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STABILITY OF EXPLOSIVES IN ENVIRONMENTAL WATER AND SOIL SAMPLES

January 1991

M. P. Maskarinec
C. K. Bayne
L. H. Johnson
S. K. Holladay
R. A. Jenkins
B. A. Tomkins

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U.S. Army Toxic and Hazardous Materials Agency

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and

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EXECUTIVE SUMMARY

This report focuses on data generated for the purpose of establishing the stability of HMX, RDX, TNT, and DNT explosives in environmental water and soil samples. The study was carried out over a one year time frame and took into account as many variables as possible within the constraints of budget and time. The objectives of the study were: 1) to provide a data base which could be used to provide guidance on pre-analytical holding times for regulatory purposes; and 2) to provide a basis for the evaluation of data which is generated outside of the currently allowable holding times for quality assurance purposes.

The experimental design consisted of three water samples and three soil samples. The water samples were distilled-in-glass water, a ground water, and a surface water. The soil samples were a U.S. Army Toxic and Hazardous Materials Agency soil, a Captina silt loam from Roane County, Tennessee, and a McLaurin sandy loam from Stone County, Mississippi. The analytes consisted of four explosives HMX, RDX, TNT and DNT. All analyses were carried out using methods similar to those in the USEPA Contract Laboratory Program. HPLC was used for all determinations. All determinations were carried out in quadruplicate along with a storage blank. Two concentration levels were studied: nominally 50 µg/L and 1000 µg/L for water samples and nominally 10 µg/g and 100 µg/g for soil samples. Water samples were stored at two temperatures, room temperature and under refrigeration (4°C). For high explosive concentrations, water samples were also stored in extraction tubes under refrigeration. Soil samples were stored at three temperatures, room temperature, 4°C, and -20°C. Samples were analyzed at intervals of 0, 3, 7, 14, 28, 56, 112, and 365 days. The maximum holding times (MHTs) were estimated by two statistical definitions.

Several approaches were taken to estimate the MHTs for each explosive because a standard definition for MHT has not been adopted by the Environmental Protection Agency (EPA). First, a procedure recommended by the American Society for Testing and Materials (ASTM) was modified and applied to the data base. Secondly, a procedure developed by Environmental Science and Engineering (ESE) for the analysis of a similar data base was applied. Each of these approaches resulted in different estimates of MHTs due to the application of different statistical procedures and criteria for the two definitions. Therefore, decisions concerning stability depend on the objective of the individual evaluating the environmental data.

The estimated MHTs depend on the different combination of levels for the experimental factors. Although HMX and RDX usually have longer MHTs than DNT and TNT, specific comparisons depend on concentration level, sample matrix, and storage condition. The matrix dependency was primarily related to the preserved biological activity of the matrix. The storage of water samples in extraction tubes did not improve the stability of the explosives.

This report is intended to summarize the findings of the study in such a way as to allow

individual decisions to be made regarding the quality of environmental data. The use of the data base may well be different for analyses conducted under RCRA, for example, than for those conducted under NPDES permit requirements. For this reason, the summary statistics for each replicate analysis is presented in the appendices of this report.

Although different concentration levels and soil types were used to estimate maximum holding times, these factors are not necessarily known prior to sampling and chemical analysis. Therefore, the choice may not be clear in practice as to which maximum holding time to select because of unknown factor combinations. The recommended maximum holding times are established for the situation when little is known about concentration levels or soil types. These recommended maximum holding times are conservative estimates made after reviewing the MHTs for all factor combinations and the explosive summary statistics in Appendices A, B, C, and D. Recommended maximum holding time for HMX and RDX contaminated ground water is 50 days under refrigeration prior to analysis. For surface water, about 30 days would be a preferred maximum pre-analytical holding time. For high levels of DNT and TNT, samples could be refrigerated for two weeks, but DNT at low levels even refrigerated will degrade very rapidly. In fact, the MHT's for DNT and TNT are so short that the data suggests that any ground water or surface water samples will not be representative of the water contamination levels, unless they are analyzed very quickly. Soil samples contaminated with HMX, RDX, and DNT should be stored at 4°C. Soil samples contaminated with TNT should be frozen immediately at -20°C. Do not permit the "minus" to get separated from the "20°C". With these sampling procedures, the recommended holding time for explosive contaminated soils is six weeks when stored at refrigerated or frozen temperatures.

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1. INTRODUCTION

During the past two decades, there has been a dramatic expansion of environmental legislation, including the Comprehensive Environmental Response, Compensation, and Liability Act; the Resource Conservation and Recovery Act; the Toxic Substances Control Act; the Clean Water Act; the Safe Drinking Water Act; the Marine Act; and, most recently, the Superfund Amendment and Reauthorization Act. One result of these regulatory measures has been a tremendous increase in the number of samples collected and distributed for analysis. One estimate is that federal, state, and local governments combined with private industry accounted for 500,000-700,000 samples in 1986. Furthermore, this number is growing at a rate of 25-40% per year [*1*]. Obviously, this has put tremendous strain on the capacity of analytical laboratories. In many cases, samples are collected at a particular site, shipped to a central distribution point, and assigned to individual laboratories on the basis of capacity. All of this is done with relatively little knowledge of the stability of the samples, and preanalytical maximum holding times (MHTs) have been established based on the best available information, much of which has been pieced together in a somewhat arbitrary fashion.

In order to provide consistent results from analytical laboratories nationwide, the United States Environmental Protection Agency (USEPA) has issued various analytical methods in the Federal Register to standardize analyses. Among the quality assurance needs in these methods is the requirement for reference samples to enable interlaboratory comparisons to be made. This work focuses on the development of a data base which allows documentation of the stability of explosives in water and soil samples, for purposes of increasing the preanalytical holding times and therefore reducing the cost associated with the analysis.

The generation of a data base establishing preanalytical holding times presents formidable experimental difficulties, including the need for a large number of identical sample aliquots, and the need for a variety of sample matrices. Two criteria must be met by such samples: They should be "real", i.e., they should closely simulate the composition of actual samples; they should also be of defined stability. Fortunately, an analytical method, high-pressure liquid chromatography (HPLC), exists which is capable of determining all of the explosive target analytes in a single run. In this work, the data base reported here can be used to make an accurate assessment of the stability of explosives in environmental water and soil samples.

2. EXPERIMENTAL

This study was designed to take into account as many experimental factors as possible within the limitations of budget and sample capacity. Six experimental factors were examined: explosive type, sample matrix, matrix type, concentration level, storage condition, and storage time.

2.1 Experimental Factors

The four explosives used in this study are: octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexahydro-1,3,5-trintro-1,3,5-triazine (RDX), 2,4,6-trinitrotoluene (TNT), and 2,4-dinitrotolune (DNT). These explosives were obtained from the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) Standard Analytical Reference Materials (SARMS) program. The explosives were studied in both a water matrix and a soil matrix. Both the water matrix and soil matrix consisted of three different types. Two explosive concentration levels were used which were dependent on the sample matrix. Concentration levels were chosen to represent values that may be encountered in practice. The choice of storage conditions was dictated by practicality as well as the possibility that the samples might not be continuously chilled during collection. The storage time was chosen on a logarithmic basis to anticipate both short term and long term degenerations. The experimental factors and their levels are presented in Table 1 for holding time study of explosive samples.

Table 1. Experimental factors for the explosive holding time study.

Factors	Factor Levels	
Explosives	HMX RDX TNT DNT	
Sample Matrix	Water Sample	Soil Sample
Matrix Type	Distilled Ground Surface	USATHAMA Tennessee Mississippi
Concentration	50 μg/L 1000 μg/L	10 μg/g 100 μg/g
Storage Condition	4°C Room Extract(4°C)	-20°C 4°C Room
Storage Time (days)	0 3 7 14 28 56 112 365	

The three types of water matrix were chosen to assess the effect of varying water quality parameters on stability. The three water types used for this study are reagent grade water (Distilled), a ground water (Ground), and a surface water (Surface). Reagent grade water was obtained from Burdick and Jackson Laboratory. The ground water was drawn from Well #1 at the Oak Ridge National Laboratory (ORNL) Aquatic Ecology Facility (well depth: 205 feet; static water level below ground level: 30 feet). Surface water was taken from the headwaters of White Oak Creek on the Oak Ridge DOE Reservation. Selected

chemical properties are given in Table 2 (based on Table 1 of [2]) for the three water types used in the pre-analytical holding time study for explosives.

Table 2. Selected chemical properties of waters used in the pre-analytical holding time study.

Characteristics	Distilled Water	Ground Water	Surface Water
Alkalinity (mg $CaCO_3$/L)	< 1	178.4	135.6
Biochemical Oxygen Demand (mg/L)	< 1	< 5	< 5
Chemical Oxygen Demand (mg/L)	< 1	2.00	3.00
Chloride (mg/L)	< 0.1	1.7	1.0
Fluoride (mg/L)	< 1	< 1	< 1
Nitrate (mg/L)	< 1	< 5	< 5
pH	6.0-7.5	7.87	8.18
Phosphate (mg/L)	< 1	< 5	< 5
Sulfate (mg/L)	< 1	7.2	< 5
Total Hardness (mg/L)	< 1	141.5	432.5

The three types of soil matrix used for this study were a U.S. Army Toxic and Hazardous Materials Agency soil (USATHAMA)[3], a Captina silt loam from Roane County, Tennessee (Tennessee), and a McLaurin sandy loam from Stone County, Mississippi (Mississippi). The USATHAMA soil is THAMA reference soil which contains no semivolatile organics. The Tennessee and Mississippi soils were furnished by the Environmental Science Division of ORNL. Both soils were slightly acidic and low in organic carbons. The Tennessee soil had a higher cation-exchange capacity and microbial respiration rate than those of the Mississippi soil. The biodegradation and microbial activity have been examined [2,4] in the Tennessee and Mississippi soils for 19 organic compounds. The results showed that most chemicals depressed carbon dioxide efflux in the two soils when applied at 1,000μg/g soil but this effect disappeared within a few days. These results cannot necessarily be extrapolated to microbial activity for the explosives in this study. Selected physical and chemical properties are given in Table 3 (based on Table 2 of [5]) for the Tennessee and Mississippi soils.

Table 3. Selected physical and chemical properties for Tennessee, Mississippi, and USATHAMA reference soils.

Characteristics	Captina Silt Loam Roane County, Tennessee	McLaurin Sandy Loam Stone County, Mississippi	USATHAMA Reference
pH (distilled water)	5.33	4.92	6.2
pH ($CaCl_2$)	4.97	4.43	-
Total Organic Carbon (%)	1.49	0.66	1.84
Sand (%)	7.7	74.9	6.73
Silt (%)	62.5	20.4	67.2
Clay (%)	29.9	4.7	26.1
Nitrogen (mg/g)	0.18	1.3	1.3
Phosphorus (mg/g)	0.04	0.49	.003
Cation-exchange Capacity			
NH_4NO_3 extraction (meq/100 g)	1.15	10.15	-
NH_4CL extraction (meq/100 g)	0.65	10.05	-

2.2 Experimental Design

The explosive holding time study was designed as a complete factorial experimental design. An example of the factorial experiment is given in Fig. 1 for water samples. During the study some variations were made on the experimental plan:

1. A nominal low concentration of 100µg/L rather than 50µg/L was used for HMX in all three water samples.

2. A nominal high concentration of 2000µg/L rather than 1000µg/L was used for HMX in the ground water and surface water samples.

3. The low concentration explosives in the three water samples were not stored in extracts (4°C).

4. For soil samples, the maximum storage time varied with soil type and concentration level. The maximum storage days are given in Table 4.

Table 4. Maximum storage days for soil samples.

Soil Type	Low Concentration	High Concentration
USATHAMA	393	375
Tennessee	344	343
Mississippi	334	333

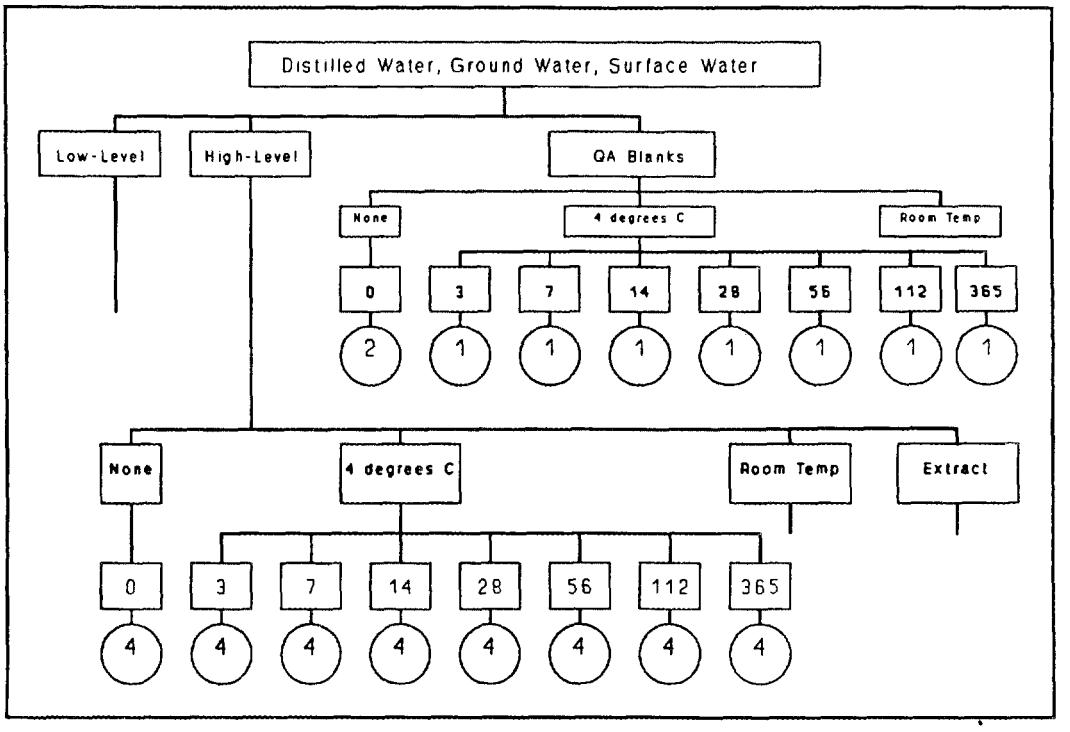

Fig. 1. Experimental design for explosives in water samples.

2.3 Analysis Procedure

Water samples were dispensed into 1-liter Tedlar gas sampling bags. One-liter Tedlar air sampling bags with dual stainless steel fittings (hose/valve fitting and replaceable septum, catalog number 231-01) were obtained from SKC, Inc. The water was allowed to degas for three days, and the gas was removed from the bag. Appropriate volumes of each stock explosive were introduced through the septum port using gas tight syringes. The contents of the Tedlar bag were mixed thoroughly by hand agitation for three minutes after which the bags were allowed to sit for thirty minutes. After mixing, samples were aliquotted into

7 mL vials by gravity flow. Teflon tubing (¼" x 6") was used to allow each vial to be filled from the bottom up, preventing mixing of the water with air. These sample storage vials were 7 mL borosilicate glass vials with teflon faced silicone septa and screw caps with holes purchased from Supelco (catalog number 2-3248). Each sample vial was completely filled with sample so that no headspace would remain after the sample vial was sealed. Each sample vial was sealed immediately with a Teflon faced septum and screw cap with hole, and stored at the appropriate temperature (4°C and 25°C).

Explosives in water samples were also stored as extracts on sorbent tubes which were XAD-4 cartridges (SKC, Inc., Eighty Four, PA). About 500 mL of water sample was passed through the XAD-4 cartridge, followed by distilled water. The XAD-4 cartridges were then stored at 4°C. Desorption was accomplished by drying each sorbent tube with nitrogen then adding a 4:1 ethyl ether-methanol solution. The solution was then evaporated to 1 mL and transferred to a 2 mL volumetric flask. Reagent grade water (Burdick & Jackson) was added to the volumetric flask to bring it to proper volume. After mixing, aliquots were pipetted into autosampler vials.

Soil samples were prepared by weighing 2 g aliquots of soil into 40 mL borosilicate glass vials with teflon faced silicone septa and screw caps with holes purchased from Shamrock Glass Company (catalog number 6-06K). Three days prior to spiking with explosives, the soil samples were wetted with 0.5 mL of reagent grade water (Burdick & Jackson) and agitated with a vortex mixer for 30 seconds. The soil samples were then stored in the dark at room temperature. This preparation step allowed bacterial growth to come to a steady state. On the day the holding time study was to begin, the soil samples were spiked with 0.5 mL of each individual explosive stock solution. These daily prepared stock solutions were acetonitrile solutions of either low explosive concentrations (10 μg/g) or high explosive concentrations (100 μg/g). The explosive soil samples were then agitated with a vortex mixer for 30 seconds and stored at the appropriate storage condition.

To extract the explosives for chemical analysis, the soil samples were ultrasonically extracted with 10 mL of acetonitrile for 18 hours in EPA VOA vials. These vials were then centrifuged for 10 minutes. From each vial, a 1 mL of extract was filtered through a 0.45 μm disposable teflon filter into a 2 mL volumetric flask for the low-level concentration samples or a 10 mL volumetric flask for the high-level concentration samples. Reagent grade water (Burdick & Jackson) was added to bring the volumetric flask to the proper volume. After mixing, aliquots were pipetted into autosampler vials.

Blank samples were aliquotted prior to addition of the stock explosive solutions. Blanks and samples were stored together in order to assess the possibility of cross contamination.

High-pressure liquid chromatography (HPLC) was the preferred analytical technique because the analytes were thermally unstable [*6-12*]. All water/soil explosive samples were eluted from an octadecylsilane (C_{18} or Zorbax-ODS, Mac-Mod, Inc., Chadds Ford, PA) reversed-phase HPLC column with a mixture of water/acetonitrile/methanol (50/25/25 v/v/v) flowing at 0.8 mL/min. The injection volume was 50 μL. An ultraviolet absorbance detector with a fixed filter (254 nm) was employed for quantifying the usual four analytes.

The order of elution (increasing time) was HMX, RDX, TNT, and 2,4-DNT. Chromatograms were recorded on both a conventional stripchart recorder (backup document) and a recording integrator (primary document). Experimentally-determined retention times, with windows of ±0.3 min, were used for the initial identification of candidate explosive peaks. Peak areas obtained from the primary document were used to quantification.

Identity confirmation for the test compounds was also provided by HPLC, but using a column (cyano groups chemically bounded to silica), which exhibits normal-phase behavior and therefore exhibits an almost inverted order of elution. In other words, the order of elution from the cyano column (increasing time) was 2,4-DNT, TNT, RDX, and HMX. A different eluent and flow rate (50/50 v/v water/methanol, 1.5 mL/min) compared to the reverse-phase column were employed, but the monitoring wavelength remains the same. Data were collected using the Winchester disk drive of the data system, and chromatograms were printed off-line. Again, peak areas were used for quantitation.

2.4 Explosive Concentrations

The response data from a chemical analysis of a water/soil sample are the area counts for the backgrounds, the external standards, and the four explosives. The explosive concentrations (C_{Exp}) were determined by comparison with external standard concentrations (C_{Std}) by:

$$C_{Exp} = C_{Std} \frac{Vol_{Std}}{Vol_{Exp}} \frac{Count_{Exp} - Bkgrd_{Exp}}{Count_{Std} - Bkgrd_{Std}}$$

Summary statistics for the explosive concentrations are tabulated in Appendix A and Appendix B for low-level and high-level concentrations in water samples and in Appendix C and Appendix D for low-level and high-level concentrations in soil samples. The appendices record the number of replicates (N), average concentration (Avg), and standard deviation (St. Dev.) for each day at the different level of the experimental factors. Note that the standard deviation is the standard deviation of the N replicate measurements and not the standard deviation of the average.

In addition, plots of the average explosive concentrations versus Time(Days) are given in the appendices for each level of the experimental factors. The average explosive concentrations are connected with a line to aid in viewing the graph and does not represent a least squares fit. The Time(Days) axis is on a logarithmic scale (base 10) which assist in distinguishing both the short-term explosive concentrations and long-term explosive concentrations. The logarithmic axis may cause distortions when viewing the graphs to judge explosive degradation. For example, Fig. 2 shows the average low-level

HMX concentrations for water samples stored at 4°C. Figure 2 uses both a linear and logarithmic Time(Days) axis which shows the effect of axis scaling. The logarithmic Time(Days) axis emphasizes the short-term explosive concentrations while the linear Time(Days) axis emphasizes the long-term explosive concentrations.

2.5 Outlier Measurements

The total number of chemical analyses used to determine maximum holding times were 1828 for water samples and 2092 for soil samples. Although 3,920 chemical analyses were performed, about 5.6% of the data for water samples and about 1.3% of the data for soil samples were not used to estimate the maximum holding time values. Potential outliers [*13*] were first identified by comparing the changes in the standard deviations of neighboringtime points for each matrix type and storage condition. Additional potential outliers were also identified by their large (e.g., > 2.5) studentized residuals for the zero-order and first-order regressions of concentrations vs storage times. Studentized residuals are the residuals (observed - predicted) divided by their standard deviations. An identified outlier value was marked in the data set not to be used for estimating maximum holding times after reexamining the corresponding HPLC chemical analysis. Chemical judgement for marking an identified outlier was based on (1) an analysis that resulted in an unusually low or high concentration due to contaminant peak interferance of poor separated peaks, or (2) an analysis corresponded to an incorrect analysis of a reference standard, or (3) an analysis that had been compromised by procedural problems (e.g., incorrect spiking concentration, HPLC pumps performing improperly, sample bottles not properly filled, data entry errors). A potential outlier found by the statistical procedure was not necessarily set aside after considering the chemical analysis.

