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**TECHNICAL REPORT** 

PHOTOCHEMISTRY OF AQUEOUS NITROGUANIDINE

W. DICKINSON BURROWS, Ph.D., P.E. MARK O. SCHMIDT RALPH H. CHYREK CHARLES I. NOSS, Sc.D.

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U.S. Army Toxic and Hazardous Materials Agency Aberdeen Proving Ground, MD 21010-5401

### U S ARMY BIOMEDICAL RESEARCH & DEVELOPMENT LABORATORY

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#### 19. ABSTRACT (Continued)

For an initial nitroguaniding concentration of 50 mg/L, photolysis exhibits zero-order kinetics through complete disappearance, regardless of pH, and the rate is somewhat faster than for other nitramine explosives and propellants, RDX, for example. The products of photolysis became a matter of concern when it was discovered that photo-nitroguanidine is more toxic to aquatic organisms by several orders of magnitude that the parent compound. The principal products from unbuffered nitroguanidine solutions are guanidine, urea and nitrite ion, with lesser quantities of cyanoguanidine, nitrate ion and ammonia, accounting for 80 percent of the carbon and virtually all of the nitrogen. Nitrosoguanidine is a transient intermediate; in separate experiments it was shown to give 90 percent conversion to guanidinium nitrite at a rate slightly faster than for nitroguanidine. All the stable products of unbuffered nitroguanidine photolysis except urea and nitrate ion are known to be much more toxic to aquatic organisms than the parent compound. Photolysis of nitroguanidine at pH 10 proceeds at nearly the same rate as the unbuffered reaction, but the product mix is different; less than 25 percent of nitroguanidine carbon is accounted for as urea, guanidine and cyanoguanidine. Elemental nitrogen is a significant product.

#### PREFACE

The research reported herein was supported by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Aberdeen Proving Ground, MD, under Project P11 - Treatment of Munition Production Wastes. The Project Officer was Janet Mahannah. This study is part of the U.S. Army Armament, Munitions, and Chemical Command (USAAMCCOM) Pollution Abatement and Environmental Control Technology Program.

High performance liquid chromatography analyses were performed at the U.S. Army Biomedical Research and Development 'aboratory (USABRDL) by Ernst E. Brueggemann; all other analyses were carried out under the direction of Dr. Steven H. Hoke. Synthesis and purification of nitrosoguanidine were performed by Alan B. Rosencrance.

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#### INTRODUCTION

Nitroguanidine, a constituent of triple-base propellant, is presently manufactured at Sunflower Army Ammunition Plant (SFAAP), DeSoto, KS. Although the production facility was designed to operate with no wastewater discharge, it now appears that as much as 400,000 gpd may be generated at the full mobilization production level of 40 tons per day. Reports that nitroquanidine is degraded by ultraviolet (UV) radiation<sup>4</sup> and by sunlight<sup>2</sup> led Noss and Chyrek to investigate UV photolysis and photooxidation as wastewater treatment technologies.<sup>3</sup> The subsequent discovery by van der Schalie that UV-photolyzad nitroguanidine in orders of magnitude more toxic to aquatic organisms than nitroguanidine alone<sup>4</sup> (Table 1) made UV photolysis unsuitable for wastewater treatment and further suggested that discharge of even small quantities of nitroguanidine may be environmentally hazardous. The present study was undertaken to develop a more detailed understanding of the consequences of nitroguanidine photolysis.

TABLE 1.	TOXICITIES O	F NITROGUANIDINE	AND PHOTO	-NITROGUANIDINE <sup>a</sup>
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	Fathead minnow 96 hr LC50, mg/L	Daphnia 48 hr EC50, mg/L		
Nitroguanidine	>2714	>2838		
Photo-nitroguanidine	34.5	24.6		
a. Reference 4.		<u> </u>		

#### EXPERIMENTAL PROCEDURES

#### EQUIPMENT

Two reactors were employed. The stainless steel reactor, described previously, is 6.6 in (16.8 cm) in diameter and 78 in (2 m) tall, with a useful volume of 38 L.<sup>3</sup> An 80-watt UV lamp (estimated 34-watt output in the UV range) encased in a 1-inch (2.5 cm) quartz tube running vertically through the center of the column emits maximum radiation at a wavelength of 253.7 nm. In the radiation-only mode, reactor contents are mixed by recirculation at <u>ca</u>. 6 L/min. For experiments involving gas collection, the apparatus pictured in Figure 1 was used.<sup>5</sup> Four 40-watt ultraviolet lamps surround a 2-inch (5 cm) quartz sample tube of 1.5 L capacity. Cooling water is circulated from a refrigerated constant temperature bath through a centor tube. The apparatus is enclosed in a close-fitting box lined with reflecting foil. Gas is collected in a calibrated bottle at the top.

