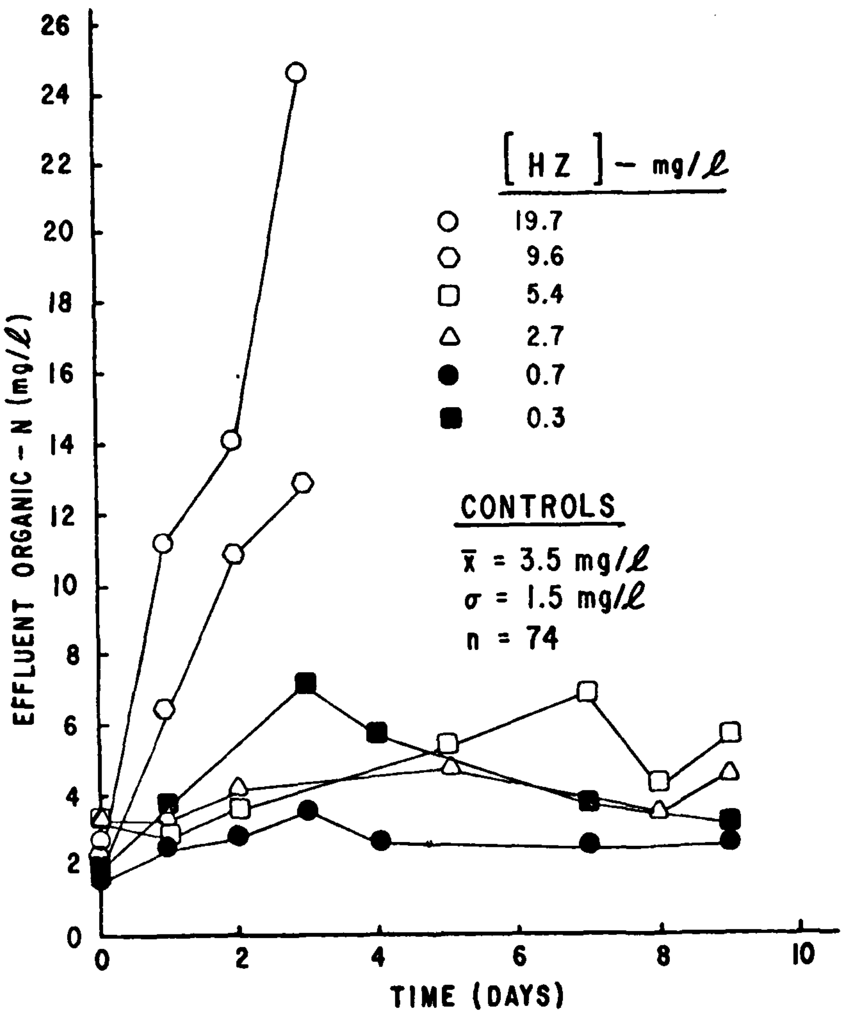

Figure 4. Effluent Organic Nitrogen as a Function of Time and Continuous Feed HZ Concentration (Mean of 4 Replicates)

TABLE 5. INFLUENT AND CONTROL EFFLUENT COD SUMMARY

Study	Study Length (Days)	Influent COD (mg/ℓ) Mean	Influent COD (mg/ℓ) σ	Control Effluent COD (mg/ℓ) Mean	Control Effluent COD (mg/ℓ) σ	Control Percent Removal
20/10	3	324	135	56	9	83
6/3	8	307	35	59	7	81
1/0.5	9	311	56	44	4	86
Overall	-	314*	67	52	10	83

* n = 20

Nitrification: The influent and control effluent nitrogen data collected over the continuous feed HZ studies are summarized in Table 6. Overall, 80-percent nitrification of influent total kjeldahl nitrogen (TKN) was achieved during these experiments. Effluent ammonia concentrations agreed well with those predicted based on the growth and substrate utilization coefficients discussed in the methods and materials section (Figure 2). While influent ammonia and TKN varied somewhat from day to day, effluent ammonia concentrations were consistently below 0.2 mg/ℓ.

From Figure 5 it is apparent that even low hydrazine concentrations (∿3 mg/ℓ) cause inhibition of nitrification. The nitrate data presented in Figure 6 reflects the effect of hydrazine or ammonia oxidation. As effluent ammonia increases, effluent nitrate decreases. The combined NH_3 and NO_3 data suggest that HZ is definitely toxic to Nitrosomonas sp. in this range. Because the conversion of ammonia to nitrite is generally considered to be the rate limiting step in the oxidation scheme, no such inferences can be made with respect to Nitrobacter sp.

Suspended Solids: The suspended solids data for the control reactors are outlined in Table 7. Recall that during the 20/10 and 6/3 runs the high reactors (20 and 6 mg/ℓ) were operated at an MLSS of 5600 mg/ℓ while the low reactors (10 and 3 mg/ℓ) were held at 4000 mg/ℓ.

The MLSS response to HZ is summarized in Figure 7. As in Table 7, all values represent concentrations prior to wasting to the desired levels. Both HZ and influent COD affected MLSS. Step increases in influent COD generally resulted in increased MLSS values as, for example, on day 2 of the 20/10 run. While HZ concentrations from 10 to 20 mg/ℓ caused elevated effluent organic nitrogen concentrations (Figure 4) it was felt that these increases were due primarily to soluble nitrogen resulting from cell lysis and that the loss of solids was not of sufficient magnitude to significantly decrease MLSS, and hence θ_c, during any of the runs. This hypothesis was supported by numerous microscopic examinations and qualitative effluent solids analyses.

