

AD-A085 186

AIR FORCE ENGINEERING AND SERVICES CENTER TYNDALL AF--ETC F/G 21/9.1
THE EFFECTS OF AMINE-BASED MISSILE FUELS ON THE ACTIVATED SLUDGE--ETC(U)
OCT 79 M G MACNAUGHTON, J A FARMWALD

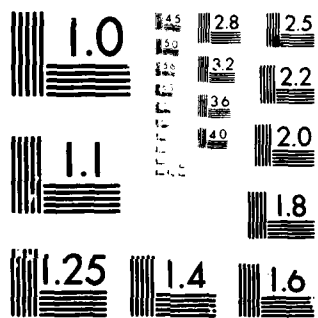
UNCLASSIFIED

AFESC/ESL-TR-79-39

NL

1 of 2
250
AD-A085 186

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000
1001
1002
1003
1004
1005
1006
1007
1008
1009
1010
1011
1012
1013
1014
1015
1016
1017
1018
1019
1020
1021
1022
1023
1024
1025
1026
1027
1028
1029
1030
1031
1032
1033
1034
1035
1036
1037
1038
1039
1040
1041
1042
1043
1044
1045
1046
1047
1048
1049
1050
1051
1052
1053
1054
1055
1056
1057
1058
1059
1060
1061
1062
1063
1064
1065
1066
1067
1068
1069
1070
1071
1072
1073
1074
1075
1076
1077
1078
1079
1080
1081
1082
1083
1084
1085
1086
1087
1088
1089
1090
1091
1092
1093
1094
1095
1096
1097
1098
1099
1100
1101
1102
1103
1104
1105
1106
1107
1108
1109
1110
1111
1112
1113
1114
1115
1116
1117
1118
1119
1120
1121
1122
1123
1124
1125
1126
1127
1128
1129
1130
1131
1132
1133
1134
1135
1136
1137
1138
1139
1140
1141
1142
1143
1144
1145
1146
1147
1148
1149
1150
1151
1152
1153
1154
1155
1156
1157
1158
1159
1160
1161
1162
1163
1164
1165
1166
1167
1168
1169
1170
1171
1172
1173
1174
1175
1176
1177
1178
1179
1180
1181
1182
1183
1184
1185
1186
1187
1188
1189
1190
1191
1192
1193
1194
1195
1196
1197
1198
1199
1200
1201
1202
1203
1204
1205
1206
1207
1208
1209
1210
1211
1212
1213
1214
1215
1216
1217
1218
1219
1220
1221
1222
1223
1224
1225
1226
1227
1228
1229
1230
1231
1232
1233
1234
1235
1236
1237
1238
1239
1240
1241
1242
1243
1244
1245
1246
1247
1248
1249
1250
1251
1252
1253
1254
1255
1256
1257
1258
1259
1260
1261
1262
1263
1264
1265
1266
1267
1268
1269
1270
1271
1272
1273
1274
1275
1276
1277
1278
1279
1280
1281
1282
1283
1284
1285
1286
1287
1288
1289
1290
1291
1292
1293
1294
1295
1296
1297
1298
1299
1300
1301
1302
1303
1304
1305
1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344
1345
1346
1347
1348
1349
1350
1351
1352
1353
1354
1355
1356
1357
1358
1359
1360
1361
1362
1363
1364
1365
1366
1367
1368
1369
1370
1371
1372
1373
1374
1375
1376
1377
1378
1379
1380
1381
1382
1383
1384
1385
1386
1387
1388
1389
1390
1391
1392
1393
1394
1395
1396
1397
1398
1399
1400
1401
1402
1403
1404
1405
1406
1407
1408
1409
1410
1411
1412
1413
1414
1415
1416
1417
1418
1419
1420
1421
1422
1423
1424
1425
1426
1427
1428
1429
1430
1431
1432
1433
1434
1435
1436
1437
1438
1439
1440
1441
1442
1443
1444
1445
1446
1447
1448
1449
1450
1451
1452
1453
1454
1455
1456
1457
1458
1459
1460
1461
1462
1463
1464
1465
1466
1467
1468
1469
1470
1471
1472
1473
1474
1475
1476
1477
1478
1479
1480
1481
1482
1483
1484
1485
1486
1487
1488
1489
1490
1491
1492
1493
1494
1495
1496
1497
1498
1499
1500
1501
1502
1503
1504
1505
1506
1507
1508
1509
1510
1511
1512
1513
1514
1515
1516
1517
1518
1519
1520
1521
1522
1523
1524
1525
1526
1527
1528
1529
1530
1531
1532
1533
1534
1535
1536
1537
1538
1539
1540
1541
1542
1543
1544
1545
1546
1547
1548
1549
1550
1551
1552
1553
1554
1555
1556
1557
1558
1559
1560
1561
1562
1563
1564
1565
1566
1567
1568
1569
1570
1571
1572
1573
1574
1575
1576
1577
1578
1579
1580
1581
1582
1583
1584
1585
1586
1587
1588
1589
1590
1591
1592
1593
1594
1595
1596
1597
1598
1599
1600
1601
1602
1603
1604
1605
1606
1607
1608
1609
1610
1611
1612
1613
1614
1615
1616
1617
1618
1619
1620
1621
1622
1623
1624
1625
1626
1627
1628
1629
1630
1631
1632
1633
1634
1635
1636
1637
1638
1639
1640
1641
1642
1643
1644
1645
1646
1647
1648
1649
1650
1651
1652
1653
1654
1655
1656
1657
1658
1659
1660
1661
1662
1663
1664
1665
1666
1667
1668
1669
1670
1671
1672
1673
1674
1675
1676
1677
1678
1679
1680
1681
1682
1683
1684
1685
1686
1687
1688
1689
1690
1691
1692
1693
1694
1695
1696
1697
1698
1699
1700
1701
1702
1703
1704
1705
1706
1707
1708
1709
1710
1711
1712
1713
1714
1715
1716
1717
1718
1719
1720
1721
1722
1723
1724
1725
1726
1727
1728
1729
1730
1731
1732
1733
1734
1735
1736
1737
1738
1739
1740
1741
1742
1743
1744
1745
1746
1747
1748
1749
1750
1751
1752
1753
1754
1755
1756
1757
1758
1759
1760
1761
1762
1763
1764
1765
1766
1767
1768
1769
1770
1771
1772
1773
1774
1775
1776
1777
1778
1779
1780
1781
1782
1783
1784
1785
1786
1787
1788
1789
1790
1791
1792
1793
1794
1795
1796
1797
1798
1799
1800
1801
1802
1803
1804
1805
1806
1807
1808
1809
1810
1811
1812
1813
1814
1815
1816
1817
1818
1819
1820
1821
1822
1823
1824
1825
1826
1827
1828
1829
1830
1831
1832
1833
1834
1835
1836
1837
1838
1839
1840
1841
1842
1843
1844
1845
1846
1847
1848
1849
1850
1851
1852
1853
1854
1855
1856
1857
1858
1859
1860
1861
1862
1863
1864
1865
1866
1867
1868
1869
1870
1871
1872
1873
1874
1875
1876
1877
1878
1879
1880
1881
1882
1883
1884
1885
1886
1887
1888
1889
1890
1891
1892
1893
1894
1895
1896
1897
1898
1899
1900
1901
1902
1903
1904
1905
1906
1907
1908
1909
1910
1911
1912
1913
1914
1915
1916
1917
1918
1919
1920
1921
1922
1923
1924
1925
1926
1927
1928
1929
1930
1931
1932
1933
1934
1935
1936
1937
1938
1939
1940
1941
1942
1943
1944
1945
1946
1947
1948
1949
1950
1951
1952
1953
1954
1955
1956
1957
1958
1959
1960
1961
1962
1963
1964
1965
1966
1967
1968
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
1984
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
2024
2025
2026
2027
2028
2029
2030
2031
2032
2033
2034
2035
2036
2037
2038
2039
2040
2041
2042
2043
2044
2045
2046
2047
2048
2049
2050
2051
2052
2053
2054
2055
2056
2057
2058
2059
2060
2061
2062
2063
2064
2065
2066
2067
2068
2069
2070
2071
2072
2073
2074
2075
2076
2077
2078
2079
2080
2081
2082
2083
2084
2085
2086
2087
2088
2089
2090
2091
2092
2093
2094
2095
2096
2097
2098
2099
2100
2101
2102
2103
2104
2105
2106
2107
2108
2109
2110
2111
2112
2113
2114
2115
2116
2117
2118
2119
2120
2121
2122
2123
2124
2125
2126
2127
2128
2129
2130
2131
2132
2133
2134
2135
2136
2137
2138
2139
2140
2141
2142
2143
2144
2145
2146
2147
2148
2149
2150
2151
2152
2153
2154
2155
2156
2157
2158
2159
2160
2161
2162
2163
2164
2165
2166
2167
2168
2169
2170
2171
2172
2173
2174
2175
2176
2177
2178
2179
2180
2181
2182
2183
2184
2185
2186
2187
2188
2189
2190
2191
2192



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

ADA 085186

DDC FILE COPY



UNCLASSIFIED

ESL-TR-79-39

2

THE EFFECTS OF AMINE BASED MISSILE FUELS ON THE ACTIVATED SLUDGE PROCESS

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

OCTOBER 1979

FINAL REPORT
JUNE 1977 - JULY 1979

DTIC
ELECTE
S JUN 9 1980 D
A

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

AFEGSC

ENGINEERING AND SERVICES LABORATORY
AIR FORCE ENGINEERING AND SERVICES CENTER
TYNDALL AIR FORCE BASE, FLORIDA 32403

80 6 6 092

NOTICE

Please do not request copies of this report from
HQ AFESC/RD (Engineering and Services Laboratory).
Additional copies may be purchased from:

National Technical Information Service
5285 Port Royal Road
Springfield, Virginia 22161

Federal Government agencies and their contractors
registered with Defense Technical Information Center
should direct requests for copies of this report to:

Defense Technical Information Center
Cameron Station
Alexandria, Virginia 22314

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ESL-TR-79-39	2. GOVT ACCESSION NO. AD-A085186	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THE EFFECTS OF AMINE BASED MISSILE FUELS ON THE ACTIVATED SLUDGE PROCESS.		5. TYPE OF REPORT/PERIOD COVERED FINAL REPORT Jun 77 - Jul 79
7. AUTHOR(s) Michael G./MacNaughton Jay A./Farmwald		8. CONTRACT OR GRANT NUMBER(s) 12 107 C
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Sciences Branch, Environics Division Air Force Engineering and Services Laboratory Tyndall Air Force Base, Florida 32403		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS JON 2103-7W-84 Program Element: 63723F 17 7W
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Engineering and Services Laboratory Tyndall Air Force Base, Florida 32403		12. REPORT DATE Oct 79
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) FE 637-3F		13. NUMBER OF PAGES 106
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) 14) AFESC/ESL-TR-79-39		
18. SUPPLEMENTARY NOTES Availability of this report is specified on verso of front cover.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Hydrazine Activated Sludge Unsymmetricaldimethylhydrazine Missile Propellants Monomethylhydrazine Toxicity Biodegradation Environmental Chemistry Environics Pollution Control Environmental Quality Amine Fuels		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The Air Force (AF) procures amine based hydrazine 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 the AF Space Shuttle Program. This report summarizes data on the effects of Hydrazine (HZ), Monomethylhydrazine (MMH), and Unsymmetricaldimethylhydrazine (UDMH) in conventional		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

394633

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. Abstract (Concluded) activated sludge systems for semi-continuous addition of waste containing the fuels and for slug doses from accidental spills.

It was concluded from the continuous feed studies that the three hydrazines could cause significant deterioration of an activated sludge plant if the concentration in the influent exceeded a few mg/l. For an aeration basin with a common hydraulic detention time of 9 hours, the efficiency of organic removal is seriously degraded when the influent concentration of HZ exceeds 10 mg/l. For UDMH and MMH this total failure results at concentrations of approximately 8 mg/l and 5 mg/l, respectively. Interpolating from these continuous feed studies, the "no effect level" would be approximately 1 mg/l for HZ and 2 mg/l for MMH and UDMH.

The influence of the hydrazines on nitrogen speciation of the sewage treatment plant effluent is more pronounced than that found for organic carbon oxidation. Inhibition of nitrification occurred at concentrations above 0.5 mg/l for MMH and 1 mg/l for the other fuels.

Only at the lowest HZ concentrations tested (<1 mg/l) was the effluent fuel concentration below detection limits, and for MMH and UDMH the maximum removal efficiency observed was 89 percent and 96 percent, respectively. Other AF-sponsored studies on the effect of these fuels on algae have established "no effect" concentrations of less than 0.001 mg/l for MMH and 1.56 mg/l for UDMH.

For slug doses (because of the short exposure) the effect of transient high fuel concentrations would be less than for a continuous exposure. The concentrations found to cause no significant effect on sewage treatment efficiency are 74 mg/l for UDMH, 44 mg/l for HZ, and ~32 mg/l for MMH. Ammonia oxidation was effected for all three fuels at the lowest concentration tested (~25 mg/l). Recovery times for the highest concentrations tested (~250 mg/l) are in the range of 2 to 5 days.

Extensive background information is presented on the theory of dispersed growth bacterial systems.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

PREFACE

This report summarizes work performed in accordance with Technical Need (TN) SAMSO-AFCEEDO-1302-76-49, "Disposal of Hydrazine Fuels Hazardous Waste," under program element 63723F, JON 21037W84. The project officers were Major Michael G. MacNaughton and Capt Jay A. Farmwald of the Civil and Environmental Engineering Development Office (CEEDO). Effective 1 March 1979, CEEDO was inactivated and became the Engineering and Services Laboratory (ESL), a directorate of the Air Force Engineering and Services Center, Tyndall Air Force Base, Florida 32403. This work was begun in June 1977 and was completed in July 1979.

This report has been reviewed by the Public Affairs Office and is releasable to the National Technical Information Service (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.

Michael G. MacNaughton
MICHAEL G. MACNAUGHTON, Major,
USAF, BSC
Chief, Environmental Sciences Div

Jay A. Farmwald
JAY A. FARMWALD, Capt, USAF, BSC
Environmental Engineer

Emil C. Frein
EMIL C. FREIN, Lt Col, USAF
Chief, Environics Division

George D. Ballentine
GEORGE D. BALLENTINE, LtCol, USAF
Director, Engineering and
Services Laboratory

APPROVED FOR PUBLICATION	
1. AUTHORITY	2
2. DATE	
3. COMMENTS	
4. SIGNATURE	
5. TITLE	
6. ORGANIZATION	
7. ADDRESS	
8. CITY	
9. STATE	
10. ZIP	
11. TELEPHONE	
12. FAX	
13. E-MAIL	
14. OTHER	
15. REMARKS	
16. DISTRIBUTION	
17. ACTION	
18. DATE	
19. SIGNATURE	
20. TITLE	
21. ORGANIZATION	
22. ADDRESS	
23. CITY	
24. STATE	
25. ZIP	
26. TELEPHONE	
27. FAX	
28. E-MAIL	
29. OTHER	
30. REMARKS	
31. DISTRIBUTION	
32. ACTION	
33. DATE	
34. SIGNATURE	
35. TITLE	
36. ORGANIZATION	
37. ADDRESS	
38. CITY	
39. STATE	
40. ZIP	
41. TELEPHONE	
42. FAX	
43. E-MAIL	
44. OTHER	
45. REMARKS	
46. DISTRIBUTION	
47. ACTION	
48. DATE	
49. SIGNATURE	
50. TITLE	
51. ORGANIZATION	
52. ADDRESS	
53. CITY	
54. STATE	
55. ZIP	
56. TELEPHONE	
57. FAX	
58. E-MAIL	
59. OTHER	
60. REMARKS	
61. DISTRIBUTION	
62. ACTION	
63. DATE	
64. SIGNATURE	
65. TITLE	
66. ORGANIZATION	
67. ADDRESS	
68. CITY	
69. STATE	
70. ZIP	
71. TELEPHONE	
72. FAX	
73. E-MAIL	
74. OTHER	
75. REMARKS	
76. DISTRIBUTION	
77. ACTION	
78. DATE	
79. SIGNATURE	
80. TITLE	
81. ORGANIZATION	
82. ADDRESS	
83. CITY	
84. STATE	
85. ZIP	
86. TELEPHONE	
87. FAX	
88. E-MAIL	
89. OTHER	
90. REMARKS	
91. DISTRIBUTION	
92. ACTION	
93. DATE	
94. SIGNATURE	
95. TITLE	
96. ORGANIZATION	
97. ADDRESS	
98. CITY	
99. STATE	
100. ZIP	
101. TELEPHONE	
102. FAX	
103. E-MAIL	
104. OTHER	
105. REMARKS	
106. DISTRIBUTION	
107. ACTION	
108. DATE	
109. SIGNATURE	
110. TITLE	
111. ORGANIZATION	
112. ADDRESS	
113. CITY	
114. STATE	
115. ZIP	
116. TELEPHONE	
117. FAX	
118. E-MAIL	
119. OTHER	
120. REMARKS	
121. DISTRIBUTION	
122. ACTION	
123. DATE	
124. SIGNATURE	
125. TITLE	
126. ORGANIZATION	
127. ADDRESS	
128. CITY	
129. STATE	
130. ZIP	
131. TELEPHONE	
132. FAX	
133. E-MAIL	
134. OTHER	
135. REMARKS	
136. DISTRIBUTION	
137. ACTION	
138. DATE	
139. SIGNATURE	
140. TITLE	
141. ORGANIZATION	
142. ADDRESS	
143. CITY	
144. STATE	
145. ZIP	
146. TELEPHONE	
147. FAX	
148. E-MAIL	
149. OTHER	
150. REMARKS	
151. DISTRIBUTION	
152. ACTION	
153. DATE	
154. SIGNATURE	
155. TITLE	
156. ORGANIZATION	
157. ADDRESS	
158. CITY	
159. STATE	
160. ZIP	
161. TELEPHONE	
162. FAX	
163. E-MAIL	
164. OTHER	
165. REMARKS	
166. DISTRIBUTION	
167. ACTION	
168. DATE	
169. SIGNATURE	
170. TITLE	
171. ORGANIZATION	
172. ADDRESS	
173. CITY	
174. STATE	
175. ZIP	
176. TELEPHONE	
177. FAX	
178. E-MAIL	
179. OTHER	
180. REMARKS	
181. DISTRIBUTION	
182. ACTION	
183. DATE	
184. SIGNATURE	
185. TITLE	
186. ORGANIZATION	
187. ADDRESS	
188. CITY	
189. STATE	
190. ZIP	
191. TELEPHONE	
192. FAX	
193. E-MAIL	
194. OTHER	
195. REMARKS	
196. DISTRIBUTION	
197. ACTION	
198. DATE	
199. SIGNATURE	
200. TITLE	
201. ORGANIZATION	
202. ADDRESS	
203. CITY	
204. STATE	
205. ZIP	
206. TELEPHONE	
207. FAX	
208. E-MAIL	
209. OTHER	
210. REMARKS	
211. DISTRIBUTION	
212. ACTION	
213. DATE	
214. SIGNATURE	
215. TITLE	
216. ORGANIZATION	
217. ADDRESS	
218. CITY	
219. STATE	
220. ZIP	
221. TELEPHONE	
222. FAX	
223. E-MAIL	
224. OTHER	
225. REMARKS	
226. DISTRIBUTION	
227. ACTION	
228. DATE	
229. SIGNATURE	
230. TITLE	
231. ORGANIZATION	
232. ADDRESS	
233. CITY	
234. STATE	
235. ZIP	
236. TELEPHONE	
237. FAX	
238. E-MAIL	
239. OTHER	
240. REMARKS	
241. DISTRIBUTION	
242. ACTION	
243. DATE	
244. SIGNATURE	
245. TITLE	
246. ORGANIZATION	
247. ADDRESS	
248. CITY	
249. STATE	
250. ZIP	
251. TELEPHONE	
252. FAX	
253. E-MAIL	
254. OTHER	
255. REMARKS	
256. DISTRIBUTION	
257. ACTION	
258. DATE	
259. SIGNATURE	
260. TITLE	
261. ORGANIZATION	
262. ADDRESS	
263. CITY	
264. STATE	
265. ZIP	
266. TELEPHONE	
267. FAX	
268. E-MAIL	
269. OTHER	
270. REMARKS	
271. DISTRIBUTION	
272. ACTION	
273. DATE	
274. SIGNATURE	
275. TITLE	
276. ORGANIZATION	
277. ADDRESS	
278. CITY	
279. STATE	
280. ZIP	
281. TELEPHONE	
282. FAX	
283. E-MAIL	
284. OTHER	
285. REMARKS	
286. DISTRIBUTION	
287. ACTION	
288. DATE	
289. SIGNATURE	
290. TITLE	
291. ORGANIZATION	
292. ADDRESS	
293. CITY	
294. STATE	
295. ZIP	
296. TELEPHONE	
297. FAX	
298. E-MAIL	
299. OTHER	
300. REMARKS	
301. DISTRIBUTION	
302. ACTION	
303. DATE	
304. SIGNATURE	
305. TITLE	
306. ORGANIZATION	
307. ADDRESS	
308. CITY	
309. STATE	
310. ZIP	
311. TELEPHONE	
312. FAX	
313. E-MAIL	
314. OTHER	
315. REMARKS	
316. DISTRIBUTION	
317. ACTION	
318. DATE	
319. SIGNATURE	
320. TITLE	
321. ORGANIZATION	
322. ADDRESS	
323. CITY	
324. STATE	
325. ZIP	
326. TELEPHONE	
327. FAX	
328. E-MAIL	
329. OTHER	
330. REMARKS	
331. DISTRIBUTION	
332. ACTION	
333. DATE	
334. SIGNATURE	
335. TITLE	
336. ORGANIZATION	
337. ADDRESS	
338. CITY	
339. STATE	
340. ZIP	
341. TELEPHONE	
342. FAX	
343. E-MAIL	
344. OTHER	
345. REMARKS	
346. DISTRIBUTION	
347. ACTION	
348. DATE	
349. SIGNATURE	
350. TITLE	
351. ORGANIZATION	
352. ADDRESS	
353. CITY	
354. STATE	
355. ZIP	
356. TELEPHONE	
357. FAX	
358. E-MAIL	
359. OTHER	
360. REMARKS	
361. DISTRIBUTION	
362. ACTION	
363. DATE	
364. SIGNATURE	
365. TITLE	
366. ORGANIZATION	
367. ADDRESS	
368. CITY	
369. STATE	
370. ZIP	
371. TELEPHONE	
372. FAX	
373. E-MAIL	
374. OTHER	
375. REMARKS	
376. DISTRIBUTION	
377. ACTION	
378. DATE	
379. SIGNATURE	
380. TITLE	
381. ORGANIZATION	
382. ADDRESS	
383. CITY	
384. STATE	
385. ZIP	
386. TELEPHONE	
387. FAX	
388. E-MAIL	
389. OTHER	
390. REMARKS	
391. DISTRIBUTION	
392. ACTION	
393. DATE	
394. SIGNATURE	
395. TITLE	
396. ORGANIZATION	
397. ADDRESS	
398. CITY	
399. STATE	
400. ZIP	
401. TELEPHONE	
402. FAX	
403. E-MAIL	
404. OTHER	
405. REMARKS	
406. DISTRIBUTION	
407. ACTION	
408. DATE	
409. SIGNATURE	
410. TITLE	
411. ORGANIZATION	
412. ADDRESS	
413. CITY	
414. STATE	
415. ZIP	
416. TELEPHONE	
417. FAX	
418. E-MAIL	
419. OTHER	
420. REMARKS	
421. DISTRIBUTION	
422. ACTION	
423. DATE	
424. SIGNATURE	
425. TITLE	
426. ORGANIZATION	
427. ADDRESS	
428. CITY	
429. STATE	
430. ZIP	
431. TELEPHONE	
432. FAX	
433. E-MAIL	
434. OTHER	
435. REMARKS	
436. DISTRIBUTION	
437. ACTION	
438. DATE	
439. SIGNATURE	
440. TITLE	
441. ORGANIZATION	
442. ADDRESS	
443. CITY	
444. STATE	
445. ZIP	
446. TELEPHONE	
447. FAX	
448. E-MAIL	
449. OTHER	
450. REMARKS	
451. DISTRIBUTION	
452. ACTION	
453. DATE	
454. SIGNATURE	
455. TITLE	
456. ORGANIZATION	
457. ADDRESS	
458. CITY	
459. STATE	
460. ZIP	
461. TELEPHONE	
462. FAX	
463. E-MAIL	
464. OTHER	
465. REMARKS	
466. DISTRIBUTION	
467. ACTION	
468. DATE	
469. SIGNATURE	
470. TITLE	
471. ORGANIZATION	
472. ADDRESS	
473. CITY	
474. STATE	
475. ZIP	
476. TELEPHONE	
477. FAX	
478. E-MAIL	
479. OTHER	
480. REMARKS	
481. DISTRIBUTION	
482. ACTION	
483. DATE	
484. SIGNATURE	
485. TITLE	
486. ORGANIZATION	
487. ADDRESS	
488. CITY	
489. STATE	
490. ZIP	
491. TELEPHONE	
492. FAX	
493. E-MAIL	
494. OTHER	
495. REMARKS	
496. DISTRIBUTION	
497. ACTION	
498. DATE	
499. SIGNATURE	
500. TITLE	
501. ORGANIZATION	
502. ADDRESS	
503. CITY	
504. STATE	
505. ZIP	
506. TELEPHONE	
507. FAX	
508. E-MAIL	
509. OTHER	
510. REMARKS	
511. DISTRIBUTION	
512. ACTION	
513. DATE	
514. SIGNATURE	
515. TITLE	
516. ORGANIZATION	
517. ADDRESS	
518. CITY	
519. STATE	
520. ZIP	
521. TELEPHONE	
522. FAX	
523. E-MAIL	
524. OTHER	
525. REMARKS	
526. DISTRIBUTION	
527. ACTION	
528. DATE	
529. SIGNATURE	
530. TITLE	
531. ORGANIZATION	
532. ADDRESS	
533. CITY	
534. STATE	
535. ZIP	
536. TELEPHONE	
537. FAX	
538. E-MAIL	
539. OTHER	
540. REMARKS	
541. DISTRIBUTION	
542. ACTION	
543. DATE	
544. SIGNATURE	
545. TITLE	
546. ORGANIZATION	
547. ADDRESS	
548. CITY	
549. STATE	
550. ZIP	
551. TELEPHONE	
552. FAX	
553. E-MAIL	
554. OTHER	
555. REMARKS	
556. DISTRIBUTION	
557. ACTION	
558. DATE	
559. SIGNATURE	
560. TITLE	
561. ORGANIZATION	
562. ADDRESS	
563. CITY	
564. STATE	
565. ZIP	
566. TELEPHONE	
567. FAX	
568. E-MAIL	
569. OTHER	
570. REMARKS	
571. DISTRIBUTION	
572. ACTION	
573. DATE	
574. SIGNATURE	
575. TITLE	
576. ORGANIZATION	
577. ADDRESS	
578. CITY	
579. STATE	
580. ZIP	
581. TELEPHONE	
582. FAX	
583. E-MAIL	
584. OTHER	
585. REMARKS	
586. DISTRIBUTION	
587. ACTION	
588. DATE	
589. SIGNATURE	
590. TITLE	
591. ORGANIZATION	
592. ADDRESS	
593. CITY	
594. STATE	
595. ZIP	
596. TELEPHONE	
597. FAX	
598. E-MAIL	
599. OTHER	
600. REMARKS	
601. DISTRIBUTION	
602. ACTION	
603. DATE	
604. SIGNATURE	
605. TITLE	
606. ORGANIZATION	
607. ADDRESS	
608. CITY	
609. STATE	
610. ZIP	
611. TELEPHONE	
612. FAX	
613. E-MAIL	
614. OTHER	
615. REMARKS	
616. DISTRIBUTION	
617. ACTION	
618. DATE	
619. SIGNATURE	
620. TITLE	
621. ORGANIZATION	
622. ADDRESS	
623. CITY	
624. STATE	
625. ZIP	
626. TELEPHONE	
627. FAX	
628. E-MAIL	
629. OTHER	
630. REMARKS	
631. DISTRIBUTION	
632. ACTION	
633. DATE	
634. SIGNATURE	
635. TITLE	
636. ORGANIZATION	
637. ADDRESS	

TABLE OF CONTENTS

Section	Title	Page
I.	INTRODUCTION.	1
II.	THEORY/BACKGROUND	2
	1. Dispersed Growth Systems.	2
	a. Substrate Utilization	2
	b. Bacterial Growth.	3
	c. Definitions	3
	d. Complete Mix-Cellular Recycle	4
	2. Hydrazines as Process Inhibitors.	8
III.	EXPERIMENTAL METHODS AND MATERIALS	9
	1. Substrate Base.	9
	2. Supplemental Requirements	11
	a. Nitrogen.	11
	b. Phosphorous	11
	c. Oxygen.	11
	d. Alkalinity.	11
	3. Operating Parameters.	14
	4. Bench Scale System.	18
	5. Experimental Matrix	18
	6. Analytical Procedures	19
	a. General	19
	b. Hydrazine	19
	c. Schedule	19

TABLE OF CONTENTS (CONTINUED)

Section	Title	Page
IV.	RESULTS - HYDRAZINE (HZ)	21
	1. Continuous Feed Studies	21
	a. HZ Degradation.	21
	b. COD	21
	c. Nitrification	31
	d. Suspended Solids	31
	2. Slug Feed Studies	32
	a. HZ Degradation	32
	b. Acute Response	32
	(1) COD	34
	(2) Nitrification	34
	c. Recovery	34
	(1) COD.	34
	(2) Nitrification	34
	(3) Suspended Solids	34
V.	RESULTS - MONOMETHYLHYDRAZINE (MMH)	40
	1. Continuous Feed Studies	40
	a. MMH Degradation	40
	b. COD	40
	c. Nitrification	44
	d. Suspended Solids	44
	2. Slug Feed Studies	49
	a. MMH Degradation	49
	b. Acute Response	49
	(1) COD	49
	(2) Nitrification	49

TABLE OF CONTENTS (CONCLUDED)

Section	Title	Page
	c. Recovery	52
	(1) COD	52
	(2) Nitrification	52
	(3) Suspended Solids	52
VI.	RESULTS - UNSYMMETRICAL DIMETHYLHYDRAZINE (UDMH)	56
	1. Continuous Feed Studies	56
	a. UDMH Degradation	56
	b. COD	56
	c. Nitrification	60
	d. Suspended Solids	60
	2. SLUG Feed Studies	64
	a. UDMH Degradation	64
	b. Acute Response.	64
	(1) COD.	64
	(2) Nitrification	67
	c. Recovery	67
	(1) COD	67
	(2) Nitrification	67
	(3) Suspended Solids	67
VII.	SUMMARY	72
	1. Continuous Feed Studies	72
	2. Slug Feed Studies	73
VIII.	CONCLUSIONS	78
	REFERENCES.	81
APPENDIX		
A.	STOICHIOMETRY	83
B.	EMPIRICAL FORMULATIONS	90
C.	CALCULATION OF ALKALINITY REQUIREMENT FOR HETEROTROPHIC REACTION	92

LIST OF FIGURES

Figure	Title	Page
1	Specific Substrate Utilization as a Function of Substrate Concentration, Monod Plot	3
2	Completely Mixed Reactor with Cellular Recycle	5
3	Tyndall Sewage Treatment Plant	10
4	Theoretical Effluent COD and Ammonia Nitrogen as a Function of Mean Cell Residence Time	13
5	Laboratory Schematic	16
6	Mixing Chamber Used to Achieve C_1 in Reactors 1 to 4, C_2 in Reactors 9 to 12, and Control Conditions in Reactors 5 to 8 During Continuous Feed Studies.	17
7	Aeration Basin and Clarifier	17
8	Continuous Influent HZ Concentrations	22
9	Influent COD and Mean Control Effluent COD Values During Continuous Feed HZ Runs	25
10	Effluent COD as a Function of Time and Continuous Feed HZ Concentration (Mean of 4 Replicates)	26
11	Effluent Organic Nitrogen as a Function of Time and Continuous Feed HZ Concentration (Mean of 4 Replicates)	26
12	Influent and Control Effluent Nitrogen Data During Continuous Feed HZ Runs.	27
13	Effluent Ammonia Nitrogen as a Function of Time and Continuous Feed HZ Concentration (Mean of 4 Replicates)	28
14	Mean Control Effluent Nitrate Nitrogen Values During Continuous Feed HZ Runs	28
15	Effluent Nitrate Nitrogen as a Function of Time and Continuous Feed HZ Runs (Mean of 4 Replicates).	29
16	Mean MLSS During Continuous Feed HZ Runs (Mean of 4 Replicates Except Controls During 20/10 and 6/3 Which Were Duplicates).	30

LIST OF FIGURES (CONTINUED)

Figure	Title	Page
17	HZ Degradation During HZ Slug Feed Experiments (Mean of Duplicates).	33
18	Calculated Half Life for HZ as a Function of Initial HZ Slug Concentration	33
19	Acute Effluent COD Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)	35
20	Acute Effluent Organic Nitrogen Response to Slug HZ Loads as a Function of Time (Mean of Duplicates).	35
21	Acute Effluent Ammonia Nitrogen Response to Slug HZ Loads as a Function of Time (Mean of Duplicates).	36
22	Acute Effluent Nitrate Nitrogen Response to Slug HZ Loads as a Function of Time (Mean of Duplicates).	36
23	Influent and Control Effluent COD and Nitrogen Data During the Slug HZ Recovery Periods	37
24	Effluent COD Recovery Following Slug HZ Loads (Mean of Duplicates).	37
25	Effluent Ammonia Nitrogen Recovery Following Slug HZ Loads (Mean of Duplicates).	38
26	Effluent Nitrate Nitrogen Recovery Following Slug HZ Loads (Mean of Duplicates).	38
27	MLSS Response to Slug HZ Loads as a Function of Time (Mean of Duplicates).	39
28	Continuous Feed Influent MMH Concentrations	41
29	Influent COD and Mean Control Effluent COD Values During Continuous Feed MMH Runs	41
30	Effluent COD as a Function of Time and Continuous Feed MMH Concentration (Mean of 4 Replicates)	45
31	Effluent Organic Nitrogen as a Function of Time and Continuous Feed MMH Concentration (Mean of 4 Replicates). . .	45
32	Influent and Control Effluent Nitrogen Data During Continuous Feed MMH Runs.	46