#### PROCEDURES

Samples of nitroguanidine and nitrosoguanidine for rate and product analyses were dissolved in 19 L of deionized water, pumped into the stainless steel reactor and irradiated at ambient temperature, 100-mL aliquots being





collected at regular intervals. For buffered samples, 20 g of sodium carbonate and 16 g of sodium bicarbonate were added. Nitroguanidine samples were stirred overnight to assure dissolution; nitrosoguanidine, however, appeared to be unstable in water, particularly at pH 10, and it was essential to initiate photolysis as soon as possible after adding the reagent to water. Nitroguanidine, nitrosoguanidine and cyanoguanidine (dicyandiamide) were determined by HPLC by methods described by Burrows, <u>et al.</u>, while nitrate, nitrite, <u>ammonia</u> nitrogen and guanidine were determined by ion chromatography. Urea was determined by a clinical method which enzymicically converts urea nitrogen to <u>ammonia</u>.

Samples prepared for gas collection were either degassed under vacuum with sonication or were deoxygenated by saturation with nitrogen. The latter method gave the best results. Product analysis was by gas chromatography using a thermal conductivity detector and helium as carrier on a molecular sieve. For nitrogen-saturated samples, gas production was measured directly; for degassed samples a correction was made for the known solubility of nitrogen in water (18 mg/L at 1 atmosphere and  $25^{\circ}$ C). Buffer proportions were the same as above.

#### RESULTS AND DISCUSSION

#### KINETICS

Ultraviolet photolysis of nitroguanidine at 50 mg/L or less is zero order with respect to nitroguanidine through complete disappearance, regardless of pH (Figure 2). As in earlier reports on nitramine photolysis, zero-order behavior is considered a likely consequence of products being relatively transparent.<sup>9,9</sup> Photolysis data for nitroguanidine at initial concentrations in the range of 100 mg/L and above could be fitted to a mixed zero-order, first-order equation as follows:

 $a(C_0 - C)/C_0 + bln(C_0/C) = kt$ 

and a + b = 1

with arbitrary values for coefficients a and b of 0.9 and 0.1, respectively, giving a specific rate constant k of 0.021 min<sup>-1</sup> for the unbuffered reaction and 0.016 min<sup>-1</sup> for the reaction at pH 10. The gas collecting apparatus was less efficient, with k equal to <u>ca</u> 0.007 min<sup>-1</sup> (Table B-1).

#### PRODUCTS: UNBUFFERED

Products of unbuffered photolysis are guanidine (Gu), cyanoguanidine (GuCN), nitrite and nitrate ions, urea and ammonia, with nitrosoguanidine (GuNO) as a transient intermediate (Tables 2 and 3), all (except urea) as noted by Noss and Chyrek.<sup>3</sup> Approximately 80 percent of nitroguanidine carbon is accounted for as quanidine, urea and cyanoguanidine (Table 3). The remaining carbon may have been present as cyanamide, which is in equilibrium with cyanoguanidine below pH  $7^{10}$  but which is not detectable at the mg/L level by the HPLC method employed.





Time	Equiv	Equivalent per initial			equivalent of nitroguani			dine	
min 	<u>ри</u>	GuNO	. Gu	6uCN	NO3N	N02-N	NH3-N		
0	1.000	<0.003	<0.11	<0.005	<0.16	<0.16	<0.077		
5	0.799	0.006	<0.11	0.018	<0.16	<0.16	<0.077		
10	0.642	0.012	0.11	0.027	<0.16	0.25	<0.077		
15	0.481	0.016	0.18	0.037	<0.16	0.43	<0.077		
20	0.317	0.019	0.22	0.047	<0.16	0.46	<0.077		
25	0.153	0.017	0.26	0.054	<0.16	0.56	0.077		
30	0.020	0.014	0.32	0.082	<0.16	0.67	0.087		
40	<0.002	0.007	0.32	0.080	<0.16	0.72	0.085		
50	<0.002	0.005	0.32	0.080	<0.16	0.74	0.084		
60	<0.002	0.003	0.33	0.081	<0.16	0.78	0.085		
72	<0.002	<0.003	0.33	0.081	<0.16	9.74	0.085		
90	<0.002	<0.003	0.29	0.081	<0.16	0.74	0.084		

TABLE 2. UV PHOTOLYSIS OF NITROGUANIDINE, 48 MG/L, UNBUFFEREDª

a. Data from Table A-1.

TABLE 3. UV PHOTOLYSIS OF NITROGUANIDINE, 96 MG/L, UNBUFFERED<sup>4</sup>

Time	Equivalent per		initi	initial equivalent of nitroguanidine						
min 	NQ	GuNO	Gu	GUCN	N03-N	NO2-N	NH3-N	Urea		
0	1,000	<0.001		<0.003	<0.05	<0.02	0.036			
5	0.943	0.003	0.24	0.013	<0.05	0.06	0.040			
11	0.776	0.008	0.06	0.017	<0.05	0.19	0.053			
15	0.686	0.011	0.10	0.026	<0.05	0.24	0.056			
20	0.581	0.014	0.12	0.035	<0.05	0.35	0.063			
30	0.418	0.019	0.18	0.050	<0.05	0.56	0.077			
40	0.244	J.020	0.26	0.059	0.06	0.71	0.092			
50	0.126	0.017	0.32	0.068	0.09	0.94	0.108			
60	0.024	0.010	0.38	0.073	0.09	0.99	0.115	0.29		
75	<0.001	0.004	0.40	0.094	0.17	1.06	0.115			
90	<0.001	0.003	0.40	0.096	0.15	1.13	0.115			
107	<0.001	0.001	0.42	0.094	0.15	1.13	0.115			
120	<0.001	<0.001	0.42	0.097	0.10	1.41	0.114	0.28		

a. Data from Table A-2.