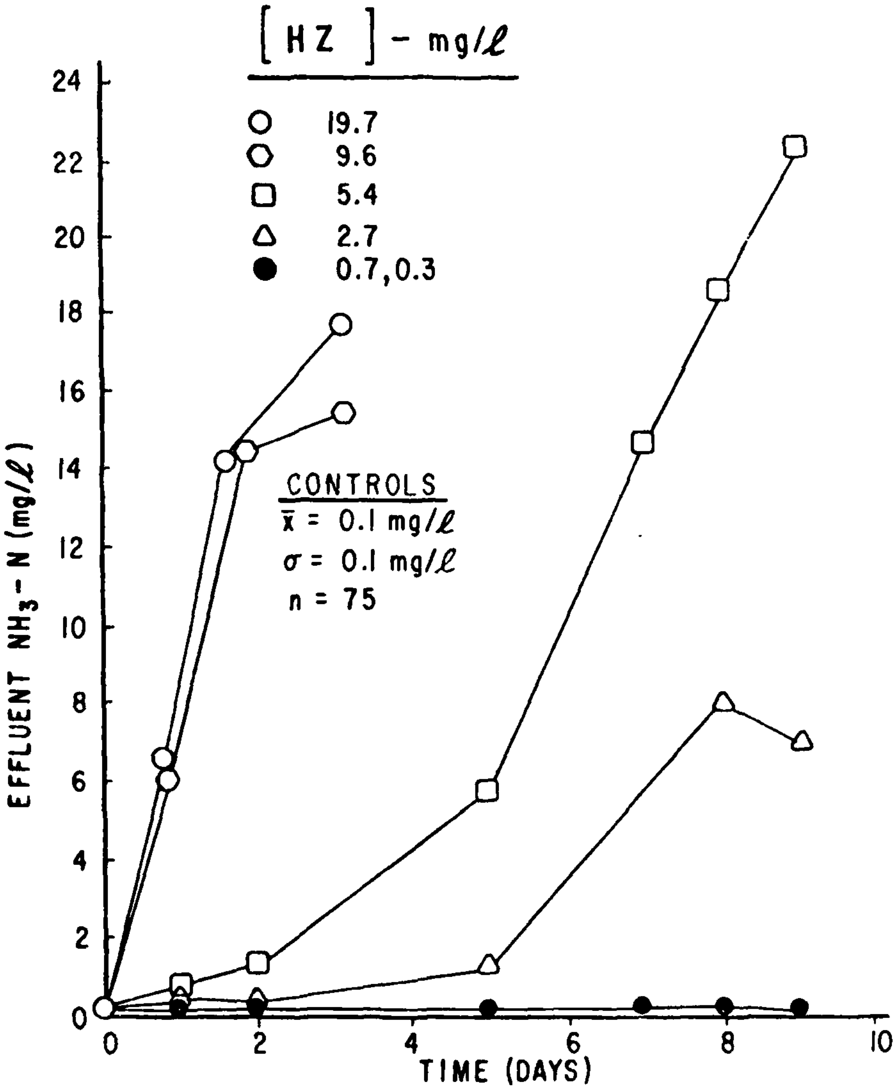

Figure 5. Effluent Ammonia Nitrogen as a Function of Time and Continuous Feed HZ Concentration (Mean of 4 Replicates)

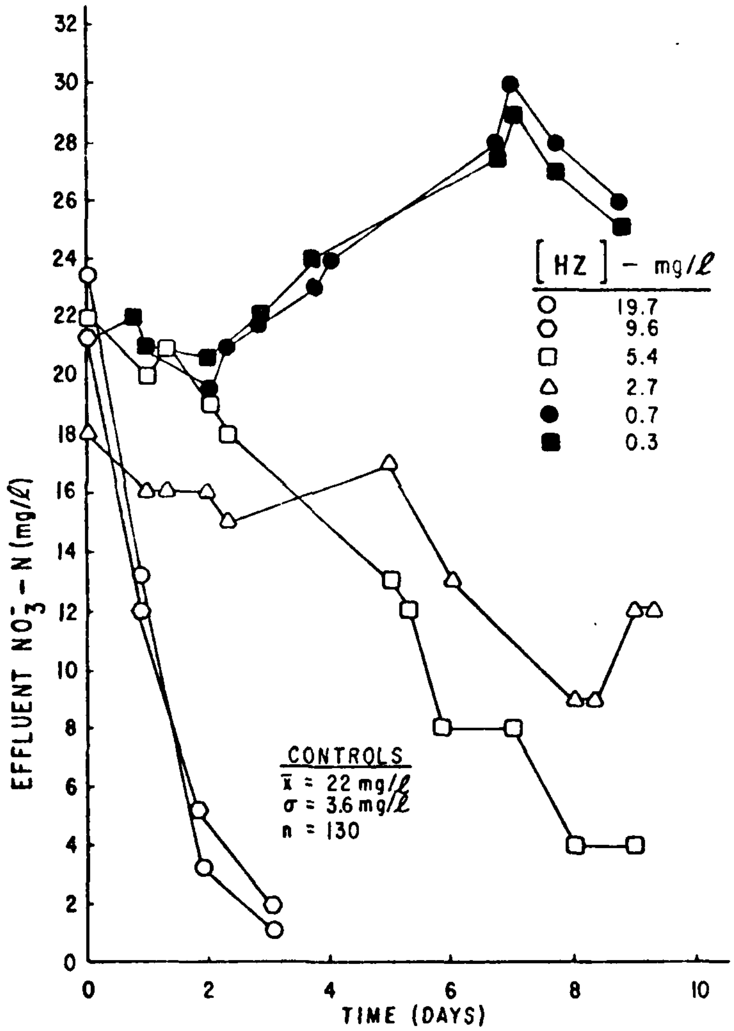

Figure 6. Effluent Nitrate Nitrogen as a Function of Time and Continuous Feed HZ Runs (Mean of 4 Replicates)

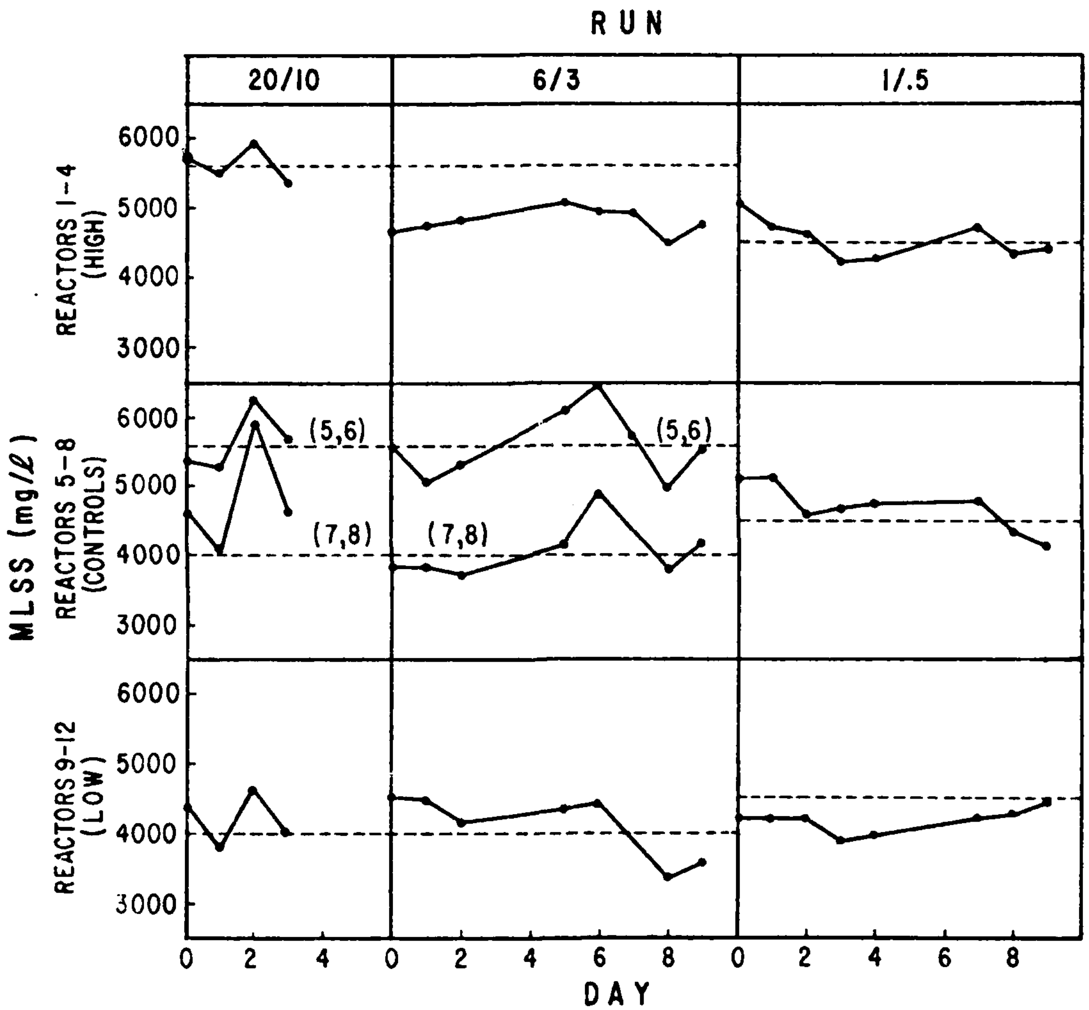

Figure 7. Mean MLSS During Continuous Feed HZ Runs (Mean of 4 Replicates Except Controls During 20/10 and 6/3 Which Were Duplicates)