LIST OF FIGURES (CONTINUED)

Figure	Title	Page
33	Effluent Ammonia Nitrogen as a Function of Time and Continuous Feed MMH Concentration (Mean of 4 Replicates). . .	46
34	Mean Control Effluent Nitrate Nitrogen Values During Continuous Feed MMH Runs.	47
35	Effluent Nitrate Nitrogen as a Function of Time and Continuous Feed MMH Concentration (Mean of 4 Replicates). . .	47
36	Mean MLSS During Continuous Feed MMH Runs (Mean of 4 Replicates)	48
37	MMH Degradation During MMH Slug Feed Experiments (Mean of Duplicates)	48
38	Calculated Halflife for MMH as a Function of Initial MMH Slug Concentration	50
39	Acute Effluent COD Response to Slug MMH Loads as a Function of Time (Mean of Duplicates)	50
40	Acute Effluent Organic Nitrogen Response to Slug MMH Loads as a Function of Time (Mean of Duplicates).	51
41	Acute Effluent Ammonia Nitrogen Response to Slug MMH Loads as a Function of Time (Mean of Duplicates).	51
42	Acute Effluent Nitrate Nitrogen Response to Slug MMH Loads as a Function of Time (Mean of Duplicates).	53
43	Influent and Control Effluent COD and Nitrogen Data During the Slug MMH Recovery Periods.	53
44	Effluent COD Recovery Following Slug MMH Loads (Mean of Duplicates)	54
45	Effluent Ammonia Nitrogen Recovery Following Slug MMH Loads (Mean of Duplicates).	54
46	Effluent Nitrate Nitrogen Recovery Following Slug MMH Loads (Mean of Duplicates).	55
47	MLSS Response to Slug MMH Loads as a Function of Time (Mean of Duplicates).	55

LIST OF FIGURES (CONTINUED)

Figure	Title	Page
48	Continuous Feed Influent UDMH Concentrations	57
49	Influent COD and Mean Control Effluent COD Values During Continuous Feed UDMH Runs	57
50	Effluent COD as a Function of Time and Continuous Feed UDMH Concentration (Mean of 4 Replicates)	58
51	Effluent Organic Nitrogen as a Function of Time and Continuous Feed UDMH Concentration (Mean of 4 Replicates) . .	58
52	Influent and Control Effluent Nitrogen Data During Continuous Feed UDMH Runs	61
53	Effluent Ammonia Nitrogen as a Function of Time and Continuous Feed UDMH Concentration (Mean of 4 Replicates) . .	62
54	Mean Control Effluent Nitrate Nitrogen Values During Continuous Feed UDMH Runs	62
55	Effluent Nitrate Nitrogen as a Function of Time and Continuous Feed UDMH Concentration (Mean of 4 Replicates) . .	63
56	Mean MLSS During Continuous Feed UDMH Runs (Mean of 4 Replicates)	63
57	UDMH Degradation During MMH Slug Feed Experiments (Mean of Duplicates)	65
58	Calculated Halflife for MMH as a Function of Initial UDMH Slug Concentration	65
59	Acute Effluent COD Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)	66
60	Acute Effluent Organic Nitrogen Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)	66
61	Acute Effluent Ammonia Nitrogen Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)	68
62	Acute Effluent Nitrate Nitrogen Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)	68
63	Influent and Control Effluent COD and Nitrogen Data During the Slug UDMH Recovery Periods	69
64	Effluent COD Recovery Following Slug UDMH Loads (Mean of Duplicates)	69

LIST OF FIGURES (CONCLUDED)

Figure	Title	Page
65	Effluent Ammonia Nitrogen Recovery Following Slug UDMH Loads (Mean of Duplicates)	70
66	Effluent Nitrate Nitrogen Recovery Following Slug UDMH Loads (Mean of Duplicates)	70
67	MLSS Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)	71
68	COD Mass Balance For Slug UDMH Load.	76
69	NH ₃ Mass Balance For Slug UDMH Load.	76
A-1	Fraction of Electron Donor Used for Energy, f_e , and for Synthesis, f_s , as a Function of θ . A is the Maximum Cell Yield Coefficient on an C_e Equivalent Basis	88

LIST OF TABLES

Table	Title	Page
1	Raw Feed Characteristics	9
2	Carnation Slender®.	10
3	Feed Solution Make-up	12
4	Final Feed Solution	13
5	Bacterial Growth and Substrate Utilization Coefficients	15
6	Design Operating Parameters	16
7	Seeding/Evaluation Sequence	19
8	Analytical Techniques	20
9	HZ Concentrations During Continuous Feed Studies	23
10	Influent and Control Effluent COD Summary	23
11	Influent and Control Effluent Nitrogen Summary	24
12	Control MLSS Data	31
13	Bacterial Decay Constants for HZ	32
14	Slug Load Response Initial Conditions	32
15	MMH Concentrations During Continuous Feed Studies	42
16	Influent and Control Effluent COD Summary	42
17	Influent and Control Effluent Nitrogen Summary	43
18	Control MLSS Data	44
19	Bacterial Decay Constants for MMH	49
20	Slug Load Response Initial Conditions	49
21	UDMH Concentrations During Continuous Feed Studies	59

LIST OF TABLES (CONCLUDED)

Table	Title	Page
22	Influent and Control Effluent COD Summary	59
23	Control MLSS Data	60
24	Influent and Control Effluent Nitrogen Summary	61
25	Bacterial Decay Constants for UDMH	64
26	Slug Load Response Initial Conditions	64
27	Gallon Equivalents of Fuel Which Will Produce Aeration Basin Concentrations of Interest.	74
A-1	Oxygen and Alkalinity Requirements	89

SECTION I

INTRODUCTION

1. BACKGROUND

The Air Force (AF) procures amine based hydrazine 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 Program. This results in an annual movement of approximately 2.36 kilograms (5.2 million pounds) of neat hydrazine (HZ), monomethylhydrazine (MMH), unsymmetricaldimethylhydrazine (UDMH), and Aerozine 50 (1:1 HZ:UDMH). Within private industry significant quantities of neat hydrazine are used as plastic blowing agents, anticorrosion agents for boiler waters, and growth inhibitors. MMH and UDMH are not widely used outside of NASA and the Department of Defense (DOD). The AF problem with respect to neat hydrazine is complicated by its use in the Emergency Power Unit (EPU) on the new F-16 aircraft which will be deployed worldwide. The EPU on the F-16 contains 24.6 liters (6.5 gallons) of a 70-percent aqueous hydrazine solution, and potential small spills during maintenance and handling of the unit require simple and effective cleanup procedures.

Documenting the ability of conventional biological waste treatment facilities to assimilate low concentration hydrazine wastes on a semi-continuous flow basis and/or slug loads resulting from transportation/operational spill situations would greatly simplify the development of preferred neutralization methodologies in single event scenarios. To evaluate the assimilative capacities of such domestic treatment systems, this research was developed to investigate both activated sludge and trickling filter unit processes. This report will summarize data on the effects of HZ, MMH, and UDMH in conventional activated sludge systems.

2. SCOPE

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

- Establish control parameters favoring the oxidation of both carbonaceous matter and ammonia (nitrification) for a supplemented primary effluent.
- Evaluate treatment efficiency under the selected operating conditions as a function of various continuous flow missile fuel concentrations.
- Document the effects of shock loadings under the selected conditions and monitor process recovery.

These data will serve as a basis for comparison with alternative physical/chemical treatment technologies in formulating AF contingency plans and should also prove useful in impact assessment exercises.

SECTION II

THEORY/BACKGROUND

1. DISPERSED GROWTH SYSTEMS

a. Substrate Utilization: The kinetics of soluble substrate utilization by dispersed bacterial populations are a function of the limiting substrate and microorganism concentrations. A relationship similar to that derived empirically by Monod (Reference 12) has been proposed for such systems (Reference 5).

$$\frac{ds}{dt} = \frac{kS X_a}{K_s + S} \quad (1)$$

$\frac{ds}{dt}$ = Substrate utilization rate per unit volume (mass/
volume - time).

k = Maximum rate of substrate utilization per unit weight
of microorganisms - at high substrate concentrations
(time⁻¹).

S = Limiting substrate concentration surrounding the micro-
organisms (mass/volume).

K_s = Half velocity coefficient (mass/volume).

X_a = Microorganism concentration (mass/volume).

Graphically, Equation (1) may be represented as shown in Figure 1. Inherent in this model is the assumption that only one substrate is limiting and that this substrate is both soluble and biodegradable.

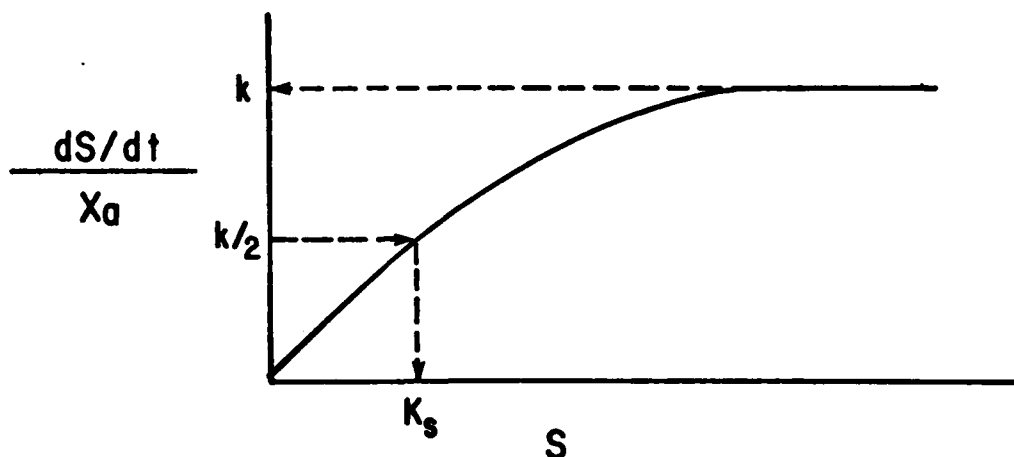


Figure 1. Specific Substrate Utilization as a Function of Substrate Concentration, Monod Plot

b. Bacterial Growth: The empirical equation for bacterial growth (Reference 13) is:

$$\frac{dX_a}{dt} = Y \frac{ds}{dt} - bX_a \quad (2)$$

$\frac{dX_a}{dt}$ = net growth rate of microorganisms per unit volume (mass/volume-time).

Y = maximum yield coefficient (mass/mass).

b = microorganism decay coefficient (time⁻¹).

Equation (2) may be rearranged to:

$$\frac{\frac{dX_a}{dt}}{X_a} = Y \frac{\frac{ds}{dt}}{X_a} - b \quad (3)$$

On a finite mass and time basis where M refers to a definite mass of microorganisms (Reference 4):

$$\frac{(\Delta X_a / \Delta t)_M}{(X_a)_M} = Y \frac{(\Delta S / \Delta t)_M}{(X_a)_M} - b \quad (4)$$

c. Definitions: Using the above relationships, many useful parameters have been defined (References 4, 5).

(1) Net Specific Growth Rate: (μ)

$$\mu = \frac{(\Delta X_a / \Delta t)_M}{(X_a)_M} \quad (5)$$

Substituting Equation (1) into (3) and using Equations (4) and (5) we may further show that:

$$\mu = \frac{YkS}{K_s + S} - b \quad (6)$$

When $b = 0$ and $S \gg K_s$, $\mu_{\max}$ can be defined:

$$\mu_{\max} = Yk \quad (7)$$

(2) Mean Cell Residence Time: (θ_c)

$$\theta_c = \frac{1}{\mu} \quad (8)$$

Equations (5) and (8) result in Equation (9).

$$\theta_c = \frac{(X_a)_M}{(\Delta X_a / \Delta t)_M} \quad (9)$$

(3) Specific Utilization: (U)

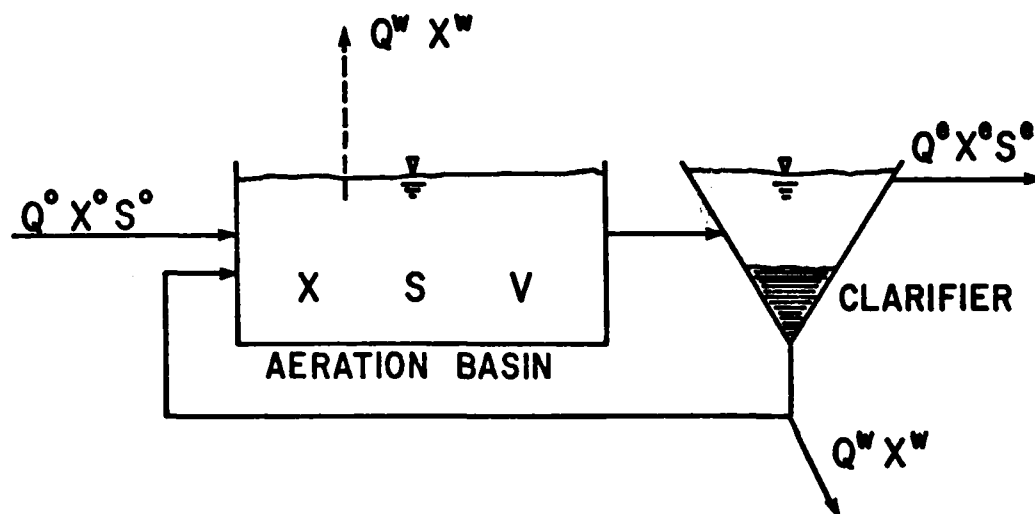
$$U = \frac{(\Delta S / \Delta t)_M}{(X_a)_M} \quad (10)$$

d. Complete Mix - Cellular Recycle :

Figure 2 illustrates this classical treatment system which employs solids (cellular) recirculation in order to make θ_c independent of the hydraulic detention time (θ). However, as pointed out by Lawrence (Reference 5), θ_c cannot be varied completely independent of θ due to the practical limitations imposed by the settling characteristics of the biomass.

In developing relationships for complete mix recycle systems, several assumptions apply:

- Waste stabilization occurs only in the aeration basin (conservative assumption).
- Instantaneous and complete mixing occurs in the aeration basin.
- The total active biological mass in the system is equal to the biological mass in the aeration basin, i.e., the clarifier simply serves as a source of biomass through constant and continuous recycle.
- $S^e = S$



NOTE : WHEN INTENTIONAL WASTING IS ACCOMPLISHED FROM THE
AERATION BASIN $X^w = X$ AND $Q^0 = Q^0 - Q^w$

Figure 2. Complete Mixed Reactor with Cellular Recycle

(1) Substrate: The effluent substrate concentration, S^e , (that soluble fraction of the influent waste escaping treatment) for a system operating under constant environmental conditions and influent characteristics may be found by combining Equations (6) and (8) (Reference 5).

$$S = \frac{K_s (1+b \theta_c)}{\theta_c (Yk-b)-1} \quad (11)$$

Thus, for a given microbial population with specified substrate utilization and growth coefficients, treatment efficiency at steady state is a function of the mean cell residence time.

(2) Biomass: A relationship for the steady state microorganism concentration in the aeration basin may be derived from a mass balance on the substrate through the system. Under steady state conditions the substrate concentration in the aeration basin is constant, therefore:

Mass rate of substrate in + Mass Rate of substrate utilization = Mass Rate of substrate out

$$Q^o S^o + V \frac{ds}{dt} = (Q^o - Q^w) S^e + Q^w S \quad (12)$$

Recalling that $S^e = S$ and using Equations (3) and (5), it can be shown that:

$$X_a = \frac{\theta_c}{\theta} \frac{Y(S^o - S)}{1 + b \theta_c} \quad (13)$$

(3) Mean Cell Residence Time: Similarly, a mass balance for the microbial mass in the treatment system may be formulated. Under steady state conditions the organism concentration in the aeration basin is constant:

Mass rate of organisms in + Mass Rate of organism growth = Mass Rate of organisms out

$$Q^o X_a^o + \frac{V dX_a}{dt} = (Q^o - Q^w) X_a^e + Q^w X_a^w \quad (14)$$

Assuming that wasting is accomplished directly from the aeration basin, substitutions involving Equations (1), (2), (6), and (8) yield the following expression for θ_c :

$$\theta_c = \frac{V X_a}{(Q^o - Q^w) X_a^e + Q^w X_a^w - Q^o X_a^o} \quad (15)$$

Under steady state conditions the growth rate, $\Delta X/\Delta t$, is constant and represents the mass of organisms which must be wasted $(Q^o - Q^w) X_a^e + Q^w X_a^w$ to maintain a constant cell residence time. Because the net specific growth rate, μ , is derived from the substrate utilization and bacterial growth relationships, the implication is that θ_c , as defined by Equation

(15), applies only to those active organisms grown in the reactor. This, then, accounts for the $Q^O X_a^O$ term which must be subtracted as derived in the mass balance. In continuous flow activated sludge treatment systems a process control parameter which accurately describes the total system microbial mass is of interest. For this reason the operational definition for θ_c has most often been defined (Reference 5) as:

$$\theta_c = \frac{X_a V}{Q^e X_a^e + Q^w X_a^w} \quad (16)$$

Again, when wasting is accomplished from the aeration basin $Q^e = Q^O - Q^w$ and $X_a^w = X_a$.

(4) θ_c^m : There exists a minimum cell residence time below which active cells will be washed out of the system at a rate which exceeds their growth rate. When this occurs $S^O = S^e$, thus, from Equation (6):

$$(\theta_c^m)^{-1} = \frac{YkS^O}{K_s + S^O} - b \quad (17)$$

(5) Sludge for Disposal: From Equation (16) it is clear that the worst case with respect to excess sludge for disposal occurs when clarification efficiency is a maximum, i.e., $X^e = 0$. If P_x equals sludge for disposal in mass/time units, then:

$$P_x = Q^w X^w = \frac{VX}{\theta_c} \quad (18)$$

(6) Suspended Solids Balance: As described by Christensen (Reference 14), there are two different kinds of suspended solids commonly recognized: (1) the inorganic portion X_{in} , and (2) the organic portion X_v , generally termed volatile suspended solids:

$$X = X_{in} + X_v \quad (19)$$

where X represents total suspended solids. Further, X_v is considered to consist of four different organic fractions: (1) biodegradable suspended solids, X_d ; (2) refractory suspended solids, X_r ; (3) active organisms, X_a ; and (4) inert organism remains after cellular decay, X_i .

Because X or X_v is most often used as a measure of X_a the relationship between θ_c and the component fractions in X or X_v is of interest. If one assumes that the fraction of a particular suspended solids component in the effluent and waste stream is the same as its proportion in the reactor:

$$\theta_c = \frac{X_a V}{Q^e X_a^e + Q^w X_a^w} = \frac{X_j V}{Q^e X_j^e + Q^w X_j^w} \quad (20)$$

where j can equal in , a , i , d , or r . For the case when X_a^O and $X_i^O = 0$ and further assuming that X_d^O degradation is proportional to S^O

degradation, a mass balance on each of the suspended solids components will lead to an expression for X_v or X as a function of θ_c and θ , given constant environmental and influent waste conditions. The term f_d represents the fraction of an active organism which is biodegradable.

$$X_v = \frac{\theta_c}{\theta} X_r^o + \frac{S}{S^o} X_d^o + \frac{Y(S^o - S)}{1 + b \theta_c} (1 + (1 - f_d)b \theta_c) \quad (21)$$

and;

$$X = \frac{\theta_c}{\theta} X_{in}^o + X_v \quad (22)$$

Equation (21) is the fundamental design equation for complete mix suspended growth systems with or without cellular recycle while Equation (22) describes the operational solids retention time (SRT) used as the process control parameter.

$$SRT = \frac{\theta_c}{\theta} = \frac{XV}{Q^e X^e + Q^w X^w} \quad (23)$$

2. HYDRAZINES AS PROCESS INHIBITORS

To date, very little research has been conducted on the effects of hydrazines in biological waste treatment systems. Tomlinson, Boon, and Tratman (Reference 15) conducted batch-screening tests on nitrifying activated sludge at various concentrations of neat hydrazine. They found that a concentration of 64 milligrams per liter (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 (Reference 16) who studied pure cultures of Nitrosomonas sp. and found 20-percent inhibition of ammonia oxidation at 32 mg/l.

Yoshida and Alexander (Reference 17) 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 even in the presence of 320 mg/l hydrazine, as evidenced by an accumulation of hydroxylamine. Verstraete and Alexander (Reference 21) 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. Currently there is no literature available on the effects of MMH or UDMH on either pure cultures or activated sludges.

SECTION III EXPERIMENTAL METHODS AND MATERIALS

1. SUBSTRATE BASE

Throughout this investigation, primary effluent from the Tyndall Air Force Base (AFB) sewage treatment plant (STP) (Figure 3), was used as the raw feed. The Tyndall AFB facility, which treats 3.0 to 6.0 million liters (0.8 to 1.6 million gallons) of combined domestic and industrial wastewater per day, employs two single-stage trickling filters for secondary waste stabilization. Each rock packed filter is subjected to hydraulic loadings which range from 7.4 to 14.7 thousand liters/square meter/day (7.9 to 15.8 million gallons/Acre/DAY) (including 1:1 recirculation), the variation being a function of seasonal precipitation. The average organic loading is 16 Kg Biochemical Oxygen Demand (BOD)/cubic meter (M³)/Day (23.2 lb BOD_L/1000 ft³/DAY) per filter.

Characterization of the raw feed solution was undertaken to aid in designing the experiment and in an effort to quantify supplemental requirements. Analytical procedures, as outlined in Section III, paragraph 6 of this report, produced the data 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 made. 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®. The ingredients, as computed from data supplied by the manufacturer, are itemized in Table 2. Stoichiometric relationships 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 fit the experimental design.

TABLE 1. RAW FEED CHARACTERISTICS

<u>PARAMETER</u>	<u>VALUE</u>	<u>UNITS</u>
COD	100	mg/l
BOD ₅	85	mg/l
Suspended Solids	62	mg/l
Volatile Suspended Solids	50	mg/l
NH ₄ ⁺ -N	12.7	mg/l
Organic -N	5.0	mg/l
NO ₃ -N	None Detected	
NO ₂ -N	None Detected	
PO ₄ -P	6.0	mg/l
Alkalinity (Total)	97.0	mg/l as CaCO ₃
pH	7.0	-

NOTE: All samples unfiltered.

TABLE 2. CARNATION SLENDER®

CONSTITUENT	VALUE, mg/l
Measured COD	222,000
Carbohydrate	118,363
Protein	37,200
Fat	16,909
Ca	676
P	676
Mg	296
Fe	8.5
Zn	8.5
Cu	1.7
I	0.12

NOTE: Also contains vitamins A, C, D, E, B₆, B₁₂, Folic Acid, Thiamine, Riboflavin, Niacin, Biotin, and Pantothenic Acid.

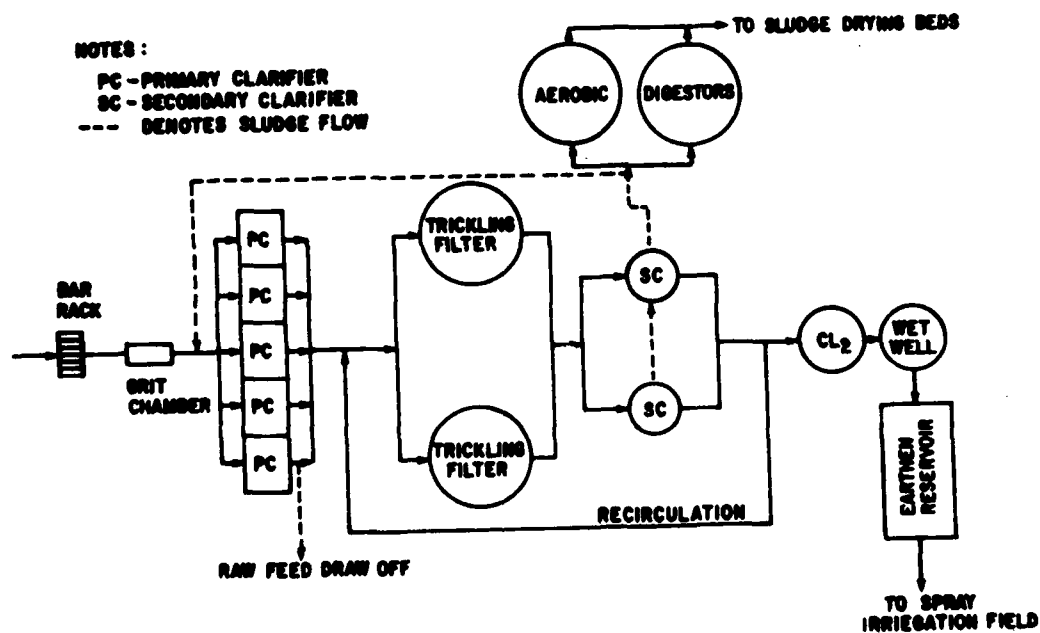


Figure 3. Tyndall Sewage Treatment Plant

2. SUPPLEMENTAL REQUIREMENTS

McCarty (Reference 6) has suggested that stoichiometric equations may be written for bacterially mediated reactions. This procedure establishes molar coefficients which may be used to predict electron acceptor utilization, cellular yield, and supplemental requirements. Such an analysis was performed on the enriched feed solution used in this study. The procedure is outlined in Appendix A. The supplemental nitrogen, phosphorous, oxygen, and alkalinity requirements derived from these calculations are discussed below.

a. Nitrogen(N): Calculations indicated that 19.2 mg/l N would be required for heterotrophic synthesis. Based on the empirical formulations derived in Appendix A, it can be shown that the total organic-N available is 16.0 mg/l. In addition, the raw feed solution contains 12.7 mg/l inorganic-N ($\text{NH}_3\text{-N}$). Obviously there will be approximately 9.5 mg/l-N remaining which should be available for nitrification. In an effort to insure nitrogen was not limiting and to increase the amount available for nitrification, 4.7 mg/l urea-N was added to the enriched feed.

b. Phosphorous(P): To insure phosphorous was not limiting, the enriched primary effluent was supplemented with 5.2 mg/l $\text{PO}_4\text{-P}$. This raised the total available phosphorous to 11.9 mg/l compared to the demand of 3.0 mg/l.

c. Oxygen(O_2): To insure an excess of dissolved oxygen (DO), humidified air was sparged through the mixed liquor at a rate of 4 liters/minute. Based on an air density of 1.2 grams (gm)/liter under the experimental conditions (1 atmosphere, 20 degrees celsius ($^{\circ}\text{C}$) and noting that air is 21 percent oxygen by weight, it can be shown that approximately 145 gm O_2 /day were made available to the system. Assuming a conservative oxygen transfer efficiency of 5 percent (Reference 18), the calculated absorptive capacity is 7.2 gm O_2 /day, or a 30-percent excess. Periodic checks on the mixed liquor to confirm a DO above 5 mg/l would later insure that oxygen was not limiting during the investigation.

d. Alkalinity: While the estimates for alkalinity suggested a requirement of 2410 mg/l (as CaCO_3), actual demands established during the initial stabilization period were much less. It was found that the pH could be maintained above 7.0 by supplementing the enriched feed with only 260 mg/l NaHCO_3 (157 mg/l as CaCO_3). This is due, in part, to the significant stripping of CO_2 from solution under actual operating conditions.

TABLE 3. FEED SOLUTION MAKE-UP

<u>Constituent</u>	<u>Formulation</u>	<u>Mass Addition</u>	<u>Supplemental Value (mg)</u>	
			Measured	Theoretical***
Enriched Feed	$C_{54}H_{96}O_{20}N_7^*$	223 mg** (1ℓ)		
COD			320	386
ORG-N			-	16.0
PO ₄ -P			6.7*	-
NH ₄ ⁺ -N			12.7	-
ALKALINITY			97	-
Supplements				
UREA	NH ₂ CONH	0.010 gm	-	4.7 as N
POTASSIUM PHOSPHATE	K ₂ HPO ₄	0.026 gm	-	5.2 as P
SODIUM BICARBONATE	NaHCO ₃	0.26 gm	-	157 as CaCO ₃

* Empirical (Appendix A)

** Measured l^o eff. value (VSS) + Slender[®] component as documented by Carnation

*** Based on empirical formulation and mass addition.

TABLE 4. FINAL FEED SOLUTION
(All values in mg/l)

Constituent	Theoretical *	Measured
COD	386	320
Org-N	20.7	20.3
NH_4^+-N	-	12.7
Total-N	33.4	29.8
PO_4-P	11.9	10.0
Alkalinity	254 as CaCO_3	275 as CaCO_3
VSS	-	100
SS	-	112

* Appendix A.

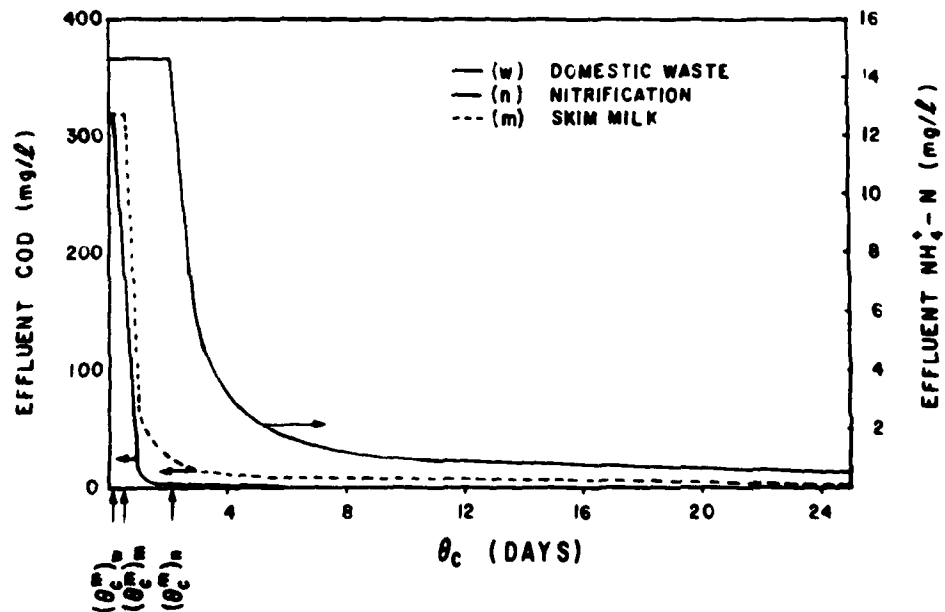


Figure 4. Theoretical Effluent COD and Ammonia Nitrogen
as a Function of Mean Cell Residence Time

3. OPERATING PARAMETERS

Knowing the bacterial growth and substrate utilization coefficients for a particular waste under specified environmental conditions, Equation (11) may be used to relate effluent soluble substrate concentration to mean cell residence time. Using the coefficient data summarized in Table 5 for COD removal (domestic waste, skim milk) and nitrification, the relationship in Figure 4 results.

It is clear from Figure 4, that 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. In a laboratory environment, it is generally more desirable to monitor and maintain a constant θ and X_v or X in an effort to realize θ^* . For the mixed treatment system of interest here, X_v can be described by a modification of Equation (27):

$$X_v = \frac{\theta}{\theta_c} X_r^o + \frac{S}{S^o} X_d^o + \frac{Y(S^o - S)}{1 + b\theta_c} (1 + (1 - f_d)b\theta_c) \theta_{cH} + \frac{Y(S^o - S)}{1 + b\theta_c} (1 + (1 - f_d)b\theta_c) \theta_{cA} \quad (24)$$

and recall that:

$$X = \frac{\theta}{\theta_c} X_{in}^o + X_v$$

where the subscripts H and A stand for heterotrophic and autotrophic, respectively. The autotrophic biomass is, however, only about four percent that of the heterotrophic, the inference being that the last term in Equation (24) can be dropped. Designing for a Mixed Liquor Suspended Solids (MLSS) of 4500 mg/l** a constant hydraulic detention time of 6.67 hours, and using the skim milk coefficients (conservative), Equations (11) and (23) lead to a θ_c of 7.5 days. These parameters are summarized in Table 6.

*Under constant influent and environmental conditions the growth rate will remain constant ($S^o \gg K_s$). When this situation is accompanied by efficient clarification, the amount of mixed liquor wasted to maintain the design MLSS will be constant and θ_c will, therefore, also remain constant.

** Assumptions: $X_a^o = X_i^o = 0$

$$X_r^o = 0.35 X_v^o$$

$$X_d^o = 0.65 X_v^o$$

TABLE 5. BACTERIAL GROWTH AND SUBSTRATE UTILIZATION COEFFICIENTS

TREATMENT OBJECTIVE	COEFFICIENT	DOMESTIC SEWAGE		SKIM MILK		BASIS
		VALUE	REFERENCE	VALUE	REFERENCE	
COD Removal	Y	0.45	5	0.48	4	mg Cells/mg COD
	b	0.05	5	0.05	4	Day ⁻¹
	k	20.9*	2	6.0*	3	mg COD/mg Cells-Day
	K	60	2	110	3	mg/l COD
Nitrification	Y	0.36	5	-	-	mg Cells/mg NH ₄ ⁺ -N
	b	0.05	5	-	-	Day ⁻¹
	k	1.8	5	-	-	mg NH ₄ ⁺ -N/mg Cells-Day
	K _s	3.6	5	-	-	mg/l NH ₄ ⁺ -N

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

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

Heterotrophic: 0.46 mg/cells/mg COD⁺
Autotrophic: 0.36 mg/cells/mg NH₄⁺-N

TABLE 6. DESIGN OPERATING PARAMETERS

θ	MLSS [*]	θ_c
6.67 Hours	4500 mg/	7.5 Days

* The first two neat hydrazine runs (20/10, 6/3) deviated slightly from the design MLSS value of 4500 mg/l. The target MLSS concentrations were: 5600 mg/l for reactors 1 to 4 (20/6 mg/l) and 4000 mg/l for reactors 9 to 12 (10/3 mg/l). Two controls were operated at each MLSS concentration. These values correspond to θ 's of 10 and 6.5 days, respectively. Solids were maintained as outlined in Table 6 for all subsequent experimentation.