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Ultraviolet photolysis of nitrosoguanidine, which is also zero order but slightly faster than nitroguanidine photolysis (Figure 3), yields almost 90 percent of its carbon as guanidine (Table 4). This strongly suggests that nitrosoguanidine is an intermediate in a major pathway to guanidine from nitroguanidine. A simple explanation for the products observed involves photodecomposition through alternative pathways: (1) disproportionation of nitroguanidine to nitrosoguanidine and an oxidized intermediate, and (2) homolysis of the nitroguanidine N-N bond (Scheme 1). The relatively small quantities of nitrate ion and ammonia detected indicate that the first pathway is more important. (The first pathway predicts that four moles of nitrite ion will be produced for every three moles of nitroguanidine photolyzed, as observed in Table 3; however, it does not predict the excess of nitrite from nitrosoguanidine photolysis reported in Table 4. We are unable to explain this discrepancy.)

TABLE 4. UV PHOTOLYSIS OF NITROSOGUANIDINE, 41 MG/L, UNBUFFERED<sup>a</sup>

Time min	Equiva GuNO	lent per Gu	initial GuCN	equivale NO <sub>3</sub> -N	nt of nii NO <sub>2</sub> -N	trosoguanidine NH <sub>3</sub> -N	
					<u> </u>		
0	1.000	<0.11	<0.005	<0.16	<0.16	<0.011	
2	0.919	<0.11	<0.005	<0.16	0.17	<0.011	
5	0.706	0.21	0.015	<0.16	0.46	<0.011	
10.25	0.394	0.52	0.032	<0.16	0.90	0.053	
15	0.100	0.80	0.050	<0.16	1.24	0.064	
20	0.004	0.90	0.060	<0.16	1.47	0.056	
25	<0.002	0.89	0.061	<0.16	1.49	0.054	
30	<0.002	0.89	0.059	<0.16	1.42	0.053	
40	<0.002	0.88	0.063	<0.16	1.47	0.048	
50	<0.002	0.89	0.063	<0.16	1.47	0.045	
60	<0.002	0.85	0.062	<0.16	1.27	0.056	
90	<0.002	0.88	0.061	<0.16	1.33	0.043	

a. Data from Table A-5.

#### PRODUCTS: BUFFERED TO pH 10

Ultraviolet photolysis of nitroguanidine at pH 10 is only slightly slower than unbuffered photolysis (Figure 2), but the product distribution is quite different (Tables 5 and 6). The maximum level of nitrosoguanidine is no more than one third that observed before, and no more than 23 percent of the nitroguanidine carbon can be accounted for as guanidine, cyanoguanidine and urea. (Note that at this pH all cyanamide would be present as cyanoguanidine.<sup>10</sup>) An unusual discovery was that as much as 23 mole percent of elemental nitrogen could be isolated from the buffered reaction, compared with none for the unbuffered reaction. Ammonium nitrite is photochemically converted to elemental nitrogen, but this bimolecular reaction is too slow to account for the production of nitrogen from nitroguanidine, as shown in Table B-3.

Ti <b>me</b> min	Equiva NQ	alent per GuNO	initial GuCN	equivalent NO <sub>3</sub> -N	of nitroqu NO <sub>2</sub> -N	uanidine Urea	
0	1.000	<0.003	<0.005	<0.16	<0.16		
5	0.811	0.003	<0.005	<0.16	<0.16		
10	0.661	0.005	<0.005	<0.16	0.22		
15	0.524	0.006	<0.005	<0.16	0.35		
20	0.375	0.006	0.012	<0.16	0.46		
25	0.237	0.004	0.016	<0.16	0.56		
30	0.092	<0.003	0.022	<0.16	0.68		
40	<0.002	<0.003	0.033	<0.16	0.60		
50	<0.002	<0.003	0.035	<0.16	0.62		
62	<0.002	<0.003	0.036	<0.16	0.59		
75	<0.002	<0.003	0.035	<0.16	0.55		
90	<0.002	<0.003	0.035	<0.16	0.63	0.19	

TABLE 5. UV PHOTOLYSIS OF NITROGUANIDINE, 47 MG/L, pH 10ª

a. Data from Table A-3.

TABLE 6. UV PHOTOLYSIS OF NITROGUANIDINE, 83 MG/L, pH 10<sup>a</sup>

Time min	Equiva NQ	lent per GuNO	initial ea Gu	quivalent GuCN	of nitroguanidine Urea	
0	1.000	<0.001	0.006	<0.003		
5	0.920	0.003	0.007	<0.003		
10	0.842	0.005	0.010	<0.003		
15	0.760	0.007	0.012	<0.003		
20	0.670	0.008	0.014	0.004		
30	0.525	0.008	0.020	0.007		
40	0.386	0.007	0.026	0.009		
50	0.254	0.005	0.033	0.013		
60	0.136	0.003	0.046	0.016	0.16	
75	0.018	<0.001	0.046	0.019		
90	0.002	<0.001	0.046	0.022		
109	<0.001	<0.001	0.046	0.022		
120	<0.001	<0.001	0.050	0.022	0.16	

a. Data from Table A-4.