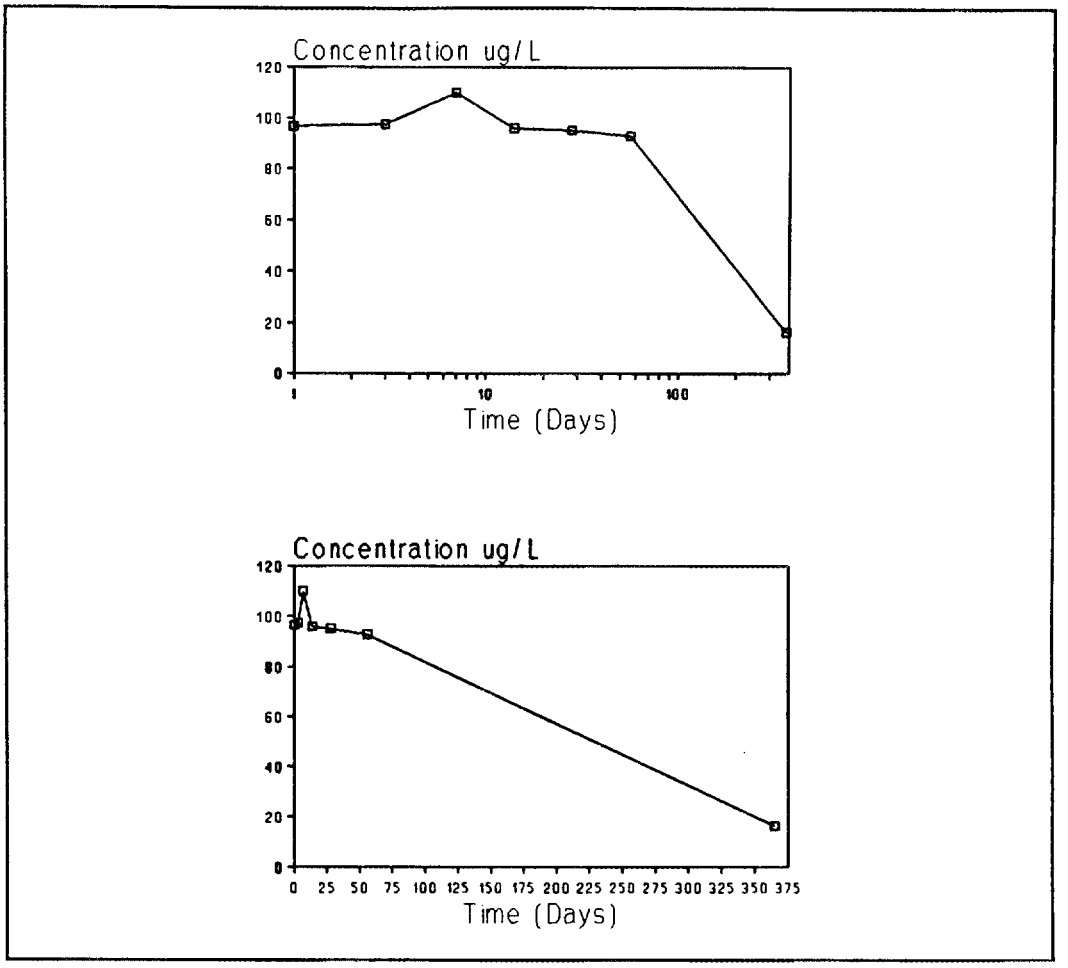

Fig. 2. Average low-level HMX concentrations for water samples stored at 4°C using both logarithm and linear scaling for the TIME (DAYS) axis.

3. RESULTS AND DISCUSSION

The results of this study are estimated maximum holding times (MHTs), which are the maximum times a sample can be held prior to analysis. Two statistical definitions were used to determine MHT criteria. The first definition was specified by the American Society for Testing and Materials [*14*, ASTM MHT]. The second definition was specified by Environmental Science and Engineering, Inc. [*15*, ESE MHT] for a holding time study conducted in cooperation with U.S. Environmental Protection Agency. The precise statistical details for these two definitions are given in Sect. 4. Both definitions are based on an approximating model for predicting concentration with time. The ASTM defines the MHT as the time the predicted concentration falls below the lower two-sided 99% confidence interval on the initial concentration. The ESE defines the MHT as the time the one-sided 90% confidence interval on the predicted concentration falls below a 10% change in the initial concentration. The main difference between the two definitions is the method of placing a lower bound on the initial concentration. The ESE MHTs are usually longer than the ASTM MHTs because decreasing the initial concentration by 10% is usually a larger reduction than the lower two-sided 99% confidence limit. The ASTM MHT definition is recommended for analytical methods with precision such that the lower bound on 99% confidence limit for an analyte concentration is less than 10% of the initial analyte concentration. Otherwise, using the ESE MHT definition would be more conservative.

The estimated MHTs depend on the different combination of factor levels. Although HMX and RDX usually have longer MHTs than TNT and DNT, specific comparisons depend on concentration level, sample matrix, and storage condition. Initially, the statistical method of a two-way analysis of variance (ANOVA) was used to determine statistically significant differences among the overall averages for storage condition and matrix type factors for each explosive and concentration combination. These differences among the averages were compared to the variation estimated from the factor interaction effects. The factor interaction effects were so large that some differences of more than 100 days could not be detected as being significant. For example, the ANOVA analysis shows no significant (5% significance level) difference between the average MHT's for storage conditions for 4°C (ASTM MHT = 225 days) and the average MHT's for room temperature storage (ASTM MHT = 75 days) for low-level concentrations of RDX in water samples. The factor interactions didn't provide an accurate estimate of the experimental error for comparison purposes because the MHTs vary substantially over the levels of storage condition and matrix type factors. Therefore, a difference of 30 days between MHTs was considered a practical difference from an operational standpoint for general comparisons of the levels of the experimental factors.

3.1 Comparisons for Water Samples

The ASTM MHTs and ESE MHTs are summarized in Table 5 and Table 6, respectively. A comparison of concentration levels shows the average MHTs for high-level concentrations are longer than the average MHTs for low-level concentrations for all explosives except RDX. For RDX, the average MHTs for low-level concentrations are longer than the average MHTs for high-level concentrations.

Table 5. ASTM MHTs in days for water samples.

Explosive	Storage Condition	Low-Level Concentration				High-Level Concentration			
		Distilled	Ground	Surface	Avg	Distilled	Ground	Surface	Avg
HMX	4°C	57	62	15	45	24	365	84	158
	Room	53	52	25	43	33	228	98	120
	Avg	55	57	20	44	29	297	91	139
RDX	4°C	365	287	23	225	112	90	75	92
	Room	78	125	19	74	53	112	57	74
	Avg	222	206	21	150	83	101	66	83
TNT	4°C	63	16	18	32	212	74	30	105
	Room	6	2	1	3	365	12	1	126
	Avg	35	9	10	18	289	43	16	116
DNT	4°C	2	4	14	7	98	365	43	169
	Room	43	3	1	16	114	71	64	83
	Avg	23	4	8	11	106	218	54	126

Table 6. ESE MHTs in days for water samples.

Explosive	Storage Condition	Low-Level Concentration				High-Level Concentration			
		Distilled	Ground	Surface	Avg	Distilled	Ground	Surface	Avg
HMX	4°C	83	50	37	57	26	365	273	221
	Room	78	71	32	60	36	365	365	255
	Avg	81	61	35	59	31	365	319	238
RDX	4°C	365	365	34	255	112	112	223	149
	Room	138	125	29	97	112	112	203	142
	Avg	252	245	32	176	112	112	213	146
TNT	4°C	125	29	17	57	365	123	41	176
	Room	7	1	1	3	365	13	1	126
	Avg	66	15	9	30	365	68	21	151
DNT	4°C	9	5	3	6	365	365	257	329
	Room	31	5	1	12	365	182	171	239
	Avg	20	5	2	9	365	274	214	284

HMX Low-Level Concentration

The average MHTs for the two storage conditions show no difference within 30 day criteria. The average ASTM MHTs show no differences between ground and distilled water samples but both averages are longer than the average ASTM MHTs for surface water. For average ESE MHTs, no differences are found between distilled and ground water samples, and ground and surface water samples. Average ESE MHTs are different for distilled and surface water samples. Shorter MHTs always occur for surface water samples.

HMX High-Level Concentrations

Comparisons depend on which MHT criteria is used. For ASTM, the average ASTM MHT for 4°C storage condition is longer than the average ASTM MHT for room temperature storage condition. This result is reversed for average ESE MHTs. However, all average MHTs for storage conditions are greater than or equal to 120 days. For water types, the average MHTs are different for all three water types. The average MHTs are ordered in decreasing magnitude by ground water, surface water, and distilled water. The biggest difference between the average ASTM and ESE MHTs are for surface water (ASTM MHT = 91 days, ESE MHT = 319 days). Note that distilled water gives the shortest average MHTs of about 30 days.

RDX Low-Level Concentrations

The average MHTs show a large decrease from a 4°C storage condition to room temperature storage condition. The average MHTs for distilled and ground water samples are longer and about the same magnitude. The average MHTs for surface water are much shorter than the average MHTs for distilled and water samples.

RDX High-Level Concentrations

The ESE MHTs for distilled and ground water samples have been truncated to 112 days because the experimental data for the last measurements (i.e., day = 365) were considered outliers. The average MHTs for the two storage conditions are about the same. For distilled and ground water samples, the average MHTs for high-concentration samples are shorter than the average MHTs for low-level concentration samples. However, for surface water samples, the average MHTs for high-concentration samples are longer than the results for low-level concentration samples. The average ASTM MHTs for the three water types are about the same with the results for surface water a little shorter than the results for ground and distilled water results. The average ESE MHTs show longer values but comparisons among the water samples cannot be made because of truncated values.

TNT Low-Level Concentrations

The average MHTs for low-level TNT concentration are much shorter than average MHTs for HMX and RDX which may suggest chemical transformation or biological degradation. Average MHTs for distilled water samples are longer than average MHTs for ground and distilled water samples which have about the same small values. Average MHTs are longer for the 4°C storage condition than average MHTs for room temperature storage condition. However, for ground and surface water samples, the individual MHTs are about the same.

TNT High-Level Concentrations

Shorter average MHTs occur for ground and surface water samples than for distilled water samples. For average ESE MHTs, the results for ground water samples are longer than

surface water samples. Average MHTs for storage temperature show an improvement for refrigeration only with the ESE MHT criteria.

DNT Low-Level Concentrations

All average MHTs for both the water samples and storage conditions are less than 30 days. The DNT samples all showed a rapid degradation.

DNT High-Level Concentrations

Average MHTs do not show the rapid degradation exhibited by low-level concentration results. Average MHTs show different results for the three water types but the relative order of ground water average MHTs and distilled water average MHTs depend on the MHT criteria. Average MHTs for surface water are always shorter than average MHTs for distilled and ground water samples.
The average MHTs for the 4°C storage condition is longer than the average MHTs for the room temperature storage condition.

3.2 Extract Storage for High-Level Concentrations of Water Samples

High-level concentrations of explosives in water samples were also stored as refrigerated (4°C) extracts. The maximum holding times estimated for these samples are given in Table 7.

Table 7. MHTs for high-level concentrations of explosives in water samples stored as extracts.

Explosive	ASTM Maximum Holding Time				ESE Maximum Holding Time			
	Distilled	Ground	Surface	Avg	Distilled	Ground	Surface	Avg
HMX	47	59	62	56	31	40	29	33
RDX	5	43	41	30	1	59	35	32
TNT	9	51	53	38	1	70	28	33
DNT	9	11	85	35	2	5	74	27
Avg	18	41	60	40	9	44	42	31

The average MHTs for the extract storage condition are much shorter, in general, than the average MHTs for the 4°C and room temperature storage conditions. Small MHTs (<14 days) occurred for RDX, TNT, and DNT in distilled water and DNT in ground water.

3.3 Comparisons for Soil Samples

The ASTM MHTs and ESE MHTs are summarized in Table 8 and Table 9, respectively. Comparisons of TNT and DNT explosives over low-level and high-level concentrations show the average MHTs for high-level concentrations are about the same for ASTM

MHTs or longer for ESE MHTs than the corresponding MHTs for low-level concentrations. For HMX and RDX, the reverse results occur. Average MHTs for low-level concentrations are longer than the average MHTs for high-level concentrations. The average MHTs over all factor levels for HMX, RDX, and DNT are about the same. For TNT, the overall average MHT is much shorter than the other three explosives.

HMX Low-Level Concentration

The average MHTs for USATHAMA soil are longer than the average MHTs for Tennessee and Mississippi soils, the latter two being about the same. The average MHTs for -20°C storage condition is shorter than average MHTs for 4°C storage conditions. For the room temperature storage condition, the average MHTs are shorter or about the same as average MHTs for the 4°C storage condition depending on the MHT criteria.

HMX High-Level Concentration

The average MHTs for USATHAMA soil are longer than the average MHTs for Tennessee and Mississippi soils. The average MHTs for Tennessee soil are about the same or slightly longer than the average MHTs Mississippi soil depending on the MHT criteria. The MHTs for the three storage conditions are about the same.

RDX Low-Level Concentration

The average MHTs for Mississippi and USATHAMA soils are longer than the average MHTs for Tennessee soil. The average ASTM MHT for Mississippi soil is longer than the average ASTM MHT for USATHAMA soil, but for ESE MHTs the results are equivalent. The average MHTs for -20°C and 4°C storage conditions are about 4 to 5 times longer than average MHTs for room temperature storage conditions. The average ASTM MHT for -20°C storage condition is longer than the ASTM MHT for 4°C but the average ESE MHTs are about the same for the two storage conditions.

RDX High-Level Concentration

The average MHTs for USATHAMA soil are 2 to 4 times longer than those for Tennessee and Mississippi soils which have about the same average MHTs. The three storage conditions have about the same average MHTs, except that the average ASTM MHT for 4°C is shorter than the average ASTM MHTs for the other storage conditions.

TNT Low-Level Concentration

The average MHTs for USATHAMA soil is much shorter than the average MHTs for Tennessee and Mississippi soils which have about the same average MHTs. The average MHTs for -20°C is much longer than the average MHTs for both 4°C and room temperature storage conditions. The average MHTs for 4°C and room temperature storage conditions shows rapid degradation under these storage conditions.

Table 8. ASTM MHTs for soil samples.

Explosive	Storage Condition	Low-Level Concentrations				High-Level Concentrations			
		USAT HAMA	Tenn essee	Miss issippi	Avg	USAT HAMA	Tenn essee	Miss issippi	Avg
HMX	-20°C	305	135	72	171	375	60	41	159
	4°C	293	318	79	230	375	56	52	161
	Room	274	24	294	197	344	53	51	149
	Avg	291	159	148	199	365	56	48	156
RDX	-20°C	393	85	334	271	375	60	50	162
	4°C	240	114	334	229	166	77	63	102
	Room	18	14	125	52	321	62	66	150
	Avg	217	71	264	184	287	66	60	138
TNT	-20°C	82	344	334	253	177	233	333	248
	4°C	49	40	0	30	13	48	149	70
	Room	0	0	0	0	1	14	47	21
	Avg	44	128	111	94	64	98	176	113
DNT	-20°C	393	68	244	235	97	135	73	102
	4°C	211	107	334	217	97	343	108	183
	Room	1	4	64	23	135	273	143	184
	Avg	202	60	214	158	110	250	108	156

Table 9. ESE MHTs for soil samples.

Explosive	Storage Condition	Low-Level Concentrations				High-Level Concentrations			
		USAT HAMA	Tenn essee	Miss issippi	Avg	USAT HAMA	Tenn essee	Miss issippi	Avg
HMX	-20°C	393	67	12	157	375	104	64	181
	4°C	393	344	13	250	375	106	76	186
	Room	393	6	334	244	375	111	73	186
	Avg	393	139	120	217	375	107	71	184
RDX	-20°C	393	134	334	287	375	152	123	217
	4°C	393	186	334	304	375	167	157	223
	Room	19	14	154	62	375	156	152	228
	Avg	268	111	274	218	375	158	144	226
TNT	-20°C	139	344	334	272	339	343	333	338
	4°C	10	6	0	5	27	56	183	89
	Room	0	0	0	0	1	4	64	23
	Avg	50	117	111	93	122	134	193	150
DNT	-20°C	393	93	334	273	199	209	137	182
	4°C	264	158	334	252	250	343	156	250
	Room	1	3	17	7	305	343	189	279
	Avg	219	85	228	177	251	298	161	237

TNT High-Level Concentration

The average MHTs for USATHAMA and Tennessee soils are shorter than the average MHTs for Mississippi soil. The average MHTs for Tennessee soil are slightly longer or about the same as the average MHTs for USATHAMA soil depending on the MHT criteria. The average MHTs for -20°C is much longer than the average MHTs for both 4°C and room temperature storage conditions. The average MHTs for 4°C is longer than the average MHTs for room temperature which can exhibit
rapid degradation.

DNT Low-Level Concentration

The average MHTs for Tennessee soil are much shorter than the average MHTs for Mississippi and USATHAMA soils which have about the same average MHTs. The large average MHTs for -20°C and 4°C storage conditions are about the same. The small average MHTs for room temperature storage condition indicates rapid degradation can occur.

DNT High-Level Concentration

Conclusions from comparisons of average MHTs for soil types depends on the MHT criteria. For the average ASTM MHTs, the result for Tennessee soil is about 2.5 times longer than the results for USATHAMA and Mississippi soils. For the average ESE MHTs, the results for both Tennessee and USATHAMA soils are about 1.5 times longer than the result for Mississippi soil. The average MHTs for -20°C are shorter than the average MHTs for both 4°C and room temperature storage conditions which have about the same average MHTs.

3.4 Conclusions and Recommendations

In reviewing the aqueous stability data, it is important to remember that data acquired in distilled water is for benchmark purposes, and has minimal environmental relevance. In general, for both the high and low concentrations of explosives, the constituents were more stable in groundwater than in surface water. In many, but not all cases, higher concentrations of explosives exhibited longer MHT's than the lower concentrations. Interestingly, in only one case was the extract more stable than the water sample itself, suggesting that performing this step early in the sample processing chain would have minimal benefit in aiding the stability of the explosives. In many cases, there were important differences in MHT's between extracts for two different water types, despite the fact that the MHT's would be expected to be quite similar. Operationally, since the data indicates that in many cases, 4°C. storage results in longer MHT's, one should be able to hold HMX and RDX contaminated ground water for up to 50 days under refrigeration prior to analysis. For surface water, about 30 days would be a preferred maximum pre-analytical holding time. For high levels of DNT and TNT, samples could be refrigerated for two weeks, but low levels of DNT - even refrigerated - will degrade very quickly. In fact, the MHT's for DNT and TNT are so short that the data suggests that any ground

water or surface water samples will not be representative of the water contamination levels, unless they are analyzed very quickly.

For the contaminated soils, the ESE criteria generally resulted in longer MHT's than those for the ASTM. However, the differences between the two may not be large enough to result in a practical difference in recommended sample handling. Interestingly, many of the explosive concentrations stored in Mississippi soil exhibited significant decreases after about a month in storage. The concentration levels then returned to values near their initial concentration levels as the study progressed. The reason for this phenomena can only be speculated. As with the water samples, the higher concentrations of explosives tended to have longer MHT's than the lower concentration samples. Among the different soils, no clear pattern emerges. The HMX and RDX do tend to be more stable in the USATHAMA soil. However, the variation of the MHT's among these three soils makes extrapolation of constituent behavior to other soils difficult. Although MHT's depend on soil types, a conservative guideline would be to use the minimum MHT for the three soils at each storage condition and concentration levels. Operationally, soil samples contaminated with HMX, RDX, and DNT should be stored immediately at 4°C or -20°C. Soil samples contaminated with TNT should be frozen immediately at -20°C. With these sampling procedures, the data suggests that explosive contaminated soils can be stored at refrigerated or frozen temperatures for six weeks, with reasonable assurance of sample stability.

Table C.2 RDX summary statistics for low-level concentrations (µg/g) in soil samples.

Soil Storage		Num Avg St Dev	Day								All Days
Soil Type	Store Cond		0	3	7	14	28	56	112	≥333	
USATHAMA	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	9.9	.	.	.	.	.	.	.	9.9
		St Dev	0.3	.	.	.	.	.	.	.	0.3
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	8.5	10.3	9.7	9.5	8.9	9.9	9.4	9.5
		St Dev	.	0.5	0.7	0.2	0.3	0.1	0.2	0.5	0.7
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	8.6	10.0	9.9	9.8	9.1	8.2	9.0	9.2
		St Dev	.	0.1	0.3	0.1	0.2	0.2	1.0	0.4	0.8
	Room	Num	.	4.0	4.0	4.0	4.0	3.0	3.0	4.0	26.0
		Avg	.	8.7	9.9	9.2	7.9	1.1	0.0	0.0	5.6
		St Dev	.	0.2	0.4	0.5	0.1	0.9	0.0	0.0	4.3
Tennessee	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	9.0	.	.	.	.	.	.	.	9.0
		St Dev	0.3	.	.	.	.	.	.	.	0.3
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	2.0	26.0
		Avg	.	9.5	9.3	9.3	7.8	9.1	9.8	10.7	9.2
		St Dev	.	0.2	0.3	0.2	0.2	0.7	0.3	0.3	0.8
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	2.0	26.0
		Avg	.	9.4	8.8	9.4	8.0	9.2	8.6	7.9	8.8
		St Dev	.	0.2	0.3	0.2	0.7	0.7	0.9	0.7	0.7
	Room	Num	.	4.0	4.0	4.0	4.0	3.0	4.0	3.0	26.0
		Avg	.	9.2	8.7	8.6	5.9	1.0	0.0	0.7	5.2
		St Dev	.	0.4	0.2	0.4	0.5	1.6	0.0	0.6	4.0
Mississippi	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	10.3	.	.	.	.	.	.	.	10.3
		St Dev	0.7	.	.	.	.	.	.	.	0.7
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	9.9	10.1	8.2	8.4	9.3	10.5	9.8	9.5
		St Dev	.	0.4	1.0	0.4	0.4	0.2	0.4	0.4	0.9
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	10.4	10.6	8.8	8.0	9.4	10.2	9.6	9.6
		St Dev	.	1.1	0.6	0.9	0.1	0.3	0.2	0.3	1.0
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	10.4	9.8	8.4	8.0	8.6	8.6	8.1	8.9
		St Dev	.	0.3	0.2	0.5	0.6	0.4	0.6	0.6	1.0

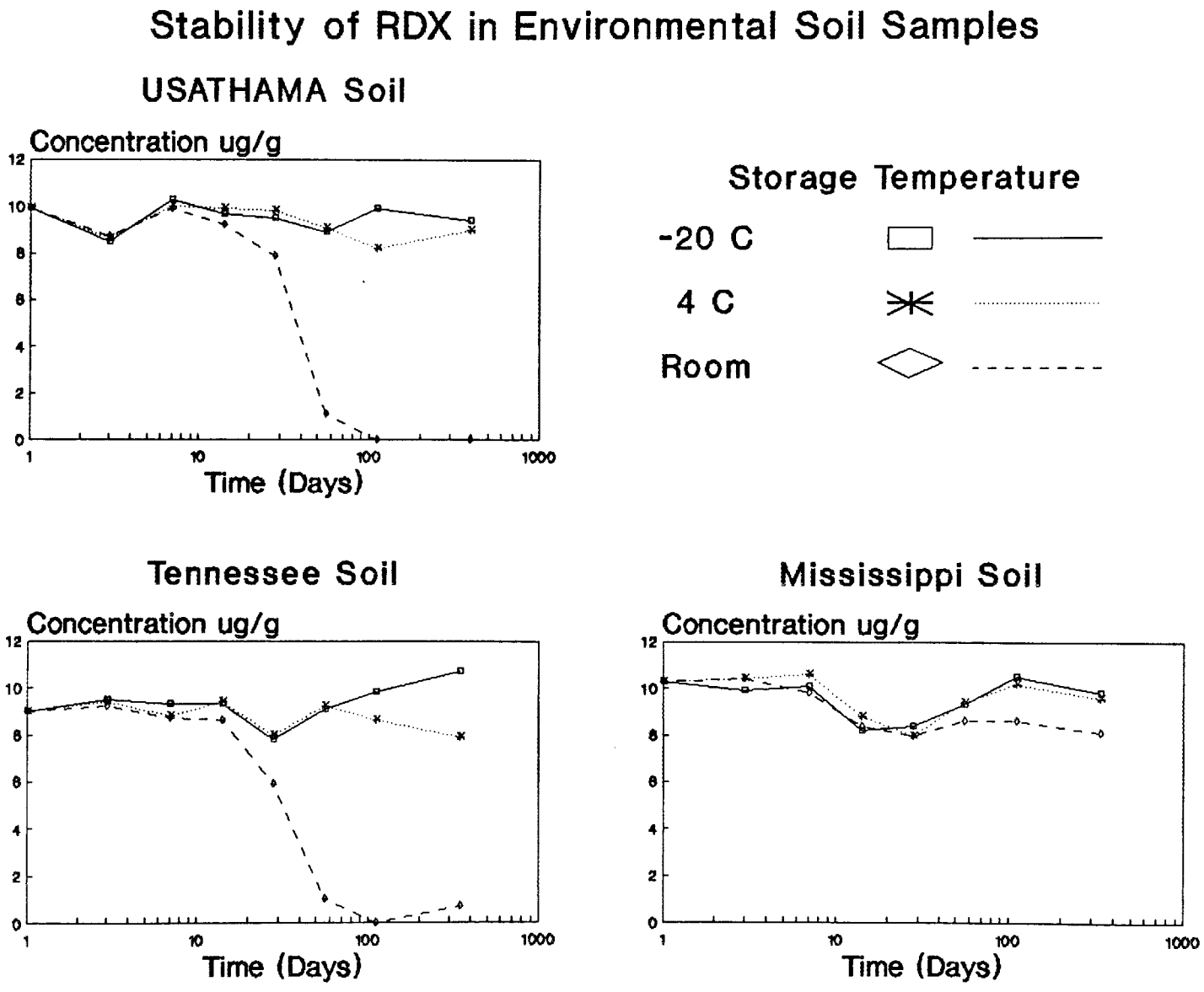

Fig. C.2 Low-level RDX in soil samples.