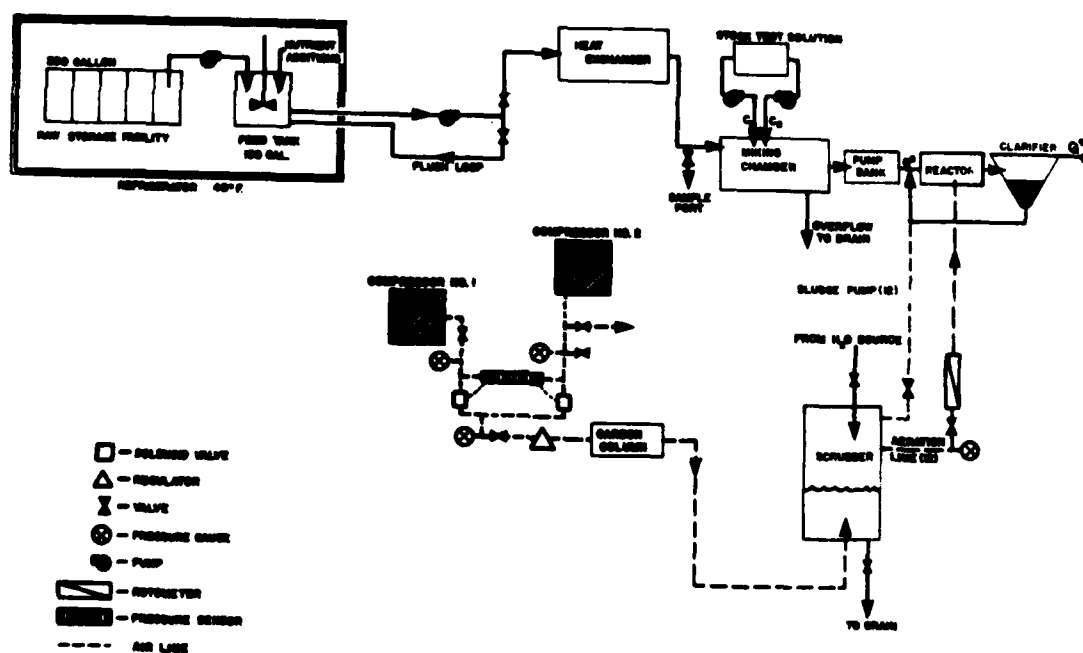


Figure 5. Laboratory Schematic

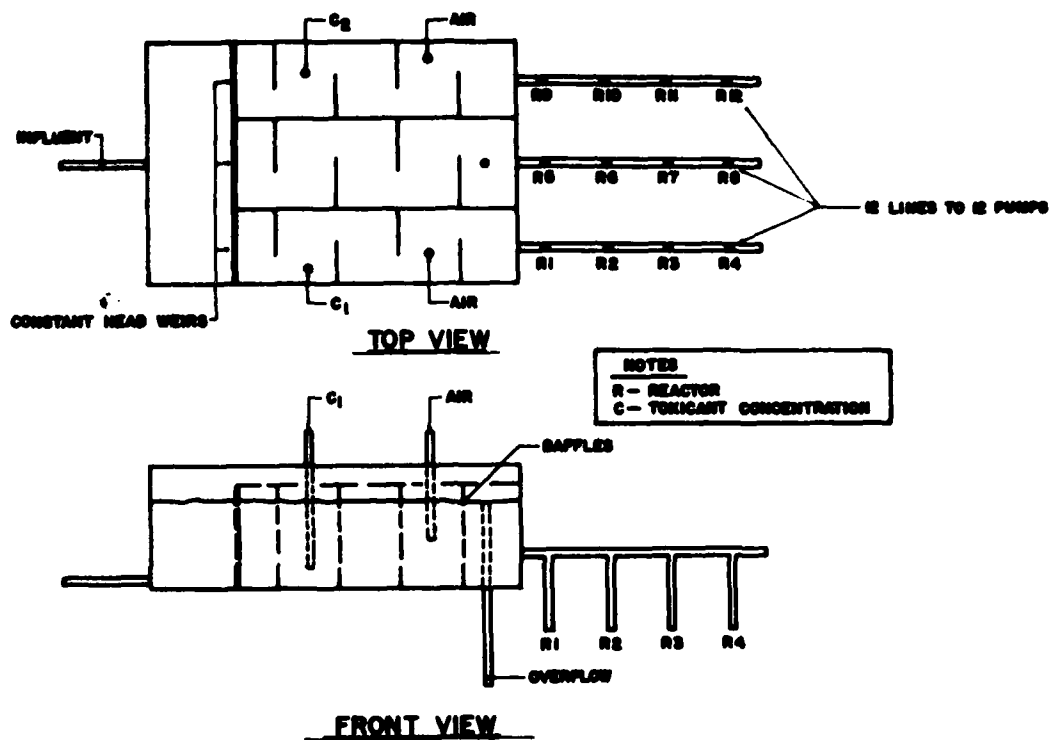


Figure 6. Mixing Chamber Used to Achieve C_1 in Reactors 1 to 4, C_2 in Reactors 9 to 12, and Control Conditions in Reactors 5 to 8 During Continuous Feed Studies

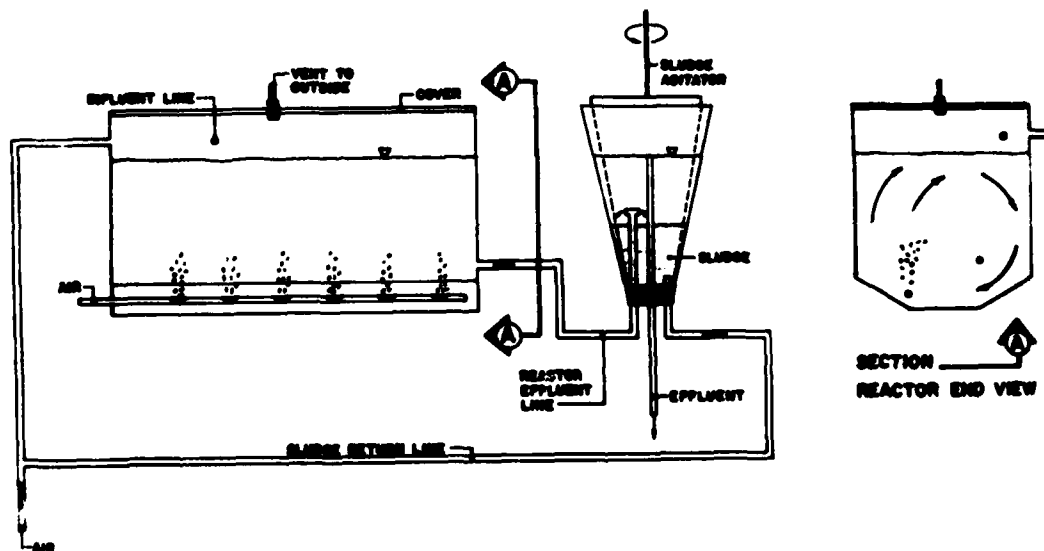


Figure 7. Aeration Basin and Clarifier

4. BENCH SCALE SYSTEM

Figure 5 is a schematic of the laboratory system developed for continuous flow studies. The 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 AFB 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 151-liter (40-gallon) containers inside a refrigeration unit (4.4°C) adjacent to the laboratory. All raw feed was stored in this configuration until utilized 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 exchange (25°F) and then into the mixing chamber, illustrated in Figure 6. This chamber was designed such that two continuous feed toxicant concentrations could be evaluated simultaneously. As indicated, the center channel received only the supplemented feed solution, serving the control series of reactors. The 6-liter Plexiglas® aeration basins detailed in Figure 7 were supplied with humidified air passed through an activated carbon filter to affect excess dissolved oxygen and complete mixing. Sludge return from the 2-liter Pyrex® clarifiers was maintained using gravity induced draw-off and an in-line air pump.

5. EXPERIMENTAL MATRIX

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 for each fuel. 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 6) on duplicate continuous flow reactors. These concentrations were realized by adding from 1 to 12 milliliters (ml) of stock fuel solutions directly to the aeration basin.

In the slug studies effluent characteristics were monitored for sufficient time to make inferences about process recovery. All reactors were allowed to achieve steady state as indicated by effluent COD and NO₃-N concentrations prior to initiating hydrazine feeds for any one particular evaluation. Table 7 summarizes the seeding/evaluation sequence employed.

TABLE 7. SEEDING/EVALUATION SEQUENCE

<u>FUEL</u>	<u>ACTION</u>
	Initial Seeding
HZ	20/20 Run
	6/3 Run
	1/0.5 Run
	Slug Loads
	Reseed
MMH	20/10 Run
	6/3 Run
	1/0.5 Run
	Reseed
UDMH	Slug Loads
	Slug Loads
	20/10 Run
	1/0.5 Run
	6/3 Run

6. ANALYTICAL PROCEDURES

a. General: Those parameters of interest included the major forms of nitrogen (NH_3 , organic, NO_3^-), COD, total and volatile suspended solids, HZ, MMH, UDMH and pH. Orthophosphate and alkalinity were monitored less frequently. All assays were performed in accordance with Standard Methods for the Examination of Water and Wastewater, 14th edition. Specific techniques are outlined in Table 8. Notable exceptions and comments are summarized below.

b. Hydrazine: The colorimetric method described by Watt and Chriss (Reference 19) was used for all HZ and MMH assays. This procedure is based on a stable yellow color which develops upon addition of p-dimethyl-aminobenzaldehyde to dilute solutions of hydrazine. Absorbance was measured at 460 anometers (nm) using a Coleman 55 digital spectrophotometer.

UDMH determinations were accomplished using the colorimetric method outlined by Pinkerton, Lauer, Diamond, and Tamas (Reference 20). The procedure develops a colored solution using trisodium pentacyanoamino ferroate (TPF) and a disodium acid phosphate/citric acid buffer. During this investigation the recommended buffer concentrations were increased by a factor of 3.5 to increase sensitivity. It was also found that a wavelength of 495 anometers (nm) provided greater accuracy than the recommended 500 anometers (nm).

c. 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

assayed for NH_4^+ -N and organic -N. Unfiltered influent samples were analyzed for these same parameters. Both influent and effluent were intermittently checked for orthophosphate, 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.

TABLE 8. ANALYTICAL TECHNIQUES

<u>Parameter</u>	<u>Method</u>	<u>Reference Standard Methods</u>
COD	Dichromate Digestion	508
Suspended Solids	Membrane Filter, Residue on Evaporation	208D
Volatile Suspended Solids	Membrane Filter, Residue Residue on Ignition	208G
NH_3 -N	Distillation/Titrimetric*	418A/D
NO_3 -N	Electrode**	419B
Organic-N	Digestion/Distillation/ Titrimetric	412/418D
Alkalinity	Titrimetric to pH 4.3	403
pH	Electrode	424
PO_4 -P	Colorimetric	425D

* Oxidized nitrogen interference not detected.

** Comparisons with Brucine method yielded good correlation.

SECTION IV

RESULTS - HYDRAZINE (HZ)

Neat hydrazine is a colorless liquid with a density of 1.000 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 and no detectable ammonia or organic nitrogen.

1. CONTINUOUS FEED STUDIES

a. HZ Degradation: Although it was the objective of this study to maintain stable hydrazine concentrations during each run, actual analyses showed that there was some variation. Figure 8 shows the measured HZ concentrations in the influent to the reactors. Each point represents the average of four reactors, and 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. The theoretical and measured average influent and effluent hydrazine concentrations for the continuous feed studies are summarized in Table 9. 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 (see Figure 17, paragraph 2a, this section), the documented reductions in HZ are assumed to be the result of microbial metabolism.

b. COD: Table 10 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. Figure 9 shows the daily influent data as well as the mean effluent CODs from the four control reactors. As can be seen, effluent quality remained very stable in the controls despite influent COD fluctuations. These findings agree with data presented by Saheh and Gaudy (Reference 22) who have reported that recycle systems can handle a 200-percent step change in influent organic substrate concentration with only a small, short-lived 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 the 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 10. For the operating parameters in this study, a 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 11. Microscopic examinations of exposed activated sludge samples

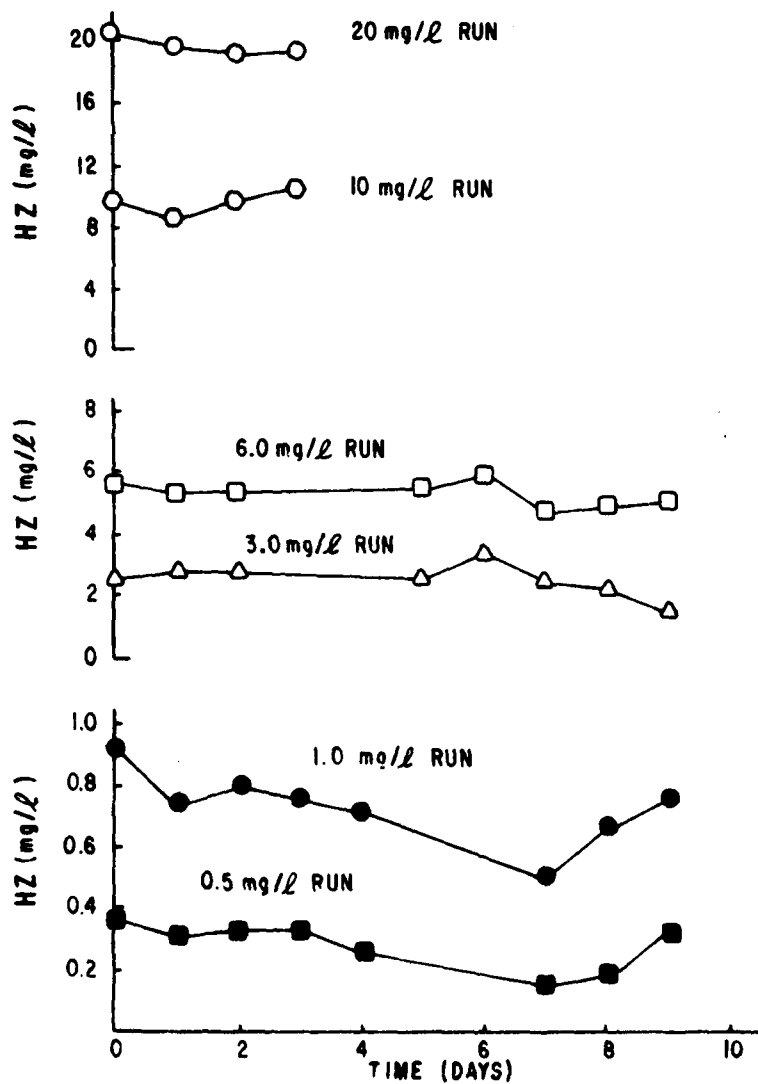


Figure 8. Continuous Influent HZ Concentrations

TABLE 9. HZ CONCENTRATIONS DURING CONTINUOUS FEED STUDIES (mg/l)

Theoretical	Study Designation	Influent		Effluent		Reduction Percent
		Mean	σ n	Mean	σ n	
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	1/0.5	0.7	0.1 52	ND	0.0 46	100
0.5	1/0.5	0.3	0.1 52	ND	0.0 36	100

NOTE: ND = None Detected

TABLE 10. INFLUENT AND CONTROL EFFLUENT COD SUMMARY

Study	Study Length (Days)	Influent COD (mg/l)		Control Effluent COD (mg/l)		Control Percent Removal
		Mean	σ	Mean	σ	
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

** n = 78

TABLE 11. INFLUENT AND CONTROL EFFLUENT NITROGEN SUMMARY (mg/l)

Study	Study Length (Days)	Influent			Control Effluent			Nitrification* Percent In Controls
		NH ₃ -N Mean	NH ₃ -N σ	TKN Mean	NH ₃ -N Mean	NH ₃ -N σ	NO ₃ -N Mean	σ
20/10	3	12.5	2.6	29.9	0.0	0.1	20	2.5
6/3	9	14.1	4.3	28.0	0.1	0.2	22	4.5
1/0.5	9	14.4	3.8	27.6	0.0	0.1	23	2.7
Overall	-	13.8	3.7	27.4	0.1	0.1	22	3.6

*Based on TKN Conversion to NO₃-N

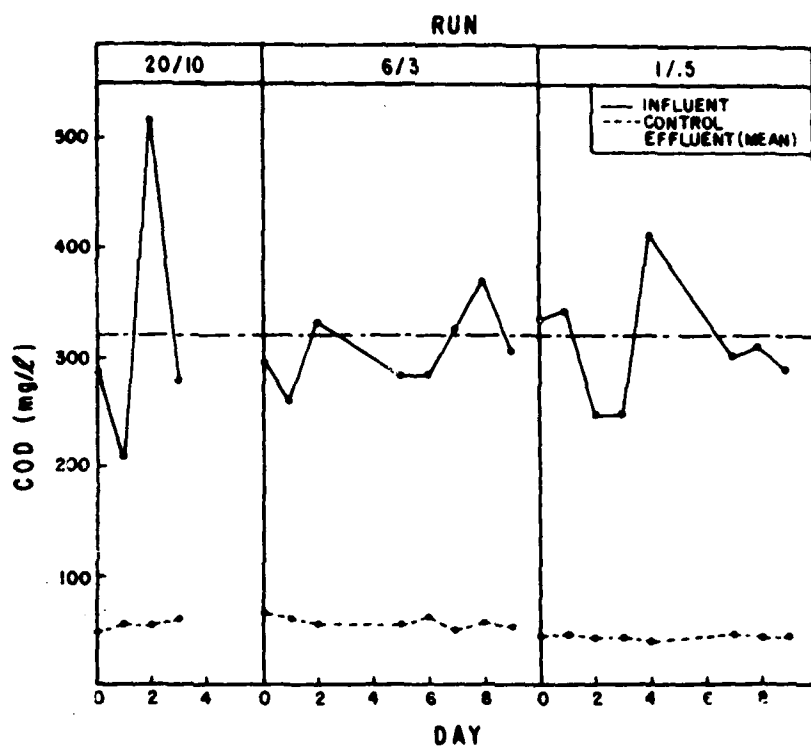


Figure 9. Influent COD and Mean Control Effluent COD Values During Continuous Feed HZ Runs

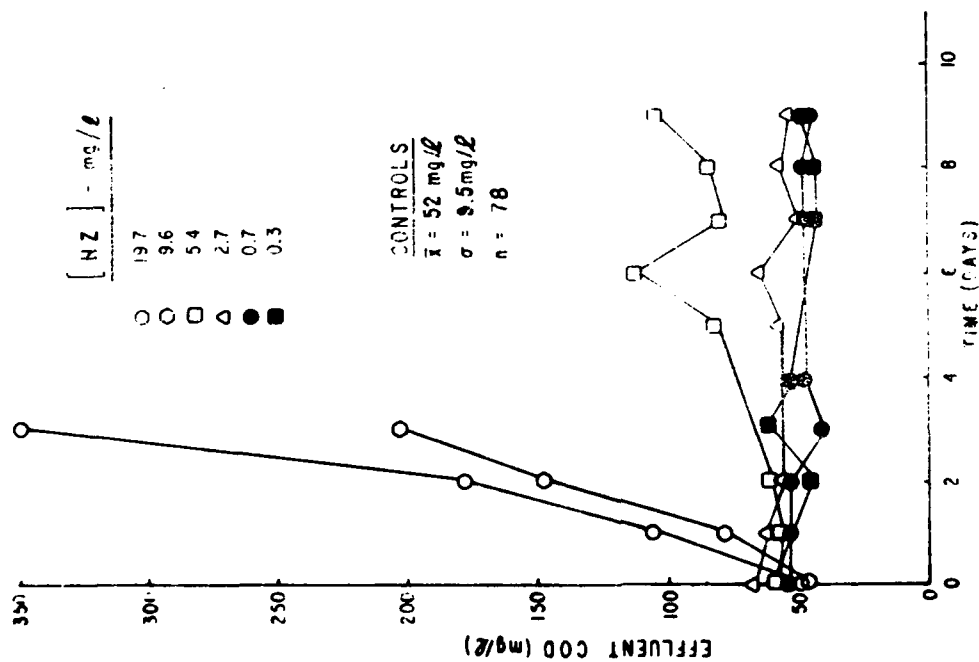


Figure 10. Effluent COD as a Function of Time and Continuous Feed HZ Concentration (Mean of 4 Replicates)

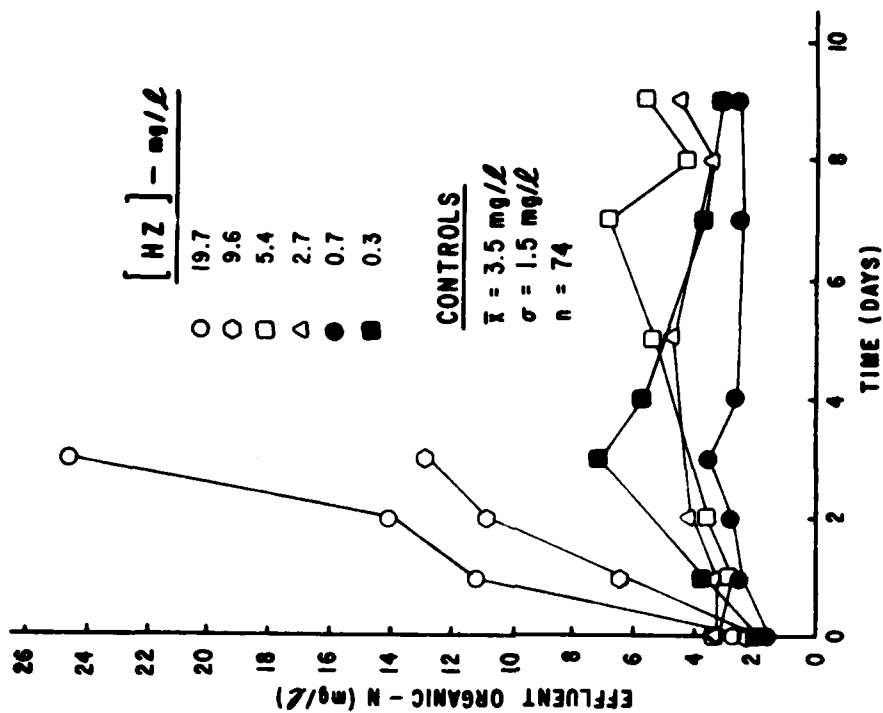


Figure 11. Effluent Organic Nitrogen as a Function of Time and Continuous Feed HZ Concentration (Mean of 4 Replicates)

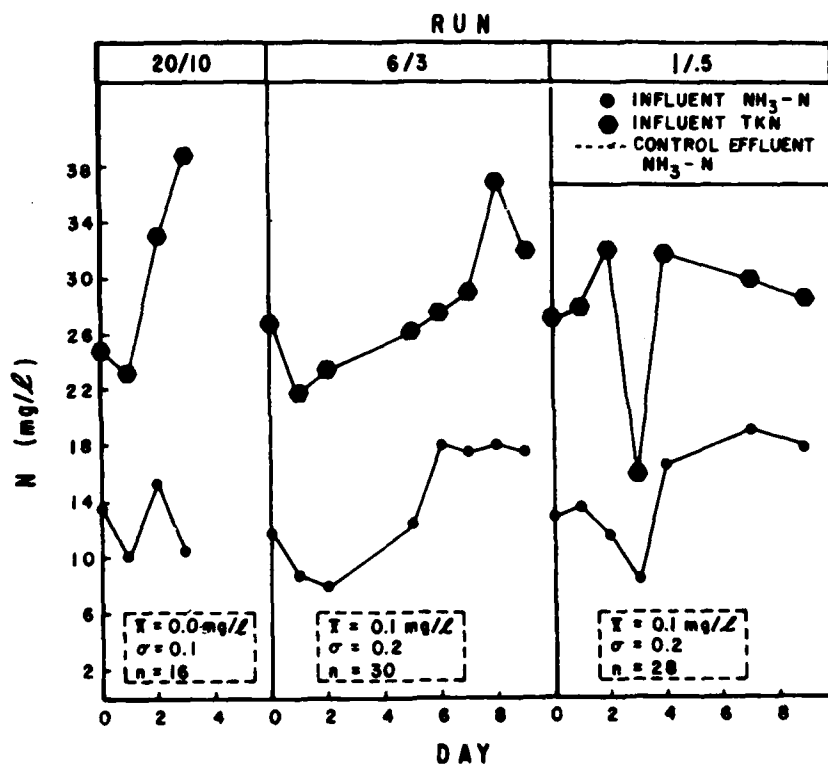


Figure 12. Influent and Control Effluent Nitrogen Data During Continuous Feed HZ Runs

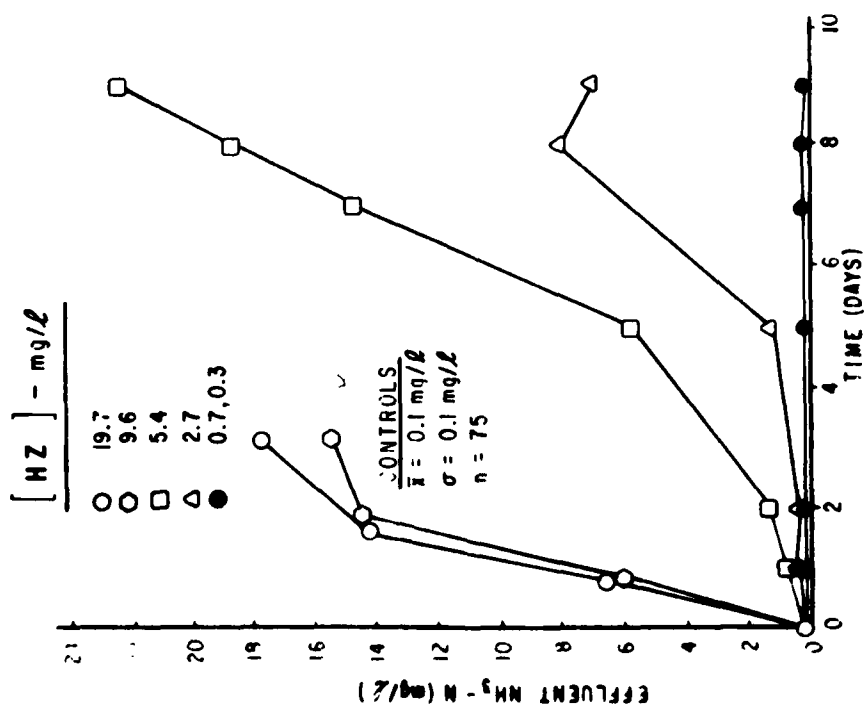


Figure 13. Effluent Ammonia Nitrogen as a Function of Time and Continuous Feed HZ Concentration (Mean of 4 Replicates)

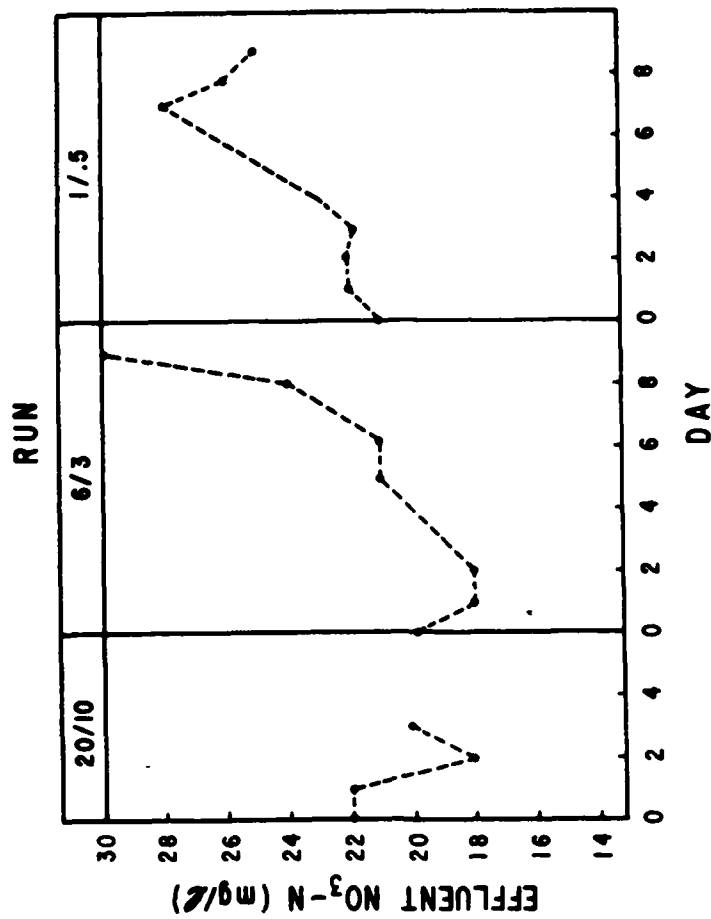


Figure 14. Mean Control Effluent Nitrate Nitrogen Values During Continuous Feed HZ Runs

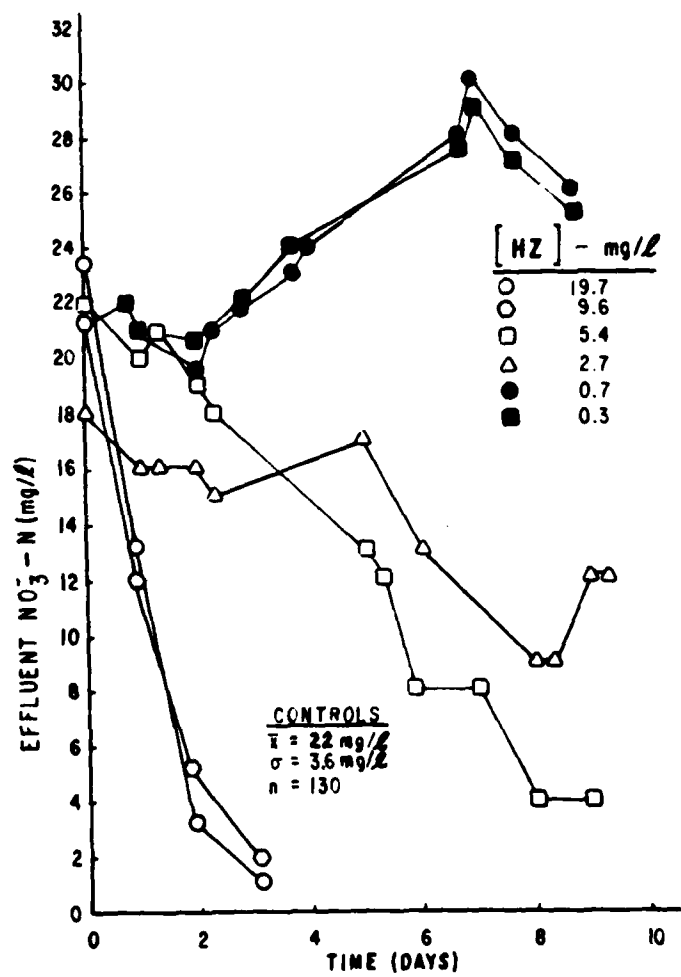


Figure 15. Effluent Nitrate Nitrogen as a Function of Time and Continuous Feed HZ Runs (Mean of 4 Replicates)

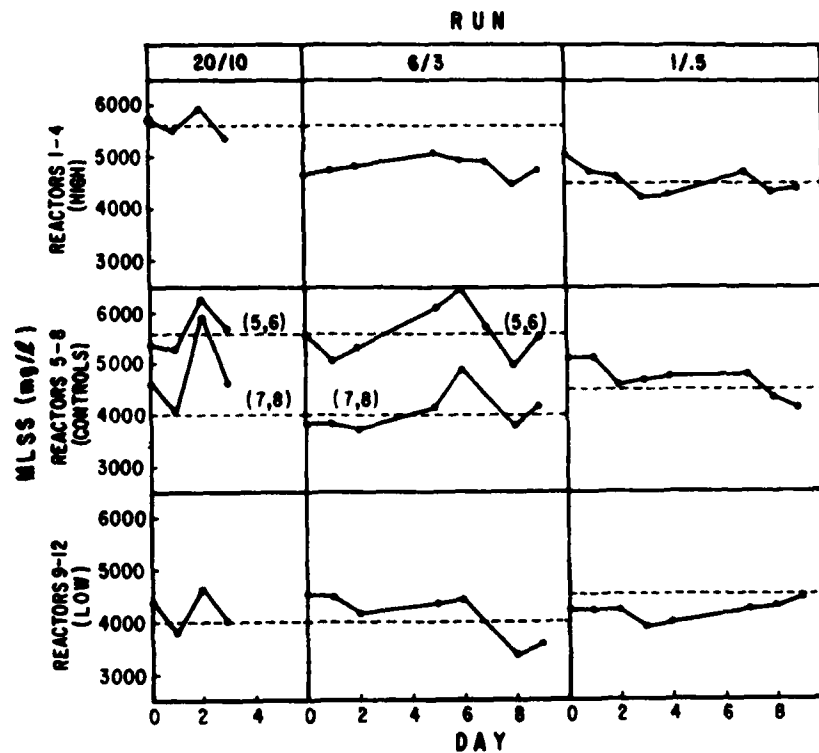


Figure 16. Mean MLSS During Continuous Feed HZ Runs (Mean of 4 Replicates Except Controls During 20/10 and 6/3 Which Were Duplicates)

verified that significant cell lysis was affected by HZ, releasing soluble organic nitrogen and other organics which contributed to soluble effluent COD as well.

c. Nitrification: The influent and control effluent nitrogen data collected over the continuous feed HZ studies are summarized in Table 11. Overall, 80-percent nitrification of influent TKN was achieved during these experiments. Effluent ammonia concentrations agreed well with those predicted based on the growth and substrate utilization coefficients discussed in Section III of this report. (Figure 4).

As for COD, the daily influent and control effluent parameters of interest have been graphically displayed in Figures 12 and 14 for comparison with daily effluent qualities in those reactors receiving HZ. The data in Figure 12 clearly indicates that while influent ammonia and TKN varied somewhat from day to day, effluent ammonia concentrations were consistently below 0.2 mg/l. From Figure 13 it is apparent that even low HZ concentrations (~ 3 mg/l) cause inhibition of nitrification. The nitrate data presented in Figure 15 agree well with the ammonia data. 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.

d. Suspended Solids: The suspended solids data for the control reactors are outlined in Table 12. 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.