About 40 percent of the carbon from buffered photolysis of nitrosoguanidine (compared with more than 90 percent for unbuffered photolysis) can be accounted for as urea, guanidine and cyanoguanidine (Table 7). The low yields of guanidine from photolysis of nitroguanidine and nitrosoguanidine may be due to the strongly basic nature of guanidine;<sup>11</sup> at high pH the driving force of protonation is lacking. Although oxidized nitrogen is well accounted for, we are unable to explain the low recovery of carbon from photolysis of these compounds. Carbon dioxide and derivatives thereof are unlikely, since the known photolysis products are hydrolytically stable at pH 10.

Time min	Equivalen GuNO	t per i Gu <sup>b</sup>	nitial GuCN	equivalent NO <sub>2</sub> -N	of nitrosoguanidine Urea <sup>C</sup>
0	1.000	•	0.005	0.28	
2	0.921	<	0.005	0.31	
5	0.806		0.005	0.39	
10	0.622		0.005	0.48	
15	0.446		0.012	0.60	
20	0.275		0.013	0.71	
25	0.103		0.015	0.83	
30	0.028		0.017	0.88	
40	0.001		0.021	0.90	
50	<0.002		0.023	0 91	
60	<0.002 0	. 15	0.024	0.91	0.22

TABLE 7. UV PHOTOLYSIS OF NITROSOGUANIDINE, 45 MG/L, pH 10<sup>a</sup>

a. Data from Table A-9.

b. Estimated from data in Table A-8.

c. Estimated from data in Table A-7.

#### PHOTO-NITROGUANIDINE TOXICITY

All the identified photolysis products of nitroguanidine (except urea<sup>12</sup>) are more toxic to aquatic organisms than the parent compound, as shown in Table 8. However, only nitrite ion is present at a level high enough to account for the greatly enhanced toxicity of photo-nitroguanidine. The concentration of nonionized ammonia, e.g., would be well below the LC50 at pH 8, the condition used by van der Schalie.<sup>4</sup> Of course, synergistic effects cannot be excluded. The US Environmental Protection Agency has declined to recommend restrictive criteria for nitrite, arguing that "concentrations of ... nitrite that would exhibit toxic effects on warm or cold water fish could rarely occur in nature.<sup>413</sup> The half-life for sunlight photolysis of nitroguanidine in natural waters is estimated to be 1-2 days, depending on season and latitude,<sup>2,14</sup> which suggests that wastewater discharged to a moving body of water would present a hazard to aquatic life only if nitroguanidire levels substantially exceeded the current SFAAP NPDES Permit limit of 25 mg/L.

Chemical/Target	Exposure hr	Endpoint	Concentration mg/L	
Guanidinium nitrate <sup>a</sup>				
Fathead minnow Daphnia magna	96 48	LC50 EC50	690 70.2	
Ammonia (nonionized)				
Fathead minnow <sup>b</sup> Daphnids <sup>C</sup>	96 48	LC50 EC50	0.35-3.4 123-189	
Nitrite (as NO <sub>2</sub> )				
Rainbow trout <sup>d</sup> Channel catfish <sup>d</sup> Fathead minnow <sup>e</sup> Daphnia magna <sup>T</sup>	96 96 96	LC50 LC50 LC50 "threshold"	0.6-1.3 13.7 2.2-2.99 18-66	
Cyanoguanidine <sup>g</sup>				
Rainbow trout(?)	48	LC50	<u>ca</u> . 6	
a. Reference 15 b. Reference 16 c. Reference 17 d. Reference 18				

## TABLE 8. ACUTE TOXICITY OF NITROGUANIDINE PHOTOLYSIS PRODUCTS

e. Reference 19 f. Reference 20 g. Reference 21

#### SUMMARY AND CONCLUSIONS

1. Nitroguanidine is readily degraded in water by ultraviolet light and by natural sunlight. The end products of UV photolysis in unbuffered waters are guanidine, urea, cyanoguanidine and nitrite ion, with lesser quantities of nitrate ion and ammonia. Nitrosoguanidine, which is even more readily photolyzed, is an intermediate in a major pathway to guanidine. Eighty percent of the carbon from nitroguanidine and virtually all of the oxidized nitrogen can be accounted for.

2. At pH 10, photolysis of nitroguanidine and nitrosoguanidine is slightly slower, but the product distribution is different. Less than 25 percent of nitroguanidine carbon can be accounted for as guanidine, cyanoguanidine and urea. Gaseous nitrogen is a significant product.

3. Photolyzed nitroguaridine has been shown by others to be much more toxic to aquatic life than nitroguanidine, but given the photolytic half-life of 1-2 days for nitroguanidine in natural waters, and considering the dilution that would take place in that timeframe, it is highly unlikely that wastewaters discharged to a body of moving water could present a hazard to aquatic life unless the nitroguanidine levels substantially exceeded the present NPDES daily average limit of 25 mg/L for Sunflower Army Ammunition Plant.