TABLE 6. INFLUENT AND CONTROL EFFLUENT NITROGEN SUMMARY (mg/ℓ)

	Influent				Control Effluent				Nitrification
	NH_3-N		TKN		NH_3-N		NO_3-N		Percent
Study	Mean	σ	Mean	σ	Mean	σ	Mean	σ	In Controls[1]
20/10	12.5	2.6	25.8	4.8	0.0	0.1	20	2.5	78
6/3	14.1	4.3	28.0	4.8	0.1	0.2	22	4.5	79
1/.5	14.4	3.8	27.6	5.7	0.0	0.1	23	2.7	83
Overall	13.8*	3.7	27.4*	4.9	0.1	0.1	22	3.6	80

[1] Based on TKN Conversion to NO_3^--N
* n = 19

TABLE 7. CONTROL MLSS DATA (mg/ℓ)

	High			Low		
Study	Mean	σ	n	Mean	σ	n
20/10	5660	450	8	4830	860	8
6/3	5600	570	16	4060	500	14
1/0.5				4670	530	32

Slug Feed Studies

HZ Degradation: Figure 8 is a plot of the reactor HZ concentration (c) over the initial added HZ concentration (c_o) versus time. The initial drop in the control plot reflects dilution due to the clarifier volume. As in the continuous feed studies, there is significant degradation of the hydrazine even at an initial hydrazine concentration of 243 mg/ℓ. Assuming exponential bacterial decay of the hydrazine, it is possible to calculate a bacterial decay constant (K) from Equation (4).

$$\ln (C/C_o) = -\frac{1}{0_s} + Kt \qquad (4)$$

C = HZ at time t (mg/ℓ)

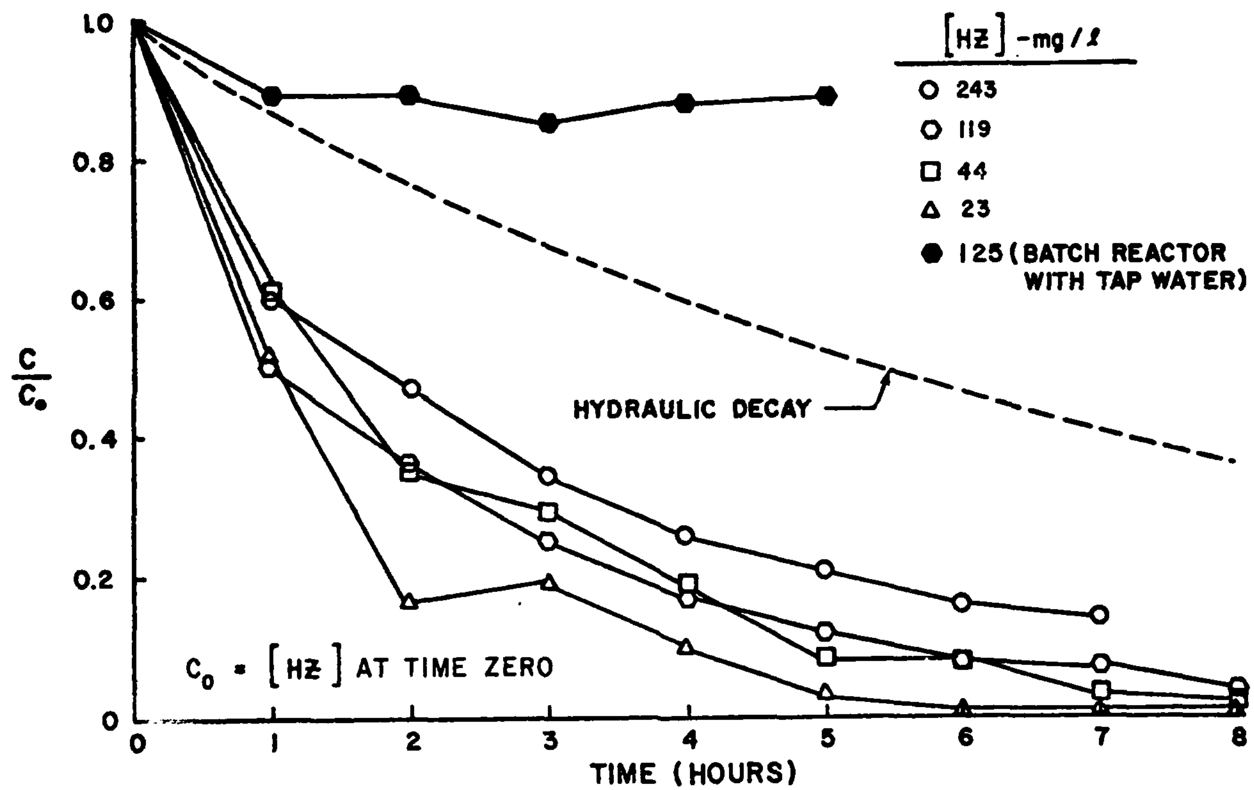

Figure 8. HZ Degradation During HZ Slug Feed Experiments (Mean of Duplicates)

C_o = HZ at time 0

Θ_s = Total system (reactor plus clarifer) hydraulic detention time = 7.78 h

t = Time (h)

K = Bacterial Decay Constant (h^{-1})

If hydrazine was not toxic to the activated sludge Equation (4) would predict K to be independent of C_o. This was not observed, as indicated in Table 8.

Acute Response: Influent parameters during the 8-hour acute response study are summarized in Table 9.

Figure 9 shows that, as would be expected from the continuous feed studies, the high initial hydrazine concentrations caused an immediate decrease in treatment efficiency. Of the 146 mg/ℓ COD in the effluent at one hour in the high run, only 33 mg/ℓ can be attributed to HZ. Further, 243 mg/ℓ samples were inadvertently lost because they exceeded the maximum value (400 mg/ℓ) for the COD protocol employed. Although there was some apparent effect at all the concentrations tested, the reduction of treatment efficiency as measured by COD removal would be minor for slug doses which did not increase the HZ concentration above 44 mg/ℓ. Figure 10 clearly shows that effluent organic nitrogen concentrations were elevated from 0 - 10 times initial effluent values depending on the HZ slug.

The effect of HZ slug feeds on nitrification is shown in Figures 11 and 12. Even at 23 mg/ℓ, there is immediate inhibition. The nitrate decay rate is approximately equal to that expected for a completely mixed reactor with no nitrate being produced, confirming that at all concentrations the oxidation of ammonia to nitrate had ceased.

Recovery: One of the objectives of this investigation was to document the time required to recover process efficiency following slug hydrazine exposures. The influent and control effluent COD and nitrogen data monitored throughout the recovery period are outlined in Figure 13.

Figure 14 illustrates that even for the 243 mg/ℓ study, there was significant recovery within 6 days. Recovery from HZ concentrations below 44 mg/ℓ was complete after approximately 3 days.