4. DETERMINATION OF MAXIMUM PRE-ANALYTICAL HOLDING TIMES BY STATISTICAL METHODS

The purpose of the work described herein was to determine the maximum length of time which a sample can be held without processing prior to analysis for a specific contaminant. One obvious criterion for "how long is too long" is the point in time where the concentration of the target constituent begins to fall outside the range of acceptability limits for the recovery of a matrix spike. However, the EPA CLP matrix spike recovery limit range can be so large that unacceptably large changes in target analyte concentration can occur without exceeding the range limits. Therefore, another approach was developed which established more stringent criteria for the concept of a pre-analytical holding time. These criteria were defined in terms of the time at which the measured sample concentration falls outside confidence interval boundaries. These boundaries were calculated from a mathematical model that approximated the change in sample concentration with time. The two primary definitions used for the MHT criteria were those by the American Society for Testing and Materials (ASTM) and by Environmental Science and Engineering, Inc. (ESE), the latter developed in cooperation with EPA's Environmental Monitoring and Support Laboratory.

4.1 Approximating Models

Maximum holding time (MHT) was defined as the maximum period of time during which a properly collected and stored sample can be stored before some degradation of the analyte occurs in the sample matrix. Calculating the MHT depends on the approximating model used to predict the expected concentration for any time during the experimental period (i.e., 365 days). Two approximating models were considered. One was based on zero-order kinetics and the other on first-order kinetics. The zero-order approximating model represents a constant change in the expected concentration with time. The first-order approximating model represents the change in the expected concentration with time which depends upon the concentration level. These two approximating models are expressed mathematically as:

Zero-Order Approximating Model:

$$dE(C)/dD = \beta,$$

or

$$E(C) = \gamma + \beta D,$$

where

$dE(C)/dD$	=	the change in the expected concentration (μg/L) with respect to time (D, days),
$E(C)$	=	the expected concentration on a specified day,
γ	=	the intercept or concentration on day = 0,
β	=	the slope or change in the expected concentration per day.

First-Order Approximating Model:

$$dE(C)/dD = \beta C,$$

or

$$E(C) = \gamma \exp(\beta D),$$

or

$$\ln[E(C)] = \ln(\gamma) + \beta D,$$

where

ln	=	the natural logarithm (i.e., base e),
β	=	the slope is now the change in the logarithm of the expected concentration per day.

The two unknown parameters γ and β are estimated from the holding time data using the method of least squares [*16*]. The method of least squares estimates the unknown parameters by minimizing the sum of squared differences between the observed concentrations and the predicted concentrations. The calculations to estimate the unknown parameters were made using the SAS [*17*] computer programming system. The estimated approximating models are:

Estimated Approximating Models:

$$C_p = C_0 + BD \text{ (zero-order)},$$

$$C_p = C_0\exp(BD) \text{ (first-order)},$$

where

C_p	=	the predicted concentration or estimated expected concentration,
C_0	=	the estimated concentration on day 0,
B	=	the estimated slope for either the expected concentration or the logarithm of the expected concentration.

The approximating model which had the smallest value for the sum of squares of the residuals (i.e., observed - predicted):

$$\Sigma(C - C_p)^2$$

was chosen to represent the behavior of the expected concentrations.

4.2 MHT Definitions

The ASTM and the ESE definitions were used to calculate the MHT criteria after choosing the approximating model for the expected concentrations. The ASTM definition [*14*] is described in volume 11.02 of the 1986 Annual Book of ASTM Standards. For the purposes of this study, the ASTM definition was applied as follows:

ASTM

1. Fit the appropriate approximating model to the holding time data by the method of least squares.

2. Estimated the intercept, C_0, and its standard deviation, S_0.

3. Calculate the two-sided 99% confidence interval on the intercept (i.e. $C_0 \pm t(df,0.005)S_0$, where $t(df,0.005)$ is the 99.5 percentile point of the t-distribution with df = degrees of freedom and S_0 is the standard deviation of the intercept).

4. The ASTM MHT is the time at which the approximating model is equal to the value of the lower confidence limit on the intercept if the estimated slope is negative. For positive estimated slopes, the MHT is the time at which the approximating model is equal to the value of the upper confidence limit on the intercept. MHT can be calculated by:

$$MHT = t(df,0.005)S_0/|B|,$$

where

$$|B| = \text{absolute value of the slope.}$$

5. Estimated MHT values greater than the time of the experimental study are set equal to maximum storage time (e.g., 365 days or Table 4).

This working definition differs slightly from the exact ASTM definition because this holding time study did not employ the same experimental design as recommended by ASTM. The differences between the two definitions are that confidence intervals on the intercepts are used rather than the confidence intervals on the mean of ten replicate concentrations measured on day 0 (it was impractical to make ten replicate analyses within one day). Also, the intercept and slope of the approximating models were estimated by the method of least squares rather than the "best graphical fit" of the average concentration for each day. Figure 3 illustrates the ASTM method for estimating the MHT for low-level concentrations of HMX in distilled water at room temperature.

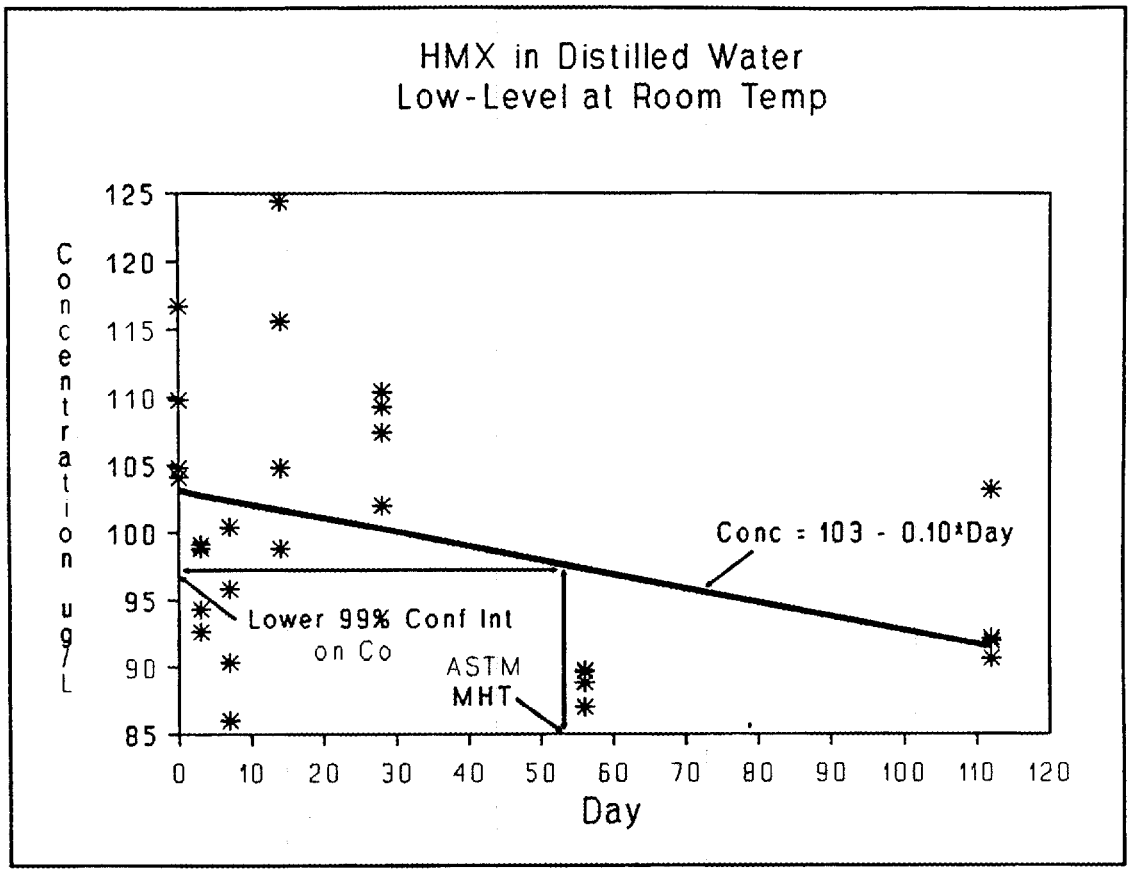

Fig. 3. ASTM method for estimating maximum holding time from data (stars) for low-levelconcentrations of HMX in distilled water at room temperature.

A second definition for MHT was used in holding time studies on inorganic analytes conducted by Environmental Science and Engineering, Inc. (ESE) in cooperation with EPA's Environmental Monitoring and Support Laboratory [*15*]. The ESE definition is based on intersecting a 10% change in the intercept with a one-sided 90% confidence interval on the predicted concentration. Figure 4 portrays the ESE method for estimating maximum holding times for the same case examined in Figure 3. For this holding time study, the ESE definition of MHT was applied as follows:

ESE

1. Fit the appropriate approximating model to the holding time data by the method of least squares.

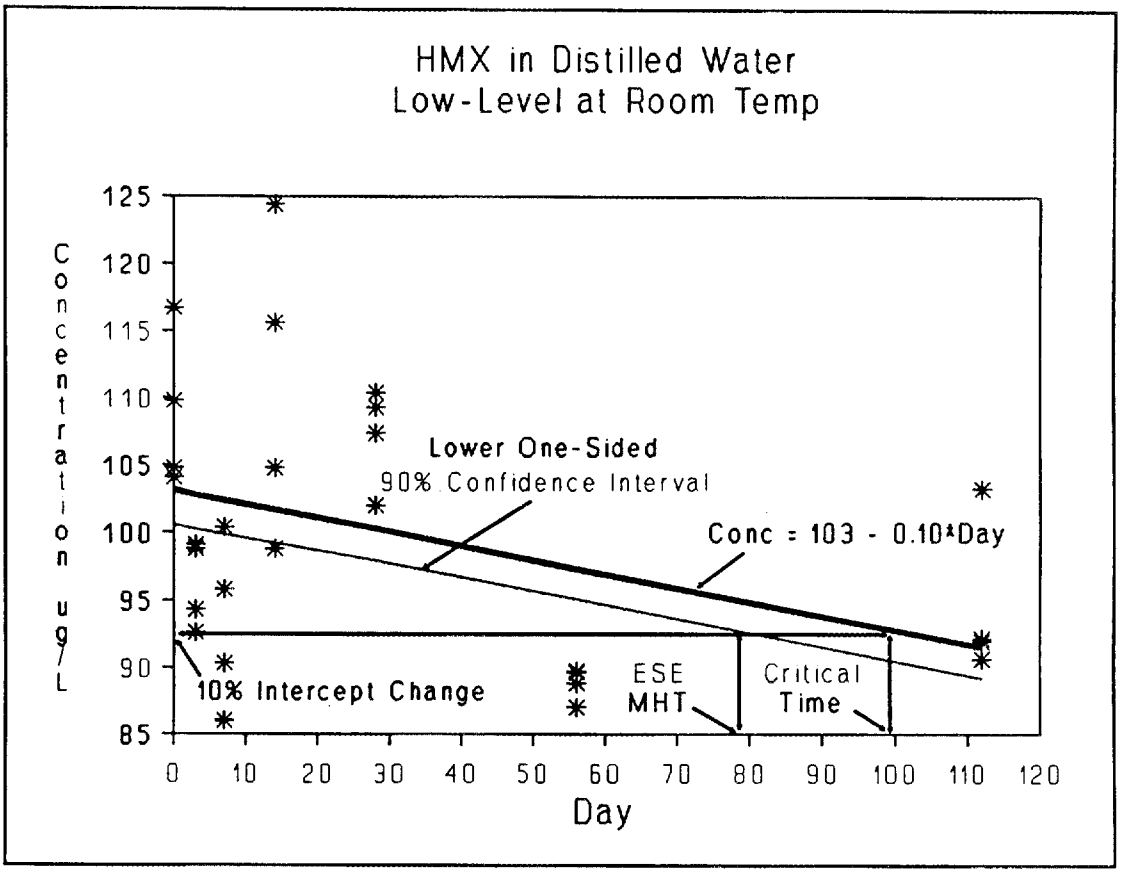

Fig. 4. ESE Method for estimating maximum holding time from data (Stars) for low-level concentrations of HMX in distilled water at room temperature.

2. Test that the slope is significantly different than zero with a two-sided t-test at 10% significance level (e.g., $|B| \geq t(df,0.05)S_1$, where t(df,0.05) is the 95 percentile point of the t-distribution with df = degrees of freedom and S_1 is the standard deviation of the slope). If the slope is not significantly different than zero then set MHT equal to the maximum storage time (e.g., 365 days or Table 4).

3. Construct a ± 10% interval about the intercept [e.g., (0.9C0, 1.1C0)]. Test that the 10% change is outside the 90% confidence interval on C_0 with a two-sided t-test at the 10% significance level [e.g., $0.1C_0 \geq t(df,0.05)S_0$ for zero-order, and $-\ln(.9) \geq t(df,0.05)S_0$ or $\ln(1.1) \geq t(df,0.05)S_0$ for first-order where t(df,0.05) is the 95 percentile point of the t-distribution with df = degrees of freedom and S_0 is the standard deviation of the intercept].

4. If a 10% change is not outside the 90% confidence interval, calculate the concentration change (i.e., $C_0 \pm KC_0$) that does occur outside the limits:

$$K = t(df,0.05)S_0/C_0 \text{ for zero-order,}$$

$$K = 1 - \exp[-t(df,0.05)S_0] \text{ for } B < 0 \text{ and first-order, and}$$

$$K = \exp[t(df,0.05)S_0] - 1 \text{ for } B > 0 \text{ and first-order.}$$

If K > 0.15, the two approximating models are usually not appropriate for estimating the expected concentrations. The MHT can't be estimated with these models and other approximating models must be investigated (see Appendix E). However, large variability in the data may also cause K > 0.15.

5. Calculate the critical time (C_T) when the predicted concentration line intersects the significant concentration change ($0.10 \leq K \leq 0.15$) by:

$$C_T = KC_0/|B| \text{ for zero-order,}$$

$$C_T = \ln(1 - K)/B \text{ for } B < 0 \text{ and first-order, and}$$

$$C_T = \ln(1 + K)/B \text{ for } B > 0 \text{ and first-order.}$$

6. The MHT is defined as the one-sided lower 90% confidence interval on CT and can be calculated by:

$$MHT = C_T - t(df,0.10)[Var(C_T)]^{1/2},$$

where,

t(df,0.10) = the 90 percentile point of the t-distribution,

and

$Var(C_T)$ = the variance of C_T approximated by:

$$Var(C_T) = C_T^2[Var(C_0)/C_0^2 + Var(B)/B^2 - 2Cov(C_0,B)/BC_0].$$

with Var, and Cov indicating estimated variance and covariance, respectively.

The one-sided lower 90% confidence interval on C_T is equivalent to the day the one-sided lower(upper) 90% confidence interval on the predicted concentration has the value $C_0 \pm KC_0$. For this equivalent definition, the MHT is the smallest solution to a quadratic equation:

$$a(MHT)^2 + b(MHT) + c = 0, \text{ so}$$

$$MHT = -(b/2a) - [b^2 - 4ac]^{1/2}/2a.$$

The coefficients for the two approximating models are:

zero-order:

$$a = B^2 - t^2(df,0.10)Var(B)$$

$$b = -2[|B|C_0 + t^2(df,0.10)Cov(C_0,B)], \text{ and}$$

$$c = (KC_0)^2 - t^2(df,0.10)Var(C_0).$$

first-order:

$$a = B^2 - t^2(df,0.10)Var(B),$$

$$b = -2[BG + t^2(df,0.10)Cov(C_0,B)], \text{ and}$$

$$c = G^2 - t^2(df,0.10)Var(C_0).$$

where,

$$G = \ln(1 + BK/|B|).$$

7. Estimated MHT values greater than the time of the experimental study are set equal to the maximum storage time (e.g., 365 days or Table 4).

The MHT values for explosives in water samples are given in Table 10 for low-level concentrations and in Table 11 for high-level concentrations. Tables 12 and 13 give the MHT values for explosives in soil samples for low-level and high-level concentrations, respectively. In addition, the tables include estimated values the intercept and the slope for the zero-order and first-order approximating models. The two models are identified by expressing the slope for the zero-order model as a number with four decimal places (e.g., -0.1038) and by expressing the slope for the first-order model as a number in exponential notation (e.g., -9.885E-04). The different values of MHT for the ASTM and ESE definitions depend on the variability of the data. This variability ultimately affects the width of the 99% confidence interval used for the ASTM definition, but does not affect the 10% intercept change used for the ESE definition. Therefore, when variability is high, the confidence interval will be broader than the 10% change. When variability is low, the confidence interval will be narrower than the 10% change.

Table 10. Estimated MHT days for low-level concentrations of explosives in water samples. First-order approximating models have slope values "B" expressed in exponential notation.

Explosive Compound	Water Type	Storage Condition	C_0	B	ASTM MHT	ESE MHT
HMX	Distilled	4°C	107	-9.885E-04	57	83
HMX	Distilled	Room	103	-0.1038	53	78
HMX	Ground	4°C	108	-0.1424	62	50
HMX	Ground	Room	106	-0.1159	52	71
HMX	Surface	4°C	102	-0.2334	15	37
HMX	Surface	Room	105	-0.2484	25	32
RDX	Distilled	4°C	51	-0.0011	365	365
RDX	Distilled	Room	52	-0.0287	78	138
RDX	Ground	4°C	50	0.0060	287	365
RDX	Ground	Room	(a)	(a)	125	125
RDX	Surface	4°C	52	-0.1173	23	34
RDX	Surface	Room	53	-0.1419	19	29
TNT	Distilled	4°C	54	-0.0346	63	125
TNT	Distilled	Room	55	-1.103E-02	6	7
TNT	Ground	4°C	54	-0.1498	16	29
TNT	Ground	Room	(a)	(a)	2	1
TNT	Surface	4°C	(a)	(a)	18	17
TNT	Surface	Room	(a)	(a)	1	1
DNT	Distilled	4°C	(a)	(a)	2	9
DNT	Distilled	Room	(a)	(a)	43	31
DNT	Ground	4°C	(a)	(a)	4	5
DNT	Ground	Room	(a)	(a)	3	5
DNT	Surface	4°C	52	-1.058E-02	14	3
DNT	Surface	Room	(a)	(a)	1	1

(a) MHT estimated by an alternative model (See Table E.2).

Table 11. Estimated MHT days for high-level concentrations of explosives in water samples. First-order approximating models have slope values "B" expressed in exponential notation.

Explosive Compounds	Water Type	Storage Condition	C_0	B	ASTM MHT	ESE MHT
HMX	Distilled	4°C	(a)	(a)	24	26
HMX	Distilled	Room	(a)	(a)	33	36
HMX	Distilled	Extract	437	-0.8668	47	31
HMX	Ground	4°C	1940	-0.0307	365	365
HMX	Ground	Room	1888	0.3372	228	365
HMX	Ground	Extract	1535	-2.3800	59	40
HMX	Surface	4°C	2003	-2.914E-04	84	273
HMX	Surface	Room	2003	-1.940E-04	98	365
HMX	Surface	Extract	1761	-3.1474	62	29
RDX	Distilled	4°C	978	0.0161	112	112[b]
RDX	Distilled	Room	997	-0.4036	53	112[b]
RDX	Distilled	Extract	(a)	(a)	5	1
RDX	Ground	4°C	975	-0.2705	90	112[b]
RDX	Ground	Room	972	-0.1632	112	112[b]
RDX	Ground	Extract	953	-1.2468	43	59
RDX	Surface	4°C	976	3.505E-04	75	223
RDX	Surface	Room	970	4.014E-04	57	203
RDX	Surface	Extract	981	-1.8772	41	35
TNT	Distilled	4°C	999	0.1207	212	365
TNT	Distilled	Room	1012	0.0454	365	365
TNT	Distilled	Extract	(a)	(a)	9	1
TNT	Ground	4°C	1042	-6.826E-04	74	123
TNT	Ground	Room	(a)	(a)	12	13
TNT	Ground	Extract	921	-1.0132	51	70
TNT	Surface	4°C	(a)	(a)	30	41
TNT	Surface	Room	(a)	(a)	1	1
TNT	Surface	Extract	806	-2.084E-03	53	28
DNT	Distilled	4°C	992	0.1885	98	365
DNT	Distilled	Room	996	0.1917	114	365
DNT	Distilled	Extract	(a)	(a)	9	2
DNT	Ground	4°C	992	-0.0430	365	365
DNT	Ground	Room	976	-4.768E-04	71	182
DNT	Ground	Extract	(a)	(a)	11	5
DNT	Surface	4°C	993	-3.636E-04	43	257
DNT	Surface	Room	929	-5.147E-04	64	171
DNT	Surface	Extract	(a)	(a)	85	74

(a) MHT estimated by an alternative model (See Table E.2).
(b) Day = 365 not used for the regression.

Table 12. Estimated MHT days for low-level concentrations of explosives in soil samples. First-order approximating models have slope values "B" expressed in exponential notation.