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### APPENDIX A

### DATA FOR PHOTOLYSIS EXPERIMENTS IN 38 L STAINLESS STEEL REACTOR

Time min	NQ <sup>a</sup> mg/L	GuNO mg/L	Gu <sup>b</sup> mg/L	GuCN mg/L	NO3-N mg/L	NO2-N mg/L	NH3-N mg/L	рH
0	47.90	<0.100	<3	<0.100	<1	<1	<0.5	7.8
5	38.27	0.256	<3	0.342	<1	<1	<0.5	7.7
10	30.759	0.497	3.3	0.726	<Ī	1.6	<0.5	7.3
15	23.042	0.657	4.8	1.017	<1	2.8	<0.5	7.2
20	15.172	0.754	5.9	1.277	<1	3.0	<0.5	6.3
25	7.314	0.699	7.2	1.480	<1	3.6	0.5	5.7
30	0.944	0.564	8.6	1.597	<1	4.3	0.56	4.8
40	<0.100	0.267	8.7	1.541	<1	4.6	0.55	4.7
50	<0.100	0.198	8.7	1.554	<1	4.8	0.54	4.7
50	<0.100	0.107	8.9	1.562	<1	5.0	0.55	
72	<0.100	<0.100	8.9	1.564	< <u>-</u>	4.9	0 55	
90	<0.100	<0.100	8.0	1.569	<1	4.8	0.54	4.7

TABLE A-1. UV PHOTOLYSIS OF NITROGUANIDINE, UNBUFFERED

a. Prepared from 0.95 g of nitroguanidine in 19 L of water.

b. Guanidine reported as guanidine, not as nitrogen.

Time min	NQ <sup>a</sup> mg/L	GuNO mg/L	Gu <sup>b</sup> mg/L	GuCN mg/L	NO3 mg/L	NO2 mg7l	NH3-N mg/L	Urea <sup>b</sup> mg/L
0	95,978	<0.100		<0.100	<3	<1	0.46	
5	90.548	0.274	0.93	0.517	<3	2.4	0.52	
11	74.471	0.685	2.45	0.677	<3	8.1	0.69	
15	65.887	0.865	4.01	1.024	<3	10.0	0.73	
20	55.752	1.145	4.50	1.371	<3	15.0	0.82	
30	40.144	1.561	7.12	1.926	<3	24.0	1.00	
40	23.447	1.653	10.26	2.273	3.4	30.0	1.19	
50	12.046	1.385	12.48	2.620	5.4	40.0	1.39	
60	2.347	0.813	14.94	2.828	5.1	42.0	1.49	7.45
75	<0.100	0.363	15.68	3.660	9.6	45.0	1.49	
90	<0.100	0.220	15.68	3.730	8.4	48.0	1.49	
107	<0.100	0.116	16.17	3.643	8.4	48.0	1.49	
120	<0.100	<0.100	16.17	3.744	5.7	60.0	1.47	7.15

TABLE A-2. UV PHOTOLYSIS OF NITROGUANIDINE, UNBUFFERED

a. Prepared from 2.0 g of nitroguanidine in 19 L of water.
 b. Guanidine and urea reported as guanidine or urea nitrogen.