TABLE 12. CONTROL MLSS DATA (mg/l)

Study	HIGH			LOW		
	Mean	σ	n	Mean	σ	n
20/10	5660	450	8	4830	860	8
6/3	5600	570	16	4060	500	14
	MEAN					
		σ	n			
1/0.5	4470	530	32			

The MLSS response to HZ are summarized in Figure 16. As in Table 12, all values represent concentrations prior to wasting to the desired levels. Wasting was accomplished once daily if the MLSS concentration was above the target value. 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 increased effluent organic nitrogen concentrations (Figure 11) and therefore effluent suspended solids, the majority of which were lysed cells (qualitative observation), the loss of solids was not of sufficient magnitude to decrease MLSS and hence θ_c significantly during any of the runs.

2. SLUG FEED STUDIES

a. HZ Degradation: Figure 17 is a plot of the ratio reactor HZ concentration (C) over the initial added HZ concentration (C_0) versus time. The initial drop in the control plot is due to the dilution effected by 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 (25).

$$\ln C/C_0 = - \frac{1}{\theta_s} + Kt \quad (25)$$

C = HZ at time t (mg/l)

C_0 = HZ at time 0

θ_s = Total system (reactor plus clarifier) hydraulic detention time (HR) = 7.78 HR

t = Time (HR)

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

If hydrazine was not toxic to the activated sludge fauna, Equation (25) would predict that K would be independent of C_0 . This was not observed, as shown in Table 13 and in Figure 18, which is a plot of the calculated half-life ($t_{1/2}$) of hydrazine at each added concentration.

TABLE 13. BACTERIAL DECAY CONSTANTS FOR HZ

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

b. Acute Response: Influent parameters during the 8-hour acute response study are summarized in Table 14.

TABLE 14. SLUG LOAD RESPONSE INITIAL CONDITIONS (mg/l)

HZ		Influent			MLSS	
Theoretical	Measured	COD	$\text{NH}_3\text{-N}$	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

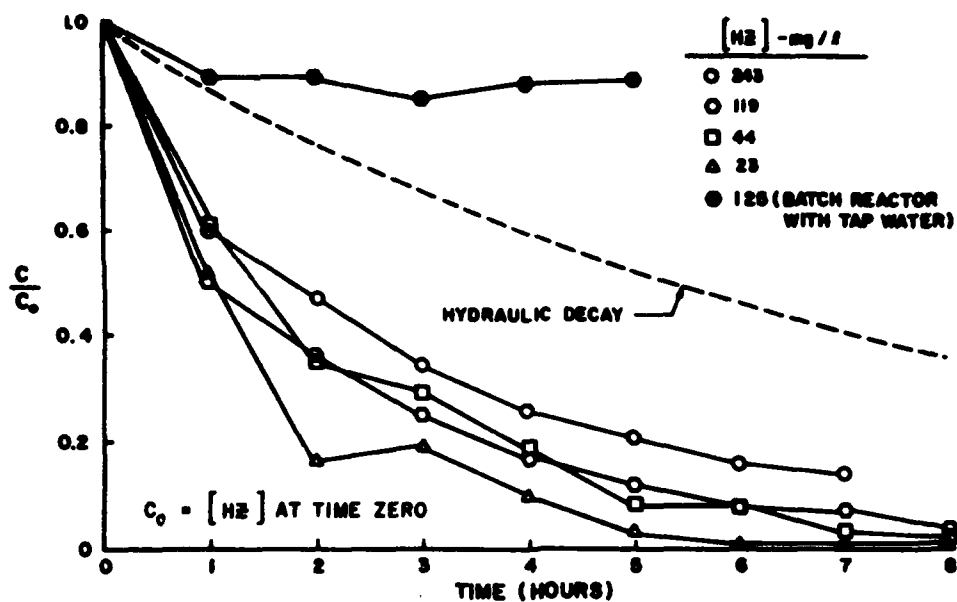


Figure 17. HZ Degradation During HZ Slug Feed Experiments (Mean of Duplicates)

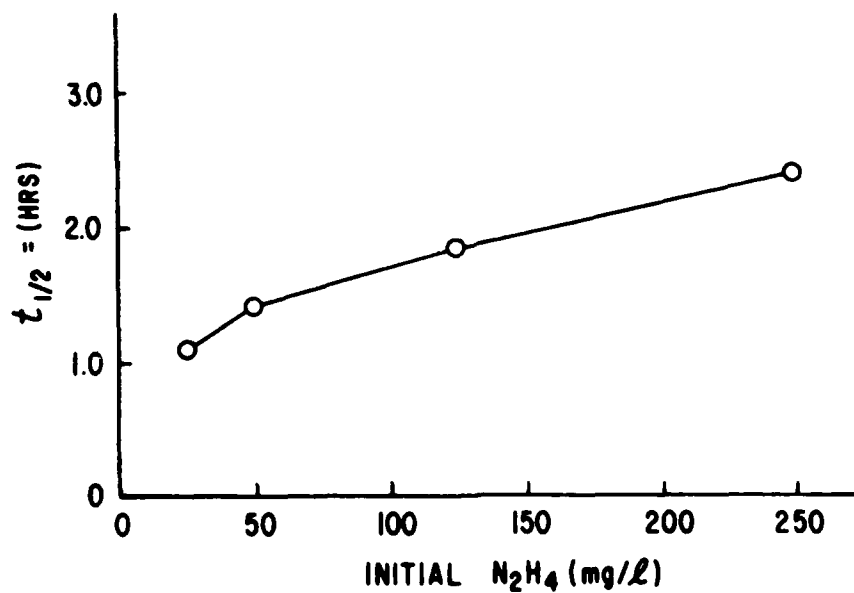


Figure 18. Calculated Half Life for HZ as a Function of Initial HZ Slug Concentration

(1) COD: Figure 19 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, only 33 mg/l can be attributed to HZ. The 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 concentration to above 44 mg/l N_2H_4 . Figure 20 clearly shows that effluent organic nitrogen concentrations were elevated from 0 to 6 times initial values depending on the HZ slug.

(2) Nitrification: The effect of HZ slug feeds on nitrification is shown in Figures 21 and 22. 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 influent nitrate, confirming that at all concentrations the oxidation of ammonia to nitrate has ceased.

c. 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 23.

(1) COD: Figure 24 illustrates that even for the 243 mg/l study there was significant recovery within 4 days and complete recovery within 6 days. Recovery from HZ concentrations below 44 mg/l was complete after approximately 3 days.

(2) Nitrification: Recovery of the nitrifying bacteria is slower than for the heterotrophs. In Figure 25 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 26, suggesting that HZ is toxic to this species as well.

(3) Suspended Solids: 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 27 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.

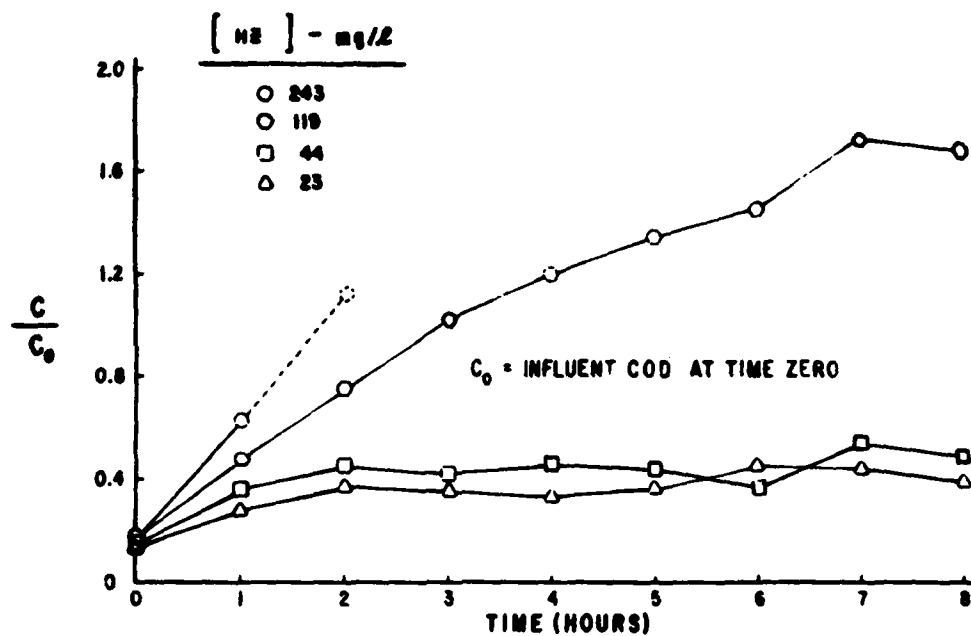


Figure 19. Acute Effluent COD Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)

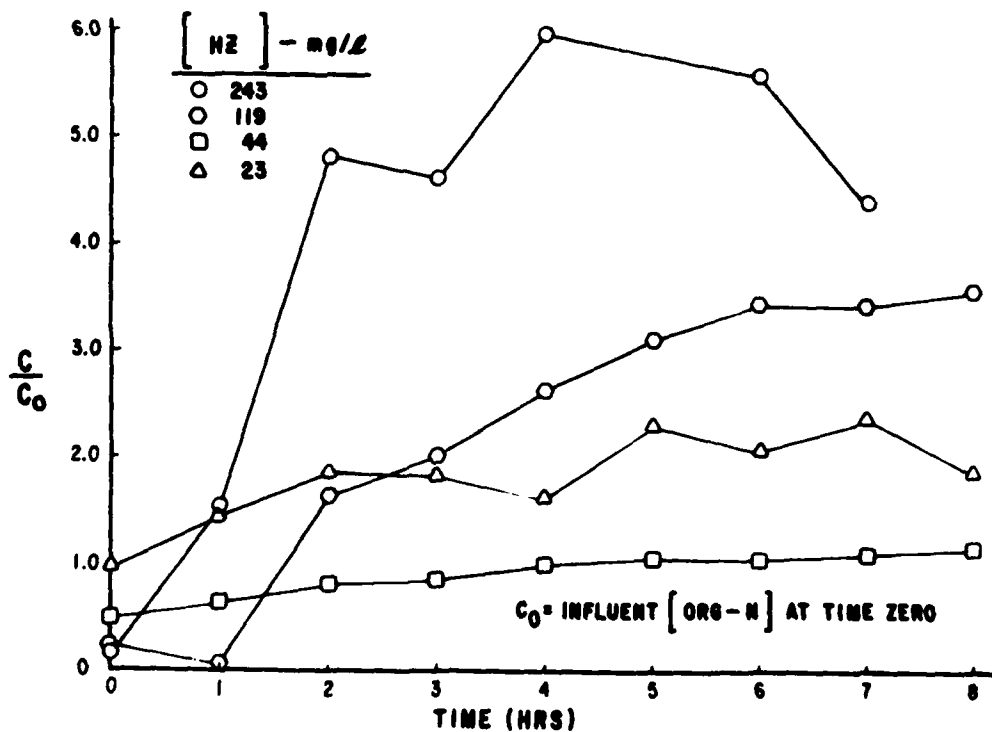


Figure 20. Acute Effluent Organic Nitrogen Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)

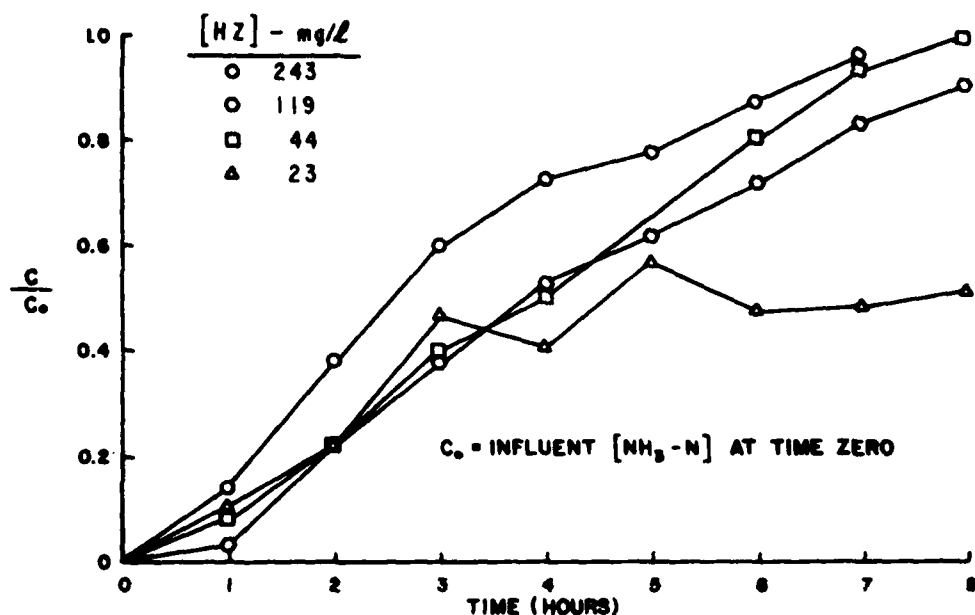


Figure 21. Acute Effluent Ammonia Nitrogen Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)

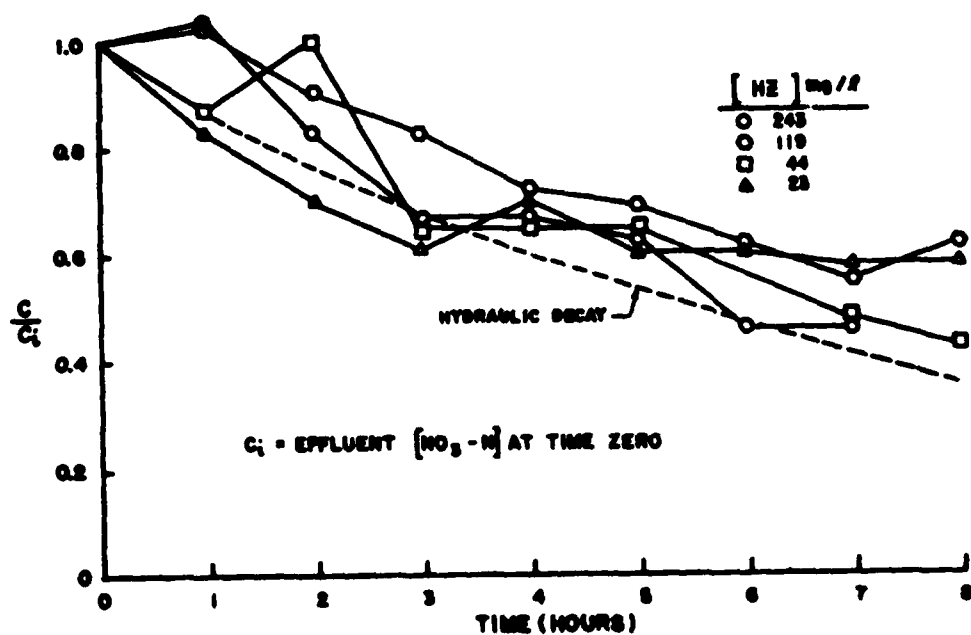


Figure 22. Acute Effluent Nitrate Nitrogen Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)

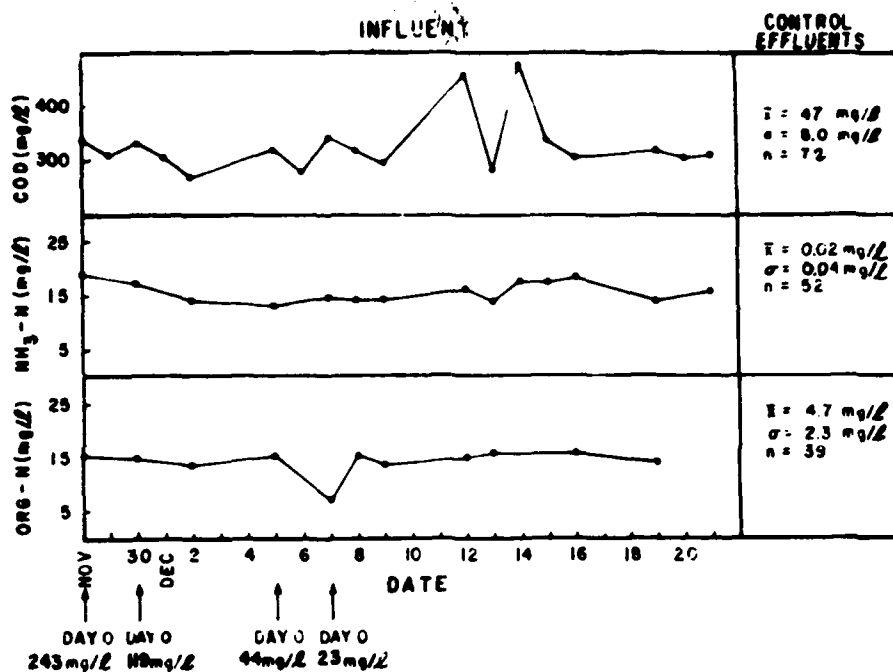


Figure 23. Influent and Control Effluent COD and Nitrogen Data During the Slug HZ Recovery Periods

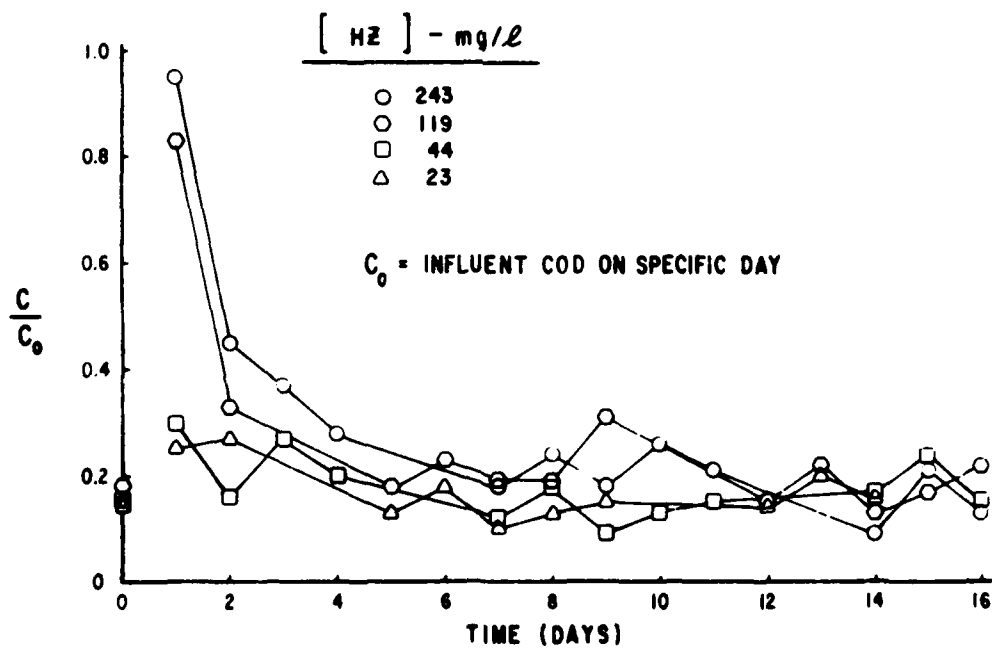


Figure 24. Effluent COD Recovery Following Slug HZ Loads (Mean of Duplicates)

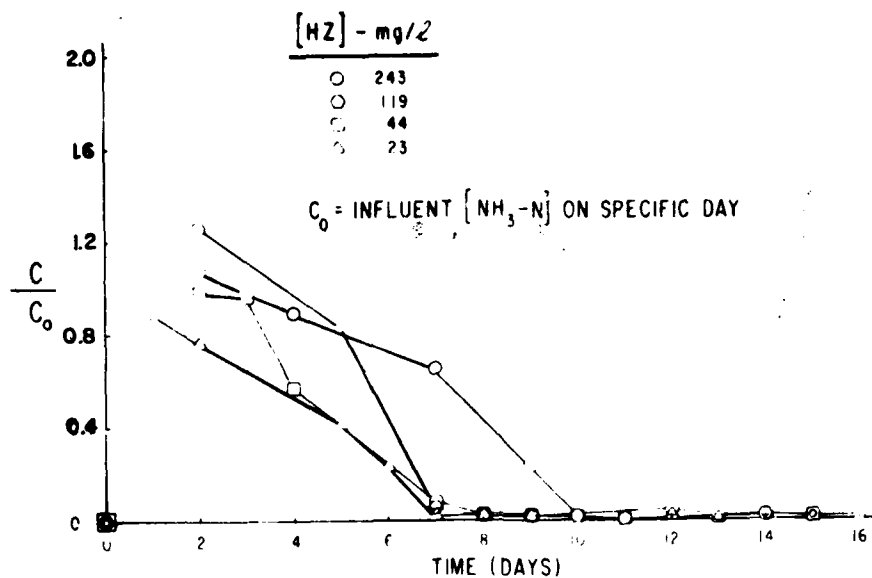


Figure 25. Effluent Ammonia Nitrogen Recovery Following Slug HZ Loads (Mean of Duplicates)

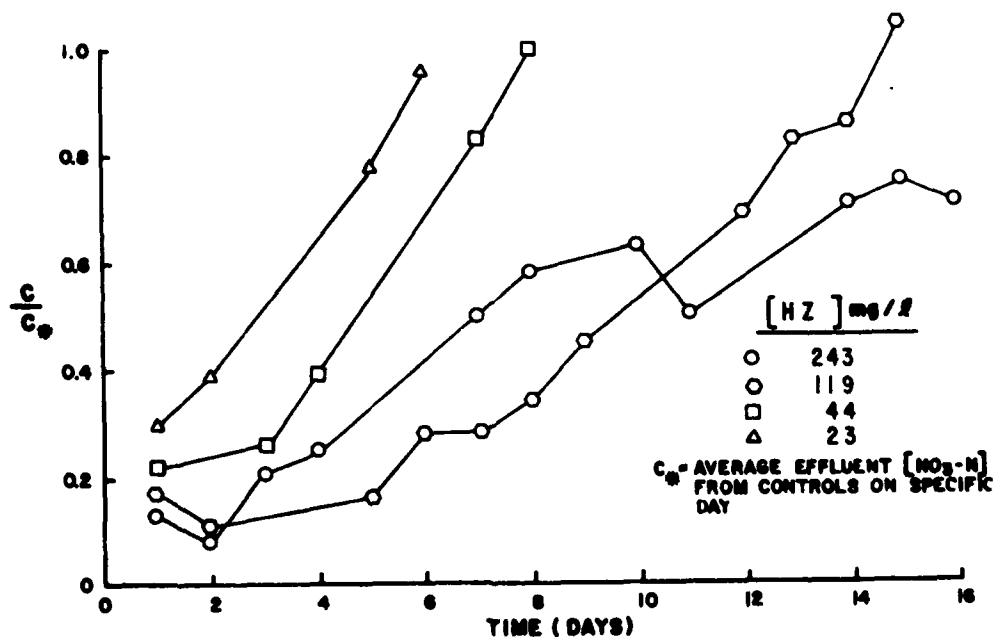


Figure 26. Effluent Nitrate Nitrogen Recovery Following Slug HZ Loads (Mean of Duplicates)

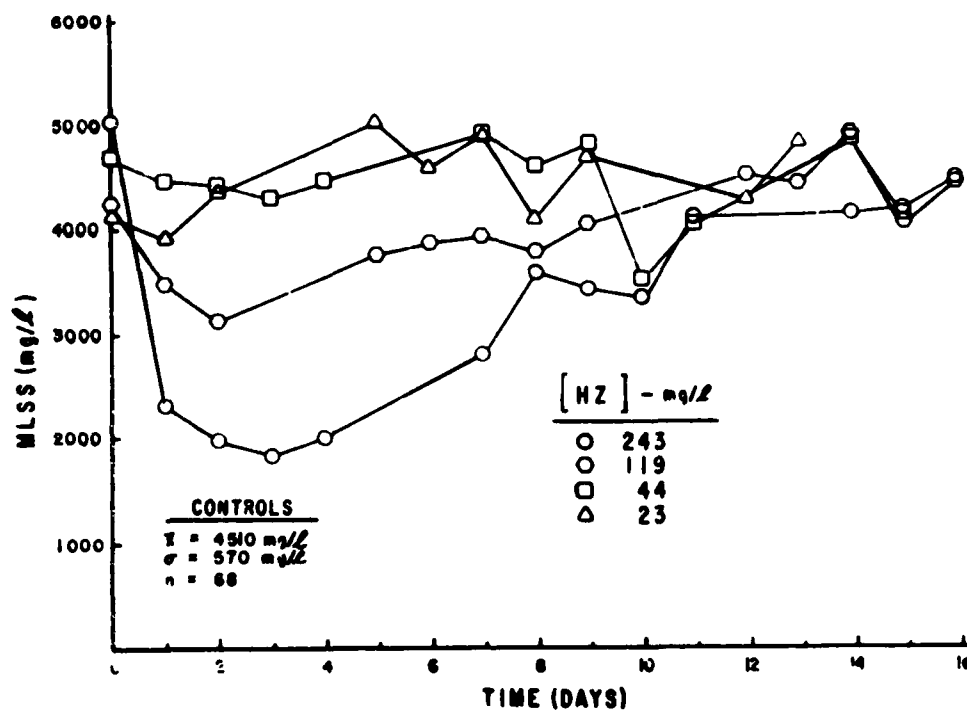


Figure 27. MLSS Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)

SECTION V

RESULTS - MONOMETHYLHYDRAZINE (MMH)

Monomethylhydrazine is a colorless liquid with a density of 0.874 gm/ml at 20°C. It is very soluble in water. Duplicate analyses of a 125 mg/l stock solution resulted in 1.56 mg COD/mg MMH, 0.03 mg NH₃-N/ mg MMH, and no detectable organic nitrogen.

1. CONTINUOUS FEED STUDIES

a. MMH Degradation: Figure 28 shows the measured influent MMH concentrations during these studies. The theoretical and measured average influent and effluent MMH concentrations are summarized in Table 15.

As for HZ, control reactors with aerated tap water showed no MMH degradation over 8 hours. The percent reductions indicate microbial degradation or degradation catalyzed by the solids in the reactor. The low percent removal observed during the 0.5 mg/l study (60 percent) is attributed to certain operational problems. During the 1/0.5 run effluent COD concentrations in the 0.5 mg/l reactors rose significantly on day 3. Effluent organic-N values were not recorded on day 3 but were very high on day 4. COD, Organic-N, and NH₃-N values remained slightly elevated throughout the remainder of the study while MLSS concentrations declined. One of the four reactors began to bulk significantly during this period.* It was also noted that the effluent quality of the controls was below normal with respect to both COD removal and nitrification during this time period; one control began to bulk on day 4*. It should be pointed out that all of the effluent parameters were extremely sensitive to bulking conditions: either directly (COD, org-N), owing to the filtration protocol (Whatman #40), or indirectly (NH₃-N, NO₃-N), as a result of decreased Q_c . The above and the fact that the heterotrophic response seemed to be on the same order of magnitude as that for the autotrophs (uncharacteristic for these fuels), might suggest a transient hydraulic anomaly in reactors 5 to 12 as the cause for these observations. The reduced MMH degradation is assumed to be primarily a function of the decreased solids level.

Assuming that the average MMH degradation level at concentrations below 1 mg/l is approximately 90 percent and 50 percent at 3 to 6 mg/l, it is difficult to explain the 75-percent removal rate at 10 to 20 mg/l. No explanation is offered at this time.

b. COD: The influent and control reactor effluent data are given in Table 16. Figure 29 shows the daily influent data as well as the mean effluent CODs from the four control reactors. Effluent quality in these reactors was clearly very stable. The high influent COD on day 1 for the 20/10 appears to be due to an unrepresentative sample (suspended matter) as the filtered sample had a COD of only 298 mg/l.

* All effluent data from the 2 bulking reactors were ignored after day 4.

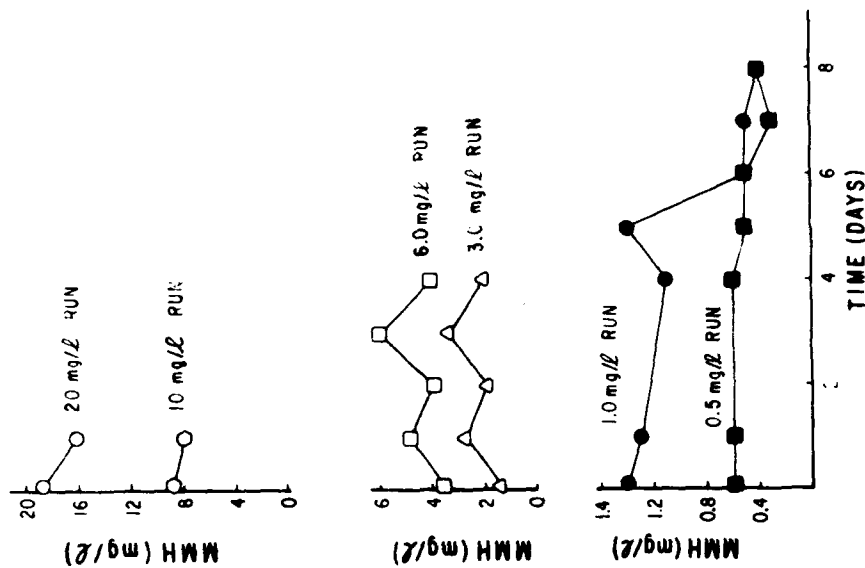


Figure 29. Influent COD and Mean Control Effluent COD Values During Continuous Feed MMH Runs

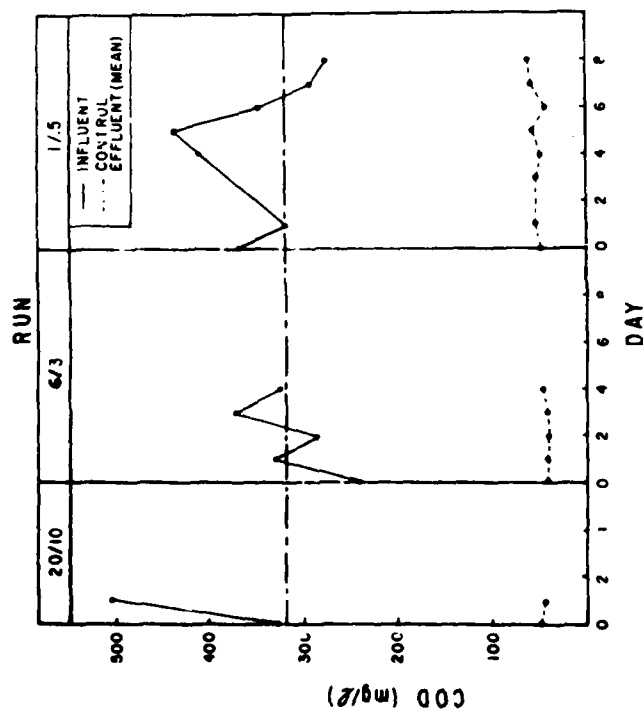


Figure 28. Continuous Feed Influent MMH Concentrations

TABLE 15. MMH CONCENTRATIONS DURING CONTINUOUS FEED STUDIES (mg/l)

Theoretical	Study Designation	Influent		Effluent		Reduction (Percent)
		Mean	σ	Mean	σ	
20	20/10	17.6	1.5	3.7	1.2	79
10	20/10	8.3	0.7	2.3	0.3	72
6.0	6/3	4.6	1.0	2.6	0.8	43
3.0	6/3	2.4	0.8	1.1	0.4	54
1.0	1/0.5	0.9	0.45	0.11	0.19	89
0.5	1/0.5	0.5	0.28	0.24	0.21	60

TABLE 16. INFLUENT AND CONTROL EFFLUENT COD SUMMARY

Study	Study Length (Days)	Influent COD (mg/l)		Control Effluent COD (mg/l)		Control Percent Removal
		Mean	σ	Mean	σ	
20/10	1	417	125	48	3	88
6/3	4	312	51	43	4	86
1/0.5	8	352	60	54	12	85
Overall	-	347*	70	49**	10	86

* n = 14

**n = 56

TABLE 17. INFLUENT AND CONTROL EFFLUENT NITROGEN SUMMARY (mg/l)

Study	Study Length (Days)	INFLUENT			CONTROL EFFLUENT			Nitrification*
		NH ₃ -N	TKN		NH ₃ -N	NO ₃ -N		
		Mean	σ	Mean	σ	Mean	σ	Percent in Control
20/10	1	12.2	0.6	44.1	24.3	0.0	0.0	70
6/5	4	11.8	2.1	29.8	2.9	0.0	0.0	91
11.5	8	8.3	1.2	27.8	9.8	0.3	1.3	68
Overall	-	10.1	2.4	31.0	11.6	0.2	0.9	81

*Based on TKN conversion to NO₃-N

Effluent COD as a function of influent MMH concentration and time is shown in Figure 30. Effluent quality was affected for all concentrations except 0.9 mg/l. Increased DODs for the 0.5 mg/l run after day 1 are unexplainable when compared with the 0.9 mg/l data. Although pumping rates were checked on days 2 and 3, influent MMH concentrations were not quantified. It is possible that at some time during day 2 or day 3 a transient hydraulic anomaly caused elevated influent MMH concentrations which resulted in these high data points. This same trend was observed for organic nitrogen, as shown in Figure 31. A close correlation exists between effluent COD and organic nitrogen, as observed for HZ.

c. Nitrification: Influent and control effluent nitrogen data collected over the continuous feed MMH studies are outlined in Table 17. Overall, 81-percent nitrification of influent TKN was achieved.