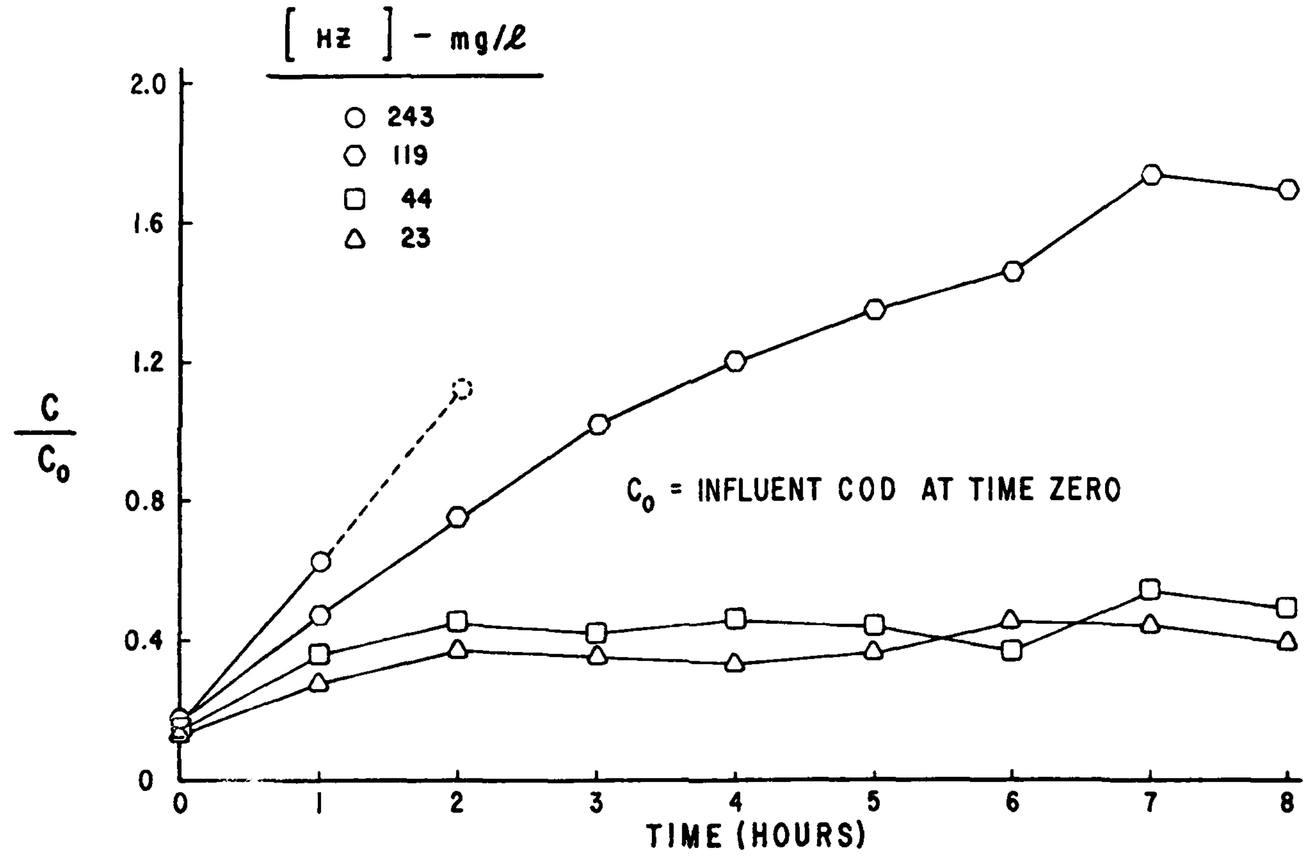

Figure 9. Acute Effluent COD Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)

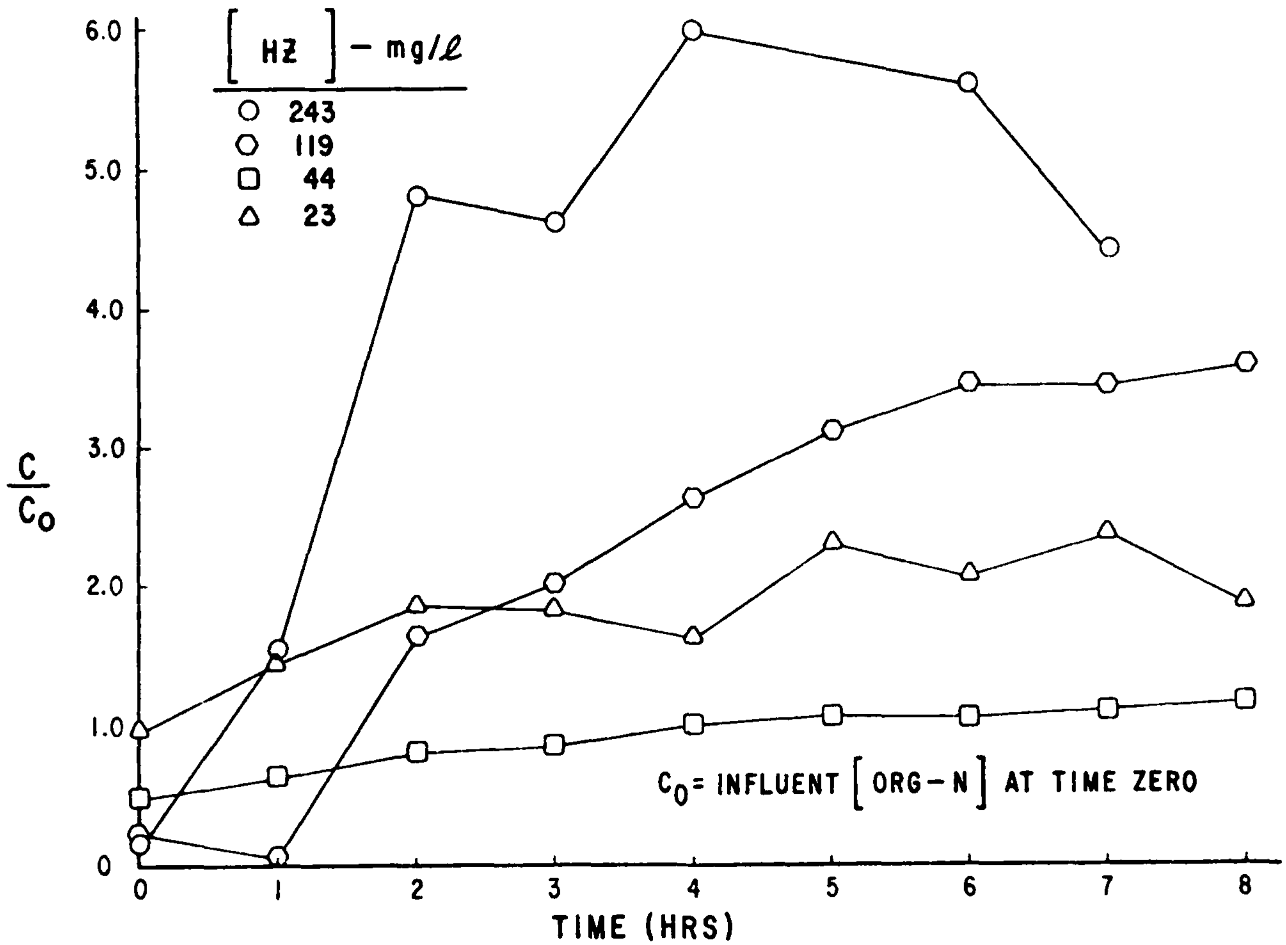

Figure 10. Acute Effluent Organic Nitrogen Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)