min	ng/L	GuNO mg/L	Gu <sup>b</sup> mg/L	GuCN mg/l	NO3-N mg/l	NO2-N mg/L	hq	Urea <sup>c</sup> mg/L
0	46.940	<0.100		<0.100	<1	<1	10.1	
5 10	38.040	0.133		<0.100			10.1	
15	24.602	0.210		<0.100	<1 <1	2.4	3.3 9 9	
20d	17.593	0.220		0.228	<1	2.9	10.0	
25	11.133	0.149		0.312	<1	3.5	10.1	
30	4.339	<0.100		0.413	<1	4.3	10.2	
40	<0.100	<0.100		0.628	<1	3.8	10.2	
5U 6 7	<0.100	<0.100		0.555		3.9	10.2	
75	<0.100	<0.100		0.666	<1	3.5	10.1	
90	<0.100	<0.100		0.667	<1	4.0	10.0	2.4
1. Pre 5. Gua 2. Ure 1. San	nidine n a report ple yel! TABLE A	om 0.95 ( ot measure ed as ure ow. 4. UV (	p of hit red. sa nitro PHOTOLYS	ogen. DIS OF NI	TROGUANI	DINE, BU	IFFERED	) TO pH
a. Pre b. Gua c. Ure d. San	nidine n a report ple yel! TABLE A NQ <sup>a</sup>	om 0.95 ( ot measure ed as ure ow. 4. UV ( GuNO	Gu <sup>b</sup>	Guch Guch	TROGUANII	DINE, BU		) TO pH Jrea <sup>d</sup>
a. Pre b. Gua c. Ure d. San Time	nidine n a report ple yel! TABLE A NQ <sup>a</sup> 82.78	om 0.99 ( ot measure ow. -4. UV ( GuNO <0.100	Gub 0.20	Guch Guch (0.100	TROGUANII	DINE, BU NO <sub>2</sub> -N	IFFERED	) TO pH Jrea <sup>d</sup>
a. Preb. Gua c. Ure d. San Time 0 5	NQ <sup>a</sup> 82.78 76.16	om 0.95 ( ot measure ow. 4. UV ( GuNO (0.100 0.202 0.255	Gub 0.20 0.25 0.22	Gucn Gucn (0.100 (0.100) (0.100)	TROGUANII	DINE, BU		) TO pH Jrea <sup>d</sup>
a. Preb. Gua c. Ure d. San Time 0 5 10 15	NQ <sup>a</sup> 82.78 76.16 69.66 62.89	om 0.95 ( ot measure ow. -4. UV ( GuNO <0.100 0.202 0.355 0.478	Gub 0.20 0.25 0.41	GuCN (0.100 (0.100 (0.100 (0.100 (0.100 (0.100	TROGUANII	DINE, BU NO <sub>2</sub> -N	IFFERED	) TO pH Jrea <sup>d</sup>
a. Pre b. Gua c. Ure d. San Time 0 5 10 15 20	NQ <sup>a</sup> 82.78 76.16 69.66 62.89 55.438	om 0.95 ( ot measure ow. 4. UV ( GuNO <0.100 0.202 0.355 0.478 0.551	Gu <sup>b</sup> 0.20 0.25 0.32 0.41 0.48	Ogen. SIS OF NI GUCN <0.100 <0.100 <0.100 <0.100 0.136	TROGUANII	DINE, BU	IFFERED	) TO pH Jrea <sup>d</sup>
a. Preb. Gua c. Ure d. San Time 0 5 10 15 20 30	Real Pares Fr nidine n a report ple yel! TABLE A NQ <sup>a</sup> 82.78 76.16 69.66 62.89 55.438 43.438	om 0.95 ( ot measure ow. -4. UV ( GuNO (0.100 0.202 0.355 0.478 0.551 0.564	0.20 0.25 0.32 0.41 0.68	Qen. SIS OF NI GUCN <0.100 <0.100 <0.100 <0.100 0.136 0.237	TROGUANII	DINE, BU		) TO pH Jrea <sup>d</sup>
a. Preb. Gua c. Ure d. San Time 0 5 10 15 20 30 40	Real Pares Fr nidine n a report ple yell TABLE A NQ <sup>a</sup> 82.78 76.16 69.66 62.89 55.438 43.438 31.961	om 0.95 ( ot measure ow. -4. UV f GuNO (0.100 0.202 0.355 0.478 0.551 0.564 0.460	Gub 0.20 0.25 0.32 0.41 0.48 0.68 0.87	GuCN (0.100 (0.100 (0.100 (0.100 (0.100 (0.136 0.237 0.315	TROGUANII	DINE, BU	IFFERED	) TO pH Jrea <sup>d</sup>
a. Preb. Gua c. Ure d. San Time 0 5 10 15 20 30 40 50 6	NQ <sup>a</sup> 82.78 76.16 69.66 62.89 55.438 43.438 31.961 21.026	om 0.95 ( ot measure ow. -4. UV ( GuNO (0.100 0.202 0.355 0.478 0.551 0.564 0.460 0.325	Gub 0.20 0.25 0.32 0.41 0.48 0.68 0.87 1.09	Qen. SIS OF NI GuCN <0.100 <0.100 <0.100 <0.100 <0.100 0.136 0.237 0.315 0.426	TROGUANII	DINE, BU	IFFERED	) TO pH Jrea <sup>d</sup>
a. Preb. Gua c. Ure d. San Time 0 5 10 15 20 30 40 50 60 60 75 6	Real Pares II nidine n a report ple yell TABLE A NQ <sup>a</sup> 82.78 76.16 69.66 62.89 55.438 43.438 31.961 21.026 11.275 1.245	om 0.95 ( ot measured as une ow. -4. UV f GuNO (0.100 0.202 0.355 0.478 0.551 0.564 0.460 0.325 0.193	0.20 0.25 0.32 0.41 0.48 0.68 0.87 1.09 1.50	Qen. SIS OF NI GUCN <0.100 <0.100 <0.100 <0.100 <0.100 0.136 0.237 0.315 0.426 0.527 0.546	TROGUANII	DINE, BU		) TO pH Jrea <sup>d</sup> 3.5
a. Preb. Gua c. Ure d. San Time 0 5 10 15 20 30 40 50 60 75 90 60	NQa 82.78 76.16 69.66 62.89 55.438 43.438 31.961 21.026 11.275 1.245 0 150	om 0.95 ( ot measured as une ow. -4. UV ( GuNO 0.202 0.355 0.478 0.551 0.564 0.460 0.325 0.193 <0.100 c0.100	Gub 0.20 0.25 0.32 0.41 0.48 0.68 0.87 1.09 1.50 1.53	Qen. GIS OF NI GUCN (0.100 (0.100 (0.100 (0.100 (0.100 (0.100 (0.100 0.136 0.237 0.315 0.426 0.527 0.649 0.750	TROGUANII	DINE, BU	IFFERED	) TO pH Jrea <sup>d</sup> 3.5
a. Preb. Gua c. Ure d. San Time 0 5 10 15 20 30 40 50 60 60 75 90 90 109	NQ <sup>a</sup> 82.78 76.16 69.66 62.89 55.438 43.438 31.961 21.026 11.275 1.245 0.150 <0.100	om 0.95 ( ot measured as une ow. -4. UV ( GuNO (0.100 0.202 0.355 0.478 0.551 0.564 0.460 0.325 0.193 <0.100 <0.100 <0.100	Gub 0.20 0.25 0.32 0.41 0.48 0.68 0.87 1.09 1.50 1.53 1.54 1.55	Qen. SIS OF NI GuCN (0.100 (0.100 (0.100 (0.100 (0.100 (0.100 0.136 0.237 0.315 0.426 0.527 0.649 0.750 0.750 0.750	TROGUANII	DINE, BU		) TO pH Jrea <sup>d</sup> 3.5