The daily influent and control effluent parameters have been graphically displayed in Figures 32 and 34 for comparison with the data presented in Figure 33. Figure 33 indicates that the autotrophs are sensitive to MMH at concentrations above 0.5 mg/l. The rising $\text{NH}_3\text{-N}$ trend for the 0.5 mg/l study after the 5-day point can be attributed to the high influent TKN on that day (Figure 32). The nitrate data in Figures 34 and 35 support this argument because, if the increased effluent ammonia concentrations were the result of MMH inhibition, nitrate concentrations would be expected to decline. Indeed, nitrate levels significantly increased in the control reactors. The nitrogen data contradicts the theory that hydraulic anomalies were responsible for elevated COD and organic nitrogen concentrations in the 0.5 mg/l study. The 0.9 mg/l plots in Figures 30 and 35 clearly show that the autotrophs are inhibited at this MMH concentration while the heterotrophs are not. MMH addition should not be expected to adversely affect COD and organic nitrogen with a concurrent rise in effluent $\text{NO}_3\text{-N}$. There remains no basis for the reduced COD removal observed for 0.5 mg/l shown in Figure 30.

d. Suspended Solids: Table 18 summarizes the control suspended solids data. MLSS response to MMH is recorded in Figure 36. No difficulty was experienced in holding MLSS concentrations at the desired 4500 mg/l even though it was qualitatively observed that effluent suspended solids increased during MMH feeds. The same dispersed fine floc was present as for the HZ runs, indicating cell lysis rather than a bulking mechanism as the cause.

TABLE 18. CONTROL MLSS DATA (mg/l)

<u>Study</u>	<u>Mean</u>	<u>σ</u>	<u>n</u>
20/10	4710	277	8
6/3	4600	413	20
1/0.5	4600	508	24
Overall	4620	440	52

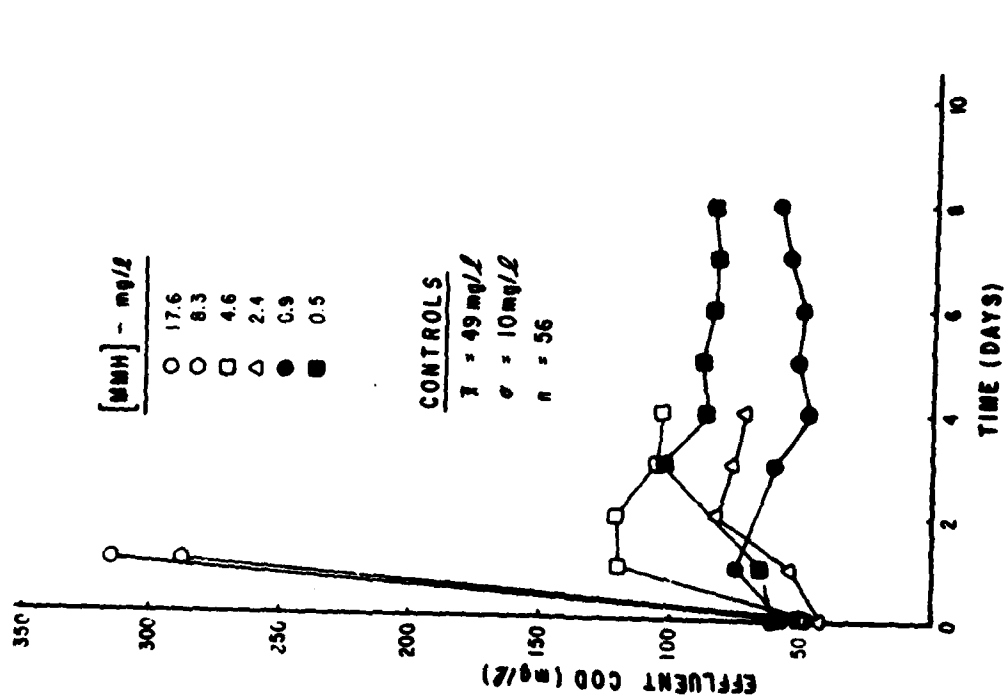


Figure 30. Effluent COD as a Function of Time and Continuous Feed MMH Concentration (Mean of 4 Replicates)

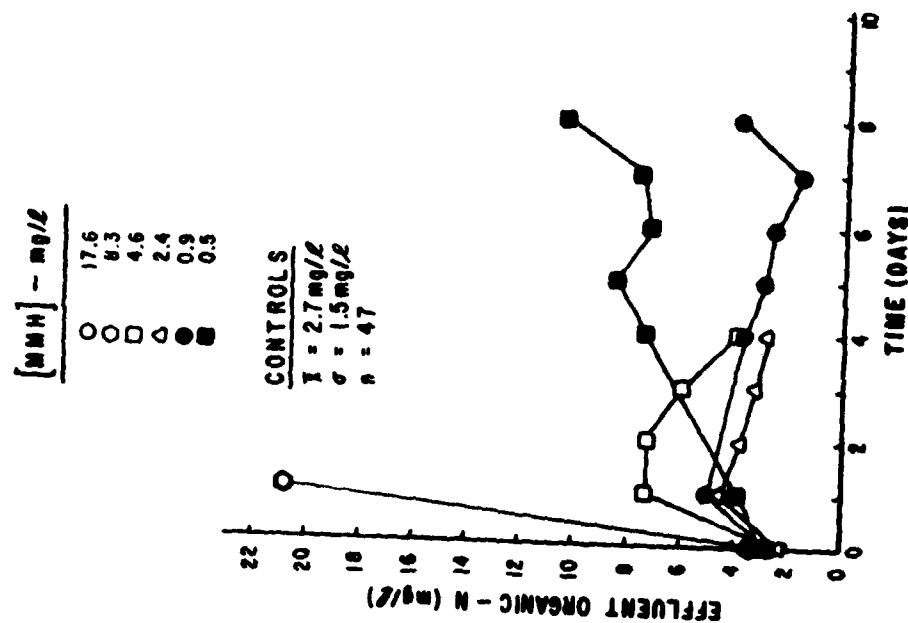


Figure 31. Effluent Organic Nitrogen as a Function of Time and Continuous Feed MMH Concentration (Mean of 4 Replicates)

[MMH] - mg/l

○	17.6
○	0.3
○	4.6
○	2.9
○	0.9
○	0.5

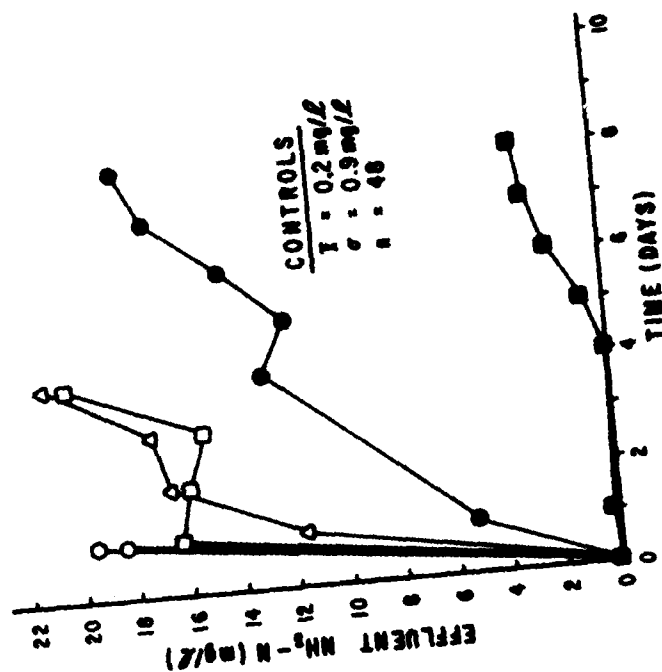


Figure 33. Effluent Ammonia Nitrogen as a Function of Time and Continuous Feed MMH Concentration (Mean of 4 Replicates)

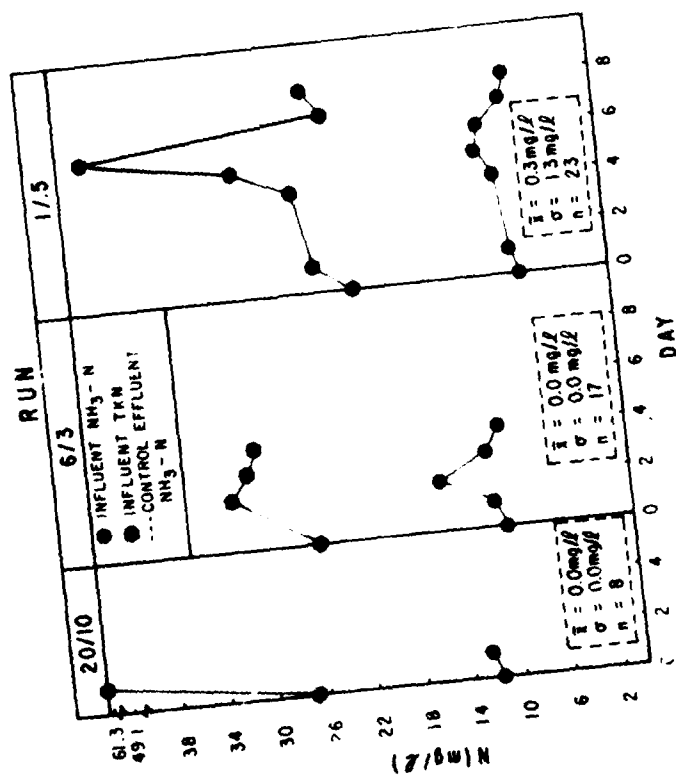


Figure 32. Influent and Control Effluent Nitrogen Data During Continuous Feed MMH Runs

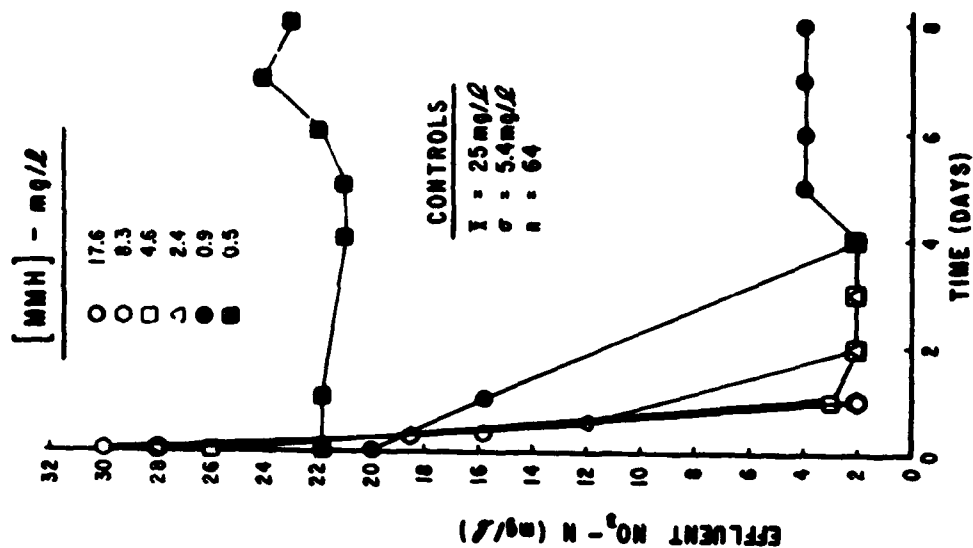


Figure 35. Effluent Nitrate Nitrogen as a Function of Time and Continuous Feed MMH Concentration (Mean of 4 Replicates)

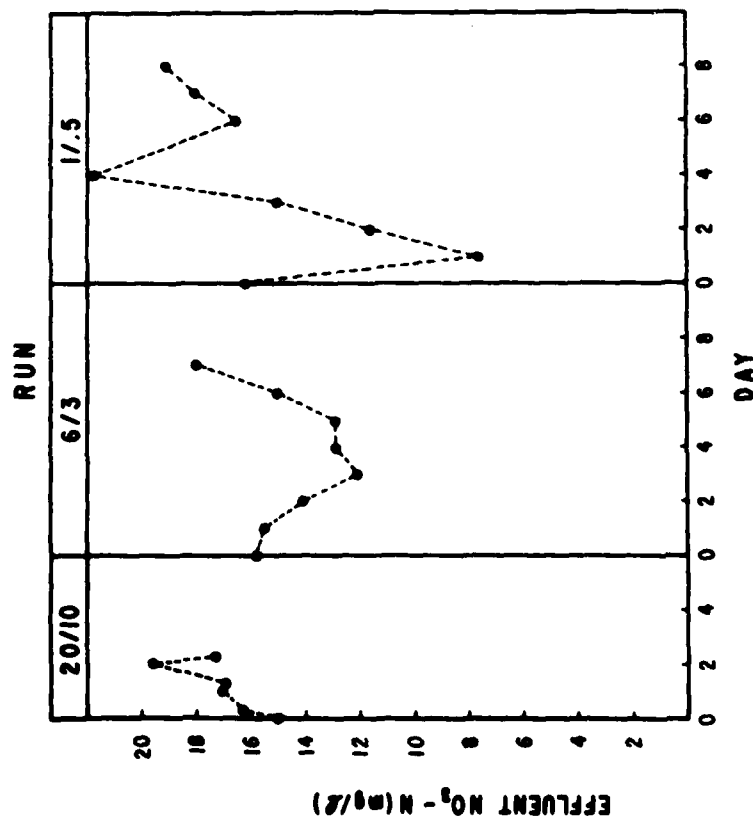


Figure 34. Mean Control Effluent Nitrate Nitrogen Values During Continuous Feed MMH Runs

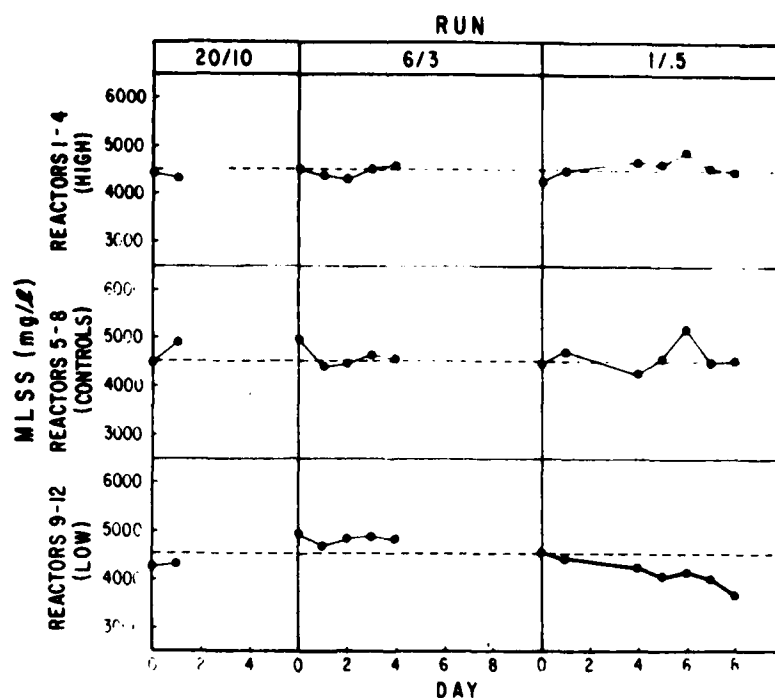


Figure 36. Mean MLSS During Continuous Feed MMH Runs (Mean of 4 Replicates)

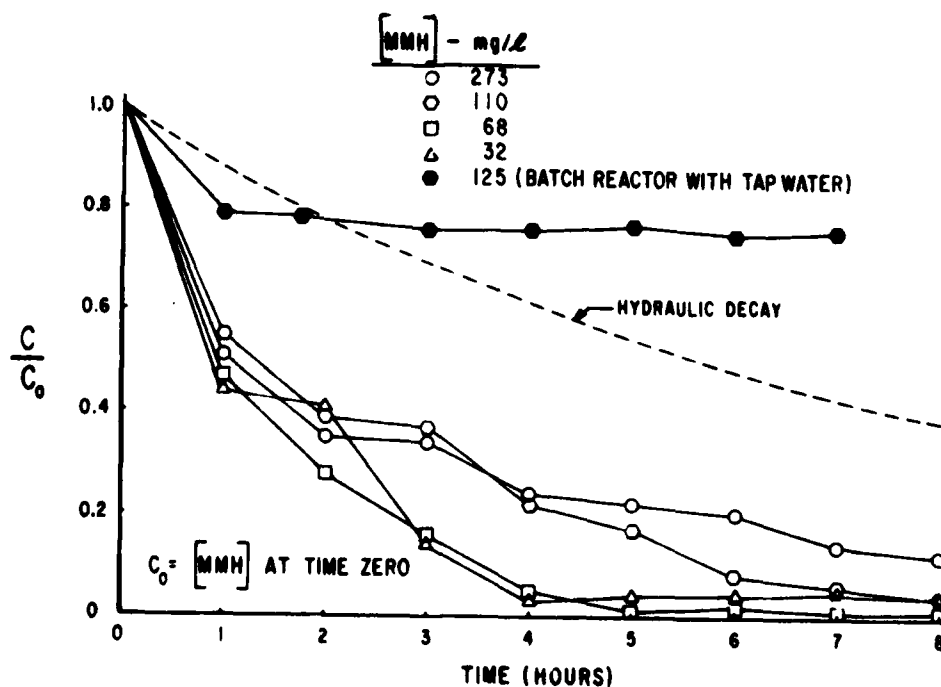


Figure 37. MMH Degradation During MMH Slug Feed Experiments (Mean of Duplicates)

2. SLUG FEED STUDIES

a. MMH Degradation: Figure 37 clearly shows that MMH was degraded during the slug feed experiments. Using Equation (25) the bacterial decay constants in Table 19 were derived. Figure 38 is a plot of the calculated half life ($t_{1/2}$) for MMH at each initial concentration.

TABLE 19. BACTERIAL DECAY CONSTANTS FOR MMH

Initial MMH (mg/l)	K(HR ⁻¹)	Correlation Coefficient
32	0.293	0.7643
68	0.505	0.9160
110	0.262	0.9811
273	0.103	0.9324

b. Acute Response: Influent parameters during the 8-hour acute response study are summarized in Table 20.

TABLE 20. SLUG LOAD RESPONSE INITIAL CONDITIONS (mg/ l)

MMH		Influent			MLSS	
Theoretical	Measured	COD	NH ₃ -N	ORG-N	Mean	σ
250	273	391	10.9	13.8	4690*	78
125	110	391	10.9	13.8	4670*	71
50	68	382	9.0	20.2	4770*	516
25	32	382	9.0	20.2	4510	78

*Wasted to 4500 mg/l prior to slug

(1) COD: Figure 39 shows that effluent COD is effected at all slug MMH concentrations except 32 mg/l. Figure 40 shows that the organic nitrogen response at 32 mg/l MMH is initially much greater than for the 110 mg/l and 68 mg/l doses. These data are not understood. It can be shown that at the one hour point, for the 273 mg/l slug, only 50 percent of the effluent COD was due to residual MMH in the reactor, indicating that cell lysis and/or metabolic inhibition had already occurred. This same data point in Figure 40 indicates that soluble organic nitrogen had been released in significant amounts at this time.

(2) Nitrification: The effect of MMH slug feeds on nitrification is shown in Figures 41 and 42. Even at 32 mg/l there is complete inhibition after 8 hours. The nitrate decay rate is somewhat faster than that predicted based solely on hydraulics. The scatter in the individual concentration plots also suggests that some interference which results in decreased NO₃-N is a function of MMH concentration. This interference could not be duplicated in distilled water solutions and is unexplained.

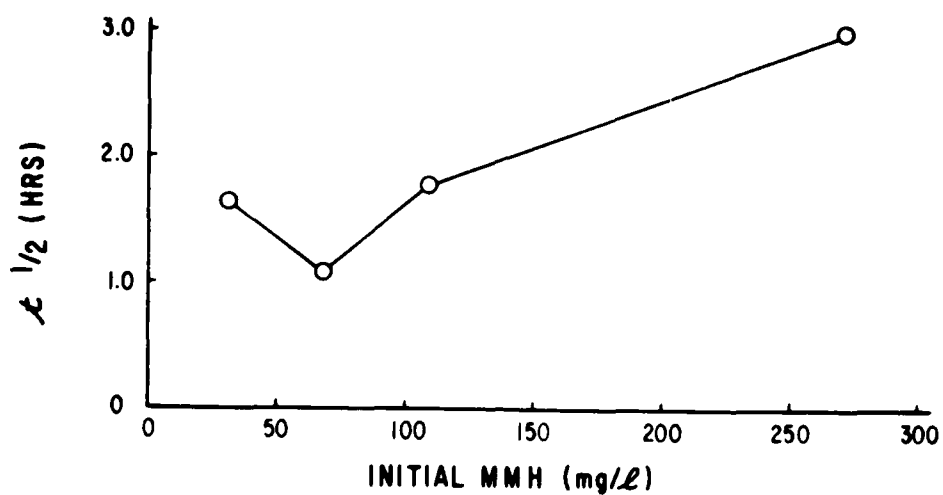


Figure 38. Calculated Halflife for MMH as a Function of Initial MMH Slug Concentration

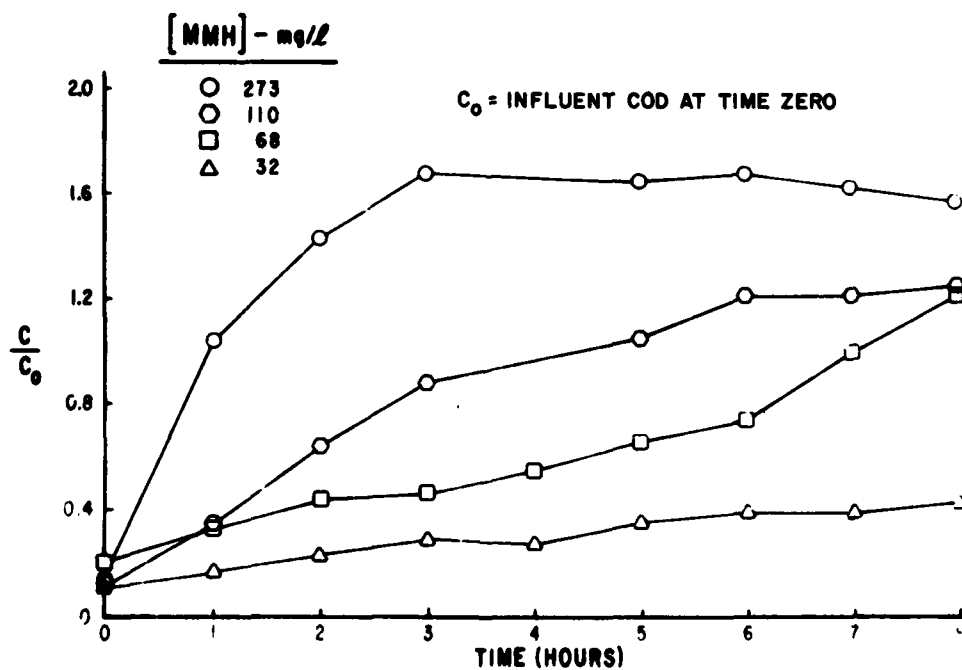


Figure 39. Actual Effluent COD Response to Slug MMH Loads as a Function of Time (Mean of Duplicates)

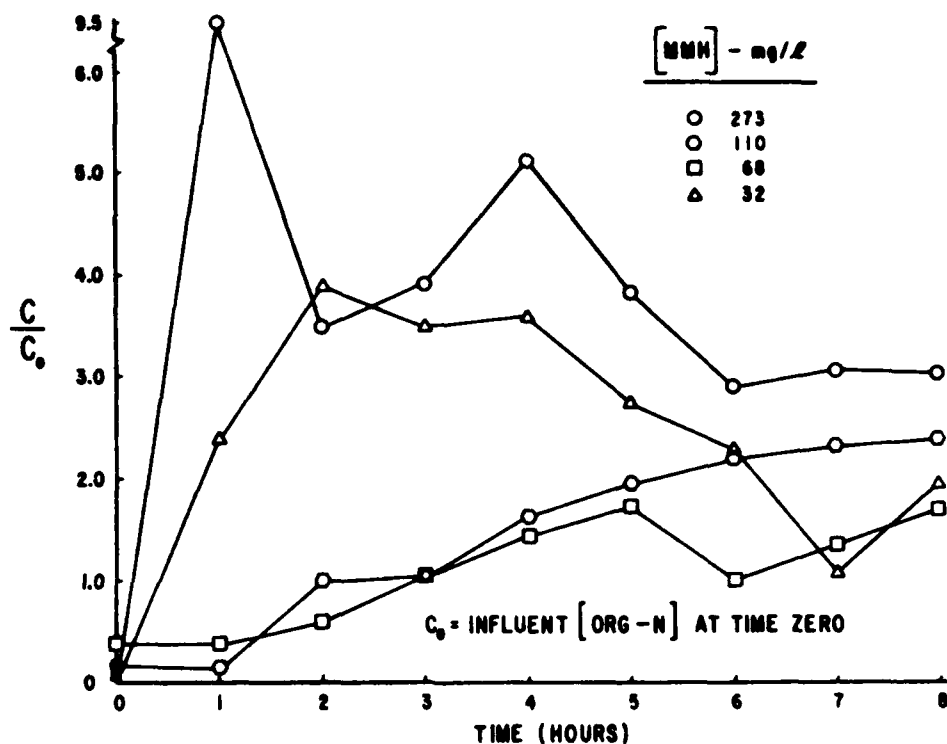


Figure 40. Acute Effluent Organic Nitrogen Response to Slug MMH Loads as a Function of Time (Mean of Duplicates)

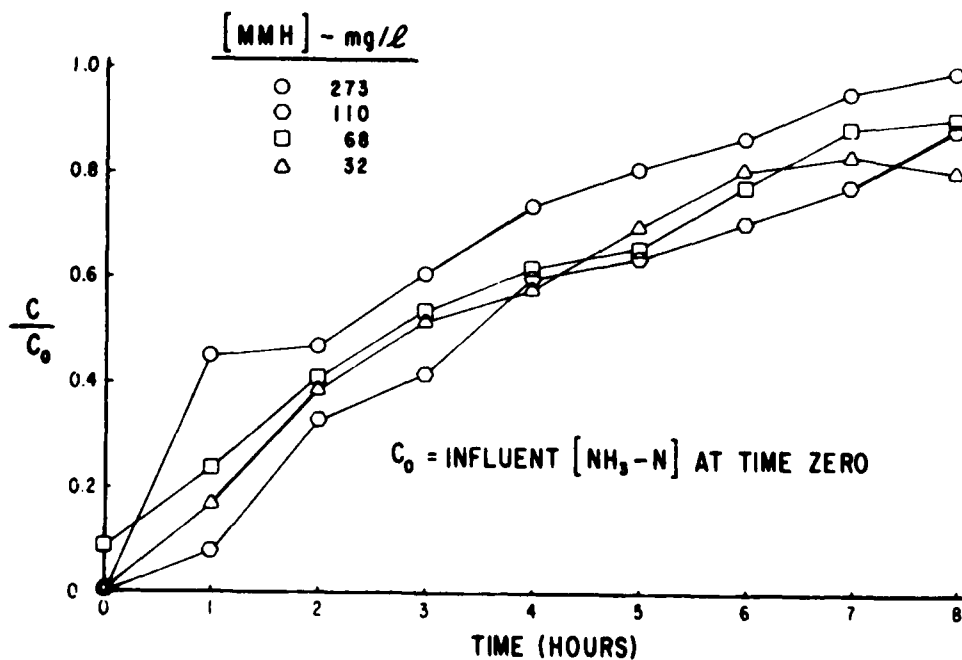


Figure 41. Acute Effluent Ammonia Nitrogen Response to Slug MMH Loads as a Function of Time (Mean of Duplicates)

c. Recovery: The influent and control effluent COD and nitrogen data monitored throughout the recovery period are outlined in Figure 43.

(1) COD: Figure 44 illustrates that there was significant recovery within 3 days even for the 273 mg/l slug.

(2) Nitrification: Recovery of the nitrifying bacteria is slower than for the heterotrophs. In Figure 45, it can be seen that 12 to 16 days were required to return effluent ammonia levels to their pre-exposure level. Figure 46 is a plot of effluent nitrate recovery for the MMH study. As no control data was available from days 6 and 8 on for the 68/32 mg/l and 273/110 mg/l slugs, respectively, a plot of actual effluent $\text{NO}_3\text{-N}$ versus time for this period has been presented as an inset. While this does not represent recovery as well as the comparison with control effluent $\text{NO}_3\text{-N}$ ($\text{C/C}_\star$), the rising trend in nitrite oxidation is dramatic enough to make inferences about nitrate recovery. The data suggest that approximately 16 days are required for complete recovery. The lag observed in establishing a *Nitrobacter* sp population during the HZ study appears to have been reproduced in the MMH study although overall MMH recovery periods were longer by 4 to 6 days.

(3) Suspended Solids: The MLSS response to MMH as shown in Figure 47 was not as drastic as for comparable HZ concentrations even though the COD and organic nitrogen effects were similar in magnitude. MLSS values never dropped below 3200 mg/l, returning to normal levels in all cases after 4 days. The decline in MLSS for the 68 mg/l and 32 mg/l studies after day 7 is attributed to bulking in 3 out of the 4 reactors (10, 11, 12) and not MMH. The reason for the bulking in these specific reactors is not known but is assumed to be related to hydraulic anomalies as this problem was noted from time to time in different reactors (including controls) but generally not in all 12 at once.

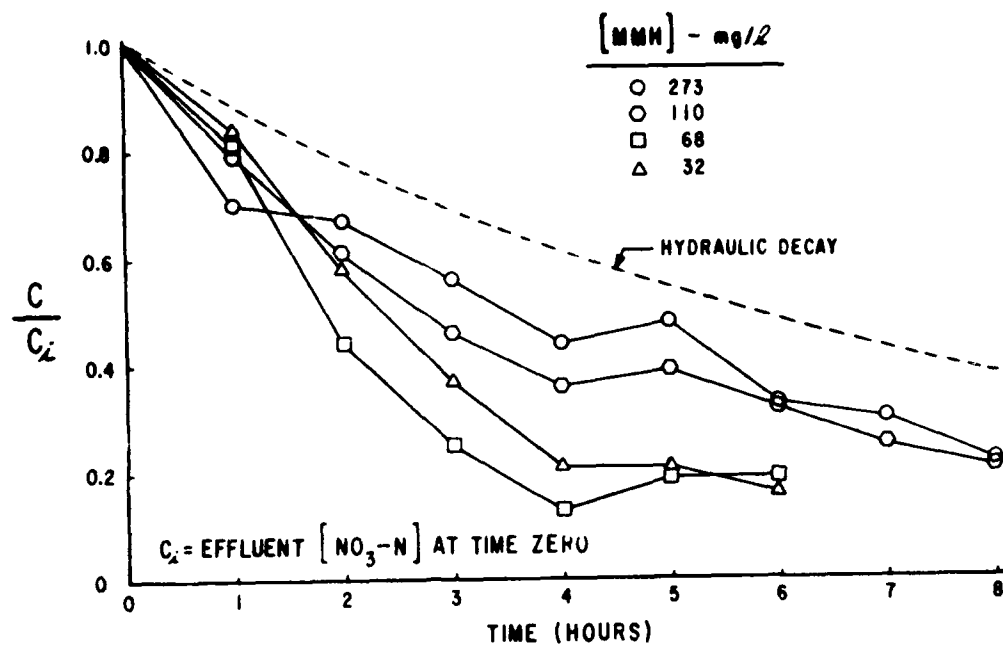


Figure 42. Acute Effluent Nitrate Nitrogen Response to Slug MMH Loads as a Function of Time (Mean of Duplicates)

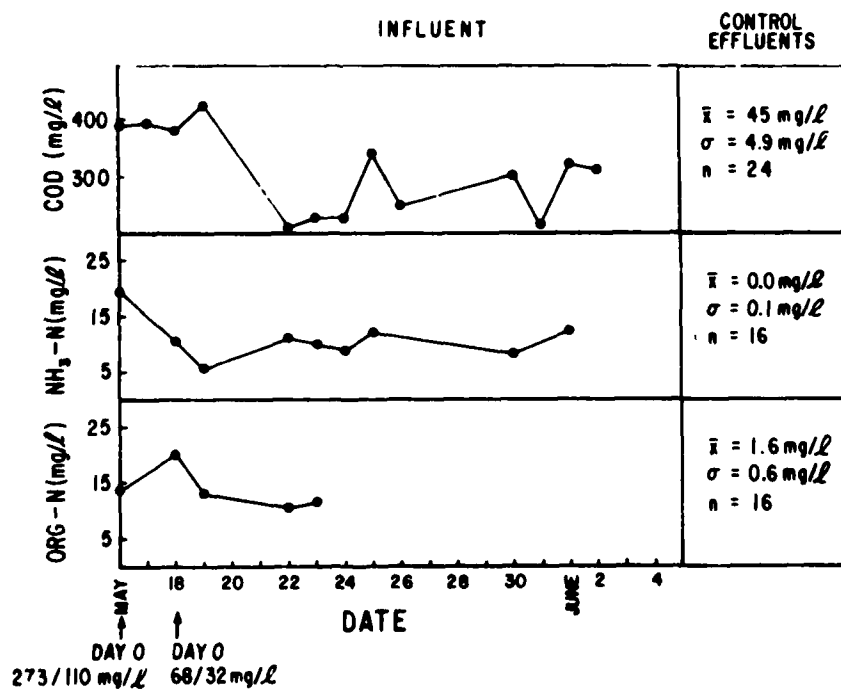


Figure 43. Influent and Control Effluent COD and Nitrogen Data During the Slug MMH Recovery Periods

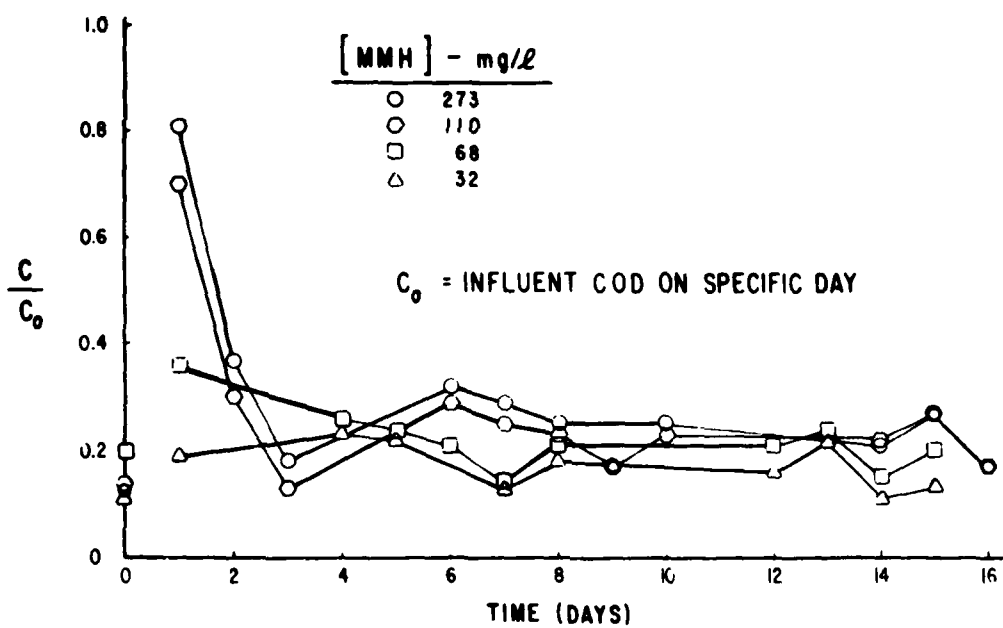


Figure 44. Effluent COD Recovery Following Slug MMH Loads (Mean of Duplicates)