Explosive Compound	Soil Type	Storage Type	C_0	B	ASTM MHT	ESE MHT
HMX	USATHAMA	-20°C	8	0.0025	305	393
HMX	USATHAMA	4°C	8	0.0025	293	393
HMX	USATHAMA	Room	7	-0.0034	274	393
HMX	Tennessee	-20°C	7	7.746E-04	135	67
HMX	Tennessee	4°C	7	-0.0024	318	344
HMX	Tennessee	Room	7	-6.102E-03	24	6
HMX	Mississippi	-20°C	6	0.0134	72	12
HMX	Mississippi	4°C	6	0.0129	79	13
HMX	Mississippi	Room	6	0.0035	294	334
RDX	USATHAMA	-20°C	10	-0.0002	393	393
RDX	USATHAMA	4°C	9	-1.955E-04	240	393
RDX	USATHAMA	Room	(a)	(a)	18	19
RDX	Tennessee	-20°C	9	5.239E-04	85	134
RDX	Tennessee	4°C	9	-0.0033	114	186
RDX	Tennessee	Room	(a)	(a)	14	14
RDX	Mississippi	-20°C	9	0.0013	334	334
RDX	Mississippi	4°C	10	-0.0003	334	334
RDX	Mississippi	Room	9	-4.828E-04	125	154
TNT	USATHAMA	-20°C	9	-0.0050	82	139
TNT	USATHAMA	4°C	6	-3.245E-03	49	10
TNT	USATHAMA	Room	(a)	(a)	0	0
TNT	Tennessee	-20°C	8	-0.0007	344	344
TNT	Tennessee	4°C	6	-5.647E-03	40	6
TNT	Tennessee	Room	(a)	(a)	0	0
TNT	Mississippi	-20°C	8	-0.0011	334	334
TNT	Mississippi	4°C	(a)	(a)	0	0
TNT	Mississippi	Room	(a)	(a)	0	0
DNT	USATHAMA	-20°C	9	-0.0003	393	393
DNT	USATHAMA	4°C	9	-2.403E-04	211	264
DNT	USATHAMA	Room	(a)	(a)	1	1
DNT	Tennessee	-20°C	9	7.738E-04	68	93
DNT	Tennessee	4°C	9	-4.633E-04	107	158
DNT	Tennessee	Room	(a)	(a)	4	3
DNT	Mississippi	-20°C	8	0.0043	244	334
DNT	Mississippi	4°C	8	-0.0011	334	334
DNT	Mississippi	Room	7	-2.347E-03	64	17

(a) MHT's estimated by an alternative model (See Table E.3).

Table 13. Estimated MHT days for high-level concentrations of explosives in soil samples. First-order approximating models have slope values "B" expressed in exponential notation.

Explosive Compound	Soil Type	Storage Condition	C_0	B	ASTM MHT	ESE MHT
HMX	USATHAMA	-20°C	93	-0.0076	375	375
HMX	USATHAMA	4°C	94	-0.0056	375	375
HMX	USATHAMA	Room	93	0.0079	344	375
HMX	Tennessee	-20°C	84	7.392E-04	60	104
HMX	Tennessee	4°C	87	7.357E-04	56	106
HMX	Tennessee	Room	86	7.163E-04	53	111
HMX	Mississippi	-20°C	82	0.1024	41	64
HMX	Mississippi	4°C	83	0.0861	52	76
HMX	Mississippi	Room	82	0.0878	51	73
RDX	USATHAMA	-20°C	89	-0.0066	375	375
RDX	USATHAMA	4°C	90	-1.251E-04	166	375
RDX	USATHAMA	Room	90	0.0072	321	375
RDX	Tennessee	-20°C	86	5.221E-04	60	152
RDX	Tennessee	4°C	89	4.577E-04	77	167
RDX	Tennessee	Room	88	5.097E-04	62	156
RDX	Mississippi	-20°C	87	6.543E-04	50	123
RDX	Mississippi	4°C	88	5.020E-04	63	157
RDX	Mississippi	Room	87	5.149E-04	66	152
TNT	USATHAMA	-20°C	85	-0.0165	177	339
TNT	USATHAMA	4°C	82	-3.241E-03	13	27
TNT	USATHAMA	Room	(a)	(a)	1	1
TNT	Tennessee	-20°C	91	-0.0257	233	343
TNT	Tennessee	4°C	89	-1.397E-03	48	56
TNT	Tennessee	Room	84	-1.023E-02	14	4
TNT	Mississippi	-20°C	82	-0.0060	333	333
TNT	Mississippi	4°C	85	-0.0315	149	183
TNT	Mississippi	Room	81	-1.273E-03	47	64
DNT	USATHAMA	-20°C	87	3.732E-04	97	199
DNT	USATHAMA	4°C	87	2.973E-04	97	250
DNT	USATHAMA	Room	87	2.248E-04	135	305
DNT	Tennessee	-20°C	88	3.212E-04	135	209
DNT	Tennessee	4°C	90	0.0093	343	343
DNT	Tennessee	Room	88	-0.0134	273	343
DNT	Mississippi	-20°C	84	5.579E-04	73	137
DNT	Mississippi	4°C	84	4.531E-04	108	156
DNT	Mississippi	Room	82	3.481E-04	143	189

(a) MHT estimated by an alternative model (See Table E.3).

The MHT values identified by (a) in Tables 8-11 indicate that neither the zero-order nor the first-order approximating models gave appropriate results. These special cases represent 19 cases for water samples and 9 cases for soil samples. The difficulty with fitting the 28 special cases is that the concentrations decreased rapidly with time to a zero or near-zero level after a possible initial period of apparent stability. Three approximating models (e.g., log-term, inverse-term, and cubic spline) were investigated in an attempt to fit the data. These models are discussed more completely in Appendix E. Half of the approximations were obtained with a cubic spline model which fits a sigmoidal shaped curve between the initial and final concentrations. The log-term model (i.e., 11 cases) and the inverse-term model (i.e., 3 cases) approximated rapid decreases in concentrations

From the results of these statistical analyses, it can be shown that each analyte has a MHT which can be established. Obviously, these are not related to the administrative/political aspects of the environmental analysis. Therefore, it is necessary to consider the end use of the data when determining the maximum holding time.

5. CONCLUSIONS

From a regulatory point of view, extension of sample holding times without compromising data quality would reduce the cost associated with waste site characterization and remedial action by reducing the possibility that additional sampling will be required due to the failure to meet the holding times. This has an important economic effect on investigations carried out under SARA. From the point of view of RCRA, where quarterly groundwater monitoring is carried out, preservation of the samples would allow direct comparison with the samples collected during the subsequent quarter. Since regulatory decisions are made based on changes in the water or soil concentrations of contaminants, this would be important in reducing analytical variability. From the standpoint of the regulated community, the ability to preserve and archive important samples for later verification would greatly reduce the possibility of error in regulatory decision-making, and would certainly eliminate the need for resampling.

From the analytical standpoint, improvements in the quality assurance process are expected. This study has shown that most explosives in water and soil samples are stable at refrigerator temperatures for a sufficient time to allow distribution and analysis. Thus for the first time, stable, long-term performance evaluation materials can be prepared and submitted in a truly blind fashion to participating analytical laboratories. Studies of interlaboratory performance of this method can now be performed. Controls can also be prepared for use in field sampling. Finally, an estimate of the intralaboratory variability in the analytical method over long periods of time is now possible.

Although different concentration levels and soil types were used to estimate maximum holding times, these factors are not necessarily known prior to sampling and chemical analysis. Therefore, the choice may not be clear in practice which maximum holding time to select from Tables 5-8 because of unknown factor combinations. The recommended maximum holding times in Table 14 are established for the situation when little is known

about concentration levels or soil types. These recommended maximum holding times are conservative estimates made after reviewing the MHTs for all factor combinations and the explosive summary statistics in Appendix A, B, C, and D.

Table 14. Recommended maximum holding tmes.

Explosive	Storage Condition	Matrix Type	Recommended MHT (days)
HMX/RDX	4°C	Ground Water	50
HMX/RDX	4°C	Surface Water	30
TNT	4°C	Ground Water	16
DNT	4°C	Ground Water	4
TNT/DNT	4°C	Surface Water	14
HMX	4°C	Soil	52
RDX	4°C	Soil	63
TNT[a]	-20°C	Soil	233
DNT	4°C	Soil	107

(a) Immediate freezing recommended.

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APPENDIX A

Explosive Summary Statistics for Low-Level Concentrations (μg/L) in Water Samples.

Table A.1 HMX summary statistics for low-level concentrations (µg/L) in water samples.

Water Storage		Num Avg St Dev	Day								All Days
Water Type	Store Cond		0	3	7	14	28	56	112	365	
Distilled	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	108.9	.	.	.	.	.	.	.	108.9
		St Dev	5.8	.	.	.	.	.	.	.	5.8
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	100.2	114.9	111.5	103.8	88.6	102.7	74.6	99.5
		St Dev	.	12.8	13.4	4.6	5.8	1.3	7.7	6.1	15.0
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	96.2	93.1	110.9	107.3	88.8	94.4	65.1	93.7
		St Dev	.	3.2	6.3	11.4	3.7	1.3	5.9	11.3	15.4
Ground	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	108.9	.	.	.	.	.	.	.	108.9
		St Dev	6.7	.	.	.	.	.	.	.	6.7
	4°C	Num	.	4.0	3.0	4.0	4.0	4.0	4.0	4.0	27.0
		Avg	.	88.1	136.4	102.8	104.7	90.5	101.8	54.2	95.5
		St Dev	.	10.0	6.6	15.0	3.8	3.5	6.5	8.3	23.5
	Room	Num	.	3.0	3.0	4.0	4.0	4.0	4.0	4.0	26.0
		Avg	.	94.5	109.1	104.5	105.1	88.6	105.3	61.2	95.0
		St Dev	.	3.9	8.4	11.6	2.2	1.4	5.5	11.3	17.4
Surface	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	96.6	.	.	.	.	.	.	.	96.6
		St Dev	4.1	.	.	.	.	.	.	.	4.1
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	.	4.0	24.0
		Avg	.	97.4	110.0	96.0	95.2	92.9	.	16.3	84.7
		St Dev	.	1.9	6.1	2.4	3.2	1.9	.	1.3	31.8
	Room	Num	.	4.0	3.0	4.0	4.0	4.0	.	4.0	23.0
		Avg	.	99.8	124.4	104.5	90.9	89.8	.	14.1	85.6
		St Dev	.	2.0	12.7	1.7	1.3	2.1	.	5.7	35.5

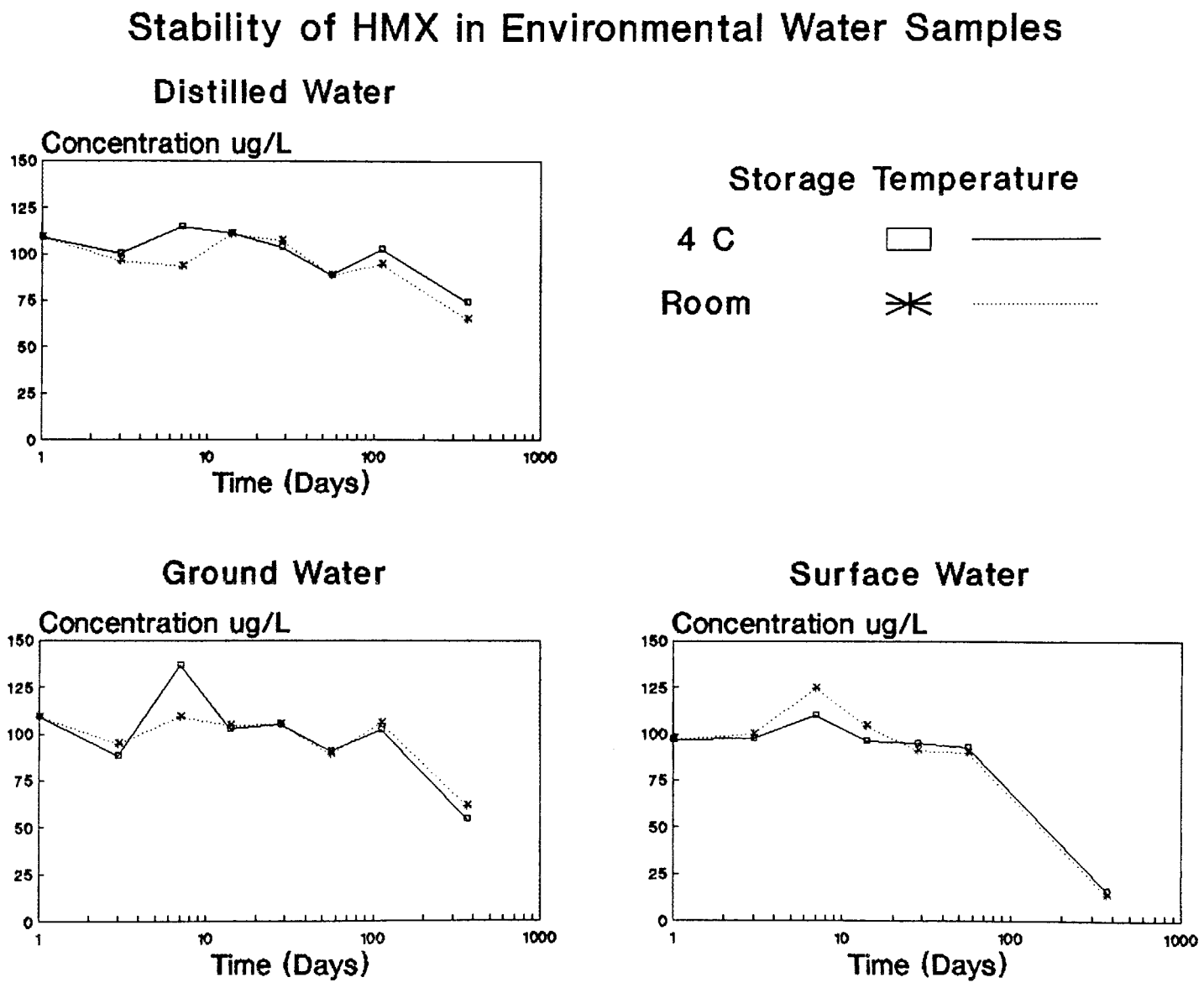

Fig. A.1 Low-level HMX in water samples.

Table A.2 RDX summary statistics for low-level concentrations (µg/L) in water samples.

Water Storage		Num Avg St Dev	Day								All Days
Water Type	Store Cond		0	3	7	14	28	56	112	365	
Distilled	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	53.1	.	.	.	.	.	.	.	53.1
		St Dev	2.0	.	.	.	.	.	.	.	2.0
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	2.0	26.0
		Avg	.	50.1	50.8	52.9	51.0	44.1	52.2	51.1	50.2
		St Dev	.	0.4	1.0	1.6	1.8	1.5	1.8	4.5	3.2
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	2.0	26.0
		Avg	.	48.9	53.8	54.8	50.7	45.1	52.4	41.0	50.2
		St Dev	.	2.0	2.5	5.3	2.1	0.6	1.6	0.8	4.8
Ground	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	51.7	.	.	.	.	.	.	.	51.7
		St Dev	1.2	.	.	.	.	.	.	.	1.2
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	3.0	27.0
		Avg	.	48.7	49.1	50.0	51.2	47.6	50.9	52.1	49.8
		St Dev	.	2.5	1.1	3.3	1.8	4.6	1.5	5.4	3.1
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	49.0	50.6	51.3	54.1	44.7	49.4	0.0	42.7
		St Dev	.	2.4	5.7	3.1	4.2	1.2	2.6	0.0	18.2
Surface	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	50.3	.	.	.	.	.	.	.	50.3
		St Dev	1.9	.	.	.	.	.	.	.	1.9
	4°C	Num	.	4.0	3.0	4.0	4.0	4.0	.	4.0	23.0
		Avg	.	48.9	58.7	51.0	44.5	47.1	.	8.9	42.5
		St Dev	.	2.2	4.6	1.0	1.9	2.2	.	6.0	16.6
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	.	4.0	24.0
		Avg	.	47.5	57.0	50.0	45.2	51.0	.	0.0	41.8
		St Dev	.	0.7	4.0	1.7	0.4	0.4	.	0.0	19.5

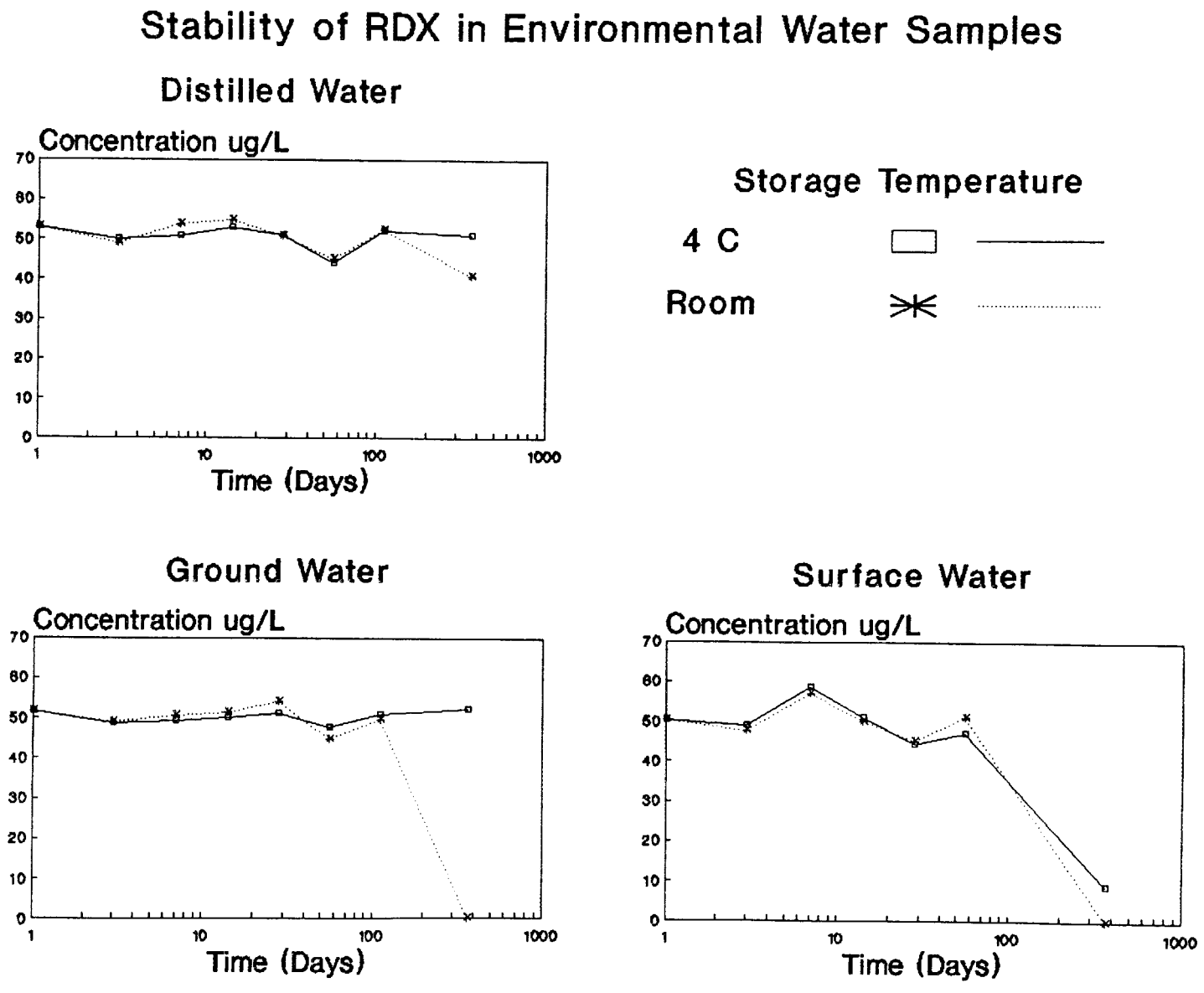

Fig. A.2 Low-level RDX in water samples.

Table A.3 TNT summary statistics for low-level concentrations (µg/L) in water samples.

Water Storage		Num Avg St Dev	Day								All Days
Water Type	Store Cond		0	3	7	14	28	56	112	365	
Distilled	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	52.1	.	.	.	.	.	.	.	52.1
		St Dev	2.2	.	.	.	.	.	.	.	2.2
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	3.0	27.0
		Avg	.	48.3	59.2	55.2	53.1	48.0	51.4	40.7	51.2
		St Dev	.	2.5	1.0	2.6	0.3	0.9	1.0	1.3	5.5
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	49.0	59.2	52.2	39.9	26.4	15.3	0.0	34.6
		St Dev	.	2.2	2.3	2.0	1.3	3.3	2.0	0.0	20.4
Ground	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	50.0	.	.	.	.	.	.	.	50.0
		St Dev	1.1	.	.	.	.	.	.	.	1.1
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	2.0	3.0	25.0
		Avg	.	50.1	58.2	56.3	51.8	42.6	34.7	0.0	44.2
		St Dev	.	0.8	1.6	2.2	1.8	3.2	0.5	0.0	18.1
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	46.1	48.6	30.0	22.4	10.6	8.2	0.0	23.7
		St Dev	.	3.5	3.4	10.5	1.3	5.6	2.6	0.0	18.3
Surface	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	48.1	.	.	.	.	.	.	.	48.1
		St Dev	1.1	.	.	.	.	.	.	.	1.1
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	47.4	54.8	63.6	8.0	0.0	0.0	0.0	24.8
		St Dev	.	1.7	0.3	3.0	5.5	0.0	0.0	0.0	27.4
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	10.7	0.0	0.0	0.0	0.0	0.0	0.0	1.5
		St Dev	.	2.5	0.0	0.0	0.0	0.0	0.0	0.0	3.9

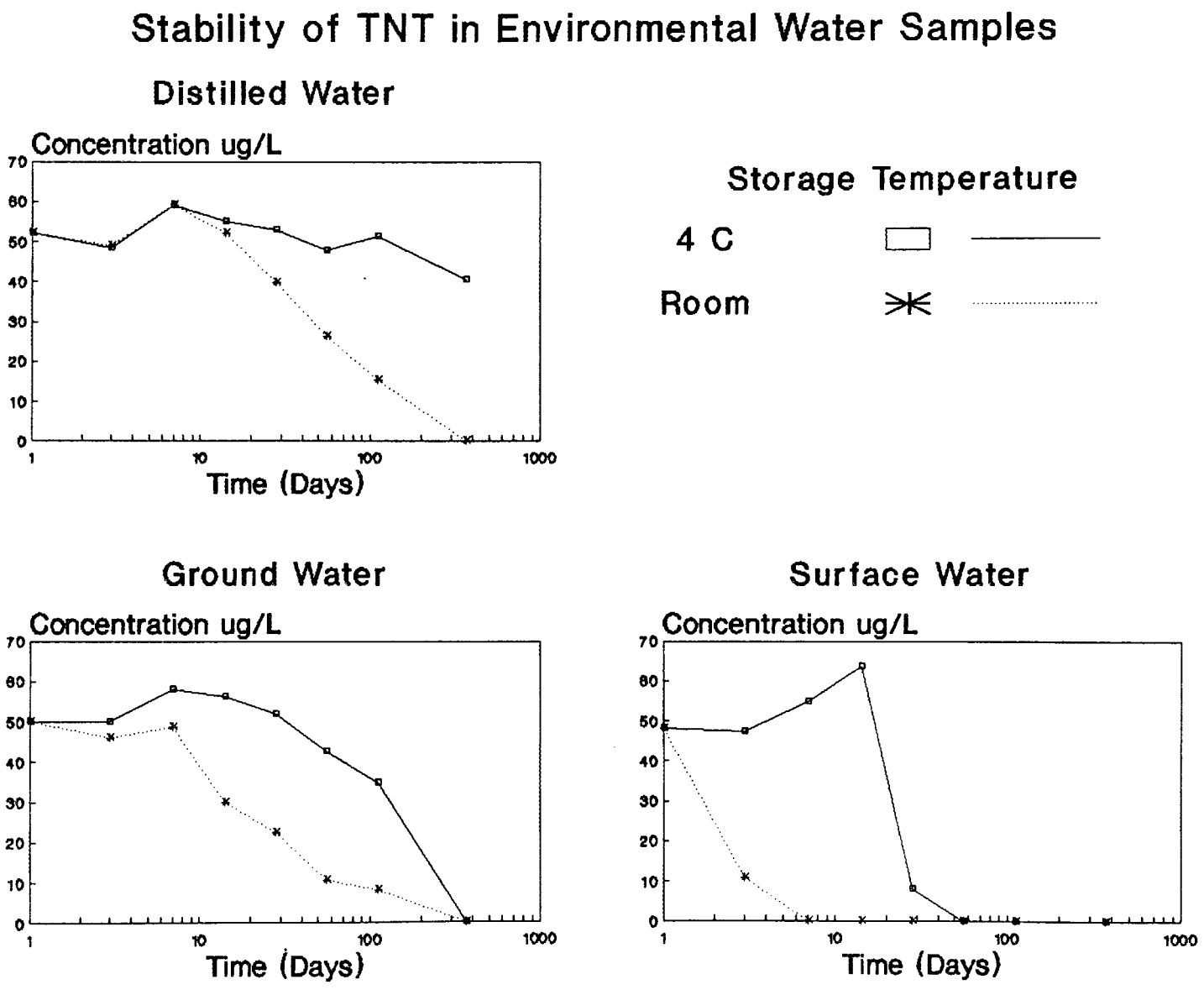

Fig. A.3 Low-level TNT in water samples.