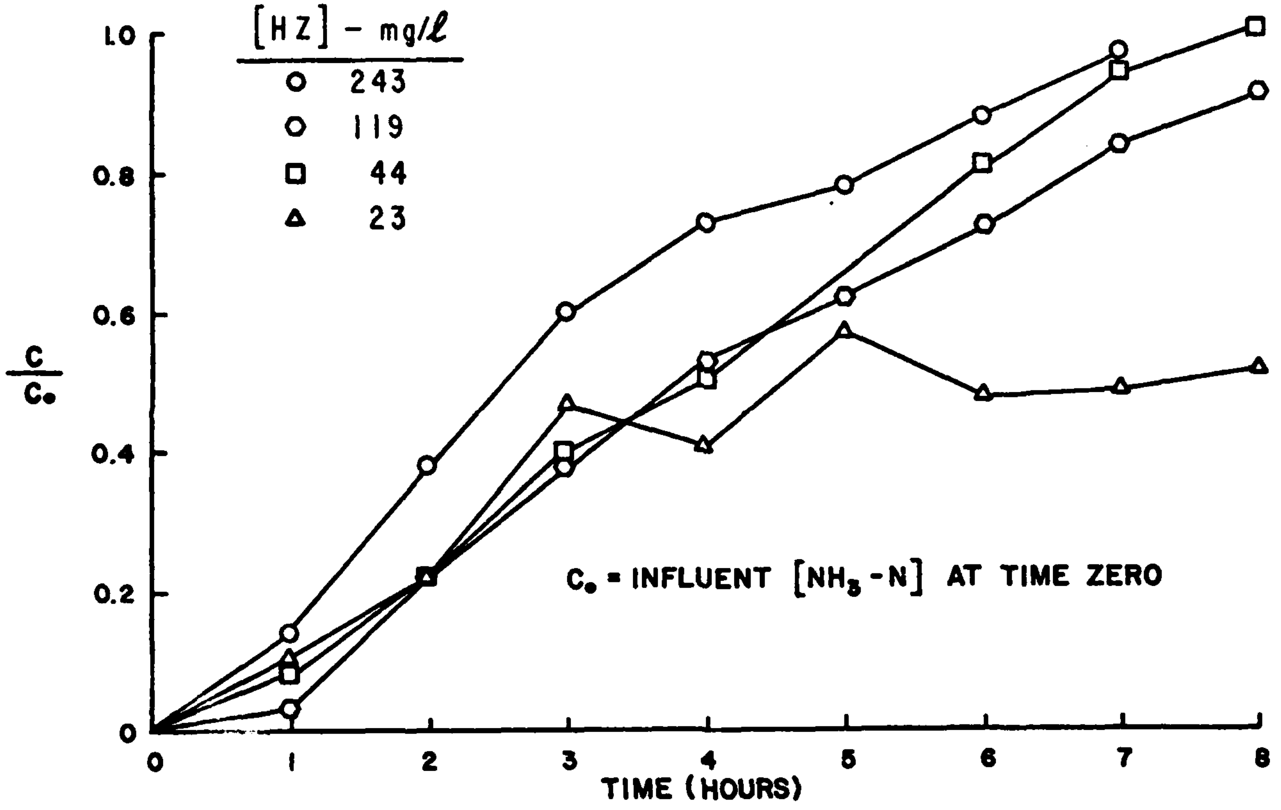

Figure 11. Acute Effluent Ammonia Nitrogen Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)

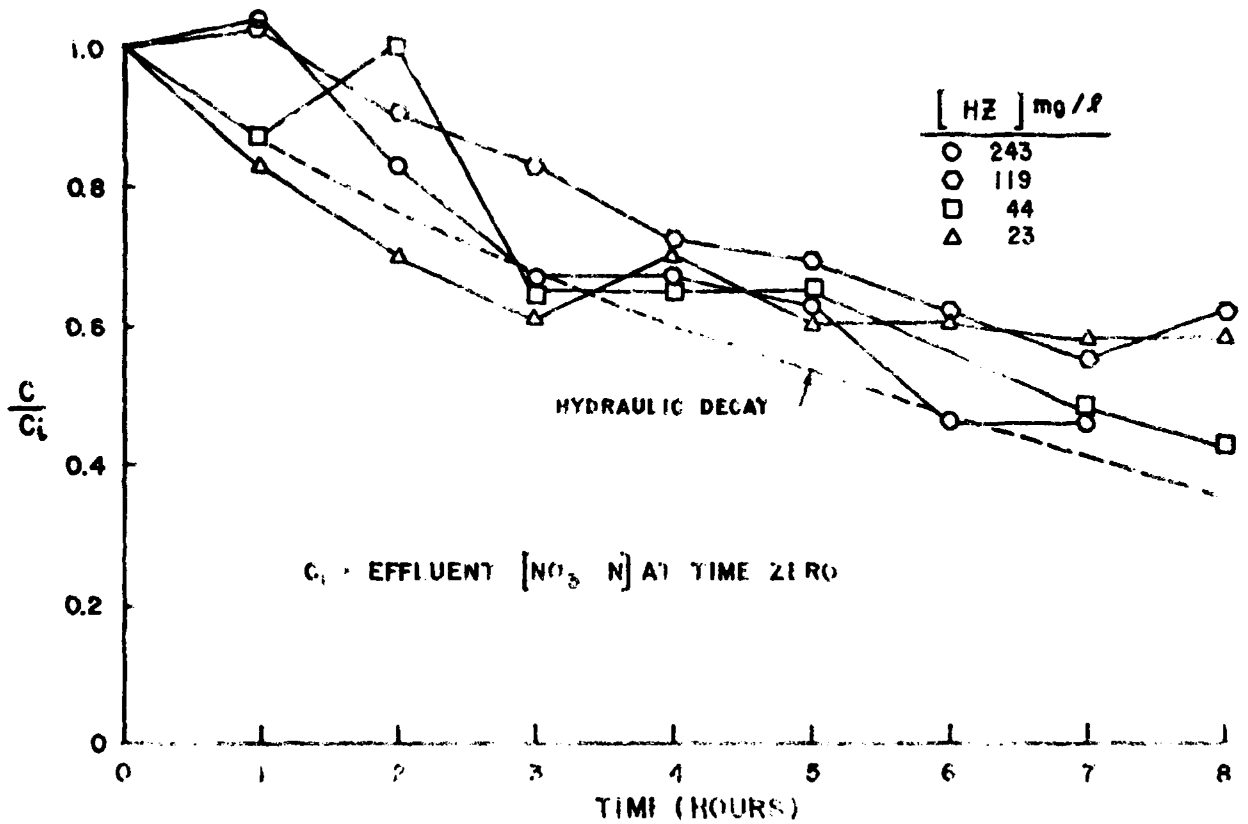

Figure [illegible] Acute Effluent [illegible] Nitrogen Response to [illegible] [illegible] (Mean of Duplicates)