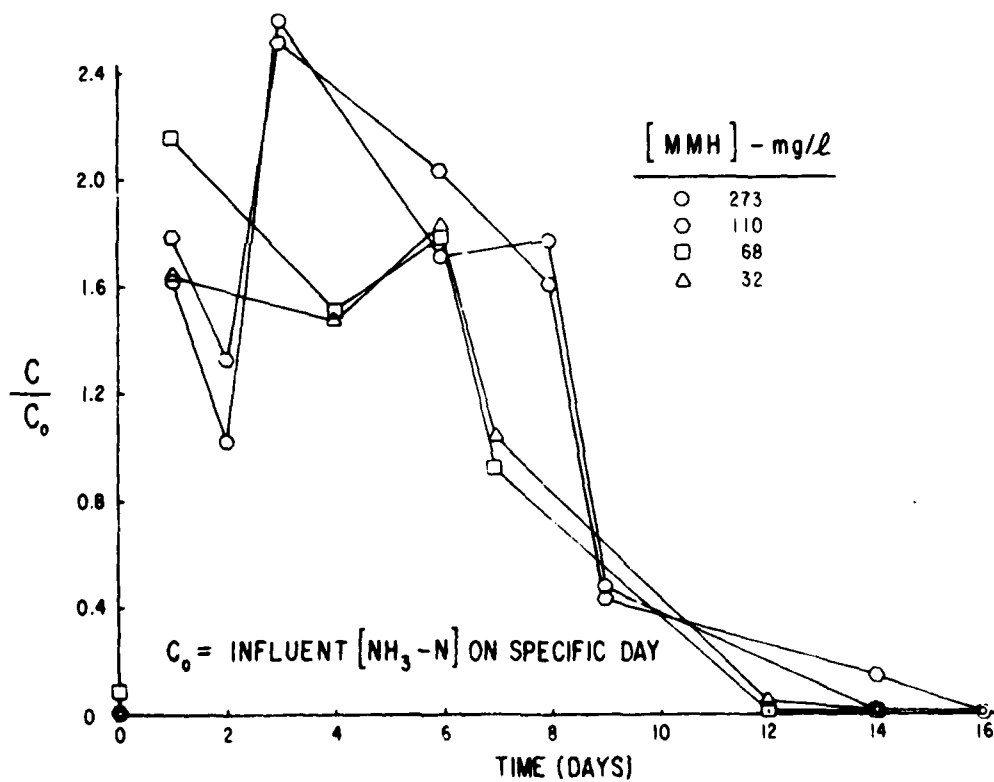


Figure 45. Effluent Ammonia Nitrogen Recovery Following Slug MMH Loads (Mean of Duplicates)

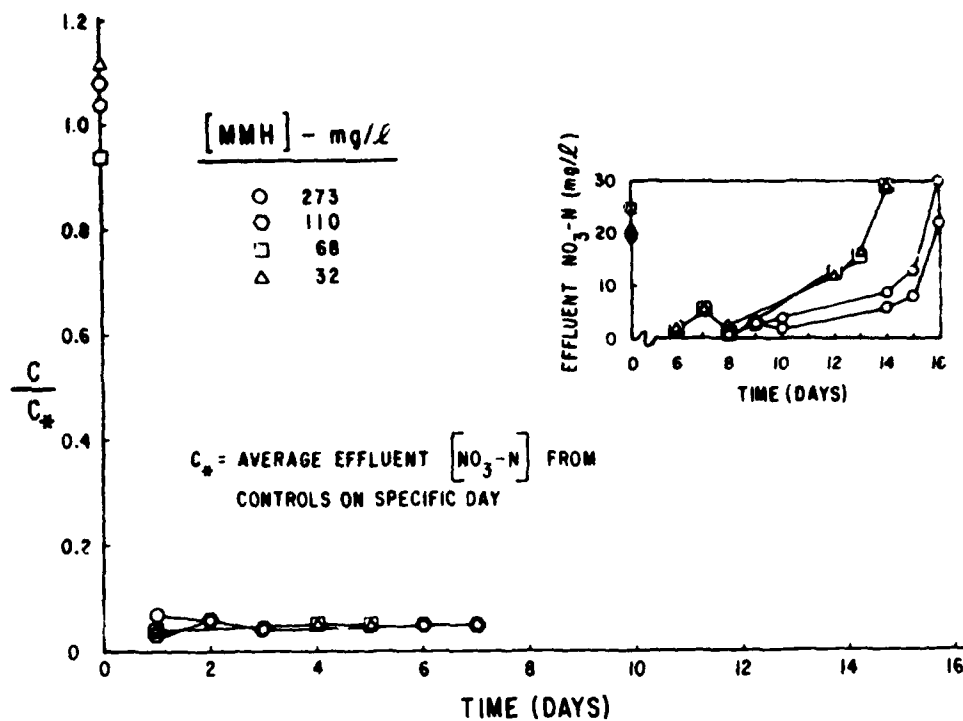


Figure 46. Effluent Nitrate Nitrogen Recovery Following Slug MMH Loads (Mean of Duplicates)

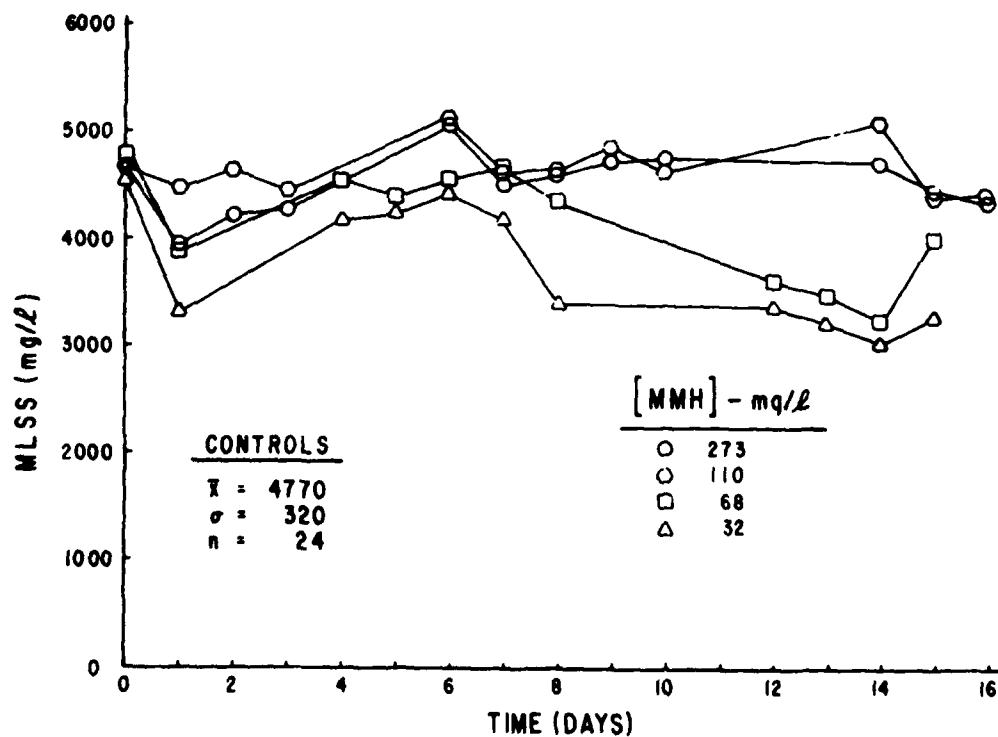


Figure 47. MLSS Response to Slug MMH Loads as a Function of Time (Mean of Duplicates)

SECTION VI

RESULTS - UNSYMMETRICAL DIETHYLHYDRAZINE (UDMH)

Unsymmetrical dimethylhydrazine is a colorless liquid with a density of 0.786 gm/ml at 20°C. It is very soluble in water. Duplicate analyses of a 125 mg/l stock solution resulted in 1.89 mg COD/mg UDMH, 0.15 mg $\text{NH}_3\text{-N}$ /mg UDMH, and no detectable organic nitrogen.

1. CONTINUOUS FEED STUDIES

a. UDMH Degradation: The influent UDMH data are shown in Figure 48 and indicate some variation about the target concentrations. Each point represents the average of 4 reactors. The influent and effluent data have been summarized in Table 21.

While degradation occurs at all concentrations investigated, it is interesting to note that the percent reductions are significantly lower than for neat hydrazine at comparable concentrations. This will be addressed in more detail in the next section.

b. COD: Table 22 summarizes the influent and control reactor effluent data for the continuous feed studies.

Figure 49 shows the daily influent data as well as the mean effluent CODs from the four control reactors. Remaining COD in the clarifier effluent as a function of influent UDMH concentration and time is shown in Figure 50. When compared with the control data, it would seem that the no effect UDMH concentration is approximately 5 mg/l. The response at 8.0 and 18.9 mg/l is essentially the same but less than that documented for HZ and MMH by a factor of two for comparable concentrations. It would also appear as if some degree of acclimation occurred as the effluent CODs exhibited a steady downward trend after day 2. This information is extremely interesting in light of the UDMH degradation data presented later. Although the toxic effects appear to be significantly less than that observed for HZ and MMH, UDMH is degraded at one-half the rate. This would suggest that UDMH was serving as an alternate carbon source to which the heterotrophic organisms may acclimate after 4 to 5 days. The HZ molecule is similar to that of ammonia, NH_3 , and it is theorized that HZ is taken into the cell by means of a like mechanism exhibiting its toxic effect once assimilated. This would account for the high degradation rate for HZ with high concurrent toxicity. The organic nitrogen data in Figure 51 also supports this argument as heterotrophic cell lysis, represented by effluent organic-N, was minimal.

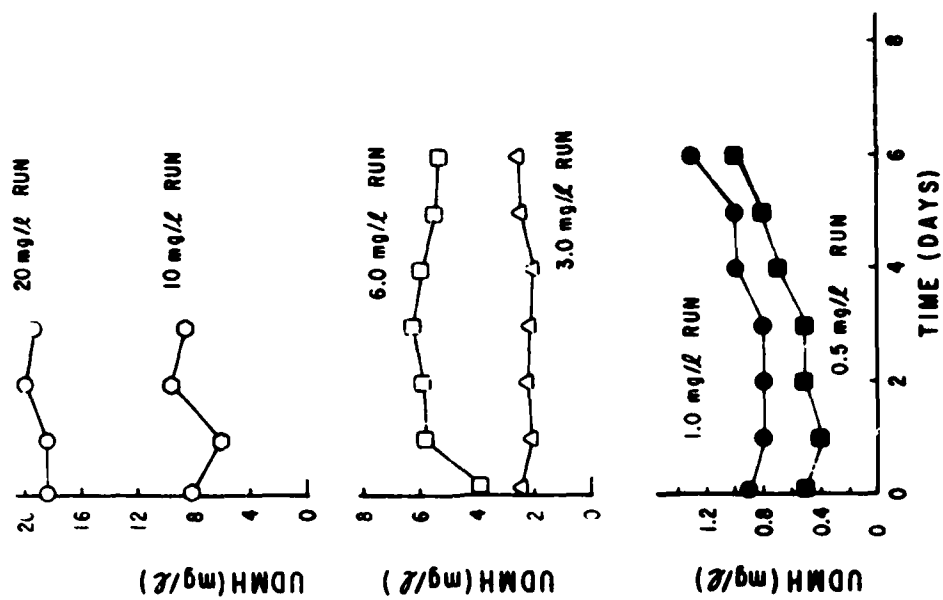


Figure 49. Influent COD and Mean Control Effluent COD Values During Continuous Feed UDMH Runs

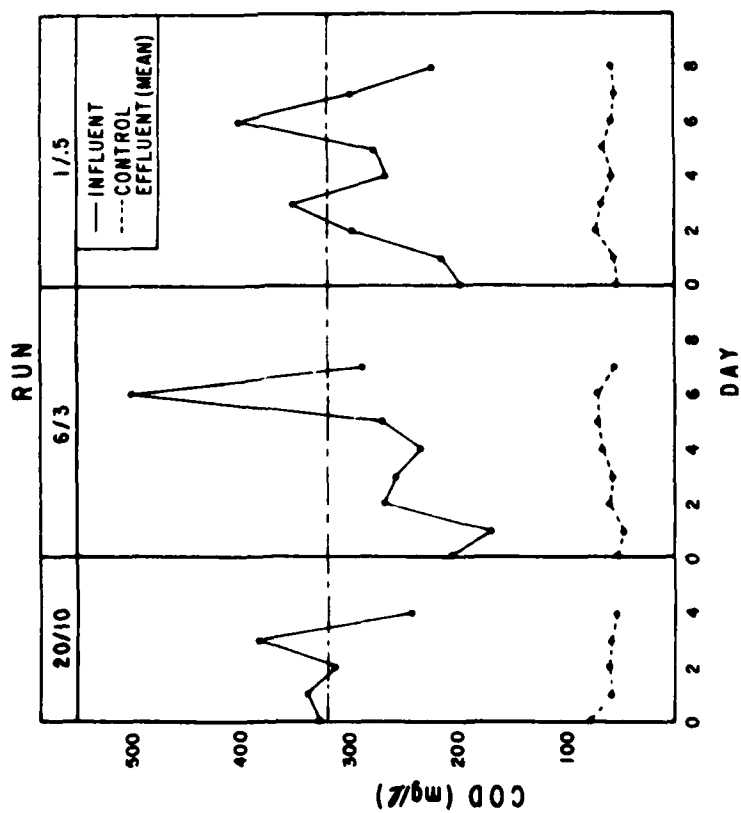


Figure 48. Continuous Feed Influent UDMH Concentrations

$[UDMH] - \text{mg/L}$

- 18.9
- 8.0
- 5.5
- △ 2.2
- 0.9
- 0.6

CONTROLS
 $\bar{x} = 61 \text{ mg/L}$
 $\sigma = 11 \text{ mg/L}$
 $n = 82$

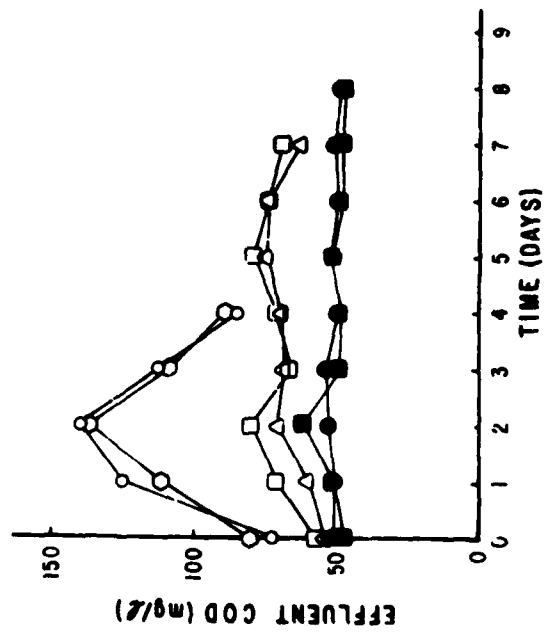


Figure 50. Effluent COD as a Function of Time and Continuous Feed UDMH Concentration (Mean of 4 Replicates)

$[UDMH] - \text{mg/L}$

- 18.9
- 8.0
- 5.5
- △ 2.2
- 0.9
- 0.6

CONTROLS
 $\bar{x} = 3.6 \text{ mg/L}$
 $\sigma = 0.9 \text{ mg/L}$
 $n = 80$

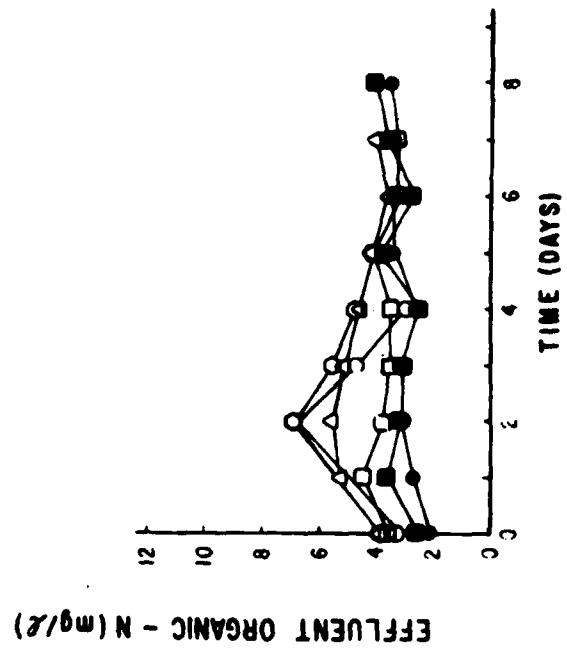


Figure 51. Effluent Organic Nitrogen as a Function of Time and Continuous Feed UDMH Concentration (Mean of 4 Replicates)

TABLE 21. UDMH CONCENTRATIONS DURING CONTINUOUS FEED STUDIES (mg/l)

Theoretical	Study Designation	Influent		Effluent		Reduction Percent
		Mean	σ	Mean	σ	
20	20/10	18.9	0.7	12.6	1.1	33
10	20/10	8.0	1.4	4.5	0.6	44
6.0	6/3	5.5	0.8	2.9	0.5	47
3.0	6/3	2.2	0.2	0.8	0.4	64
1.0	1/0.5	0.9	0.2	0.15	0.07	83
0.5	1/0.5	0.6	0.2	0.04	0.08	93

TABLE 22. INFLUENT AND CONTROL EFFLUENT COD SUMMARY

Study	Study Length (Days)	Influent COD (mg/l)		Control Effluent COD (mg/l)		Control Percent Removal
		Mean	σ	Mean	σ	
20/10	4	320	51	63	15	80
6/3	7	276	99	60	9	78
1/0.5	8	284	64	61	11	79
Overall	-	278*	87	61**	11	78

* n = 22

** n = 82

c. Nitrification: The influent and control effluent nitrogen data collected over the continuous feed UDMH studies are presented in Table 24.

The daily influent and control effluent parameters have been graphically displayed in Figures 52 and 54 for comparison with the daily effluent qualities in those reactors receiving UDMH. From Figure 53, it is apparent that concentrations above approximately 1 mg/l cause inhibition of nitrification. The nitrate data presented in Figure 55 agree well with the ammonia data. The drop in effluent $\text{NO}_3\text{-N}$ on day 1 was observed in the control reactors (Figure 54) as well as for the 0.9 and 0.6 mg/l UDMH reactors. Unlike the heterotrophs, there appears to be no autotrophic acclimation to UDMH.

d. Suspended Solids: The suspended solids data for the control reactors are outlined in Table 23. Figure 56 summarizes all MLSS data.

TABLE 23. CONTROL MLSS DATA (mg/l)

<u>Study</u>	<u>Mean</u>	<u>σ</u>	<u>n</u>
20/10	4710	360	15
6/3	4660	530	32
1/0.5	4630	460	36
Overall	4660	470	83

No difficulty was experienced in holding MLSS concentrations at the desired 4500 mg/l. As noted earlier cell lysis, and hence effluent solids, was minimal during the UDMH studies.

TABLE 24. INFLUENT AND CONTROL EFFLUENT NITROGEN SUMMARY (mg/L)

Study	Study Length (Days)	Influent			Control Effluent			Nitrification* Percent in Controls
		NH ₃ -N Mean	NH ₃ -N σ	TKN Mean	NH ₃ -N Mean	NO ₃ -N Mean	σ	
20/10	4	14.7	2.2	27.6	0.3	22	1.0	80
6/3	7	5.7	2.1	20.9	0.1	15	2.2	72
1/0.5	8	8.7	2.7	23.0	0.3	16	4.7	70
Overall	-	8.7	4.0	23.1	0.7	17	4.2	74

* Based on TKN conversion to NO₃-N

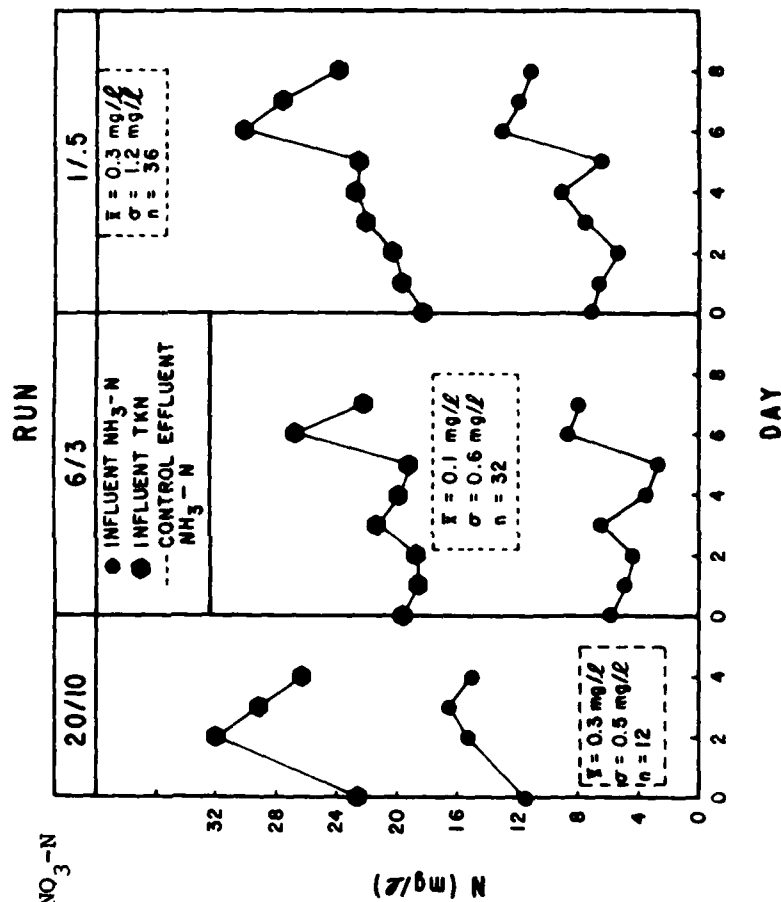


Figure 52. Influent and Control Effluent Nitrogen Data During Continuous Feed UDMH Runs

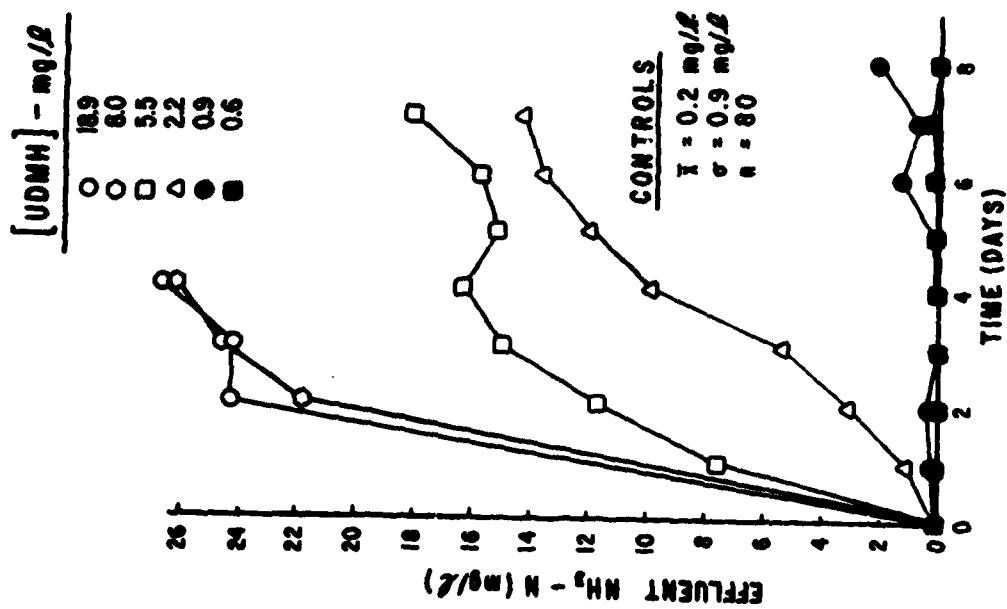


Figure 53. Effluent Ammonia Nitrogen as a Function of Time and Continuous Feed UDMH Concentration (Mean of 4 Replicates).

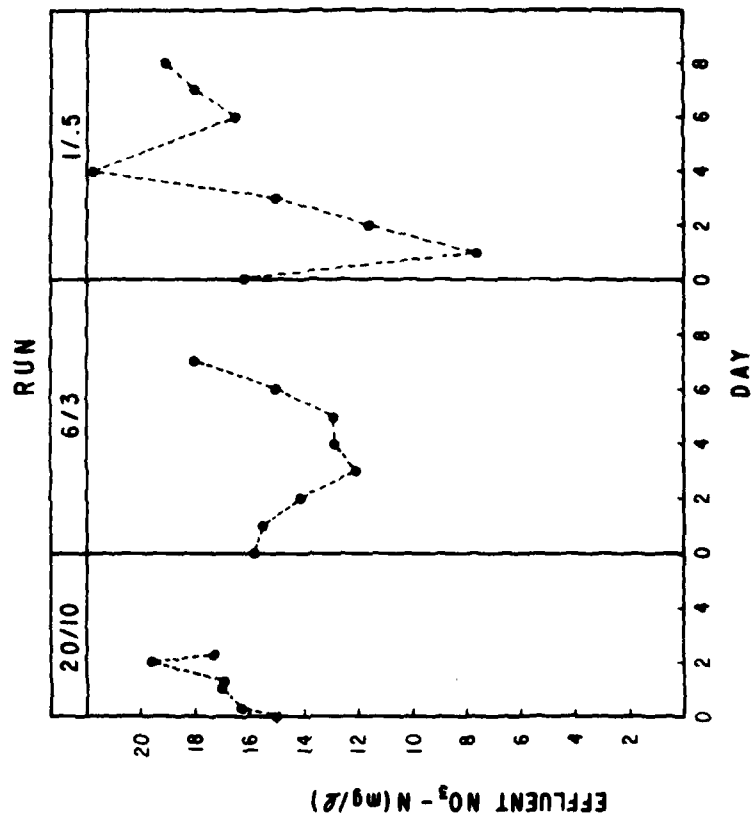


Figure 54. Mean Control Effluent Nitrate Nitrogen Values During Continuous Feed UDMH Runs.

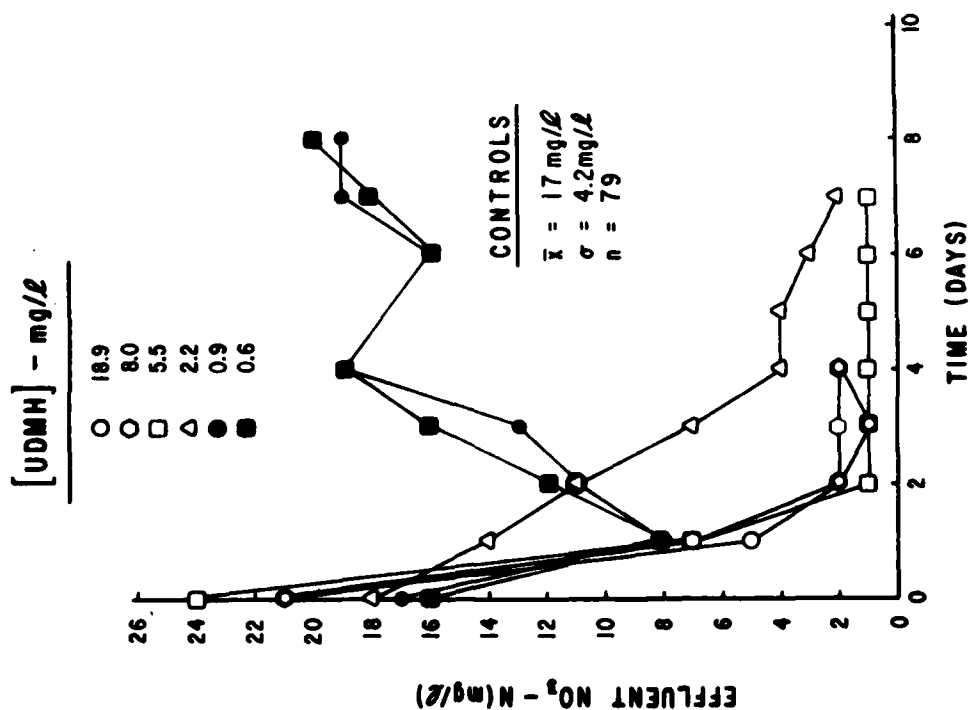


Figure 55. Effluent Nitrate Nitrogen as a Function of Time and Continuous Feed UDMH Concentration (Mean of 4 Replicates)

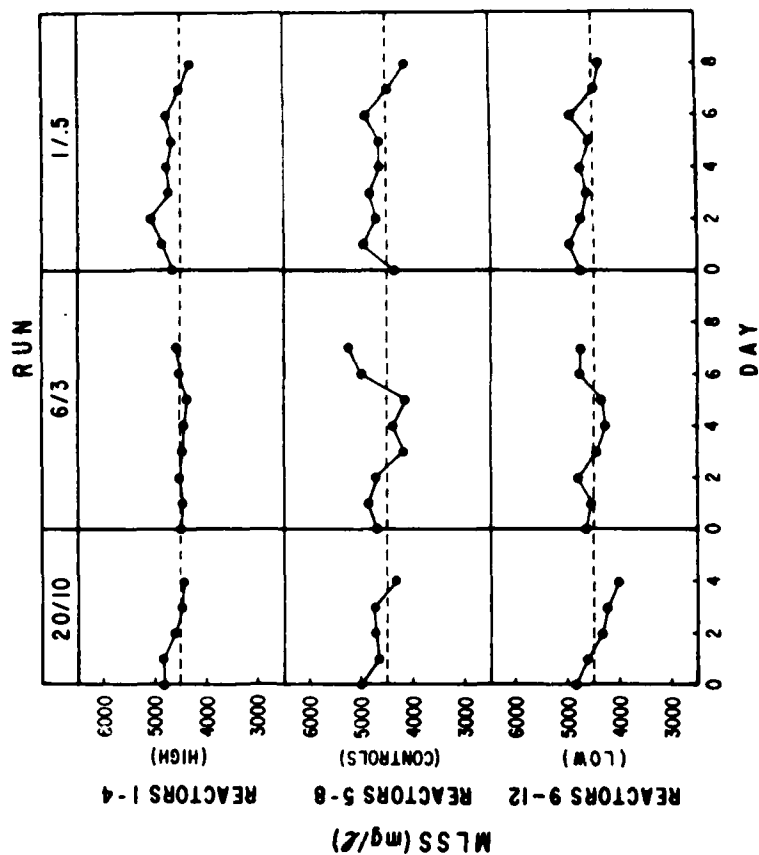


Figure 56. Mean MLSS During Continuous Feed UDMH Runs (Mean of 4 Replicates)

2. SLUG FEED STUDIES

a. UDMH Degradation: Figure 57 clearly shows that UDMH was degraded during the slug feed experiments but at a lower rate than for HZ or MMH. The bacterial decay constants and half lives were computed as described earlier and are shown in Table 25 and Figure 58. These data agree well with the degradation theory proposed for the continuous feed results.

TABLE 25. BACTERIAL DECAY CONSTANTS FOR UDMH

<u>Initial UDMH (mg/l)</u>	<u>K(HR⁻¹)</u>	<u>Correlation Coefficient</u>
255	0.075	0.9754
128	0.053	0.9858
74	0.1192	0.9592
22	0.095	0.9827

b. Acute Response: Influent parameters during the 8-hour acute response study are summarized in Table 26 below.

TABLE 26. SLUG LOAD RESPONSE INITIAL CONDITIONS (mg/l)

<u>UDMH</u>		<u>Influent</u>			<u>MLSS</u>	
<u>Theoretical</u>	<u>Measured</u>	<u>COD</u>	<u>NH₃-N</u>	<u>ORG-N</u>	<u>Mean*</u>	<u>σ</u>
250	255	226	10.0	11.6	4730	230
125	128	226	10.0	11.6	4800	40
50	74	336	12.2	18.3	5120	300
25	22	314	11.6	21.5	5170	400

*Wasted to 4500 mg/l prior to slug

(1) COD: Figure 59 shows that effluent COD is not effected at slug doses below 74 mg/l. At the two hour point approximately 84 percent of the effluent COD was due to residual UDMH in the reactor. The remainder, 57 mg/l, representing no decline in substrate degradation. The organic nitrogen data in Figure 60 correlates well as it shows essentially no system upset even at 255 mg/l UDMH. However, at 3 hours some 90 mg/l of the effluent COD cannot be attributed to UDMH. Effluent organic nitrogen concentrations rose only slightly at this time, the implication being that the heterotrophic effects of slug UDMH doses in the range investigated are more related to inhibition than to toxicity and that these effects do not become manifest until approximately 3 hours post exposure. Concentrations below 74 mg/l UDMH produced no adverse effect.