Table A.4 DNT summary statistics for low-level concentrations (µg/L) in water samples.

Water Storage		Num Avg St Dev	Day								All Days
Water Type	Store Cond		0	3	7	14	28	56	112	365	
Distilled	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	55.4	.	.	.	.	.	.	.	55.4
		St Dev	2.4	.	.	.	.	.	.	.	2.4
	4°C	Num	.	4.0	4.0	2.0	4.0	4.0	4.0	3.0	25.0
		Avg	.	48.5	49.5	49.6	47.4	45.3	40.4	38.7	45.6
		St Dev	.	1.6	0.6	0.7	0.7	1.1	0.5	1.6	4.1
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	3.0	27.0
		Avg	.	48.4	50.8	50.9	47.3	42.1	33.7	32.3	44.1
		St Dev	.	1.3	1.9	0.9	1.2	1.7	0.6	1.7	7.3
Ground	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	54.1	.	.	.	.	.	.	.	54.1
		St Dev	1.9	.	.	.	.	.	.	.	1.9
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	50.2	50.7	48.0	48.9	45.8	36.6	43.5	46.3
		St Dev	.	1.8	1.7	2.2	0.8	0.8	1.5	8.1	5.5
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	3.0	2.0	25.0
		Avg	.	48.7	51.4	48.1	46.0	41.5	38.0	42.1	45.6
		St Dev	.	3.6	1.5	5.5	0.9	1.5	3.6	1.8	5.1
Surface	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	51.0	.	.	.	.	.	.	.	51.0
		St Dev	2.6	.	.	.	.	.	.	.	2.6
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	2.0	4.0	26.0
		Avg	.	48.1	48.5	46.6	35.8	22.3	35.3	0.0	33.7
		St Dev	.	0.9	0.6	0.7	5.0	3.3	2.8	0.0	17.4
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	40.5	30.0	18.6	7.8	0.9	0.0	0.0	14.0
		St Dev	.	1.8	1.4	1.5	1.6	1.0	0.0	0.0	15.4

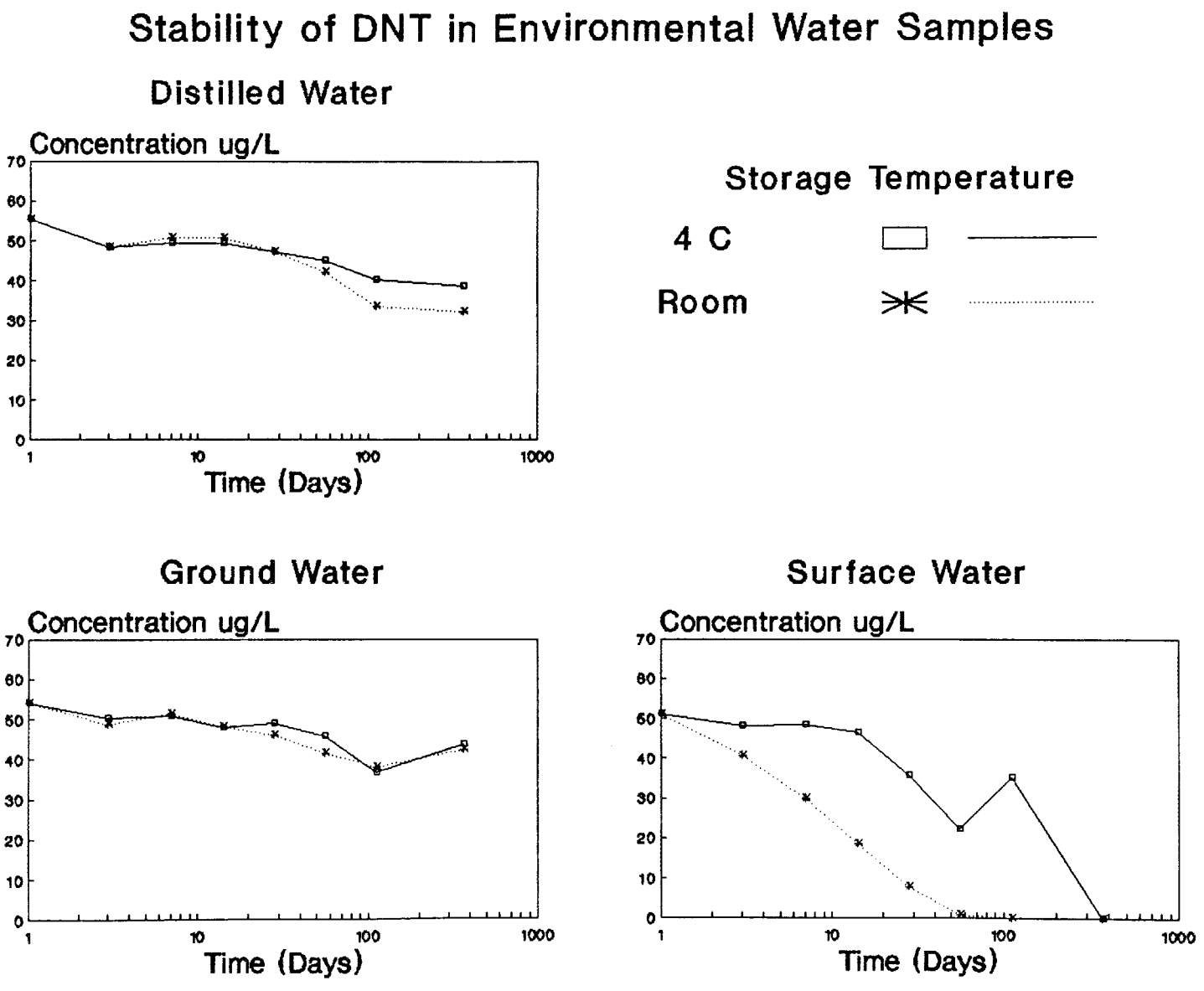

Fig. A.4 Low-level DNT in water samples.

APPENDIX B

Explosive Summary Statistics for High-Level Concentrations (μg/L) in Water Samples

Table B.1 HMX summary statistics for high-level concentrations (μg/L) in water samples.

Water Storage		Num Avg St Dev	Days								All Days
Water Type	Store Cond		0	3	7	14	28	56	112	365	
Distilled	None	Num	4	.	.	.	.	.	.	.	4
		Avg	978	.	.	.	.	.	.	.	978
		St Dev	19	.	.	.	.	.	.	.	19
	4°C	Num	.	4	4	4	4	4	4	4	28
		Avg	.	945	1003	929	866	433	525	565	752
		St Dev	.	22	23	23	11	10	15	8	223
	Room	Num	.	4	4	4	4	4	3	4	27
		Avg	.	937	1023	934	934	446	504	559	772
		St Dev	.	26	25	13	19	20	3	14	232
	Extract	Num	4	.	3	3	4	4	4	4	26
		Avg	435	.	372	530	414	336	362	119	360
		St Dev	41	.	52	9	56	14	40	33	124
Ground	None	Num	4	.	.	.	.	.	.	.	4
		Avg	1773	.	.	.	.	.	.	.	1773
		St Dev	25	.	.	.	.	.	.	.	25
	4°C	Num	.	4	4	4	4	4	4	4	28
		Avg	.	1834	2129	2149	1946	1782	1950	1937	1961
		St Dev	.	16	37	121	65	48	94	32	142
	Room	Num	.	4	4	3	4	4	4	4	27
		Avg	.	1825	1996	2068	1966	1727	1978	2010	1934
		St Dev	.	29	39	189	51	34	86	72	132
	Extract	Num	4	4	4	4	3	4	4	4	31
		Avg	1377	1785	1686	1257	1518	1282	1323	669	1357
		St Dev	172	220	38	111	219	80	388	129	370
Surface	None	Num	4	.	.	.	.	.	.	.	4
		Avg	2024	.	.	.	.	.	.	.	2024
		St Dev	57	.	.	.	.	.	.	.	57
	4°C	Num	.	4	4	3	4	4	4	2	25
		Avg	.	2021	2101	1889	2004	1980	1832	1863	1966
		St Dev	.	42	43	28	32	51	49	24	98
	Room	Num	.	4	4	4	4	4	4	4	28
		Avg	.	2011	2100	1914	2008	1930	1939	1880	1969
		St Dev	.	21	26	26	49	64	46	35	80
	Extract	Num	4	4	4	4	4	4	3	4	31
		Avg	1669	1702	1704	1645	1613	2019	1271	585	1534
		St Dev	137	252	55	465	482	293	439	220	501

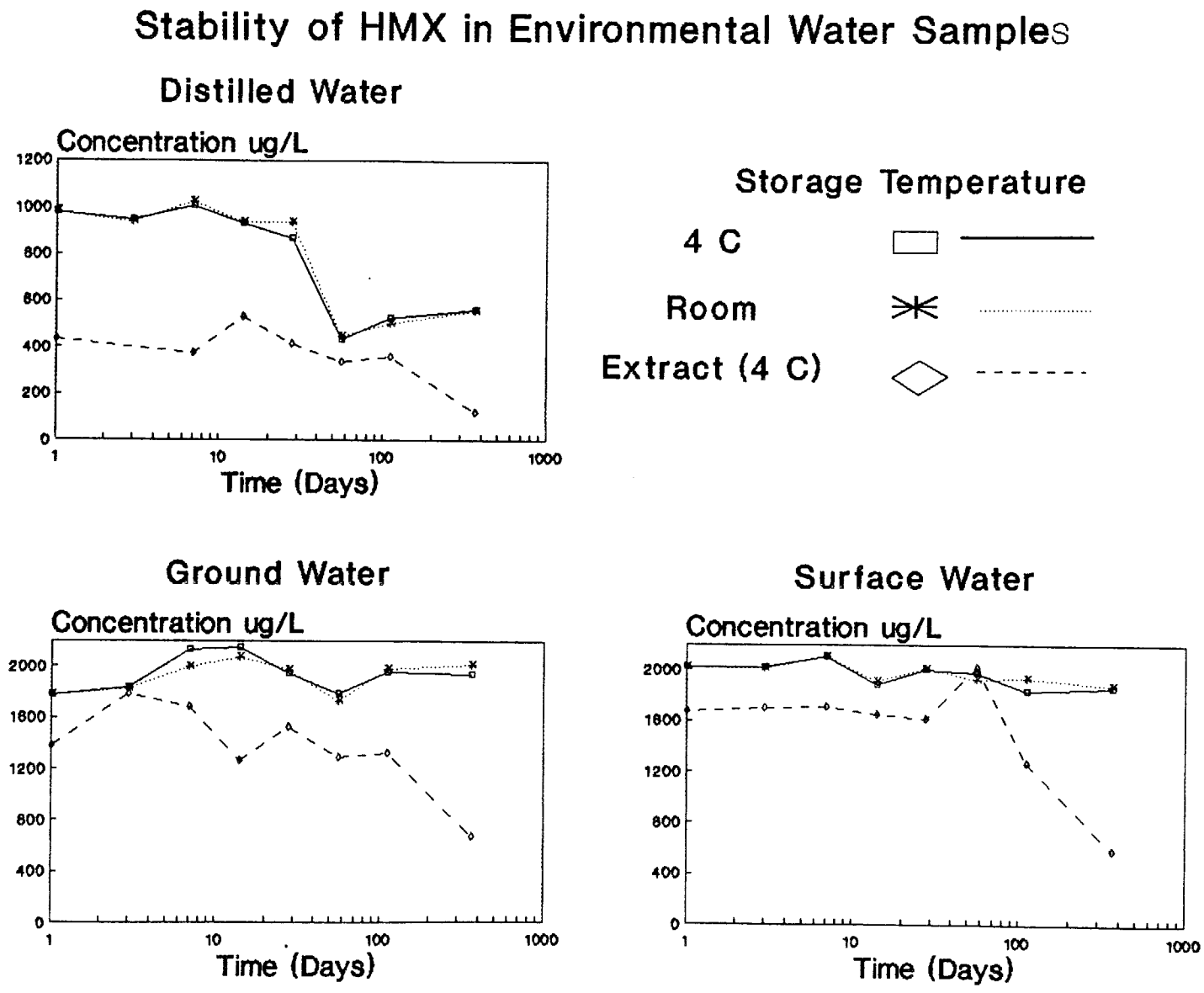

Fig. B.1 High-level HMX in water samples.

Table B.2 RDX summary statistics for high-level concentrations (µg/L) in water samples.

Water Storage		Num Avg St Dev	Day								All Days
Water Type	Store Cond		0	3	7	14	28	56	112	365	
Distilled	None	Num	4	.	.	.	.	.	.	.	4
		Avg	1000	.	.	.	.	.	.	.	1000
		St Dev	31	.	.	.	.	.	.	.	31
	4°C	Num	.	4	4	4	4	4	4	.	24
		Avg	.	1000	992	932	943	997	983	.	974
		St Dev	.	22	11	33	20	19	12	.	33
	Room	Num	.	4	4	4	4	4	3	.	23
		Avg	.	996	1025	947	979	998	943	.	983
		St Dev	.	18	15	14	20	28	21	.	34
	Extract	Num	4	4	4	4	4	4	4	4	32
		Avg	860	702	938	949	936	1019	980	303	836
		St Dev	82	100	64	69	169	73	27	74	238
Ground	None	Num	4	.	.	.	.	.	.	.	4
		Avg	948	.	.	.	.	.	.	.	948
		St Dev	21	.	.	.	.	.	.	.	21
	4°C	Num	.	4	4	4	4	4	4	.	24
		Avg	.	965	998	978	997	932	950	.	970
		St Dev	.	36	22	48	34	24	24	.	38
	Room	Num	.	4	4	2	4	4	4	.	22
		Avg	.	971	980	1056	969	920	969	.	971
		St Dev	.	16	9	32	13	3	36	.	39
	Extract	Num	4	4	4	4	4	4	4	3	31
		Avg	885	1005	978	907	883	895	861	481	874
		St Dev	43	40	33	87	112	20	191	77	161
Surface	None	Num	4	.	.	.	.	.	.	.	4
		Avg	979	.	.	.	.	.	.	.	979
		St Dev	19	.	.	.	.	.	.	.	19
	4°C	Num	.	4	4	4	4	4	4	4	28
		Avg	.	994	1047	935	948	1032	966	1124	1007
		St Dev	.	16	27	11	11	7	45	12	66
	Room	Num	.	4	4	4	4	4	4	4	28
		Avg	.	993	1043	954	935	987	971	1142	1004
		St Dev	.	13	26	9	6	11	22	11	67
	Extract	Num	4	4	4	4	4	4	4	4	32
		Avg	931	960	1022	935	928	980	689	305	844
		St Dev	41	112	54	76	118	183	208	193	258

Stability of RDX in Environmental Water Samples

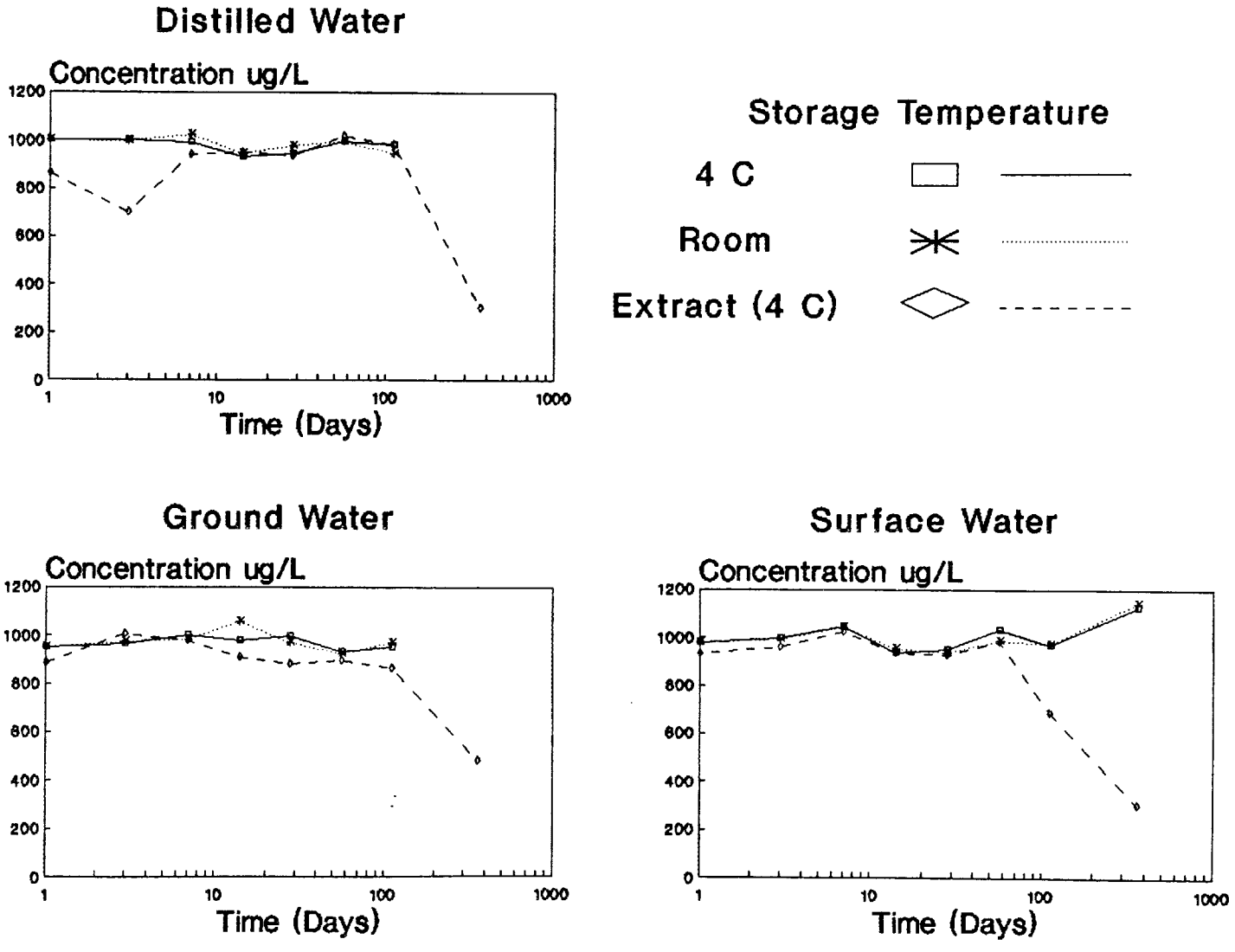

Fig. B.2 High-level RDX in water samples.

Table B.3 TNT summary statistics for high-level concentrations (µg/L) in water samples.