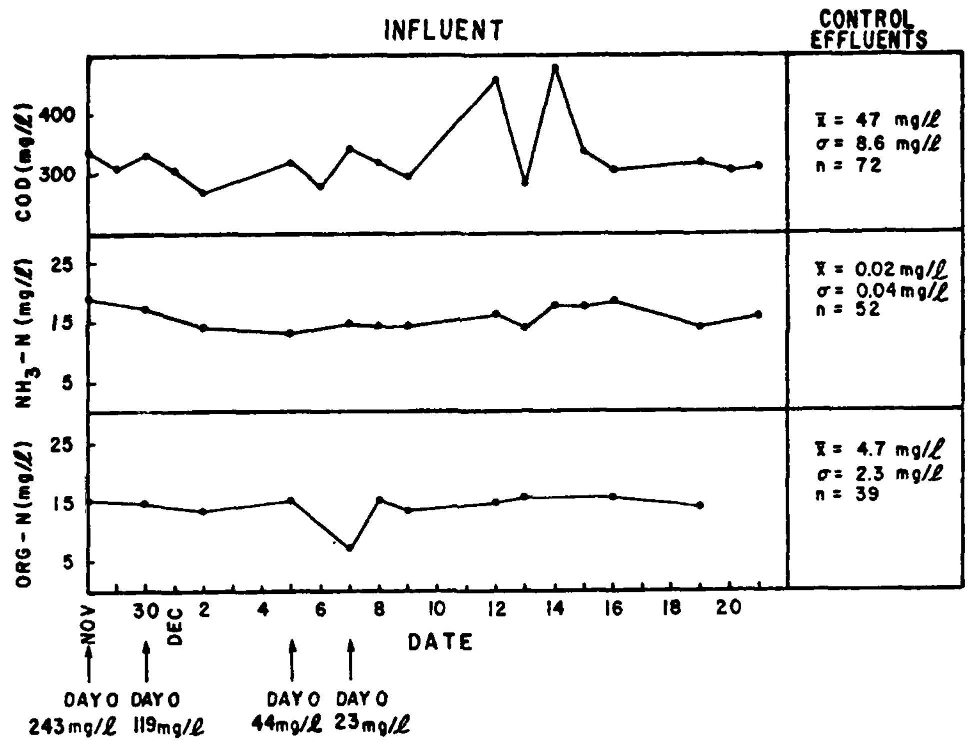

Figure 13. Influent and Control Effluent COD and Nitrogen Data During the Slug HZ Recovery Periods.

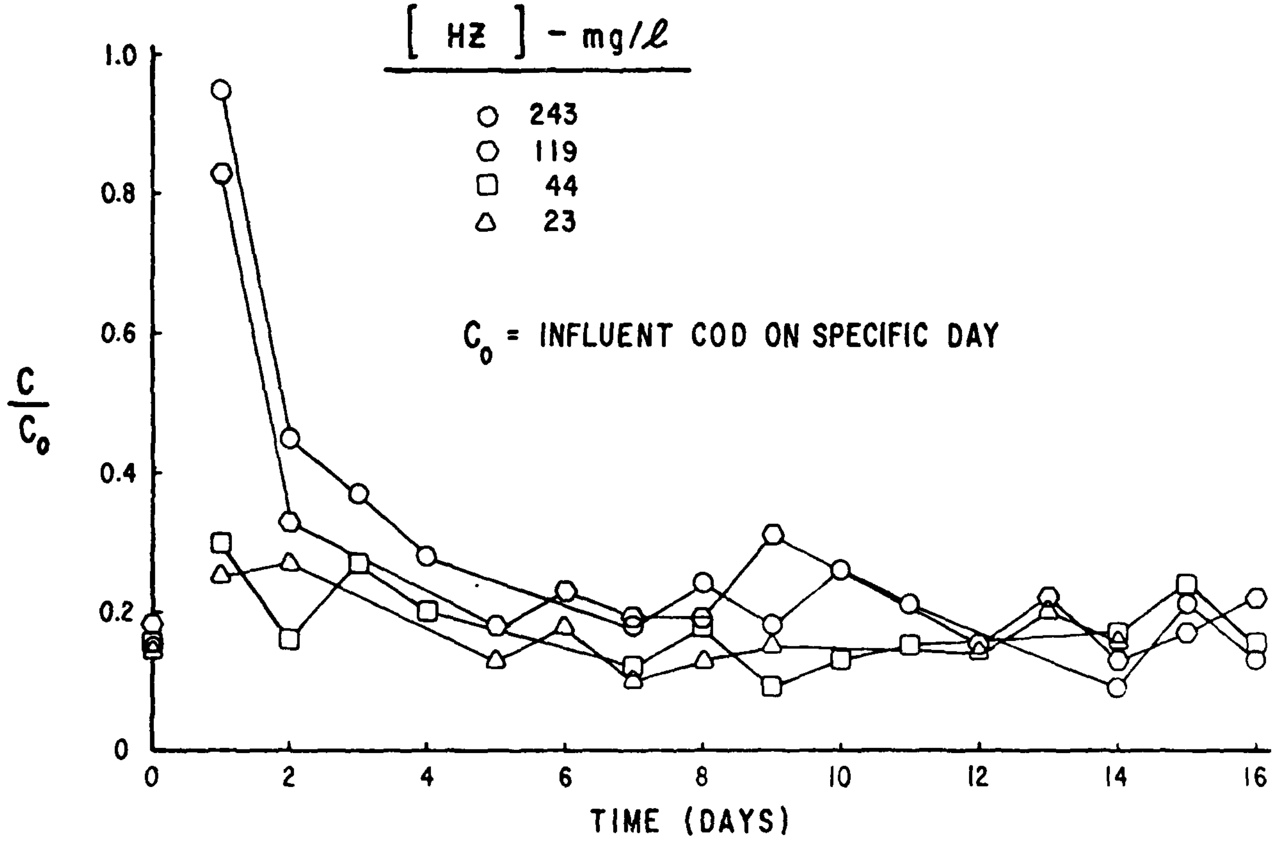

Figure 14. Effluent COD Recovery Following Slug HZ Loads (Mean of Duplicates)

TABLE 8. BACTERIAL DECAY CONSTANTS FOR HZ

Initial HZ (mg/ℓ)	K_1 (h^{-1})	Correlation Coefficient
23	0.498	0.9730
44	0.353	0.9912
119	0.246	0.9914
243	0.160	0.9916

TABLE 9. SLUG LOAD RESPONSE INITIAL CONDITIONS (mg/ℓ)

HZ			Influent		MLSS	
Theoretical	Measured	COD	NH_3-N	ORG-N	Mean	σ
250	243	338	18.7	15.4	5030*	850
125	119	337	17.2	14.8	4260	46
50	44	319	13.0	15.3	4700*	113
25	23	340	14.6	6.5	4130	615

* Wasted to 4500 mg/ℓ

Recovery of the nitrifying bacteria is slower than for the heterotrophs. In Figure 15, it can be seen that ammonia oxidation had not returned to normal until after 7 to 10 days. There appears to be an additional lag of from 1 to 8 days until a viable Nitrobacter sp. population is reestablished, as indicated by Figure 16, suggesting that HZ is toxic to this species as well.

As noted earlier, the slug doses of 243 mg/ℓ and 119 mg/ℓ produced significant cell lysis, the end result being increased solids in the effluent. Figure 17 indicates that, at 243 mg/ℓ, the MLSS dropped to a low of approximately 2000 mg/ℓ for about 4 days while those reactors receiving 119 mg/ℓ HZ declined to approximately 3000 mg/ℓ in this same time frame. Recovery at these high concentrations was not complete until 12 to 14 days post-exposure. The 44 mg/ℓ and 23 mg/ℓ slug reactors were not significantly affected with respect to MLSS concentrations although effluent solids increased slightly for the first few days following introduction of the HZ.