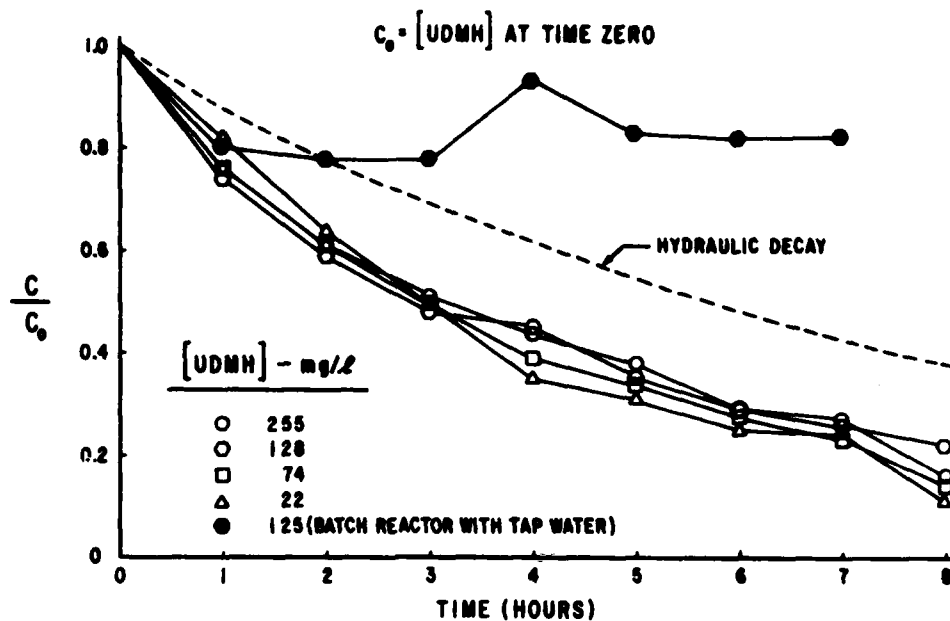


Figure 57. UDMH Degradation During MMH Slug Feed Experiments (Mean of Duplicates)

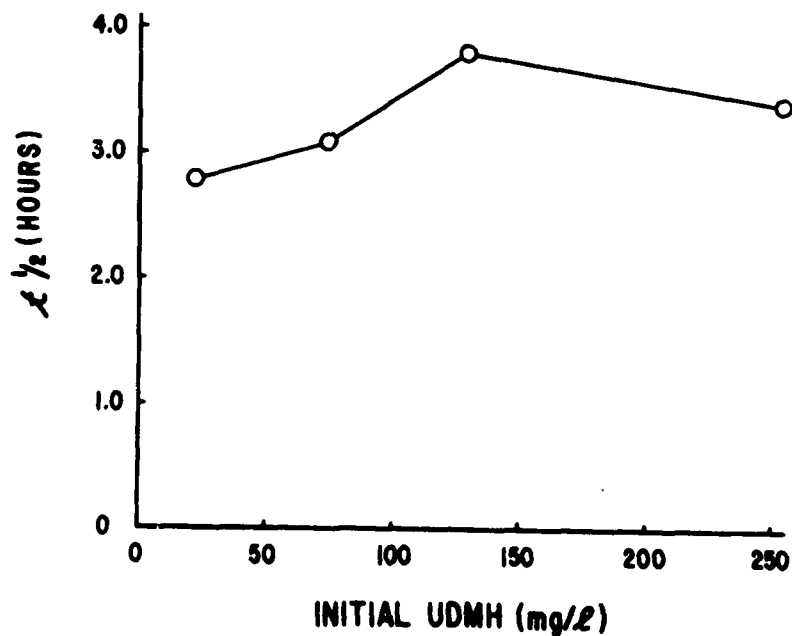


Figure 58. Calculated Halflife for MMH as a Function of Initial UDMH Slug Concentration

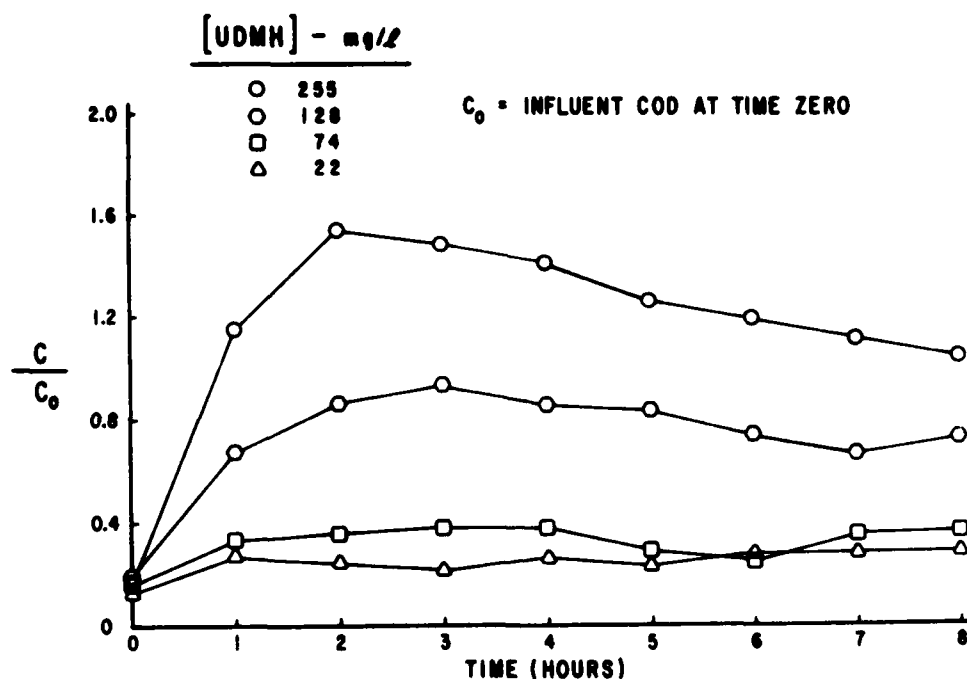


Figure 59. Acute Effluent COD Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)

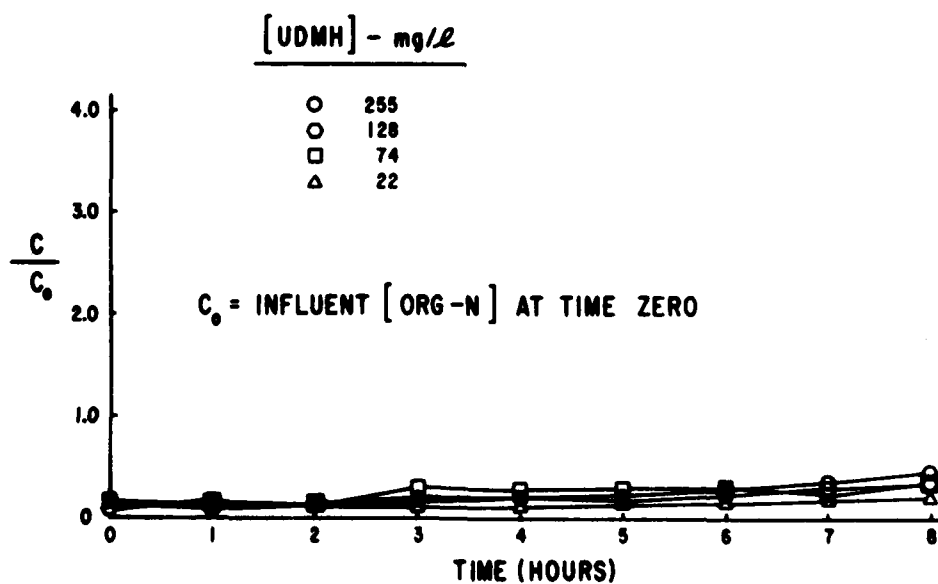


Figure 60. Acute Effluent Organic Nitrogen Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)

(2) Nitrification: The effect of UDMH slug feeds on nitrification is shown in Figures 61 and 62. Even at 22 mg/l, inhibition is complete after 8 hours. At 255 mg/l, it can be shown that inhibition is complete at 2 hours post exposure. The nitrate decay rate is essentially equal to that expected for a completely mixed reactor with no influent nitrate, indicating that at all concentrations the oxidation of ammonia to nitrate has ceased. Note that all of the plots are slightly above the predicted decay curve, an observation which suggests that inhibition was not instantaneous. If time zero is taken at 1 hour, the hydraulic decay and 255 mg/l curves are almost identical.

c. Recovery: The influent and control effluent COD and nitrogen data monitored throughout the recovery period are outlined in Figure 63.

(1) COD: Figure 64 indicates significant recovery after 48 hours for both the 255 mg/l and 128 mg/l slug feeds.

(2) Nitrification: Recovery of the nitrifying bacteria was again slower than for the heterotrophs. Figure 65 shows that 8 to 9 days were required to return to the pre-exposure ammonia oxidation levels. Effluent nitrate concentrations (Figure 66) are displayed as the slug reactor mean over the mean control value for all days except 0 to 9 during the 252 mg/l and 128 mg/l studies. As no control data was available, a plot of actual effluent $\text{NO}_3\text{-N}$ versus time has been presented as an inset. The nitrate recovery times match the ammonia recovery times very closely. This again implies that the autotrophic bacteria were inhibited rather than eliminated by the UDMH. No explanation can be offered with respect to the C/C_0 values in excess of unity for $\text{NH}_3\text{-N}$. Note that this same phenomena occurred during the MMH slug studies.

(3) Suspended Solids: The MLSS response to UDMH was minimal, as shown in Figure 67. The low value on day 7 for the 255 mg/l run was due to a low MLSS determination (2500 mg/l). This anomaly was attributed to unrepresentative sampling noting that the MLSS was 4470 mg/l the following day.

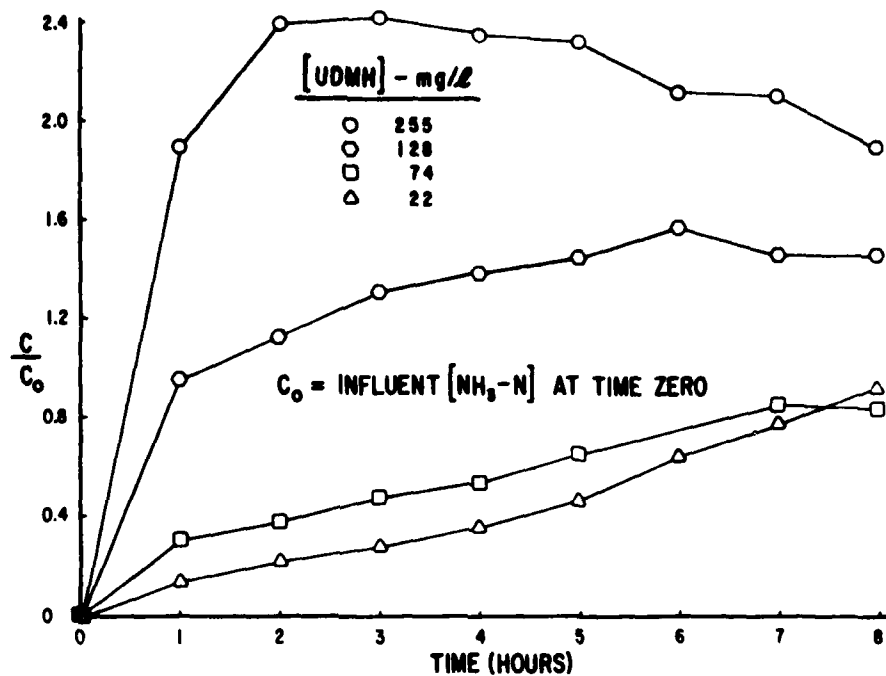


Figure 61. Acute Effluent Ammonia Nitrogen Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)

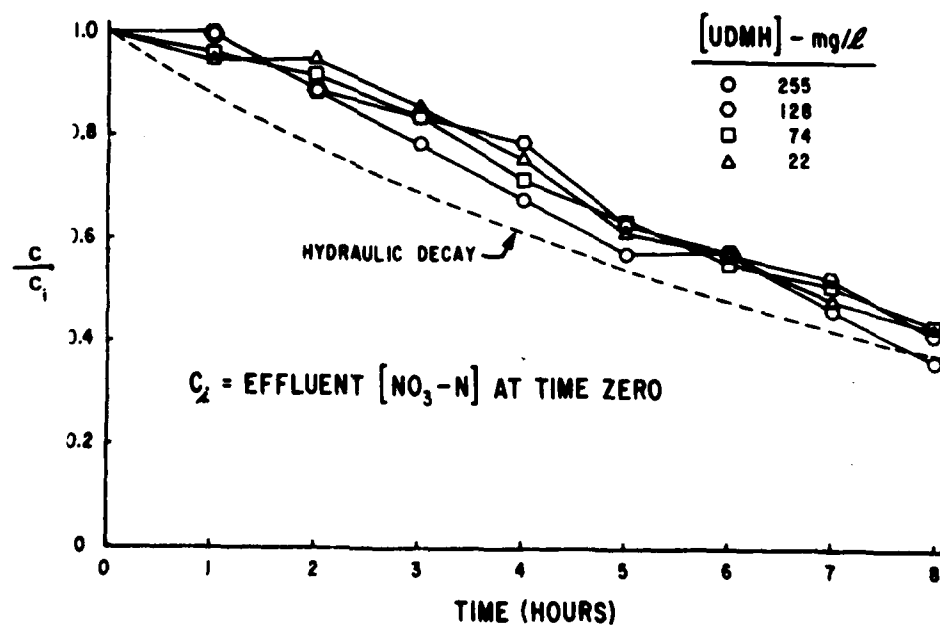


Figure 62. Acute Effluent Nitrate Nitrogen Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)

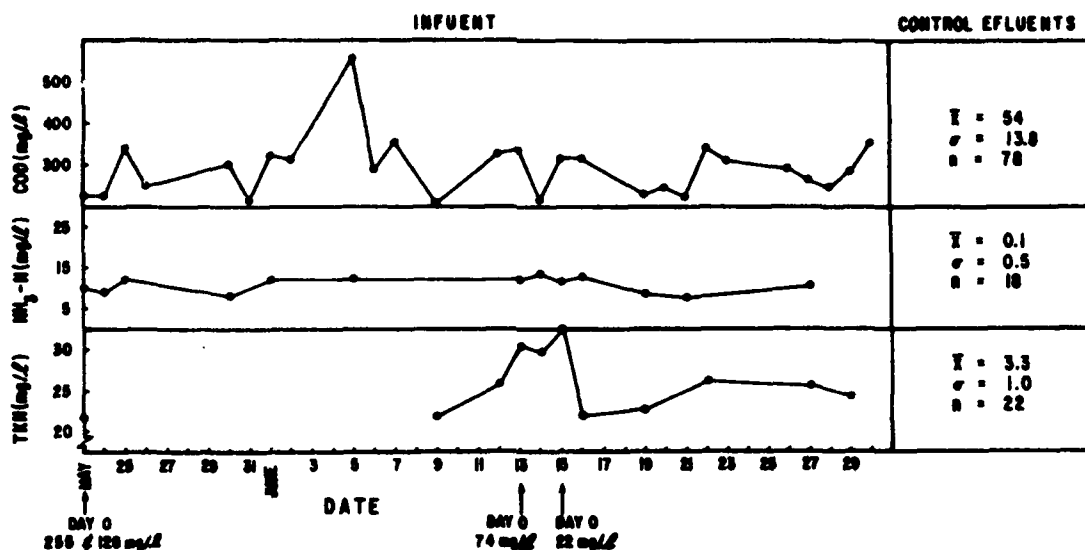


Figure 63. Influent and Control Effluent COD and Nitrogen Data During the Slug UDMH Recovery Periods

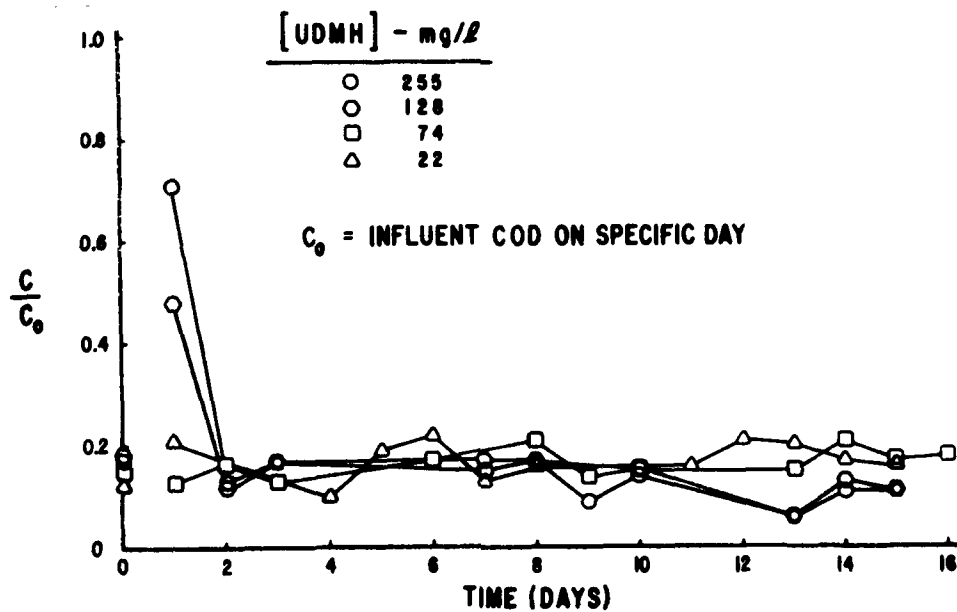


Figure 64. Effluent COD Recovery Following Slug UDMH Loads (Mean of Duplicates)

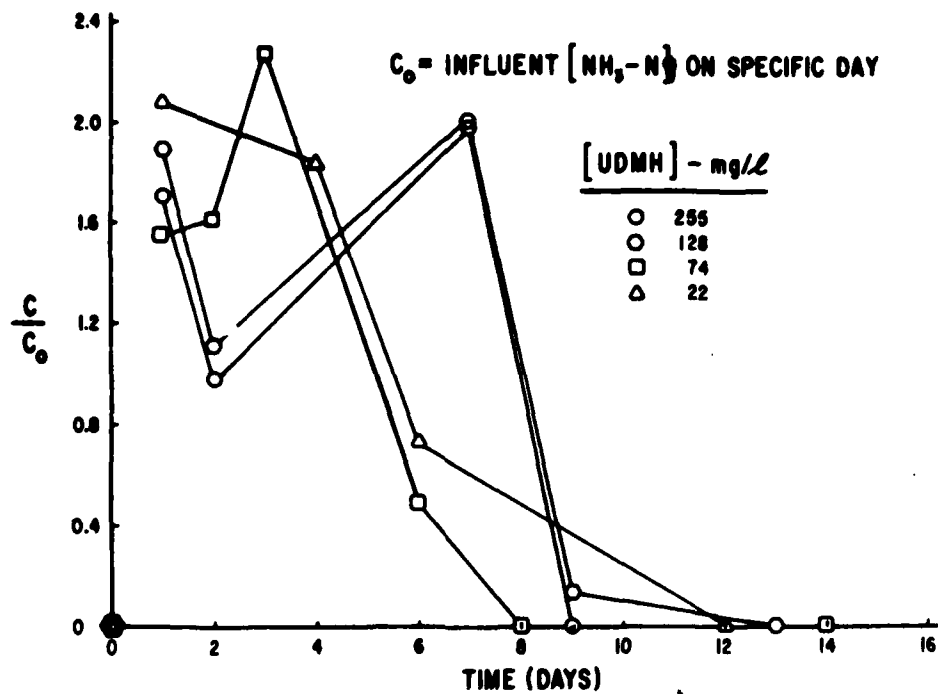


Figure 65. Effluent Ammonia Nitrogen Recovery Following Slug UDMH Loads (Mean of Duplicates).

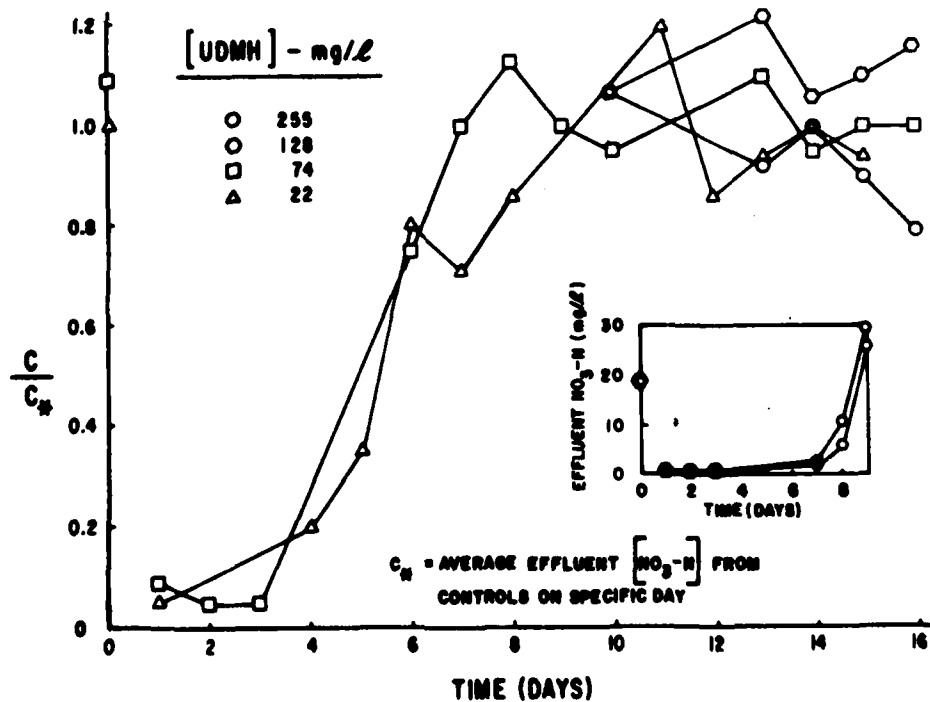


Figure 66. Effluent Nitrate Nitrogen Recovery Following Slug UDMH Loads (Mean of Duplicates)

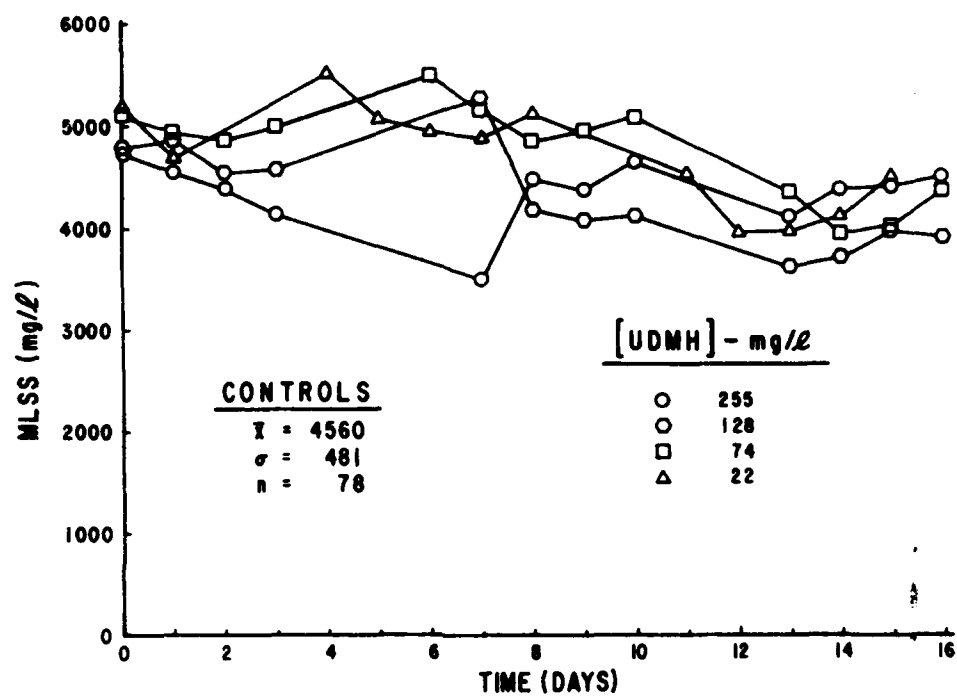


Figure 67. MLSS Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)

SECTION VII

SUMMARY

1. CONTINUOUS FEED STUDIES

It is apparent from the continuous feed studies that the three hydrazines could cause significant deterioration of an activated sludge plant if the concentration in the influent exceeded a few mg/l. For a reactor with hydraulic detention time (θ) of 9 hours and solids recycle ($\theta^C \sim 7$ days), the efficiency of organic carbon removal as measured by COD is seriously degraded when the influent concentration of hydrazine exceeds 10 mg/l. For UDMH and MMH, total failure is caused by concentrations of approximately 8 mg/l and 5 mg/l, respectively. In contrast to hydrazine and MMH, it appears that after 2 days the heterotrophic organisms begin to acclimate even to the ~ 20 mg/l UDMH feed concentration. Unfortunately, this test was terminated after 4 days so this conclusion should be made cautiously. Interpolating for the continuous feed studies reported here, the no effect level would be approximately 2 mg/l for hydrazine and 1 mg/l for MMH and UDMH.

Even if sufficient control could be maintained to insure dilution to these levels, complete degradation of the influent hydrazine would not be achieved. Only at the lowest hydrazine concentrations tested (< 1 mg/l) was the effluent feed concentration below detection limits. For MMH and UDMH, the maximum removal efficiency observed was 89 percent and 96 percent, respectively. Studies on the effect of these fuels on algae have established no effect concentrations of less than 0.001 mg/l for MMH and 1.56 mg/l for UDMH (Reference 24). To maintain these low effluent concentrations would require restricting influent concentrations to below 1 mg/l for the three fuels.

The influence of the hydrazines on nitrogen speciation is more pronounced than that found for carbon oxidation. Other nitrogen compounds shown to be powerful selective inhibitors of nitrification include thiourea, thioacetamide dithio-oxamide and cyanide. Inhibition of nitrification occurred at concentrations above 0.5 mg/l for MMH and 1 mg/l for the other fuels. These concentrations are significantly lower than the 10^{-3} M (32 mg/l) concentrations found by Yoshida and Alexander Reference 17) to inhibit Nitrosomonas. Indeed, they stated that ammonia oxidation still proceeded in the presence of 10^{-2} M (320 mg/l) hydrazine. This was indirectly inferred from data on the formation of hydroxylamine which could result from some other mechanism rather than ammonia oxidation. This selective effect could not be observed for hydrazine and MMH in the studies reported here. Both organisms appeared to be equally effected by comparison of the ammonia oxidation and nitrate formation data in Figure 13 and 15 and Figures 33 and 35. From Figures 53 and 55 it is possible to infer a less immediate effect on ammonia oxidation than nitrate formation; however, in the operation of an activated sludge plant, such information is of minor importance. The results shown in Figure 13 illustrate that in this study ammonia oxidation ceased or was severely reduced at hydrazine concentrations greater than 1 mg/l as reflected in increasing ammonia and decreasing nitrate concentrations in the reactor effluents. Maintaining a stable organic nitrogen concentration

proved difficult and so quantitative evaluation of the effect of the fuels on effluent ORG-N is difficult to ascertain. Qualitatively, removal of organic nitrogen closely parallels removal of COD. This is particularly evident in the UDMH studies which exhibit a much lesser disruption even at 20 mg/l, although from data on degradation of the three fuels (Tables 9, 15, and 21) the reduced toxicity cannot be attributed to lower equilibrium UDMH concentrations in the reactors. UDMH displayed the highest stability to degradation with an average reactor concentration of 12.6 mg/l compared to 6.1 mg/l for hydrazine and 3.7 mg/l for MMH for a nominal feed concentration of 20 mg/l. The percentage fuel degradation in the reactors can be estimated from the decay constants determined in the spill studies. Using a mass balance on the completely mixed flow reactor (CMFR) and assuming steady state conditions, the ratio of effluent concentrations to influent concentration can be calculated:

$$\frac{C}{C_0} = \frac{1}{1 + K\theta} \quad (26)$$

The percentage removals were calculated using a hydraulic detention time (θ) of 6.67 hours and the decay constants for the fuels at the lowest slug concentration, nominally 25 mg/l. The steady state percentage reductions (77 percent for hydrazine, 67 percent for MMH, and 39 percent for UDMH) compare favorably with the measured levels except for MMH. The low degradation of UDMH and the corresponding reduced toxicity implies that UDMH is taken up less by the heterotrophs and autotrophs than both hydrazine and MMH.

The impact on nitrification again reflects the correlation between percentage degradation of the fuel and toxicity. The reason for MMH displaying a more toxic effect to autotrophs than hydrazine is not apparent. This is the opposite trend shown in algae and fish batch studies. These studies, however, are biased by the different degradation rates of the fuels (References 23 and 24).

Mixed liquor suspended solids (MLSS) were relatively stable for all the experiments even though the reactors had quit functioning. It must be assumed that non-viable cells are a major portion of the remaining sludge.

2. SLUG FEED STUDIES

Although continuous addition of hydrazine to the sanitary sewage system is not recommended, it is important to know the effect of one time fuel doses on a treatment plant. Slug loads could result from an accidental spill that reaches the sanitary sewer system or the disposal of an improperly neutralized waste solution. Because of the short exposure, the effect of transient high concentrations of fuel would be expected to be less than a continuous exposure. Figures 17, 37, and 57 show the concentrations of hydrazines expected from strictly hydraulic decay (dilution) in a completely mixed flow reactor (CMFR) and the measured concentrations. It is apparent that there is uptake or break-down of the fuel which is not experienced in the absence of the biological solids.

TABLE 27. GALLON EQUIVALENTS OF FUEL WHICH WILL PRODUCE AERATION BASIN CONCENTRATIONS OF INTEREST

(1, 5, 25, 250 mg/l) DURING SPILL SITUATIONS FOR VARIOUS HYDRAULIC DETENTION TIMES AND FLOW RATES

HYDRAULIC DETENTION TIME, θ

FLOW	4 HOURS						8 HOURS						12 HOURS						9 DAYS					
	1	5	25	250	1	5	25	250	1	5	25	250	1	5	25	250	1	5	25	250	1	5	25	250
50,000 GPD	0.008	0.04	0.21	2.1	0.016	0.08	0.4	4	0.024	0.12	0.6	6	0.43	2.2	10.8	108								
100,000 GPD	0.016	0.08	0.4	4	0.032	0.16	0.8	8	0.048	0.24	1.2	12	0.86	4.3	21.5	215								
200,000 GPD	0.032	0.16	0.8	8	0.064	0.32	1.6	16	0.096	0.48	2.4	24	1.73	8.7	43.3	433								
500,000 GPD	0.08	0.4	2	20	0.16	0.8	4	40	0.24	1.2	6	60	4.32	21.6	108	1080								
1 MGD	0.16	0.8	4	40	0.32	1.6	8	80	0.48	2.4	12	120	8.64	43.2	216	2160								
2 MGD	0.32	1.6	8	80	0.64	3.2	16	160	0.96	4.8	24	240	17.3	86.4	432	4320								
10 MGD	1.6	8	40	400	3.2	16	80	800	4.8	24	120	1200	86.4	432	2160	21600								
20 MGD	3.2	16	80	800	6.4	32	160	1600	9.6	48	240	2400	173	864	4320	43200								
50 MGD	8	40	200	2000	16	80	400	4000	24	120	600	6000	432	2160	10800	108000								

NOTE: Volumes of fuel were calculated based on a density of 1.00 gm/ml (i.e. HZ). These values will be conservative for MMH and UDMH. The appropriate multiplication factors are:

MMH : 1.14
UDMH: 1.27

These bacterial decay constants are given in Tables 13, 19, and 25. The use of the term constant is a misnomer since, as shown for each fuel, the rate constant decreases with increasing fuel concentrations. Even though a simple first order reaction was assumed, this may not be the case and some complex reaction may be required to account for the disappearance of the fuel at a molecular level. The additional decay of the fuels observed in the reactors could be due to catalysis of the oxidation due to metals released from the stressed and lysed cells; however, without more rigorous experiments, it is not possible to speculate on a mechanism. It is important to note that if a spill is large enough to produce the concentrations studied here (25 to 250 mg/l) fuel will still remain in the plant effluent. Even for the lowest concentration used, ~25 mg/l, the effluent still contained hydrazine concentrations well above those found toxic to fish, algae, and other aquatic organisms.

Table 27 outlines the quantity of fuel required to produce concentrations from 1 to 250 mg/l for different size reactors (sewage treatment plant aeration basins). For a (1 MGD) plant with a hydraulic detention time of ~8 hours, typical of some AF installations, a 24.6-liter (6.5-gallon) spill from a F-16 emergency power unit would create a concentration of 14 mg/l in a completely mixed aeration basin. Since the basin is completely mixed, the immediate effluent concentration would also be 14 mg/l. In contrast to the continuous feed situation, however, an acute dose of this magnitude produces a minimal effect on plant operation. Figures 19, 39, and 59 present data on the influence of acute doses up to 273 mg/l on COD removal. The concentration which causes no significant effect is 74 mg/l for UDMH, 44 mg/l for hydrazine, and ~32 mg/l for MMH. Since both MMH and UDMH contribute COD, this must be accounted for to realistically compare the removal of COD from the substrate feed. For instance, 2 hours following a 225-mg/l UDMH slug, 295 mg/l of the 347 mg/l measured COD can be attributed to the fuel itself. Using semibatch reactor kinetics, it is possible to calculate the effluent COD given the influent COD, initial reactor COD, and the COD of the specific fuel using Equation (27).

$$COD_{EFF} = COD_{INIT} - \frac{1}{\theta} t + COD_{INF} \left(1 - e^{-\frac{1}{\theta} t} \right) \quad (27)$$

Comparing calculated effluent COD with measured COD in Figure 68 reveals a significant difference at the first hour. Measured CODs are only ~60 percent of the calculated value. For longer times, the calculated and measured values are remarkably close. The discrepancy at the short reaction times may be due to poor circulation between the clarifier and reactor. This same trend is apparent for effluent ammonia concentration, as shown in Figure 69. Figures 24, 44, and 64 illustrate that, for single exposures, COD removal returns to normal after 7 days for hydrazine and only 2 days for MMH and UDMH.

As in the continuous feed studies, the influence of slug fuel doses on the autotrophic organism is much more significant than on the heterotrophs. Ammonia oxidation is effected for all three fuels at the lowest concentrations tested. The decrease in nitrate exhibited by reactors dosed with hydrazine and UDMH is slightly slower than would be expected from simple wash-out from the reactor. The rapid decrease seen with MMH is unexplained.