TABLE A-3. UV PHOTOLYSIS OF NITROGUANIDINE, BUFFERED TO PH 10

d. Urea reported as urea nitrogen.e. Sample yellow

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Time min	NQ mg/L	GuNO <sup>a</sup> mg/L	Gu <sup>b</sup> mg/L	GuCN mg/L	NG3-N mg/L	NO <sub>2</sub> -N mg7L	NH3-N mg/L	рH	
0	<0.100	40.533	<3	<0.100	<1	<1	<0.7	7.7	
2	<0.100	37.269	<3	<0.100	<1	1.1	<0.7	7.6	
5	<0.100	28.600	5.7	0.287	<1	3.0	<0.7	7.4	
10.25	<0.100	15.960	14.0	0.617	<1	5.8	0.34	7.1	
15	<6.100	4.034	21.7	0.970	< <u>1</u>	8.0	0.41	6.4	
20	<0.100	0.157	24.5	1.170	٩	9.5	0.36	6.4	
25	<0.100	<0.100	24.3	1.178	đ	9.6	0.35	6.3	
30	<0.100	<0.100	24.2	1.145	٨Ī	9.2	0.34	6.2	
40	<0.100	<0.100	23.9	1.222	<1	9.5	0.31	6.1	
50	<0.100	<0.100	24.2	1.228	d	9.5	0.29	6.2	
60	<0.100	<0.100	23.2	1.202	<1	8.2	0.35	4.1	
75	<j.100< td=""><td>&lt;0.100</td><td>24.0</td><td>1.189</td><td>&lt;1</td><td>8.6</td><td>0.28</td><td>5</td><td></td></j.100<>	<0.100	24.0	1.189	<1	8.6	0.28	5	

TABLE A-5. UV PHOTOLYSIS OF NITROSOGUANIDINE, UNBUFFERED

a. Prepared from 0.97 g Of nitrosoguanidine in 19 L of water. b. Guanidine reported as guanidine.

TABLE A-6. UV PHOTOLYSIS OF NITROSOGUANIDINE, UNBUFFERED

Time min	GuNO <sup>a</sup> mg/L	GuCN mg/L
0	45.68	<0.10
2	41.43	<0.10
5	33.57	<0.10
10	20.64	<0 10
15	6.39	0.23
20	0.11	0.53
27	<0.19	0.70
35	<0.10	0.78
45	<g.10< td=""><td>0.90</td></g.10<>	0.90
60	<0.10	1.00
75	<0.10	1.12

a. Prepared from J.95 g of nitrosoguanidine in 19 L of water.

Time min	NQ mg/L	GuNO <sup>a</sup> mg/l	Gu <sup>b</sup> mg/L	GuCN mg/L	NO3-N mg/L	NO2-N mg7L	Urea <sup>C</sup> mg/L	pH	
0	<0.100	34.749		<0.100	<1	<1		10.3	
2	<0.100	33.159		<0.100	<1	<1		10.3	
5	<0.100	28.504		<0.100	<1	1.9		10.3	
10	<0.100	21.918		<0.100	<1	3.6		10.3	
15	<0.100	16.036		<0.100	<1	4.7		10.3	
20	<0.100	10.102		<0.100	<1	7.0		10.3	
25	<0.100	4.612		0.5358	<1	8.2		10.3	
30	<0.100	1.127		0.4172	<1 -	8.6		10.4	
40	<0.100	<0.100		0.5735	<1	9.1		10.3	
50d	<0.100	<0.100		0.5757	<1	9.1		10.3	
60	<0.100	<0.100		0.6261	<1	9.3		10.3	
75	<0.100	<0.100		0.6183	<1	8.6	3.1	10.2	

TABLE A-7. UV PHOTOLYSIS OF NITROSOGUANIDINE, BUFFERED TO pH 10

a. Prepared from 0.95 g of nitrosoguanidine in 19 L of water.

b. suanidine not measured.

c. Urea reported as urea nitrogen.d. Sample yellow.