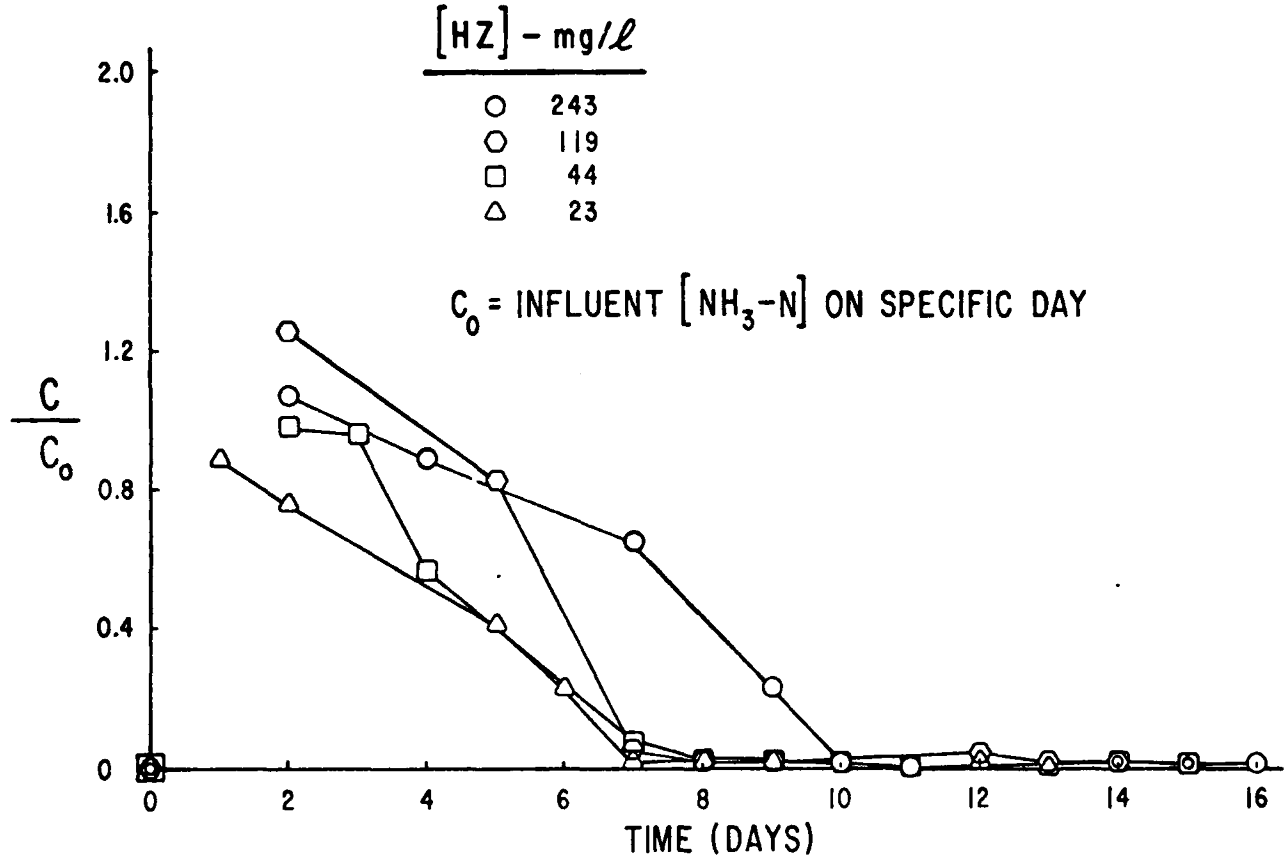

Figure 15. Effluent Ammonia Nitrogen Recovery Following Slug HZ Loads (Mean of Duplicates)

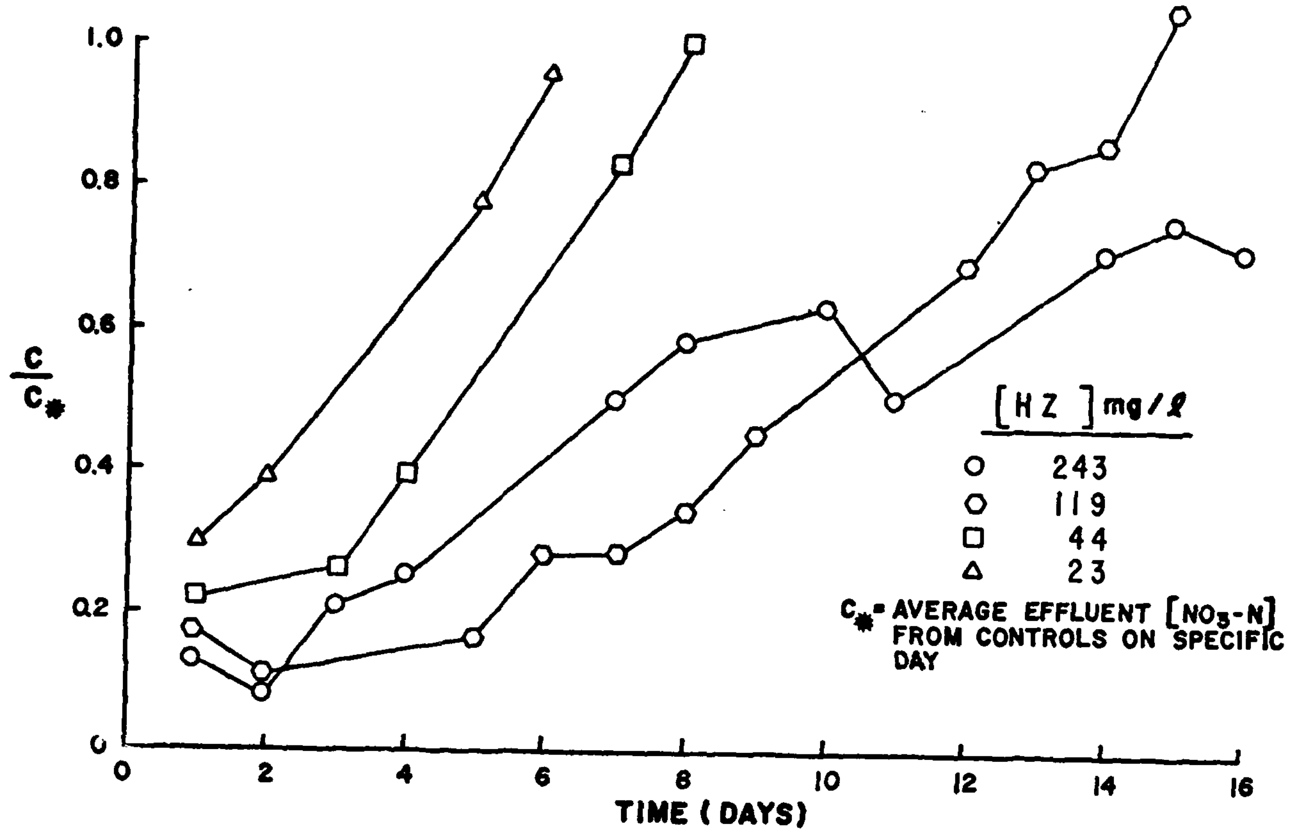

Figure 16. Effluent Nitrate Nitrogen Recovery Following Slug HZ Loads (Means of Duplicates)