Water Storage		Num Avg St Dev	Day								All Days
Water Type	Store Cond		0	3	7	14	28	56	112	365	
Distilled	None	Num	3	.	.	.	.	.	.	.	3
		Avg	1005	.	.	.	.	.	.	.	1005
		St Dev	22	.	.	.	.	.	.	.	22
	4°C	Num	.	4	4	4	4	4	4	4	28
		Avg	.	1000	995	944	984	1031	1087	1021	1009
		St Dev	.	19	4	17	47	33	19	3	47
	Room	Num	.	4	4	4	4	4	3	4	27
		Avg	.	1000	1027	942	1013	1064	1069	1011	1016
		St Dev	.	18	18	18	23	40	9	33	46
	Extract	Num	3	4	4	4	.	3	4	4	26
		Avg	838	794	864	835	.	946	1038	475	822
		St Dev	31	112	147	143	.	147	46	42	195
Ground	None	Num	4	.	.	.	.	.	.	.	4
		Avg	947	.	.	.	.	.	.	.	947
		St Dev	23	.	.	.	.	.	.	.	23
	4°C	Num	.	4	4	2	4	4	4	4	26
		Avg	.	1010	1181	1079	1068	966	921	829	1002
		St Dev	.	16	13	11	22	12	29	104	118
	Room	Num	.	4	4	4	4	4	4	4	28
		Avg	.	1004	1047	887	674	294	94	9	573
		St Dev	.	35	26	54	39	25	64	17	413
	Extract	Num	4	4	4	3	4	4	3	4	30
		Avg	843	913	1002	817	906	894	858	535	847
		St Dev	51	65	55	115	54	38	124	79	149
Surface	None	Num	4	.	.	.	.	.	.	.	4
		Avg	988	.	.	.	.	.	.	.	988
		St Dev	18	.	.	.	.	.	.	.	18
	4°C	Num	.	4	4	4	4	4	3	4	27
		Avg	.	1005	1072	991	978	858	608	590	881
		St Dev	.	30	24	13	21	27	37	41	183
	Room	Num	.	4	4	4	3	3	3	3	24
		Avg	.	903	526	229	152	84	68	70	323
		St Dev	.	12	21	60	6	15	26	17	310
	Extract	Num	4	3	4	3	4	4	4	4	30
		Avg	814	858	733	651	869	892	535	388	715
		St Dev	19	51	84	108	68	59	130	47	188

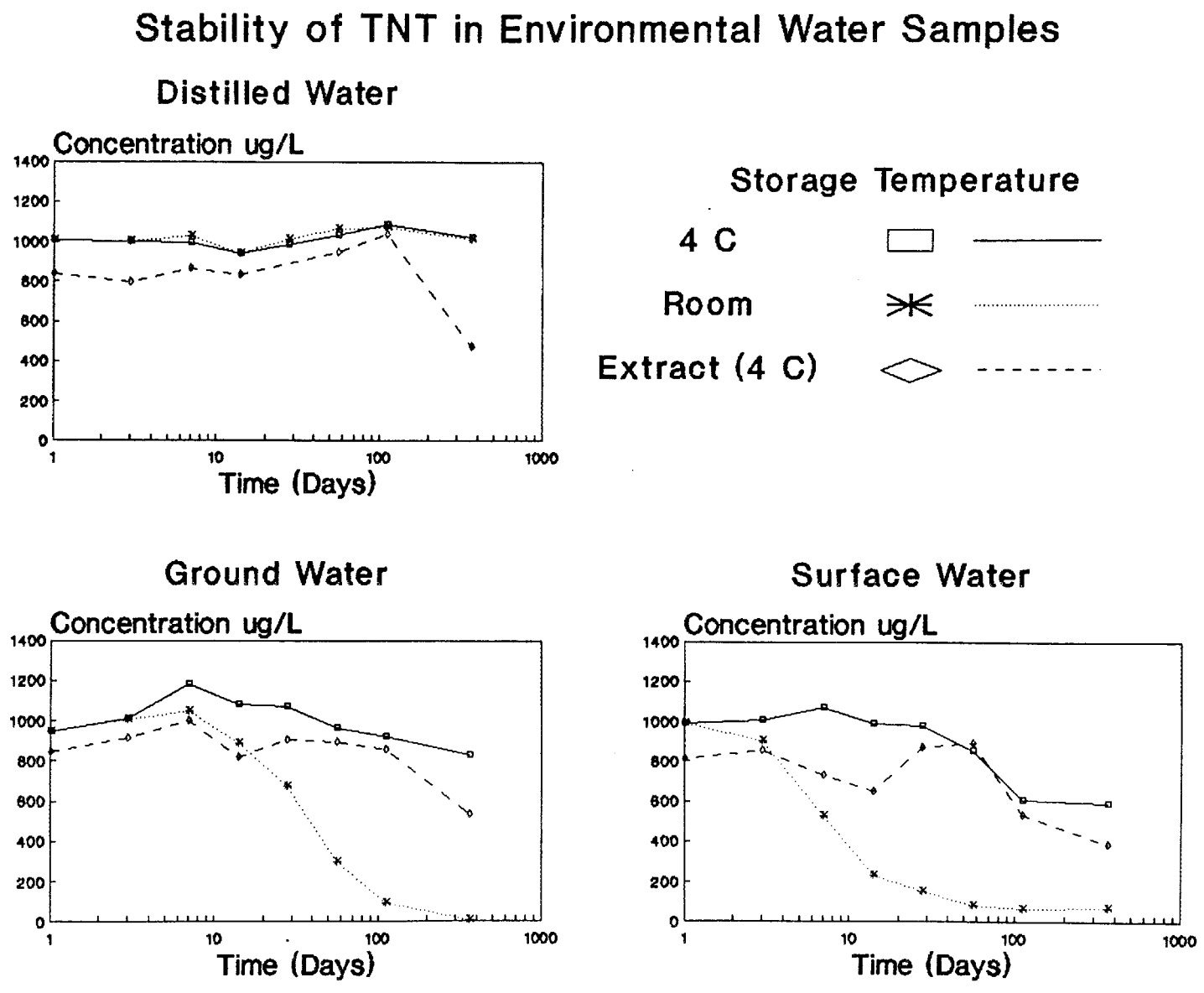

Fig. B.3 High-level TNT in water samples.

Table B.4 DNT summary statistics for high-level concentrations (µg/L) in water samples.

Water Storage		Num Avg St Dev	Day								All Days
Water Type	Store Cond		0	3	7	14	28	56	112	365	
Distilled	None	Num	4	.	.	.	.	.	.	.	4
		Avg	1000	.	.	.	.	.	.	.	1000
		St Dev	26	.	.	.	.	.	.	.	26
	4°C	Num	.	4	4	3	4	4	4	4	27
		Avg	.	1000	1003	956	976	988	1063	1050	1007
		St Dev	.	15	14	19	30	27	17	11	40
	Room	Num	.	4	4	4	4	4	3	4	27
		Avg	.	1000	1006	935	1003	1033	1058	1055	1011
		St Dev	.	17	49	9	25	34	2	12	46
	Extract	Num	4	4	4	4	3	4	3	4	30
		Avg	840	856	847	884	850	958	1150	573	861
		St Dev	76	44	59	104	85	120	64	22	162
Ground	None	Num	4	.	.	.	.	.	.	.	4
		Avg	950	.	.	.	.	.	.	.	950
		St Dev	20	.	.	.	.	.	.	.	20
	4°C	Num	.	4	4	2	4	4	4	4	26
		Avg	.	1005	1013	1037	998	979	969	982	995
		St Dev	.	19	18	45	25	12	22	15	27
	Room	Num	.	4	4	4	4	4	4	4	28
		Avg	.	1008	1010	1044	947	897	863	845	945
		St Dev	.	11	16	36	37	16	36	60	80
	Extract	Num	4	4	4	4	4	4	3	4	31
		Avg	864	922	886	911	891	1021	964	550	873
		St Dev	36	51	37	154	95	44	91	74	153
Surface	None	Num	4	.	.	.	.	.	.	.	4
		Avg	996	.	.	.	.	.	.	.	996
		St Dev	20	.	.	.	.	.	.	.	20
	4°C	Num	.	4	4	4	4	4	4	4	28
		Avg	.	977	1018	948	1006	996	930	872	964
		St Dev	.	6	16	3	15	13	14	10	49
	Room	Num	.	4	4	4	3	4	4	4	27
		Avg	.	965	972	865	893	868	826	792	883
		St Dev	.	6	14	21	9	30	34	16	67
	Extract	Num	4	4	4	4	4	4	3	4	31
		Avg	954	946	925	959	1057	953	510	338	841
		St Dev	32	122	109	117	136	54	79	32	256

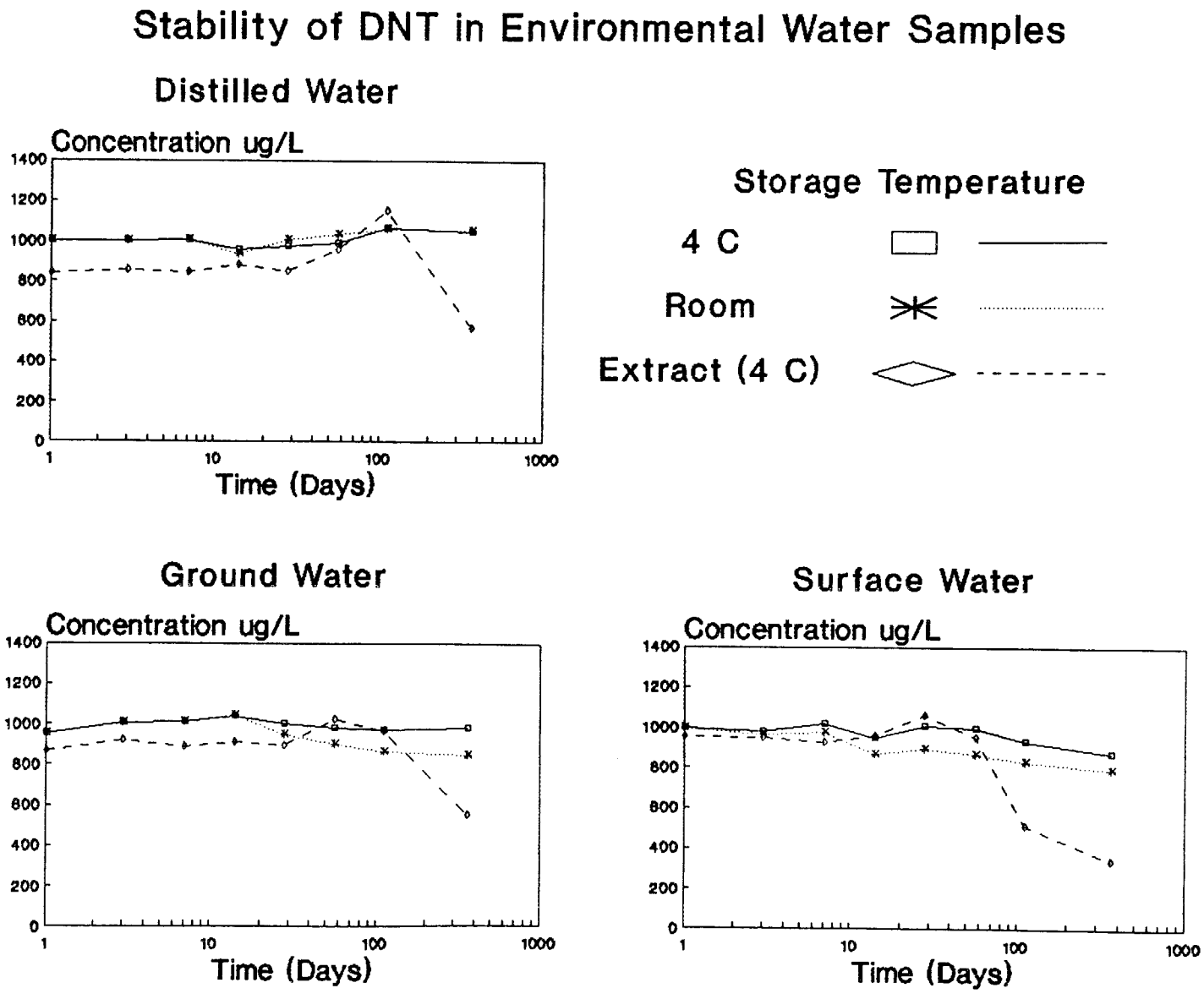

Fig. B.4 High-level DNT in water samples.

APPENDIX C

Explosives Summary Statistics for Low-Level Concentrations (μg/g) in Soil Samples

Table C.1 HMX summary statistics for low-level concentrations (µg/g) in soil samples.

Soil Storage		Num Avg St Dev	Day								All Days
Soil Type	Store Cond		0	3	7	14	28	56	112	≥333	
USATHAMA	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	10.3	.	.	.	.	.	.	.	10.3
		St Dev	0.2	.	.	.	.	.	.	.	0.2
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	8.7	6.5	8.2	6.6	7.8	9.2	9.0	8.0
		St Dev	.	0.5	0.3	1.4	0.3	0.1	0.3	0.2	1.2
	4°C	Num	.	4.0	4.0	4.0	3.0	4.0	4.0	4.0	27.0
		Avg	.	8.4	7.5	7.7	6.3	7.9	6.9	9.4	7.8
		St Dev	.	0.3	0.1	0.6	0.0	0.7	0.8	0.4	1.0
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	3.0	27.0
		Avg	.	8.3	7.0	6.2	5.5	6.4	6.4	6.5	6.6
		St Dev	.	0.2	0.8	0.2	0.3	1.2	1.6	0.7	1.1
Tennessee	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	9.5	.	.	.	.	.	.	.	9.5
		St Dev	0.3	.	.	.	.	.	.	.	0.3
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	2.0	26.0
		Avg	.	7.9	6.0	8.0	6.0	7.4	7.0	10.5	7.3
		St Dev	.	0.1	0.2	0.8	0.5	0.7	0.4	1.3	1.3
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	2.0	26.0
		Avg	.	7.9	7.4	7.4	5.7	6.2	6.4	7.6	6.9
		St Dev	.	0.4	0.9	0.1	1.3	0.1	0.1	0.9	1.0
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	3.0	27.0
		Avg	.	7.9	5.8	7.1	5.6	5.9	3.3	0.0	5.3
		St Dev	.	0.4	0.2	1.2	0.5	1.1	1.7	0.0	2.5
Mississippi	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	7.0	.	.	.	.	.	.	.	7.0
		St Dev	0.2	.	.	.	.	.	.	.	0.2
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	7.4	6.7	3.4	4.4	7.7	9.0	10.2	7.0
		St Dev	.	0.3	0.2	0.2	0.6	1.4	0.9	0.5	2.3
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	7.5	7.3	3.2	4.6	7.0	9.3	10.0	7.0
		St Dev	.	0.2	0.2	0.2	0.2	1.5	0.7	0.4	2.4
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	7.6	6.5	3.2	4.4	6.6	7.6	6.9	6.1
		St Dev	.	0.3	0.2	0.4	1.0	0.8	1.0	2.6	1.9

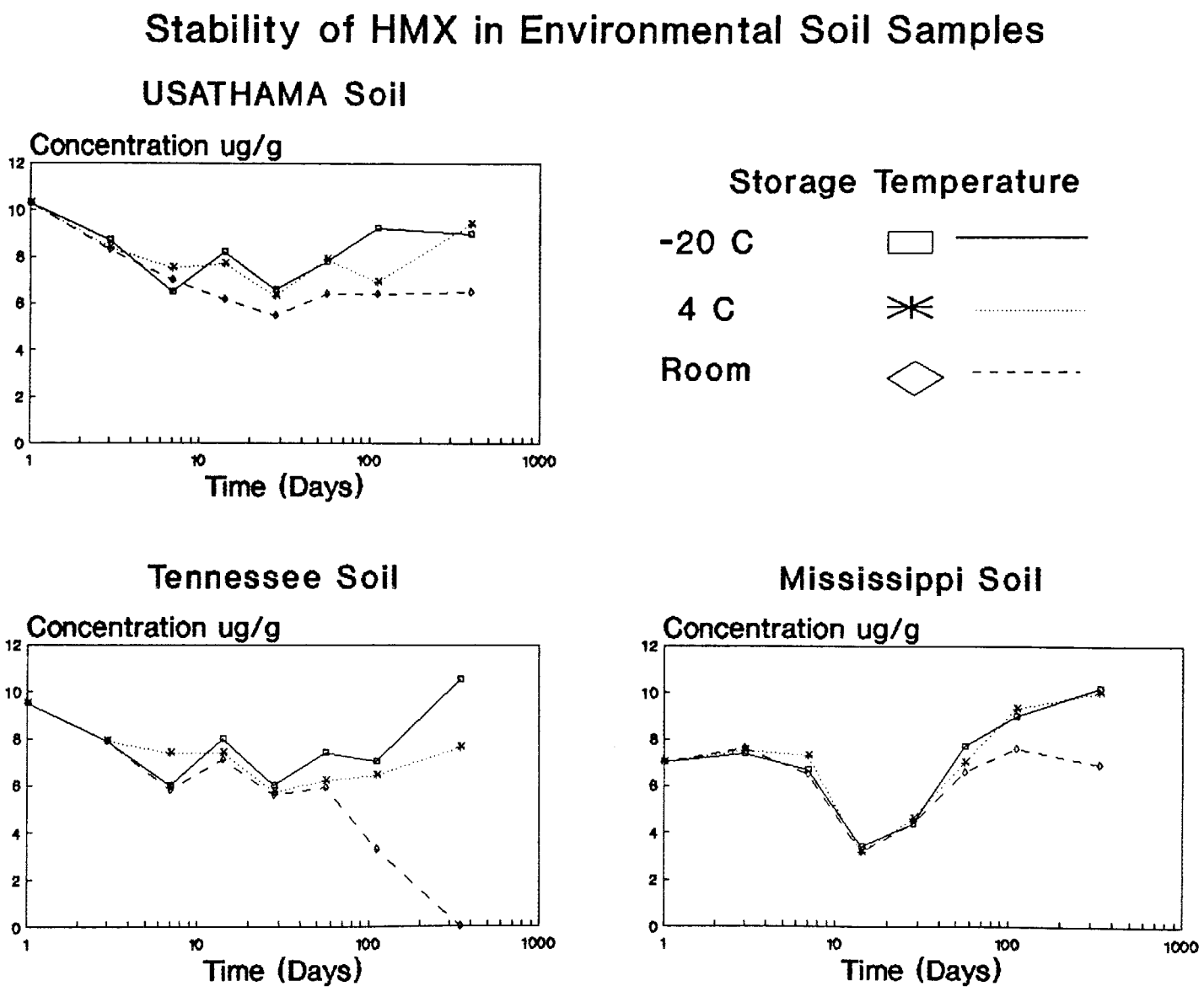

Fig. C.1 Low-level HMX in soil samples.

Table C.3 TNT summary satistics for low-level concentrations (µg/g) in soil samples.

Soil Storage		Num Avg St Dev	Day								All Days
Soil Type	Store Cond		0	3	7	14	28	56	112	≥333	
USATHAMA	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	8.9	.	.	.	.	.	.	.	8.9
		St Dev	0.2	.	.	.	.	.	.	.	0.2
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	8.0	7.9	8.9	8.9	8.6	9.4	6.5	8.3
		St Dev	.	0.4	0.1	0.2	0.2	0.4	0.8	0.7	1.0
	4°C	Num	.	4.0	4.0	4.0	4.0	3.0	4.0	3.0	26.0
		Avg	.	7.0	6.2	6.7	6.1	4.5	2.7	2.3	5.2
		St Dev	.	0.4	0.2	0.7	0.3	0.9	0.6	0.3	1.8
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		St Dev	.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Tennessee	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	9.1	.	.	.	.	.	.	.	9.1
		St Dev	0.2	.	.	.	.	.	.	.	0.2
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	2.0	26.0
		Avg	.	8.7	8.6	8.1	6.7	8.1	8.8	8.1	8.1
		St Dev	.	0.3	0.4	0.3	0.2	0.6	0.2	0.7	0.8
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	2.0	26.0
		Avg	.	6.7	6.7	5.3	3.0	3.0	2.3	1.2	4.2
		St Dev	.	0.2	0.2	0.3	1.0	0.2	0.4	0.2	2.0
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	3.0	27.0
		Avg	.	1.4	0.1	0.0	0.0	0.0	0.0	0.2	0.2
		St Dev	.	0.2	0.1	0.0	0.0	0.0	0.0	0.4	0.5
Mississippi	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	10.8	.	.	.	.	.	.	.	10.8
		St Dev	1.8	.	.	.	.	.	.	.	1.8
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	7.8	8.4	5.0	2.5	8.3	10.7	6.5	7.0
		St Dev	.	0.5	0.4	1.3	0.9	0.1	0.3	1.9	2.6
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	5.9	5.2	2.7	2.9	2.9	2.4	2.1	3.4
		St Dev	.	0.3	0.4	0.5	0.3	0.6	0.7	0.8	1.5
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	1.6	0.5	0.0	0.0	0.0	0.0	0.0	0.3
		St Dev	.	0.3	0.1	0.0	0.0	0.0	0.0	0.0	0.6

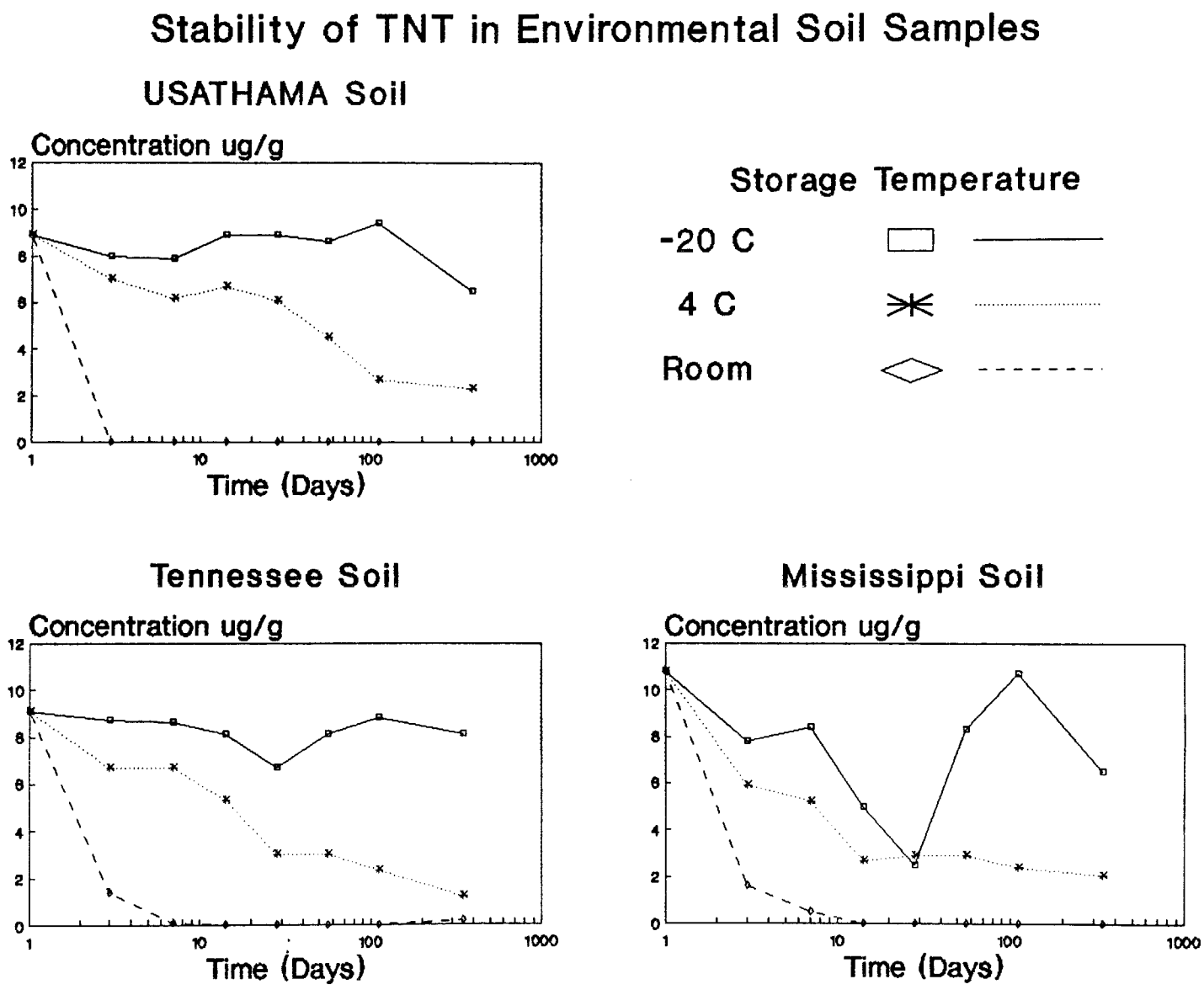

Fig. C.3 Low-level TNT in soil samples.

Table C.4 DNT summary statistics for low-level concentrations (µg/g) in soil samples.