TABLE A-8. UV PHOTOLYSIS OF NITROSOGUANIDINE, BUFFERED TO pH 10

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Time min	GuNO <sup>a</sup> mg/L	Gu <sup>b</sup> mg/L	GuCN mg/L	
0	24.46		<0.10	
2	24.43		<0.10	
5	16.21		0.35	
10	8.69		0.44	
15	3.15		0.46	
20	2.47		0.48	
27	<0.10		0.51	
35	<0.10		0.50	
45	<0.10		0.51	
60	<0.10		0.51	
76	<0.10	3.25	0.51	

a. Prepared from U.95 g of nitrosoguanidine in 19 L of water b. Guanidine reported as guanidine nitrogen.

Time min	6uN0 <sup>a</sup> mg/L	Gu <sup>b</sup> mg/L	GuCN mg/L	NO2-N mg7L	Urea <sup>c</sup> mg/L	
0	45,002		<0.100	2.01		
ž	41.430		<0.100	2.19		
5	36.272		<0.100	2.77		
10	27.994		<0.100	3.41		
15	20.067		0.259	4.33		
20	12.367		0.288	5.09		
25	4.632		0.326	5.95		
30	1.276		0.370	6.29		
40	0.032		0.440	6.44		
50	<0.100		0.497	6.48		
60	<0.100		0.522	6.53	0.0	

TABLE A-9. UV PHOTOLYSIS OF NITROSOGUANIDINE, BUFFERED TO pH 10

a. Prepared from 1.0 g of nitrosoguanidine in 19 L of water.
b. Guanidine analysis by fluorescence method unsatisfactory.
c. Urea reported as urea nitrogen.

### APPENDIX B

### DATA FOR PHOTOLYSIS EXPERIMENTS IN GAS COLLECTING APPARATUS

Time hrs	NQ mg/'.	GuNO mg/L	GuCN mg/L	NO3-N mg/L	NO2-N mg?L	
0	923.385	<0.100	<0,100	NDª	ND <sup>a</sup>	
0.5	724.480	7.500	0.844	NDª	NDª	
1	381.909	11.167	2.205	1.6	85	
1.5	333.520	9.855	4.044	2.0	108	
2	274.470	10.094	7.293	2.7	158	
2.5	213.982	9.548	8.869	3.0	200	
3	148.465	7.463	13.393	3.3	177	
4	34.648	2.475	16.431	4.3	222	
5	2.732	<0.100	18.691	4.3	261	
6	<0.100	<0.100	18.897	4.3	302	
7	<0.100	<0.100	18.132	4.3	237	
8	<0.100	<0.100	19.336	4.4	221	
9	<0.100	<0.100	16.9 <b>86</b>	4.3	199	
10	<0.100	<0.100	17.493	4.5	215	
11	<0.100	<0.100	17.697	5.1	211	
12	<0.100	<0.100	17.259	4.9	213	
13	<0.100	<0.100	17.758	5.5	203	
14	<0.100	<0.100	17.291	5.8	222	
15	<0.100	<0.100	17.787	5.8	211	
16	<0.100	<0.100	19.051	5.9	212	
17	<0.100	<0.100	20.726	6.2	199	
18	<0.100	<0.100	19.607	6.3	181	
19	<0.100	<0.100	20.134	6.2	183	
20	<0.100	<0.100	20.288	6.7	195	
21	<0.100	<0.100	20.337	6.8	166	
22	<0.100	<0.100	19.862	7.1	163	
23	<0.100	<0.100	20.365	6.6	190	

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TABLE B-1. UV PHOTOLYSIS OF NITROGUANIDINE, BUFFERFD TO pH 10

a. ND = Below detection limits.

	Run 9ª	Run 10 <sup>4</sup>	Run 11 <sup>b</sup>	
NQ initial, mg/L	1267	1140	1130	
NQ final, mg/L	37.7	0.74	3.08	
pH initial	10.25	10.0	10.25	
pH final	9.76	9.95	10.00	
Vol gas collected, mL	78	42	100	
Correction for N <sub>2</sub> solubility, mL	27	27		
Total gas, mL	105	69	100	
Percent N <sub>2</sub> in gas	96.5	93.5	93.6	
Temperature, <sup>O</sup> C	25	25	25	

TABLE 8-2. UV PHOTOLYSIS OF NITROGUANIDINE, BUFFERED TO pH 10

a. Sample initially degassed.b. Sample presaturated with nitrogen.

Time hr	NOZ-N mg/L	NH3-N ( mg/L	Gas collected mL
0	70	70	0
24			35
55			75
81	47	35	100

### TABLE B-3. UV PHOTOLYSIS OF AMMONIUM NITRITE®

a. Prepared as 0.005 M NaNO2, 0.005 N (NH4)SO4 and 0.1 M NaHCO3.

### APPENDIX C

### GLOSSARY OF TERMS

Gu	guanidine
GuCN	cyanoguanidine (dicyandiamide)
GuNO	nitrosoguanidine
HPLC	high performance liquid chromatography
NPDES	National Pollution Discharge Flimination System
NO	nitroguanidine
SFAAP	Sunflower Army Ammunition Plant
UV	ultraviolet

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