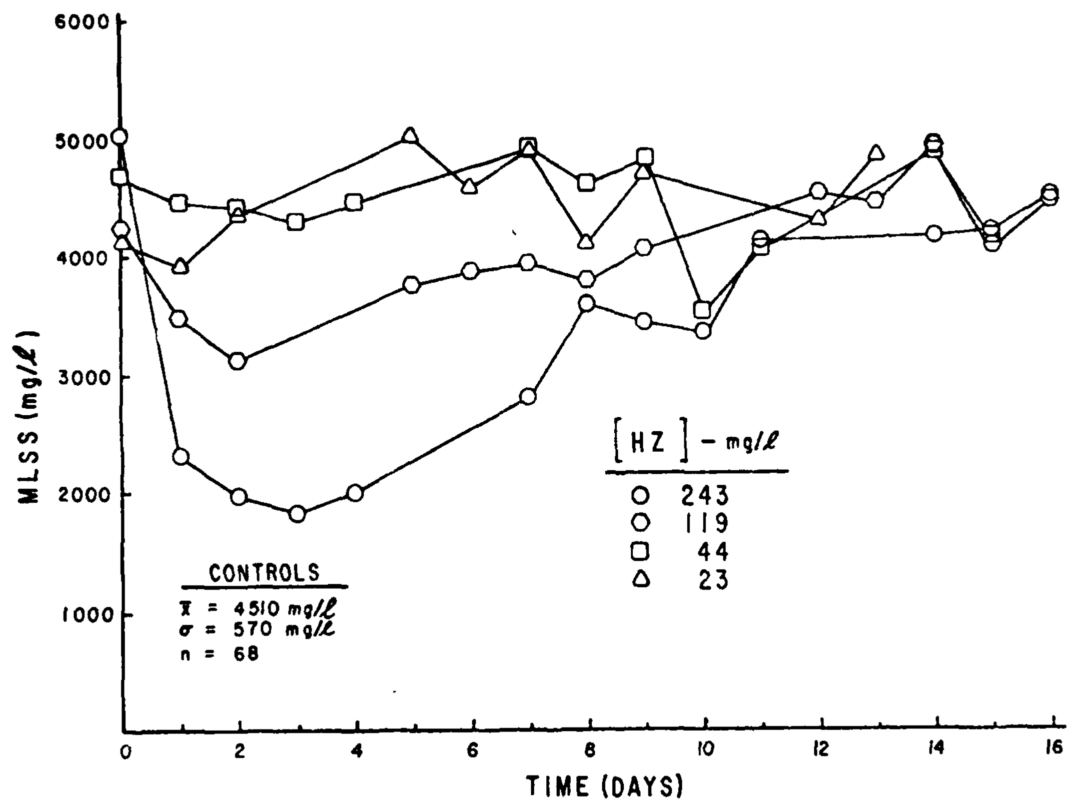

Figure 17. MLSS Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)

SECTION IV

SUMMARY

Continuous Feed Studies

It is apparent from the continuous feed studies that hydrazine could cause significant deterioration of an activated sludge plant if the concentration in the influent exceeded 5 to 10 mg/ℓ. For reactors with hydraulic detention times (θ) of 6 to 7 hours and solids retention times on the order of 7 days, the efficiency of organic carbon removal as measured by COD is seriously degraded when the influent concentration of hydrazine exceeds 10 mg/ℓ, the "no effect level" being approximately 2 mg/ℓ. Only at the lowest hydrazine concentrations tested (<1 mg/ℓ) was the effluent fuel concentration below detectable limits. Studies by Scherfig et al[13] on the effect of hydrazine on algae have established "no effect" concentrations of less than 0.001 mg/ℓ. For sticklebacks fish, the LC_{96} was determined to be 3.4 mg/ℓ by Klein and Jenkins[14].

The influence of the hydrazines on nitrogen speciation is more pronounced than that found for carbon oxidation. Inhibition of ammonia nitrification occurred at concentrations above 1 mg/ℓ. This concentration is significantly lower than the 10^{-3} M (32 mg/ℓ) concentrations found by Yoshida and Alexander[3] to inhibit Nitrosomonas sp. and 10^{-2} M (320 mg/ℓ) at which they reported measurable ammonia oxidation. This was implied from their data on the formation of hydroxylamine which could have resulted from some other mechanism rather than ammonia oxidation. The results shown in Figure 5 illustrate that in this study ammonia oxidation ceased, or was severely reduced, at hydrazine concentration greater than 1 mg/ℓ, as reflected by increasing ammonia and decreasing nitrate in the reactor effluents. Qualitatively, the removal of organic nitrogen closely parallels removal of COD. As noted earlier. hydrazine is reported to be more toxic to Nitrobacter sp. than Nitrosomonas sp. which oxidizes ammonia through hydroxylamine to nitrite. This selective effect could not be observed for hydrazine in the studies reported here. Both organisms appeared to be equally affected by comparison of the ammonia oxidation and nitrate formation data in Figures 5 and 6.

Mixed liquor suspended solids (MLSS) were relatively stable for all the experiments, even though treatment efficiencies were dramatically reduced. It must be assumed that a significant amount of the solids were nonviable.

Slug Loading

Treatment plant efficiency (as measured by COD removal) is not seriously impaired for slug doses which increase the activated sludge basin hydrazine concentration up to 44 mg/ℓ. For an aeration basin of 3.78×10^6 ℓ (3 MGD at an 8 hour detention time), the hydrazine spilled would have to exceed 189 ℓ (50 gallons). At present hydrazine is transported by rail and over some 3.22×10^5 Km (200,000 miles) of public highway annually. Table 10, taken from Watje[15], lists the common modes of transportation for HZ and suggests there is potential for slug doses in the range of concern. Based on the data developed here, washing a spill into the sanitary system is not recommended. In any spill cleanup operation, physical recovery of the fuel and chemical neutralization should be the accepted practice.

TABLE 10. EQUIPMENT USED TO TRANSPORT HYDRAZINE AND AEROZINE 50

Container	DOT Spec	Capacity
Rail Car	103AALW	22690 ℓ (6000 gallons)
Trailer	MC-311	18150 ℓ (4800 gallons)
Drum	SC (HZ)	200 ℓ (53 gallons)
	42C (Aerozine)	170 ℓ (45 gallons)

SECTION V

CONCLUSIONS

1. The use of activated sludge for continuous treatment of waste hydrazine fuel is not recommended. The rigid controls required to insure influent concentrations are maintained below the "no effect" level (1 mg/ℓ would not be practical).

2. Discharges from pretreatment processes must be held to concentrations low enough to prevent values greater than 1 mg/ℓ in the influent to POTWs using activated sludge treatment to insure they are not adversely affected and that final fuel discharges into receiving waters are below environmentally significant levels.

3. Treatment plant efficiency as measured by COD removal is not seriously impaired for slug doses which result in aeration basin fuel concentrations up to 44 mg/ℓ.

4. COD recovery times for slug doses up to 243 mg/ℓ are on the order of 4 to 5 days.

5. Nitrification ceased at slug doses above 23 mg/ℓ. The "no effect" concentration with respect to ammonia oxidation is between 1 to 23 mg/ℓ.

6. Ammonia recovery times for slug doses up to 243 mg/ℓ are on the order of 7 to 10 days.

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