Soil Storage		Num Avg St Dev	Day								All Days
Soil Type	Store Cond		0	3	7	14	28	56	112	≥333	
USATHAMA	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	9.0	.	.	.	.	.	.	.	9.0
		St Dev	0.1	.	.	.	.	.	.	.	0.1
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	8.6	9.1	9.4	9.3	9.0	8.4	9.0	9.0
		St Dev	.	0.4	0.2	0.1	0.3	0.2	0.2	0.2	0.4
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	3.0	27.0
		Avg	.	8.5	9.0	9.1	9.0	8.3	7.0	8.5	8.5
		St Dev	.	0.2	0.1	0.1	0.2	0.5	0.3	0.3	0.8
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	5.4	2.1	0.0	0.0	0.0	0.0	0.0	1.1
		St Dev	.	0.5	0.8	0.1	0.0	0.0	0.0	0.0	2.0
Tennessee	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	9.1	.	.	.	.	.	.	.	9.1
		St Dev	0.3	.	.	.	.	.	.	.	0.3
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	2.0	26.0
		Avg	.	9.2	9.2	9.3	7.4	8.6	10.0	11.5	9.2
		St Dev	.	0.2	0.2	0.1	0.1	0.4	0.3	0.6	1.1
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	2.0	26.0
		Avg	.	8.7	9.0	9.2	7.4	8.1	8.2	7.6	8.4
		St Dev	.	0.3	0.1	0.2	0.5	0.3	0.9	0.7	0.8
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	3.0	27.0
		Avg	.	7.9	5.5	3.3	0.8	0.3	0.2	0.8	2.8
		St Dev	.	0.2	1.0	1.0	0.2	0.1	0.1	0.5	2.9
Mississippi	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	9.5	.	.	.	.	.	.	.	9.5
		St Dev	0.1	.	.	.	.	.	.	.	0.1
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	9.2	9.2	6.4	4.7	8.9	9.9	9.3	8.2
		St Dev	.	0.1	0.3	0.7	1.4	0.1	0.1	0.7	1.9
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	8.8	9.2	6.7	7.0	8.1	8.8	8.0	8.1
		St Dev	.	0.2	0.1	0.5	0.1	0.2	0.2	0.5	0.9
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	8.4	7.7	4.9	4.6	4.7	4.3	3.4	5.4
		St Dev	.	0.2	0.2	0.3	0.5	0.4	0.3	0.3	1.8

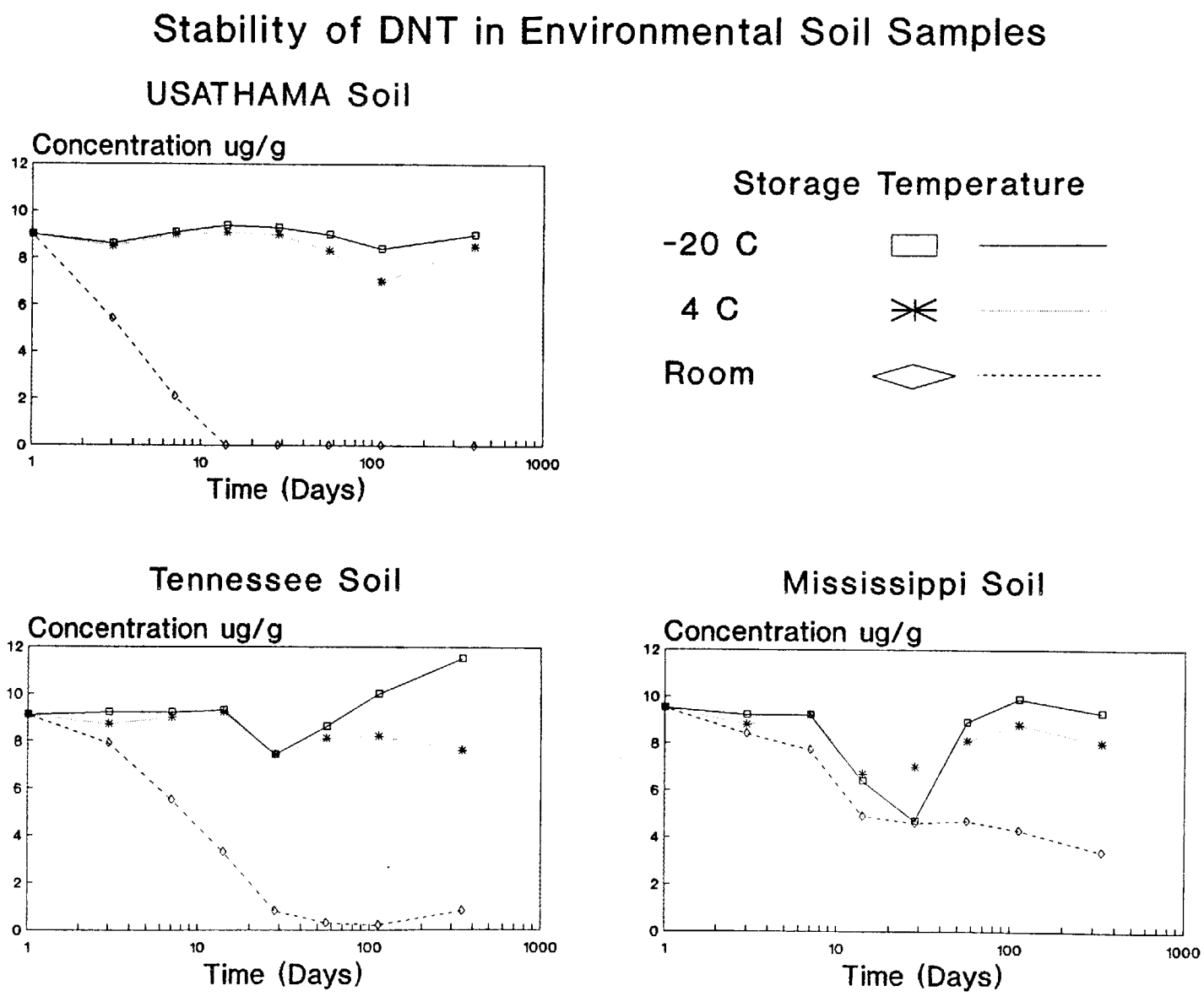

Fig. C.4 Low-level DNT in soil samples.

APPENDIX D

Explosives Summary Statistics for High-Level Concentrations (μg/g) in Soil Samples

Table D.1 HMX summary statistics for high-level concentrations (µg/g) in soil samples.

Soil Storage		Num Avg St Dev	Day								All Days
Soil Type	Store Cond		0	3	7	14	28	56	112	≥333	
USATHAMA	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	91.4	.	.	.	.	.	.	.	91.4
		St Dev	3.6	.	.	.	.	.	.	.	3.6
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	95.2	88.4	100.8	97.0	88.3	85.0	92.2	92.4
		St Dev	.	2.5	3.4	2.5	5.2	1.3	2.3	2.9	5.9
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	95.3	91.3	98.5	99.1	89.9	87.4	93.3	93.5
		St Dev	.	1.9	1.4	4.5	3.7	1.4	0.5	1.5	4.7
	Room	Num	.	4.0	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Avg	.	96.2	91.9	94.5	98.2	89.0	86.8	97.8	93.7
		St Dev	.	3.5	1.2	4.5	2.8	1.1	0.5	3.0	4.8
Tennessee	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	85.1	.	.	.	.	.	.	.	85.1
		St Dev	1.5	.	.	.	.	.	.	.	1.5
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	94.3	92.4	83.3	78.8	81.4	87.0	112.6	90.0
		St Dev	.	2.6	2.0	1.8	0.9	3.5	5.4	3.0	11.1
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	3.0	4.0	27.0
		Avg	.	94.0	96.9	86.9	80.1	92.4	88.1	115.1	93.5
		St Dev	.	2.9	2.3	1.7	3.5	1.2	3.9	2.0	10.8
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	91.7	93.4	86.0	79.7	88.8	86.1	112.8	91.2
		St Dev	.	5.5	3.6	1.5	1.3	1.5	0.7	5.1	10.3
Mississippi	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	93.6	.	.	.	.	.	.	.	93.6
		St Dev	3.5	.	.	.	.	.	.	.	3.5
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	82.5	75.2	75.9	79.7	89.9	100.3	114.1	88.2
		St Dev	.	2.6	1.6	1.6	5.1	1.5	2.5	2.6	13.8
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	87.3	76.3	77.2	77.4	90.7	99.1	110.2	88.3
		St Dev	.	2.8	1.3	1.7	7.6	2.1	4.3	3.5	12.6
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	86.8	74.3	75.3	79.1	89.3	100.5	109.7	87.8
		St Dev	.	2.3	1.5	2.8	2.1	4.0	2.7	2.9	12.8

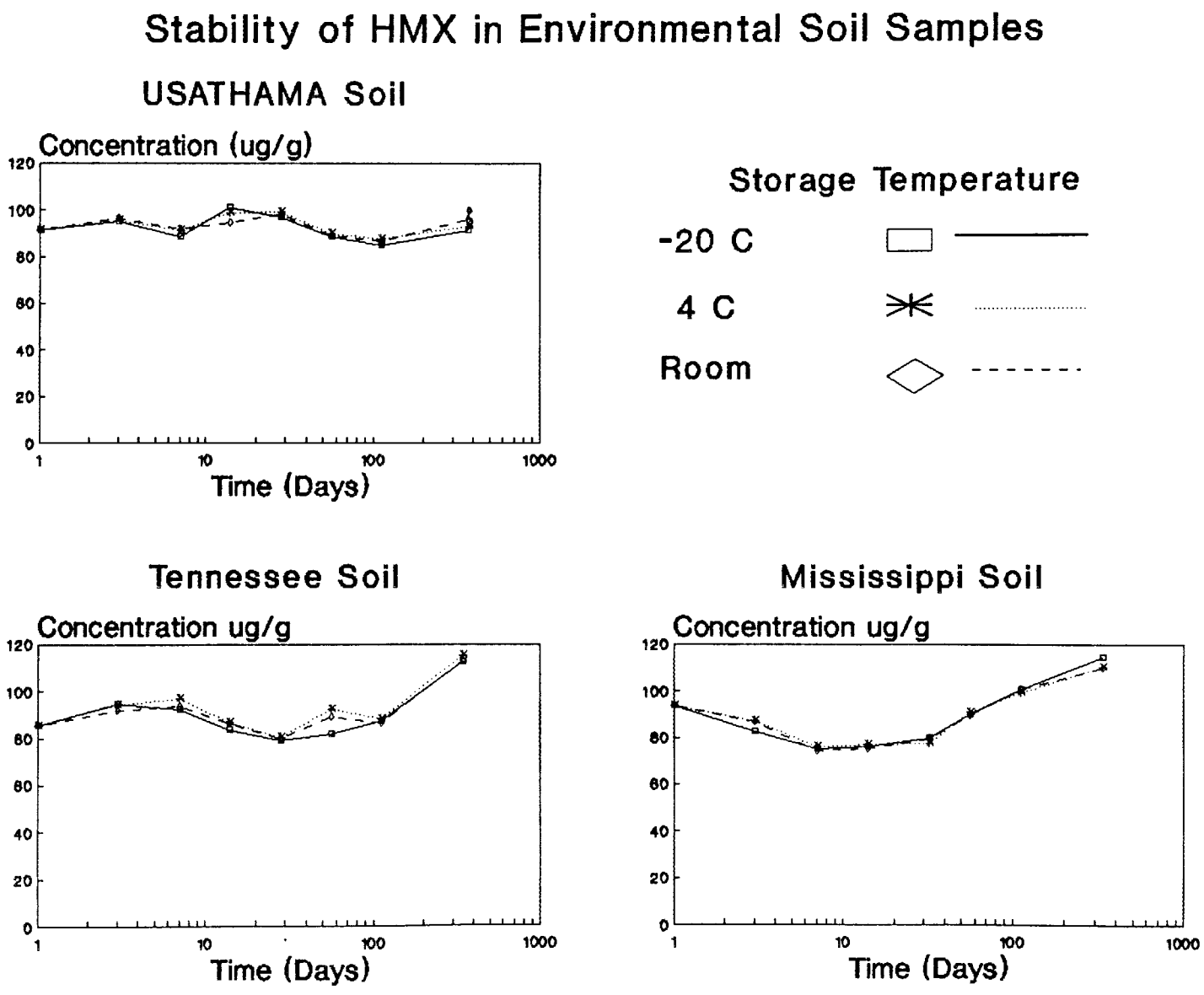

Fig. D.1 High-level HMX in soil samples.

Table D.2 RDX summary statistics for high-level concentrations (μg/g) in soil samples.

Soil Storage		Num	Day								All
Water Type	Store Cond	Avg St Dev	0	3	7	14	28	56	112	≥333	Days
USATHAMA	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	88.0	.	.	.	.	.	.	.	88.0
		St Dev	3.0	.	.	.	.	.	.	.	3.0
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	94.5	87.9	93.5	87.4	89.8	80.4	89.2	89.0
		St Dev	.	1.6	3.4	1.4	4.3	2.1	1.9	3.1	5.0
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	92.0	90.0	91.5	91.4	89.0	83.5	87.1	89.2
		St Dev	.	2.5	1.5	1.2	4.4	1.1	1.0	1.9	3.5
	Room	Num	.	4.0	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Avg	.	94.1	92.7	91.6	90.6	89.6	83.9	95.0	91.1
		St Dev	.	2.3	2.0	1.4	1.0	1.5	1.1	4.2	4.0
Tennessee	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	87.0	.	.	.	.	.	.	.	87.0
		St Dev	1.7	.	.	.	.	.	.	.	1.7
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	88.6	92.3	89.1	79.1	85.5	91.3	104.3	90.0
		St Dev	.	2.7	1.6	2.5	0.9	2.7	4.4	2.5	7.6
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	3.0	4.0	27.0
		Avg	.	92.8	94.7	90.7	79.4	92.5	93.9	104.3	92.6
		St Dev	.	2.6	2.4	2.4	2.2	1.1	4.8	3.1	7.4
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	89.2	92.5	91.9	79.6	90.7	91.6	105.3	91.6
		St Dev	.	2.8	3.1	2.0	0.9	0.9	0.7	6.3	7.6
Mississippi	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	95.2	.	.	.	.	.	.	.	95.2
		St Dev	2.8	.	.	.	.	.	.	.	2.8
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	88.0	86.9	80.3	86.0	87.6	96.8	107.6	90.5
		St Dev	.	2.5	1.7	1.8	4.0	0.8	2.3	3.5	8.8
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	91.5	87.7	83.0	84.7	90.9	93.6	104.7	90.9
		St Dev	.	1.8	1.8	1.8	5.2	3.0	3.2	3.6	7.3
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	91.0	83.8	80.4	84.7	89.1	94.2	103.0	89.5
		St Dev	.	1.7	0.8	1.9	1.2	2.1	4.9	2.7	7.5

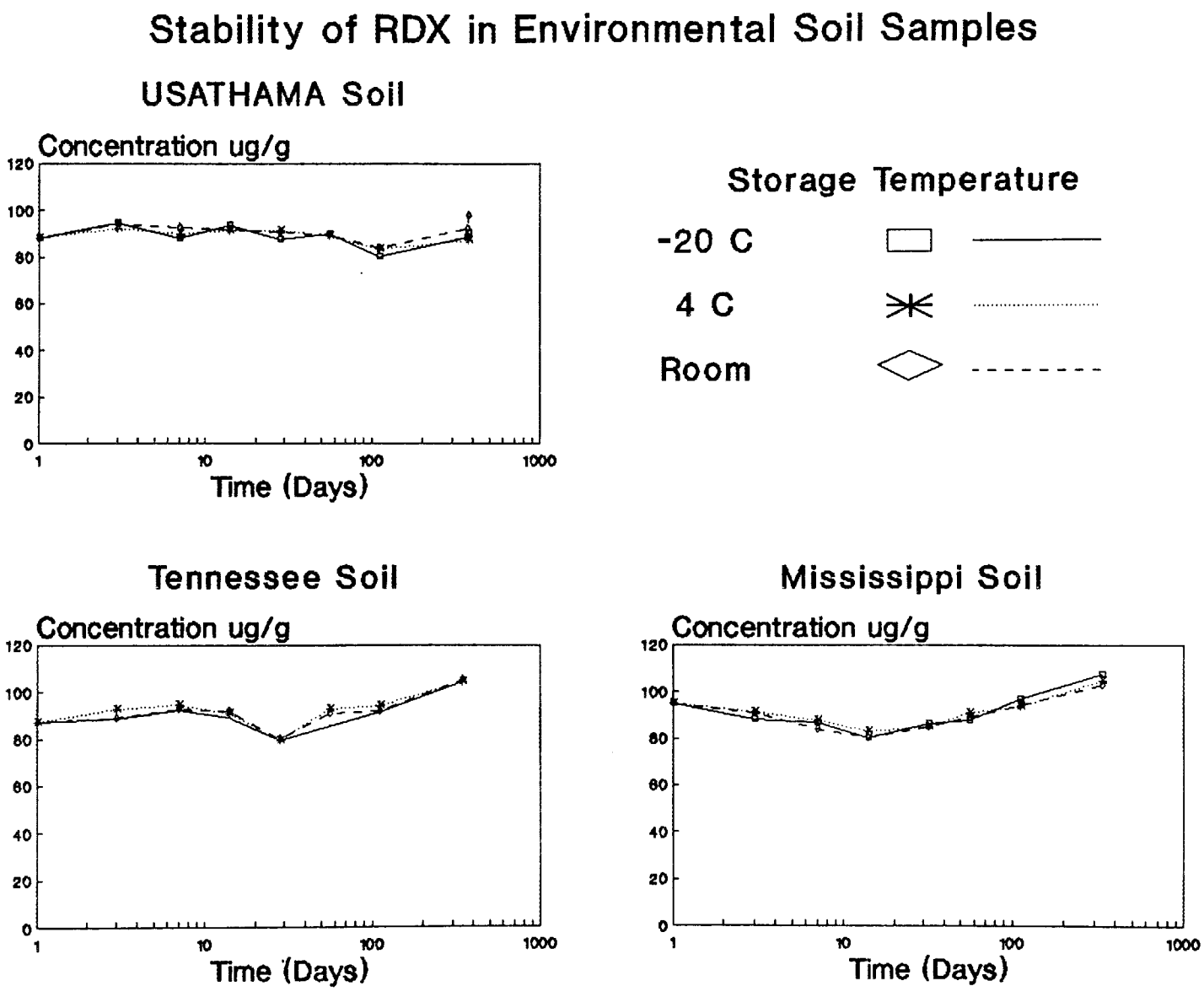

Fig. D.2 High-level RDX in soil samples.

Table D.3 TNT summary statistics for high-level concentrations (μg/g) in soil samples.

Soil Storage		Num Avg St Dev	Day								All Days
Soil Type	Store Cond		0	3	7	14	28	56	112	≥333	
USATHAMA	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	85.6	.	.	.	.	.	.	.	85.6
		St Dev	3.9	.	.	.	.	.	.	.	3.9
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	80.1	82.8	87.8	90.2	86.0	78.5	79.6	83.6
		St Dev	.	2.0	8.3	1.8	2.7	3.3	2.2	3.9	5.6
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	73.2	83.4	80.1	77.6	70.4	52.5	25.1	66.0
		St Dev	.	0.7	2.0	6.2	4.0	1.4	3.1	2.7	19.7
	Room	Num	.	4.0	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Avg	.	68.8	70.8	54.8	46.2	29.0	11.0	0.3	40.5
		St Dev	.	2.8	1.2	3.5	1.7	1.5	0.8	0.5	26.5
Tennessee	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	102.	.	.	.	.	.	.	.	102.1
		St Dev	3.4	.	.	.	.	.	.	.	3.4
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	86.0	105.8	87.1	71.1	87.1	89.6	83.2	87.1
		St Dev	.	2.2	2.2	2.2	3.0	3.4	2.5	2.8	9.9
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	90.8	89.9	91.2	68.3	79.7	78.7	56.0	79.2
		St Dev	.	6.6	5.9	1.4	3.9	5.4	4.7	6.0	13.3
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	83.8	91.3	73.4	51.9	46.1	20.8	3.1	52.9
		St Dev	.	6.5	4.8	1.2	1.8	5.6	4.6	1.6	31.0
Mississippi	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	91.9	.	.	.	.	.	.	.	91.9
		St Dev	5.4	.	.	.	.	.	.	.	5.4
	-20°C	Num	.	4.0	4.0	4.0	3.0	3.0	3.0	4.0	25.0
		Avg	.	80.5	80.5	71.3	80.9	82.3	93.6	78.1	80.5
		St Dev	.	5.4	2.1	5.3	4.7	1.7	3.6	6.1	7.2
	4°C	Num	.	4.0	4.0	4.0	3.0	3.0	4.0	4.0	26.0
		Avg	.	86.2	82.9	71.5	78.9	85.7	89.4	71.7	80.8
		St Dev	.	3.7	2.5	4.1	5.4	5.8	2.0	5.8	7.8
	Room	Num	.	4.0	4.0	3.0	4.0	3.0	4.0	4.0	26.0
		Avg	.	85.7	78.5	72.0	72.7	72.4	72.6	54.0	72.6
		St Dev	.	3.4	3.4	1.8	1.3	6.7	7.9	7.2	10.5

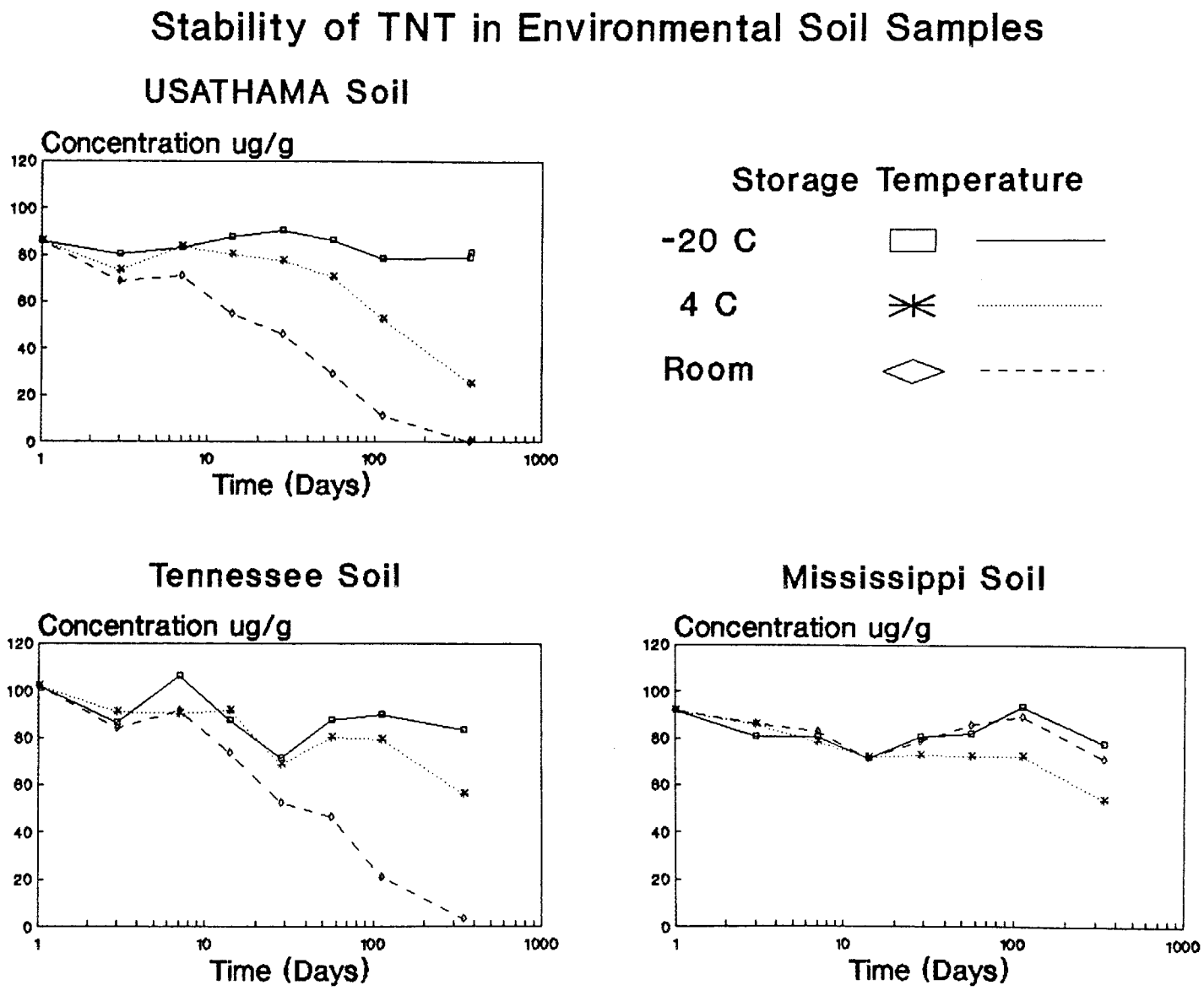

Fig. D.3 High-level TNT in soil samples.