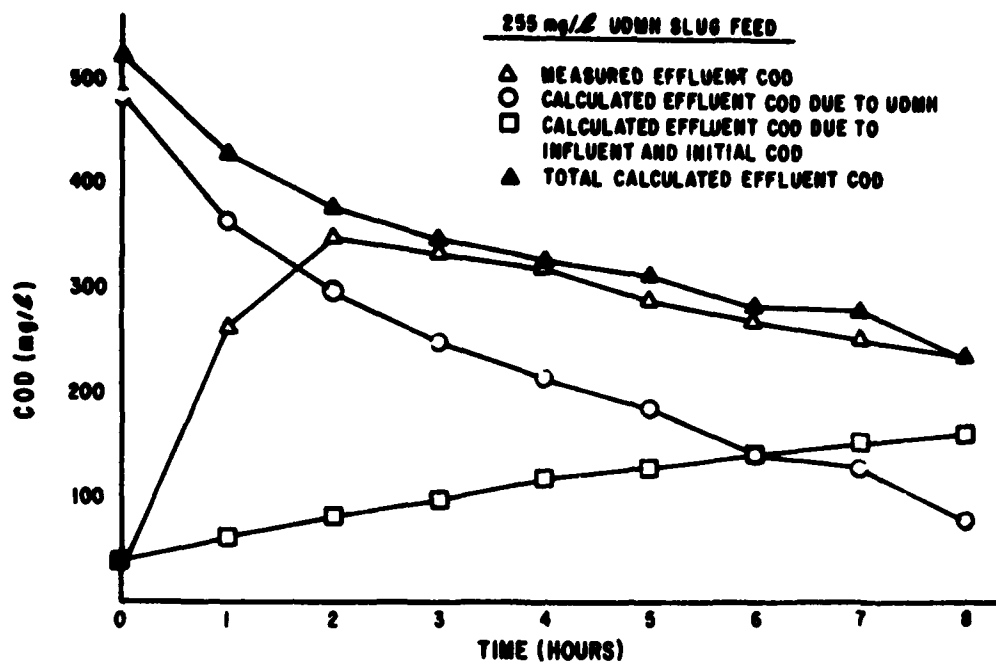


Figure 68. COD Mass Balance for Slug UDMH Load

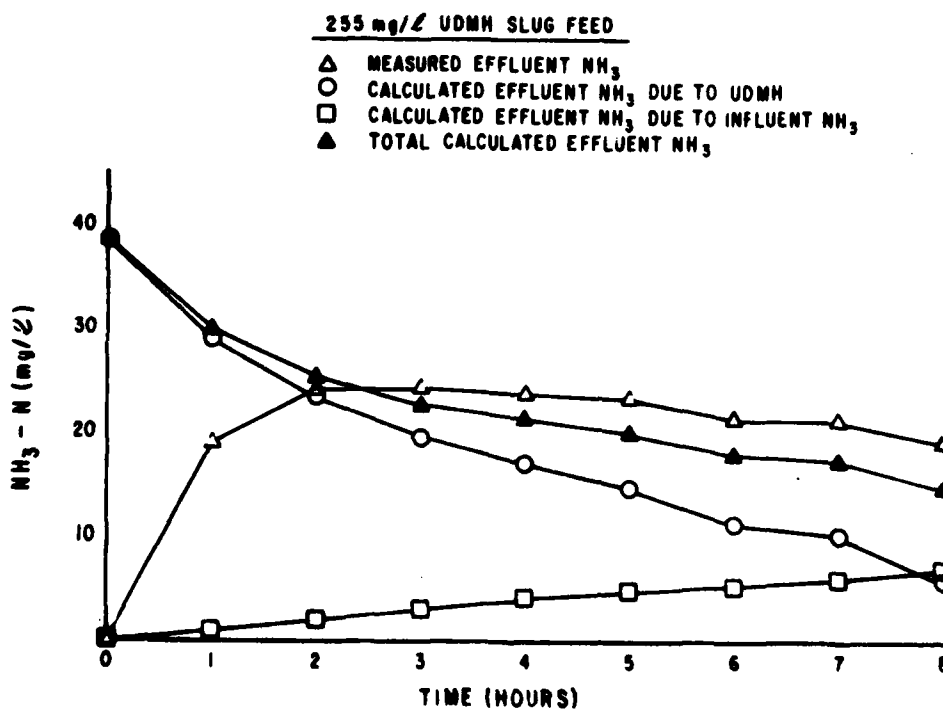


Figure 69. NH₃ Mass Balance for Slug UDMH Load

Attempts to document a reaction between MMH and NO_3^- or an interference with the nitrate probe were negative; nor is it likely that anaerobic denitrification could explain the rapid decrease seen for all 4 initial concentrations studied. A possible explanation might be that, under the conditions existing in the reactors, a catalyzed reaction between MMH and NO_3^- occurred. Unfortunately this was not evaluated while the reactors were operating.

SECTION VIII

CONCLUSIONS

Continuous Feed-All Fuels

- 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.

- Discharges from pretreatment processes must be held to concentrations low enough to prevent values greater than 1 mg/l in the influent to Privately Owned Treatment Works (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.

Slug Loads-HZ

- 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.
- COD recovery times for slug doses up to 243 mg/l are on the order of 4 to 5 days.
- 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.
- Ammonia recovery times for slug doses up to 243 mg/l are on the order of 7 to 10 days.

Slug Loads-MMH

- Treatment plant efficiency, as measured by COD removal, is not seriously impaired for slug doses which result in aeration basin MMH concentrations up to 32 mg/l.
- COD recovery times for slug doses up to 273 mg/l are on the order of 2 to 3 days.
- Nitrification ceased at slug doses above 32 mg/l. The no effect concentration with respect to ammonia oxidation is between 1 to 32 mg/l.
- Ammonia recovery times for slug doses up to 273 mg/l are on the order of 12 to 16 days.

Slug Loads-UDMH

- Treatment plant efficiency, as measured by COD removal, is not seriously impaired for slug doses which result in aeration basin UDMH concentrations up to 74 mg/l.
- COD recovery times for slug doses up to 255 mg/l are on the order of 2 to 3 days.

- Nitrification ceased at slug doses above 32 mg/l. The no effect concentration with respect to ammonia oxidation is between 1 to 22 mg/l.
- Ammonia recovery times for slug doses up to 255 mg/l are on the order of 8 to 12 days.

REFERENCES

1. Sherrard, J. H., "Kinetics and Stoichiometry of Completely Mixed Activated Sludge", Journal Water Pollution Control Fed., Sep 1977.
2. Piel, K.M., and A. F. Gaudy, Jr, "Kinetic Constants for Aerobic Growth of Microbial Populations Selected with Various Single Compounds and with Municipal Wastes as Substrates", Applied Microbiology, 21, 253-256, 1971.
3. Eckhoff, D. W., and D. Jenkins, "Activated Sludge Systems, Kinetics of the Steady and Transient States", Report No. 67-12 of the Sanitary Engineering Research Laboratory, University of California, Berkley, 1967.
4. Metcalf and Eddy, Wastewater Engineering, McGraw-Hill Book Co., New York, New York 1972.
5. Lawrence, A. L. and P. L. McCarty, "A Unified Basis for Biological Treatment Design and Operation", Journal of the Sanitary Engineering Division, ASCE, 96, 1970.
6. McCarty, P. L., "Stoichiometry of Biological Reactions." Paper presented at the International Conference, "Toward a Unified Concept of Biological Waste Treatment Design," Atlanta, Georgia (October 6, 1974).
7. Stanill, Roger Y., The Microbial World, 4th Edition, Prentice-Hall Inc., Englewood Cliffs, NJ, 1976.
8. Hoover, S. R., and Porges, N., "Assimilation of Dairy Wastes by Activated Sludge II, The Equation of Synthesis and Oxygen Utilization." Sewage and Industrial Wastes, 24 306 (1952).
9. McCarty, P. C., "Phosphorous and Nitrogen Removal by Biological Systems", presented at 2nd Sanitary Engineering Research Laboratory Workshop, Tahoe City, California, June 26, 1970.
10. Wild, H. E., Sawyer and McMahon, "Factors Affecting Nitrification Kinetics," JWPCF, 43, 1971.
11. Stratton, Frank E., and P. L. McCarty, "Prediction of Nitrification Effects on the Dissolved Oxygen Balance of Streams", Environmental Science and Technology, (5) May 67.
12. Monod, J., "La Technique of Culture Continue; Theorie et Applications," Annals Institute Pasteur, Vol. 79, 1950.

13. Heukelekian, H., Orford and Manganello, "Factors Affecting the Quantity of Sludge Production in the Activated Sludge Process," *Sewage and Industrial Wastes*, Vol. 23, No. 8, August 1951.
14. Christensen, Douglas R. and P. L. McCarty, "Biotreat: A Multi-Process Biological Treatment Model", Presented at the Annual WPCF Conference, Denver, Colorado, October 1974.
15. Tomlinson, T. G., et al, "Inhibition of Nitrification in the Activated Sludge Process of Sewage Disposal," *Journal Applied Bacteriology*, 29, 266, 1966.
16. Meyerhof, O., "Die Atmung des Nitritbildners und ihre Beeinflussung durch chemische Substanzen," *Pflugers Arch. ges. Physiol.* 166, 240.
17. Yoshida, T. and Alexander, "Hydroxylamine Formation by *Nitrosomonas europaea*", *Canadian Journal of Microbiology*, Vol. 10, 1964.
18. Water Pollution Control Fed., Wastewater Treatment Plant Design; Manual of Practice No. 8, WPCF, Washington, DC, 1977.
19. Watt, George W. and Chrisp, "A Spectrophotometric Method for the Determination of Hydrazine," *Analytical Chemistry*, Vol. 24, No. 12, December, 1952.
20. Pinkerton, M. K., et al, "A Colorimetric Determination for 1,1-Dimethylhydrazine (UDMH) in Air, Blood and Water," *American Industrial Hygiene Association Journal*, Vol. 24, May-June 1963.
21. Verotrack, W. and M. Alexander, "Heterotrophic Nitrification by Arthrobacter sp.", *Journal of Bacteriology*, June 1972.
22. Saleh, M.M. and A. F. Gaudy, Jr., "Shock Load Response of Activated Sludge with Constant Recycle Sludge Concentration," *Journal Water Pollution Control Fed.*, April 1978.
23. Klein, S. A., and D. Jenkins, "Environmental Quality Research. Fish and Aufwuchs Bioassay. Third Annual Report" AMRL-TR-78-65, Aerospace Medical Research Laboratory, Wright-Patterson Air Force Base, Ohio, November 1978.
24. Scherfig, J., P. S. Dixon, and C. A. Justice, "Environmental Quality Research, Use of Unicellular Algae for Evaluation of Potential Aquatic Contaminants, Third Annual Report". AMRL-TR-78-86, Aerospace Medical Research Laboratory, Wright-Patterson AFB, Ohio, November 1978.

AD-A085 186

AIR FORCE ENGINEERING AND SERVICES CENTER TYNDALL AF--ETC F/G 21/9.1
THE EFFECTS OF AMINE-BASED MISSILE FUELS ON THE ACTIVATED SLUDGE--ETC(U)
OCT 79 M G MACNAUGHTON, J A FARMWALD

UNCLASSIFIED

NL

211 2
211 2



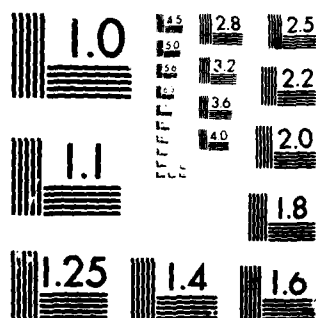
END

DATE

FILED

6-80

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

APPENDIX A

STOICHIOMETRY

A. General: The stoichiometric relationship developed by McCarty (Reference 6) is as follows:

$$R = R_d - f_e R_a - f_s R_c \quad (A-1)$$

R = overall reaction

R_d = half reaction for electron donor

R_a = half reaction for electron acceptor

R_c = half reaction for cell synthesis

f_e = fraction of e^- donor used for energy

f_s = fraction of e^- donor used for synthesis

where: $f_e + f_s = 1$.

In suspended growth systems, f_e and f_s are a function of cellular yield and the organism decay rate, the latter being a function of solids retention time. Using the classical growth equation for microorganisms and mass balance relationships for a suspended growth system, McCarty developed the following relationship:

$$f_s = a_e \left(1 - \frac{f_d b \theta_c}{1 + b \theta_c} \right) \quad (A-2)$$

where: a_e = cell yield coefficient expressed as equivalents of cells per equivalent^e of donor consumed (Figure A-1). a_e and b can be estimated from kinetic studies for a particular waste or from thermodynamic considerations. Oftentimes values are assumed based on previous work with similar wastes. The fraction f_d is most often assumed to be 0.8 for both aerobic and anaerobic organisms (Reference 1). Thermodynamic relationships, as reported by McCarty (Reference 6), are given by Equations (A-3) and (A-4).

$$a_e = \frac{1}{1 + A} \quad (A-3)$$

$$A = - \frac{\Delta G_p / k^m + \Delta G_n / k + 7.5}{k \Delta G_r} \quad (A-4)$$

ΔG_p = energy required to convert cell carbon source to an intermediate stage

$$= \Delta G^0(w)_d + 8.54$$

= 27.22 Kcal for inorganic e^- donors

$\Delta G^\circ(w)_d$ = free energy per mole of electrons for donor half reaction.

m = +1 if ΔG_p is >0 , -1 if <0

$$\Delta G_r = \Delta G^\circ(w)_d - \Delta G^\circ(w)_a$$

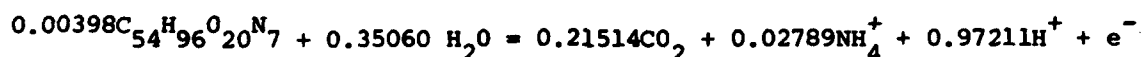
$\Delta G^\circ(w)_a$ = free energy per mole of electrons for acceptor half reaction.

k = efficiency of energy transfer for bacterial growth, ranging from 0.4 - 0.7.

ΔG_n = energy required to convert the nitrogen source for cell synthesis to NH_3 .

B. Heterotrophic Reactions: Using the data presented in Tables 1 and 2 and McCarty's procedure for constructing empirical formulations based on electron equivalent fractions of each component in the waste (Appendix B), the following relationship was developed for the enriched primary effluent and has been taken to represent the heterotrophic donor half reaction, R_d . The balanced equation has been normalized to 1 electron equivalent:

(A-5)



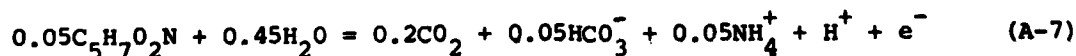
* $\Delta G^\circ(w) = -7.9$ Kcal/ e^- equivalent

The electron acceptor is oxygen; thus R_a is:

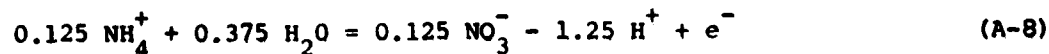


* $\Delta G^\circ(w) = 18.675$ Kcal/ e^- equivalent

Assuming an empirical formula for aerobic bacterial protoplasm (Reference 8) and noting that ammonia serves as the nitrogen source, R_c becomes:



C. Autotrophic Reactions: The following half reaction applies when NH_4^+ serves as the electron donor.



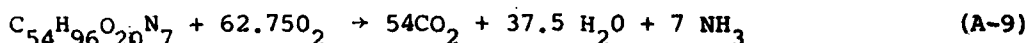
$$\Delta G^\circ(w) = 8.245$$

The reactions R_a and R_c are the same as for the heterotrophic situation.

*Reactants and products at unit activity except $H^+ = 10^{-7}$

D. Yield Coefficients: The bacterial yield coefficient, Y, expressed as grams cells/gram substrate removed may be estimated by writing the overall reaction, R, for the condition $\theta_c = 0$ (reference Figure A-1). The substrate of interest in the autotrophic reaction is NH_4^+-N which is amenable to direct measurement. However, since this is not the case for the heterotrophic substrate, it becomes advantageous to develop a relationship between organic substrate concentration and a standard parameter such as COD.

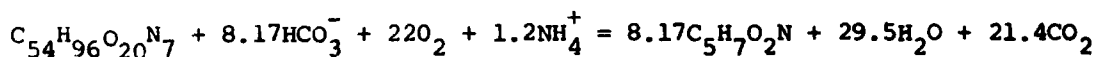
1. COD: The theoretical chemical oxygen demand for the supplemented feed solution may be calculated from the empirical formulation, thus:



On a molar basis, 1 mole donor $\equiv$ 2008 gm COD. Based on a total organic fraction of 223 mg/l in the enriched feed (118.7 mg carbohydrate + 37.3 mg protein + 16.9 mg fat + 50 mg l^o effluent (measured value), a value of 433 mg/l COD results. Actual analyses of the primary effluent yielded 100 mg COD/50 mg yss/l which is, in fact, equal to the value predicted from the empirical formula $\text{C}_{10}\text{H}_{19}\text{O}_3\text{N}$ used in constructing the donor half reaction. The composite Slender[®] formulation, $\text{C}_{42}\text{H}_{71}\text{O}_{16}\text{N}_6$, does, however, yield a value 29 percent higher (286,000 mg/l) than that determined experimentally.

2. Heterotrophic Y: Assuming a k value of 0.6 (Reference 6) and employing $\Delta G^\circ(w)$ values developed in paragraph B, Equations (A-3) and (A-4) are used to find that $a_e = 0.65$. If $f_d = 0.8$, it follows from Equation (A-2) that $f_s = a_e$ and therefore $f_e = 0.35$. Substituting into Equation (A-1) yields the following relationship for R.

(A-10)

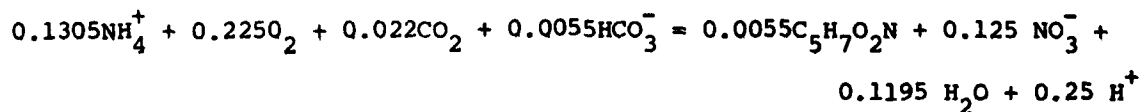


From the above coefficients and those relationships derived from equation (A-9) Y is 0.46 gm cells/gm COD removed. This value compares well with values reported in the literature for similar wastes (Reference 5).

3. Autotrophic Y: Again a_e may be calculated from thermodynamic considerations assuming $k = 0.6$. Thus, when $\theta_c = 0$; $a_e = 0.11$, $f_s = 0.11$, and $f_e = 0.89$.

The overall autotrophic reaction is constructed and used to estimate Y on a gram cells/gram NH_4^+-N removed basis.

(A-11)



$$Y = 0.34 \text{ gm cells/gm } \text{NH}_4^+-\text{N}$$

E. Supplemental Requirements: As discussed in paragraph A, f , f_s , and hence R , under actual operating conditions, are a function of $\bar{S}$, f_s^s , and θ_c . By writing balanced Stoichiometric reactions as a function of θ_c (Constant b , f_c), it can be shown that oxygen and alkalinity demands increase with increasing cell residence times. The advantages of approaching such an extended aeration system are lower observed yields ($Y_{OBS} = Y/(1+b\theta_c)$), effluent soluble substrate concentrations, and nutrient requirements.

1. Nutrients: In the interest of making conservative estimates the worst case was considered for the desired influent substrate concentrations, i.e., maximum yield ($\theta_c = 0$) and complete substrate utilization ($S_e = 0$). The assumption indicates that Equations (A-10) and (A-12) should be used to estimate maximum yield nitrogen and phosphorous requirements.

a. Nitrogen:

(1) Heterotrophic: Using the appropriate stoichiometric Equation (A-10), it is clear that one mole of donor requires 1.2 moles of NH_4-N for complete oxidation to occur. Based on an influent donor mass of 223 mg/l (organic fraction), it can be shown that a nitrogen requirement of 3.2 mg/l exists, the theoretical organic nitrogen supplied by the donor being 160 mg/l. Note that rule-of-thumb estimates are often made, based on the same yield and utilization assumptions employed here, assuming the typical aerobic cell contains 12-percent nitrogen. In this case, the resultant 17.6 mg/l value compares well with the stoichiometric total of 19.2 mg/l. Referring to Table 1, it is seen that approximately 12.7 mg/l of inorganic nitrogen is present in the raw feed solution. While this should provide an adequate excess of nitrogen, an additional 4.7 mg/l urea-N was routinely added to insure nitrogen was not limiting.

(2) Autotrophic: Considering all sources, the total organic and inorganic nitrogen in the described system is approximately 33.4 mg/l*. Of this, 19.2 mg/l is required for heterotrophic synthesis, the remainder, 14.2 mg/l, being available for nitrification. This total value agrees well with the average Kjeldahl nitrogen (29.8 mg/l) in the supplemented feed which was monitored throughout the study.

b. Phosphorous: As stated earlier, the phosphorous requirement is generally considered to be about 1/5 that of nitrogen. This rule of thumb assumes the typical aerobic cell contains approximately 2-percent phosphorous. In lieu of stoichiometry which includes a phosphorous component, this information, again based on maximum yield and complete substrate utilization, may be used to estimate the phosphorous demands.

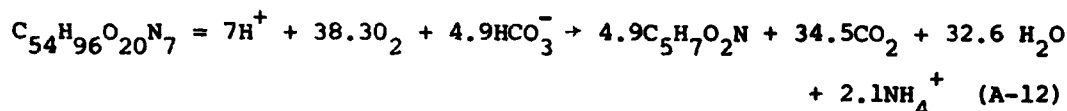
- * 1° Effluent inorganic-N: 12.7 mg/l
 Electron donor organic-N: 16.0 mg/l; based on empirical formulation.
 Supplemental organic-N: 4.7 mg/l UREA-N

(1) Heterotrophic: Using a yield coefficient of 0.46 and an influent substrate concentration of 320 mg/l as CO₂, the resultant phosphorous requirement is 2.9 mg/l.

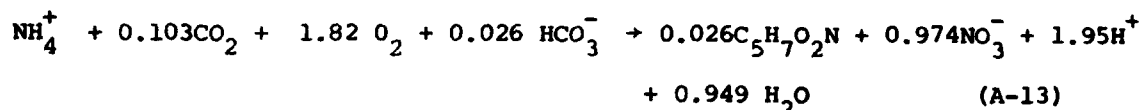
(2) Autotrophic: The autotrophic demand for phosphorous is expected to be low. Using the appropriate values, the calculations indicate a demand of 0.10 mg/l-P.

2. Oxygen and alkalinity: Conservative estimates of oxygen and alkalinity requirements were made based on a mean cell residence time of 20 days. The appropriate stoichiometry is summarized below.

HETEROTROPHIC: $a_e = 0.65$ $f_s = 0.39$, $f_e = 0.61$



AUTOTROPHIC: $a_e = 0.11$ $f_s = 0.066$, $f_e = 0.934$



The above relationships lead to the requirements outlined in Table A-1, assuming complete substrate utilization.

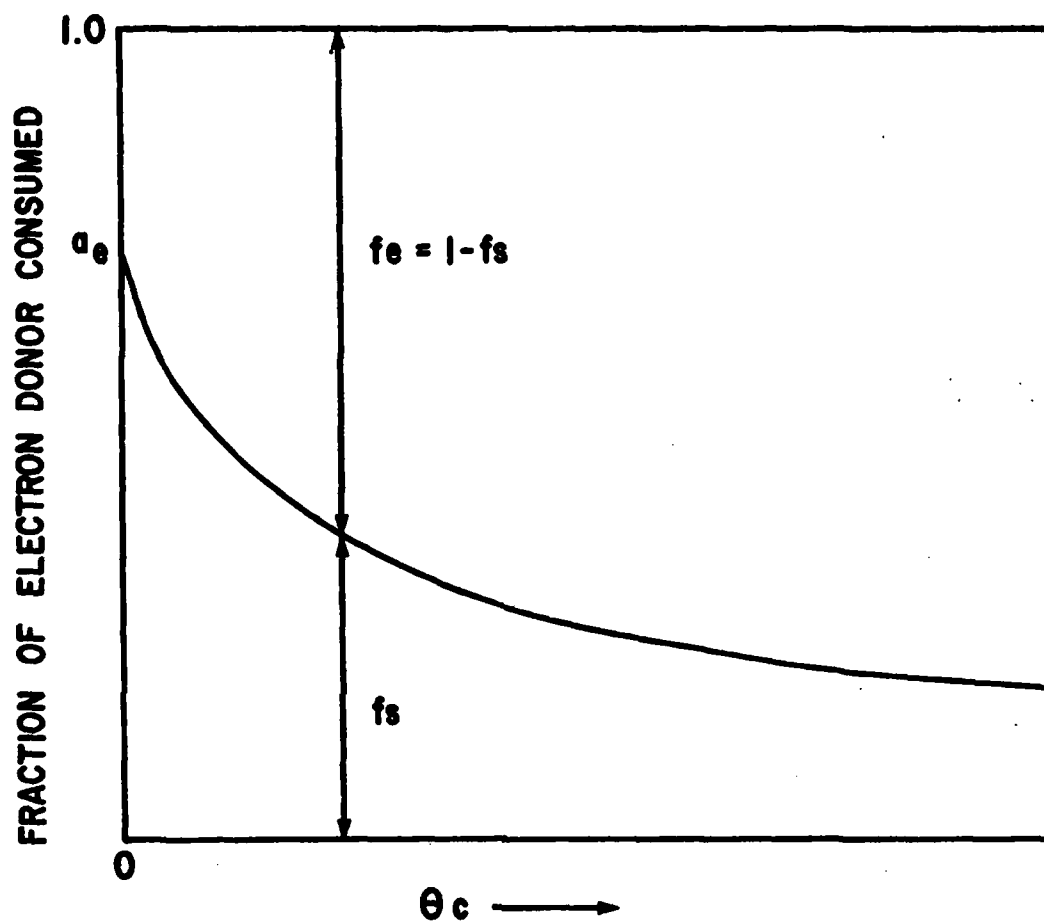


Figure A-1. Fraction of Electron Donor Used for Energy, f_e , and for Synthesis, f_s , as a Function of θ_c . A_e is the Maximum Cell Yield Coefficient on an Equivalent Basis

TABLE A-1. OXYGEN AND ALKALINITY REQUIREMENTS $\theta_c = 20$ DAYS

	Design S^0	O_2 gm/DAY	Alkalinity mg/l as $CaCO_3$
Heterotrophic	320 mg/l COD	4.20	2260*
Autotrophic	15 mg/l NH_4^+-N	1.35	150**
Total		5.55	2410

* Based on Carbonic Acid Equilibria, $pH \geq 7.0$ (Appendix C) and HCO_3^- requirements for synthesis.

** Assumed 10 times the NH_4^+-N to be oxidized (Reference 9).

APPENDIX B

EMPIRICAL FORMULATIONS

Raw Feed

1° EFF (Domestic Sewage) $1/50 \text{ C}_{10}\text{H}_{19}\text{O}_3\text{N}$

50 mg/l vss (measured value)

$$(0.05 \text{ gm}) \frac{\text{mole}}{201 \text{ gm}} = 0.0002488 \text{ Mole} \quad \frac{50 \text{ eq}}{\text{Mole}} = \underline{\underline{0.0124 \text{ eq}}}$$

Slender®

Carbohydrate $1/4 \text{ CH}_2$ 0.1187 gm/l (Slender® Label)

$$(0.1187 \text{ gm}) \frac{1 \text{ mole}}{14 \text{ gm}} \frac{4 \text{ eq}}{\text{mole}} = \underline{\underline{0.0339 \text{ eq}}}$$

Fat $1/46 \text{ C}_8\text{H}_{16}\text{O}$ 0.0169 gm/l (Slender® Label)

$$(0.0169 \text{ gm}) \frac{1 \text{ mole}}{128 \text{ gm}} \frac{46 \text{ eq}}{\text{mole}} = \underline{\underline{0.00607 \text{ eq}}}$$

Protein $1/66 \text{ C}_{16}\text{H}_{24}\text{O}_5\text{N}_4$ 0.0373 gm/l (Slender® Label)

$$(0.0373 \text{ gm}) \frac{1 \text{ mole}}{352 \text{ gm}} \frac{66 \text{ eq}}{\text{mole}} = \underline{\underline{0.00699 \text{ eq}}}$$

Total equivalents = 0.0594

Total Slender equivalents = 0.04696

FRACTIONS ON EQ BASIS

<u>Component</u>	<u>Slender Only®</u>	<u>Enriched Feed</u>
1° EFF	--	0.21
Carbohydrate	0.72	0.57
Protein	0.15	0.12
Fat	0.13	0.10

Enriched Feed Formulation:

$$0.21 (C_{10}H_{19}O_3N) + 0.57 (CH_2O) + 0.12 (C_{16}H_{24}O_5N_y) + 0.1 (C_8H_{16}O) =$$

$$C_{5.39} H_{9.61} O_{1.9} N_{0.69} \sim \underline{\underline{C_{54}H_{96}O_{20}N_7}}$$

$$\Delta G^{\circ}(w) = \epsilon (\text{Fractions}) (\text{Component } \Delta G^{\circ}(w))$$

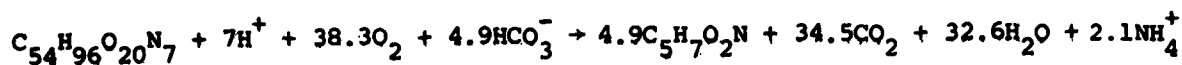
$$\Delta G^{\circ}(w) = 0.21(-7.6) + 0.57(-10.0) + 0.12(-7.7) + 0.10(-6.6) =$$

$$-7.9 \text{ Kcal/e}^- \text{ equivalent}$$

$$\text{Similarly Slender Formulation} = \underline{\underline{C_{42}H_{71}O_{16}N_6}}$$

APPENDIX C

CALCULATION OF ALKALINITY REQUIREMENT FOR HETEROTROPHIC REACTION



$$pH = 6.4 + \log \frac{HCO_3^-}{H_2CO_3^*} \quad pK_1 = 6.4$$

$$\text{where } H_2CO_3^* = CO_2(aq) + HCO_3^-$$

$$\text{Assume } H_2CO_3 \ll CO_2(aq) \quad \text{i.e. } H_2CO_3^* \equiv CO_2(aq)$$

Desire pH > 7.0

$$\log \frac{HCO_3^-}{H_2CO_3^*} = \log \frac{HCO_3^-}{CO_2(aq)} \geq 0.6$$

For each mole of waste 34.5 moles CO_2 produced assume worst case, i.e.,

all CO_2 becomes $CO_2(aq)$

$$\log \frac{HCO_3^-}{34.5} \geq 0.6$$

$$\frac{HCO_3^-}{34.5} \geq 3.98$$

$$HCO_3^- \geq 137.3 \text{ moles}$$

In addition: HCO_3^- is destroyed to produce cellular matter, i.e., 4.9

moles per the stoichiometry $HCO_3^- \geq 142 \text{ moles}$

$$\frac{142 \text{ moles } HCO_3^-}{1 \text{ mole waste}} \times \frac{1 \text{ mole } C_aCO_3}{1 \text{ mole } HCO_3^-} \times \frac{100 \text{ gm } C_aCO_3}{1 \text{ mole } C_aCO_3} = 14200 \text{ gm } C_aCO_3/\text{mole waste}$$

$$(320 \text{ mg COD})/\ell \times \frac{1 \text{ mole waste}}{2008 \text{ gm COD}} \times \frac{14200 \text{ gm } C_aCO_3}{\text{mole waste}} = 2260 \text{ mg}/\ell \text{ as } C_aCO_3$$

INITIAL DISTRIBUTION LIST

OASD/(I&L)EES	1	HQ USAFE/SGB	1
OUSDR&E	1	HQ USAFE/DEVS	1
OSAF/MIQ	1	HQ USAFE/DEPV	1
DDC/DDA	2	USAF Hospital	1
ARPA	1	Weisbaden	
OSAF/OI	1	HQAUL/LSE 71-249	1
HQ USAF/LEEV	2	HQ USAFA/Library	1
HQ USAF/SGES	1	AFIT/Library	1
AFMSC/SGPA	1	AFIT/DE	1
HQ AFSC/DL	1	AFRES/SGB	1
HQ AFSC/SD	1	USAFSS/DEE	1
HQ AFSC/DEV	1	USAFRCE/DEEV	3
HQ AFSC/SGB	1	USAFRCE/CR/DEEV	3
AMD/RDU	1	USAFRCE/ER/DEEV	3
AMD/RDB	1	US Army, MIRADCOM	1
AMRL/THE	1	Ch, Environmental Chem	1
OEHL/CC	3	Dev/USAEHA	
USAFSAM/EDE	4	USA Med Bioengrg R&D Lab	2
USAFSAM/VNL	1	Ch, Industrial Hyg Div	2
Strughold Aeromedical	1	USAEHA	
Library		USA Chief, R&D/EQ	1
AFOSR/NL	1	USN Chief, R&D/EQ	1
SAMSO/SGX	1	Ch, Pollution Abatement	1
SAMSO/DEV	1	NAVFAC	
AFRPL/Library	1	NAPC/Code PE71:AFK	1
AFRPL/LKDP	1	NESO	1
ADTC/DLODL (Tech Library)	1	US Coast Guard/GDD	1
ASD/AEL	1	HQ NASA	1
FTD/LGM	1	NCEL	1
AFWL/SUL (Tech Library)	1	NASA/MD-E	1
AFTEC/SG	1	FAA/AEE-300	1
HQ SAC/DEPA	1	FAA/ARD-550	1
HQ SAC/SGPA	1	EPA/ORD	1
HQ TAC/SGPA	1	Federal Lab Program	1
HQ TAC/DEEV	1	Library, Chem Abstract	1
HQ AFLC/SGP	1	Service	
HQ AFLC/DEEPV	2	Toxic Materials Info Ctr	1
HQ AFLC/IGYG	1	HQ AFESC/DEV	4
HQ AFLC/MAXF	1	HQ AFESC/TST	2
HQ MAC/SGPE	1	HQ AFESC/RDVC	15
HQ MAC/DEEV	1		
HQ ADCOM/SGPAP	1		
HQ ADCOM/DEEV	1		
HQ ATC/SGPAP	1		
HQ ATC/DEEV	1		
HQ PACAF/SGPE	1		
HQ PACAF/DEEV	1		
1 Med Severice Wg/SGB	1		
HQ AFISC/SG	2		
HQ AAC/SGB	1		
HQ AAC/DEEV	1		