Table D.4 DNT summary statistics for high-level concentrations (μg/g) in soil samples.

Soil Storage		Num Avg St Dev	Day								All Days
Soil Type	Store Cond		0	3	7	14	28	56	112	≥333	
USATHAMA	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	89.5	.	.	.	.	.	.	.	89.5
		St Dev	3.6	.	.	.	.	.	.	.	3.6
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	91.7	88.3	89.6	87.9	89.1	79.3	104.4	90.0
		St Dev	.	1.6	4.3	0.9	2.9	0.9	2.3	2.9	7.4
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	87.8	89.5	88.2	89.1	88.3	80.6	100.4	89.1
		St Dev	.	1.5	2.0	0.7	3.0	1.4	1.8	2.9	5.8
	Room	Num	.	4.0	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Avg	.	89.6	88.6	86.9	87.0	88.7	79.3	97.6	88.2
		St Dev	.	1.4	0.9	1.2	0.4	1.0	0.8	3.6	5.4
Tennessee	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	93.3	.	.	.	.	.	.	.	93.3
		St Dev	2.0	.	.	.	.	.	.	.	2.0
	-20°C	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Avg	.	87.5	94.9	91.9	76.3	84.0	94.6	98.8	89.7
		St Dev	.	1.3	0.9	0.9	0.7	2.5	4.2	1.9	7.5
	4°C	Num	.	4.0	4.0	4.0	4.0	4.0	3.0	4.0	27.0
		Avg	.	91.2	95.6	93.3	78.6	85.5	94.3	93.8	90.2
		St Dev	.	3.2	1.6	1.8	2.8	1.3	4.3	3.3	6.3
	Room	Num	.	4.0	4.0	4.0	4.0	4.0	4.0	3.0	27.0
		Avg	.	89.4	91.4	91.9	74.4	82.4	87.2	84.7	85.9
		St Dev	.	1.9	1.5	1.9	1.6	2.4	2.9	3.2	6.2
Mississippi	None	Num	4.0	.	.	.	.	.	.	.	4.0
		Avg	91.3	.	.	.	.	.	.	.	91.3
		St Dev	3.8	.	.	.	.	.	.	.	3.8
	-20°C	Num	.	4.0	4.0	3.0	3.0	4.0	4.0	4.0	26.0
		Avg	.	87.1	87.3	74.9	81.2	83.6	90.4	102.2	87.3
		St Dev	.	2.3	2.6	1.9	4.2	2.3	4.8	1.9	8.3
	4°C	Num	.	4.0	4.0	4.0	3.0	4.0	4.0	4.0	27.0
		Avg	.	91.6	86.7	74.2	80.1	82.0	90.3	98.7	86.4
		St Dev	.	1.1	1.0	5.1	5.7	3.1	1.1	4.4	8.3
	Room	Num	.	4.0	4.0	3.0	4.0	4.0	4.0	4.0	27.0
		Avg	.	90.0	84.0	73.2	74.6	80.0	84.4	94.2	83.3
		St Dev	.	2.2	0.5	1.8	0.9	2.9	4.7	2.7	7.5

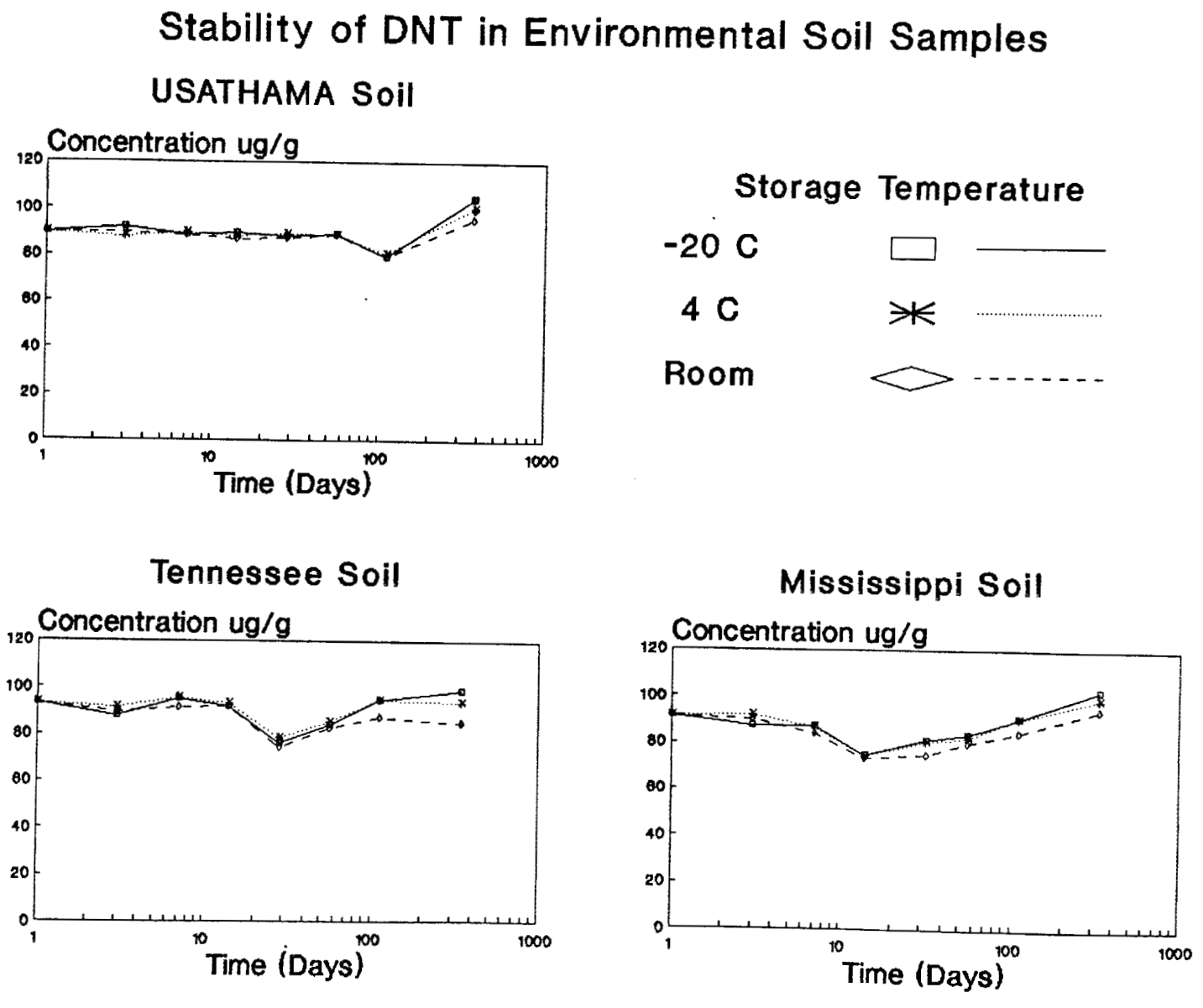

Fig. D.4 High-level DNT in soil samples.

APPENDIX E

Alternative Models for Estimating Maximum Preanalytical Holding Times

Alternative Models for Estimating Maximum Preanalytical Holding Times

The problems encountered with fitting zero-order and first-order models to the preanalytical holding time data are illustrated in Fig. E.1 for high-level concentrations of TNT in surface water stored at 4°C. The concentrations are approximately constant for the first 28 days then rapidly decrease to a plateau of about 590 µg/L. Basically, there are only two concentration levels. Both the zero-order and first-order models try to average these low and high concentrations levels.

To approximate the rapidly decreasing concentrations, additional linear models (e.g., linear with respect to the coefficients) were examined which have derivatives that also decreased rapidly. The zero-order model, first-order model, and the additional models are given in Table E.1. The log-term model and inverse-term model were able to approximate the rapid concentration decreases for many of the special cases. The coefficients for these models can be estimated by the usual linear regression methods. However, these models couldn't approximate any cases which had an initial constant-concentration plateau. An empirical model was then applied which had an initial constant-concentration for days less than day = D_0, and a final concentration for days greater than day = D_1. The concentrations between day D_0 and day D_1 were modelled by a cubic spline which is a cubic polynomial with a sigmoidal shape curve. The cubic spline starts at the initial concentration at day D_0 and ends at the final concentration at day D_1. In addition, the cubic spline is required to be continuous at day D_0 and day D_1.

Table E.1 Models and their derivatives used to approximate special cases of explosives in water and soil samples.

Model	Equation	Derivative
Zero-Order	$C = C_0 + B(day)$	$dC/d(day) = B$
First-Order	$C = C_0 exp[B(day)]$	$dC/d(day) = BC_0 exp[B(day)]$
Log-Term	$C = C_0 + B(day) + Aln(day)$	$dC/d(day) = B + A/(day)$
Inverse-Term	$C = C_0 + B(day) + A/(day)$	$dC/d(day) = B - A/(day)^2$

Mathematically, the cubic spline approximates the concentrations by a function of time, f(D) with D = day:

$$f(D) = \begin{cases} C_0 & \text{if } D \le D_0 \\ a + bD + cD^2 + dD^3 & \text{if } D_0 \le D \le D_1 \\ C_1 & \text{if } D \ge D_1 \end{cases}$$

The continuity condition and the initial and final concentration conditions place two restrictions on f(D):

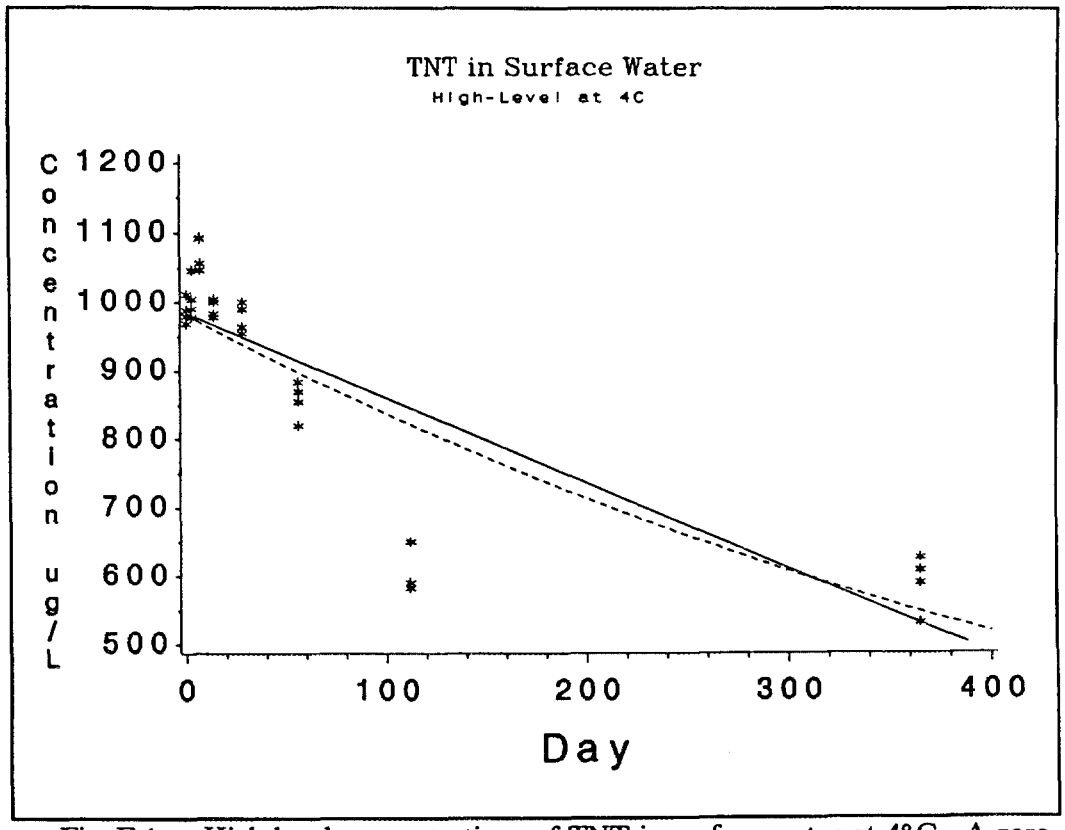

Fig. E.1 High-level concentrations of TNT in surface water at 4°C. A zero-order model (solid line) and first-order model (dashed line) are fitted to the concentration data (stars).

1. $f(D_0) = C_0$ and $f(D_1) = C_1$.

2. $f'(D_0) = 0$ and $f'(D_1) = 0$, where f' is the derivative with respect to D_0 and D_1, respectively.

Using these two restrictions for the cubic spline, the coefficients a, b, c, and e can be determined in terms of D_0 and D_1.

$$a = (C_0H_1 - C_1H_0)/(H_1 - H_0) \qquad c = -1.5(C_1 - C_0)(D_0 + D_1)/(H_1 - H_0)$$

$$b = 3(C_1 - C_0)D_0D_1/(H_1 - H_0) \qquad e = (C_1 - C_0)/(H_1 - H_0)$$

where $H_0 = 0.5D_0^2(3D_1 - D_0)$ and $H_1 = 0.5D_1^2(3D_0 - D_1)$.

The estimates of the parameters D_0 and D_1 for the cubic splines are calculated by the method of non-linear least squares. The cubic splines were estimated for 9 special cases of explosives in water samples and 5 special cases of explosives in soil samples. The

estimated parameters were calculated with the non-linear procedure PROC NLIN with METHOD=MARQUARDT in the SAS computer programming language [*17*]. The fitted cubic spline is plotted in Fig. E.2 for high-level concentrations of TNT in surface water at 4°C.

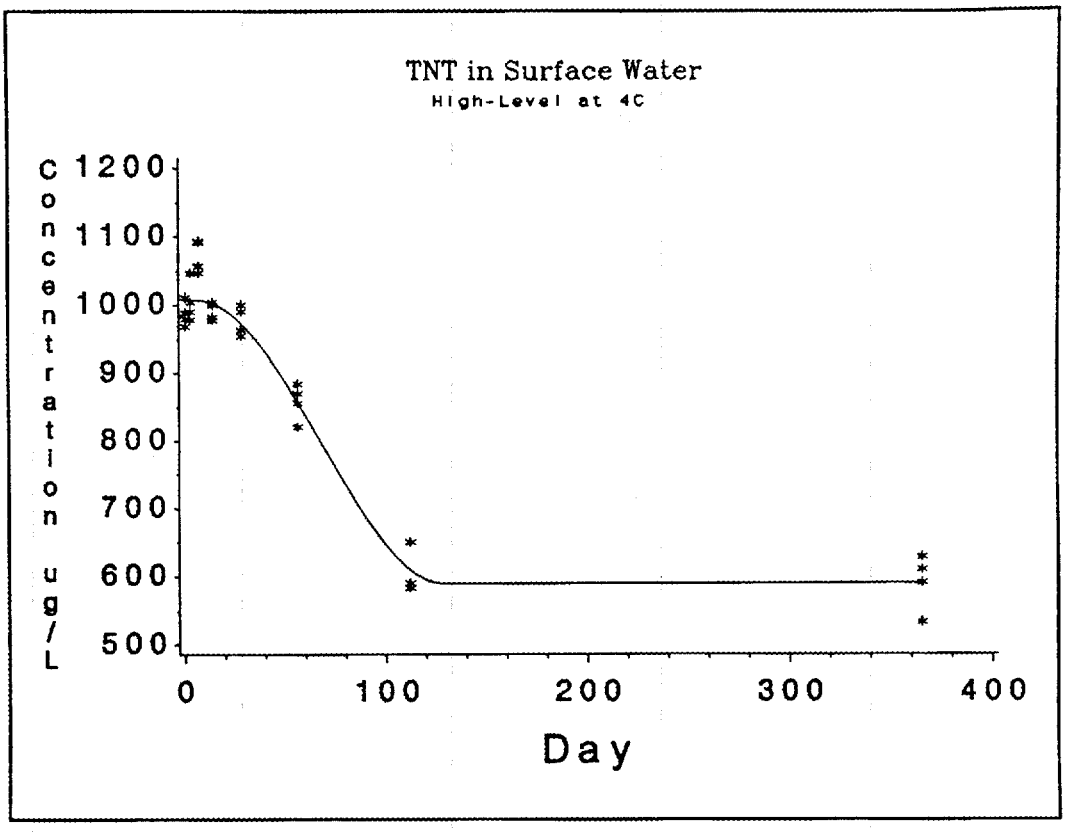

Fig. E.2 Cubic spline fitted to high-level concentrations of TNT in surface water stored at 4°C.

Maximum Holding Time

The ASTM and ESE definitions for MHT are adapted to the cubic spline using the following procedures:

ASTM MHT procedure for the cubic spline:

1. Fit the data with a cubic spline using C_0 = the average of concentrations on day = 0 and C_1 = the average of concentrations on day = 365 or one-half the average for concentrations of day = 112 and day = 365.

2. Construct a 99% confidence interval about the initial concentration $C_0 \pm t(0.005,df)S_p/\sqrt{n}$ where t(0.005,df) is the 99.5 percentile point of the t-distribution

with df = degrees of freedom for S_p. The pooled standard deviation, S_p, is estimated from all within standard deviations for days $\leq D_0$ and n is the number of observations on day = 0.

3. The MHT is found by iteratively calculating the cubic spline for days in the interval (D_0,D_1) until the following conditions are achieved:

   a) $C_0 - t(0.005,df)S_p/\sqrt{n} \leq f(MHT)$.

   b) $C_0 - t(0.005,df)S_p/\sqrt{n} > f(MHT+1)$.

<u>ESE MHT procedure for the cubic spline</u>:

1. Fit the data with a cubic spline using C_0 = the average of concentrations on day = 0 and C_1 = the average of concentrations on day = 365, or one-half the averages for concentrations on day = 112 and day = 365.

2. Construct a ± 10% interval on C_0 [e.g., $(0.9C_0,1.1C_0)$]. Test that the 10% change is outside the 90% confidence interval on C_0 [e.g., $0.1C_0 \geq t(0.05,df)S_p/\sqrt{n}$ where t(0.05,df) is the 95 percentile point of the t-distribution with df = degrees of freedom for S_p]. The pooled standard deviation, S_p, is estimated from all within standard deviations for days $\leq D_0$ and n is the number of observations on day = 0.

3. If a 10% change is not outside the 90% confidence interval on C_0, calculate the concentration change (i.e. $C_0 - KC_0$) that is outside the 90% confidence interval by:

   $$K = t(0.05,df)S_p/(C_0\sqrt{n})$$

   If K > 0.15, the cubic spline model does not give an appropriate fit for estimating MHT.

4. The MHT is defined as the one-sided lower 90% confidence interval on the critical time (i.e., the day the cubic spline equals $C_0 - KC_0$). This MHT definition is equivalent to the day the lower 90% confidence interval on the cubic spline equals $C_0 - KC_0$. The MHT is found by iteratively calculating the cubic spline for days in the interval (D_0,D_1) until the following conditions are achieved:

   a) $C_0 - KC_0 \leq f(MHT) - t(0.10,df)\{Var[f(MHT)]\}^{1/2}$.

   b) $C_0 - KC_0 > f(MHT+1) - t(0.10,df)\{Var(f(MHT+1)]\}^{1/2}$.

The value of t(0.10,df) is the 90 percentile point of the t-distribution with df = N - 2 degrees of freedom for N observations in the data set. The variance of the cubic spline

Var[f(D)] is calculated by error propagation formulas [*18*] using the derivatives with respect to D_0 and D_1.

$$Var[f(D)] = (df/dD_0)^2 Var(D_0) + (df/dD_1)^2 Var(D_1) + 2(df/dD_0)(df/dD_1)Cov(D_0,D_1).$$

The variance terms $Var(D_0)$,$Var(D_1)$ and covariance term $Cov(D_0,D_1)$ are estimated from the non-linear least squares fit of the cubic spline to the observed data. The derivatives of the cubic spline are:

$$(df/dD_0) = da/dD_0 + (db/dD_0)D + (dc/dD_0)D^2 + (de/dD_0)D^3, \text{ and}$$

$$(df/dD_1) = da/dD_1 + (db/dD_1)D + (dc/dD_1)D^2 + (de/dD_1)D^3.$$

Let $K = 1/(D_0 - D_1)^4$, then the derivatives of the coefficients are:

$$da/dD_0 = 6K(C_1 - C_0)D_0D_1^2 \qquad dc/dD_0 = 6K(C_1 - C_0)(D_0 + 2D_1)$$

$$db/dD_0 = -6K(C_1 - C_0)D_1(2D_0 + D_1) \qquad de/dD_0 = -6K(C_1 - C_0)$$

$$da/dD_1 = -6K(C_1 - C_0)D_0^2D_1 \qquad dc/dD_1 = -6K(C_1 - C_0)(2D_0 + D_1)$$

$$db/dD_1 = 6K(C_1 - C_0)D_0(D_0 + 2D_1) \qquad de/dD_1 = 6K(C_1 - C_0)$$

Figure E.3 illustrates the ASTM and ESE definitions for high-level concentrations of TNT in surface water stored at 4°C. The maximum holding times for the special cases of explosives are tabulated in Tables E.2 and E.3.

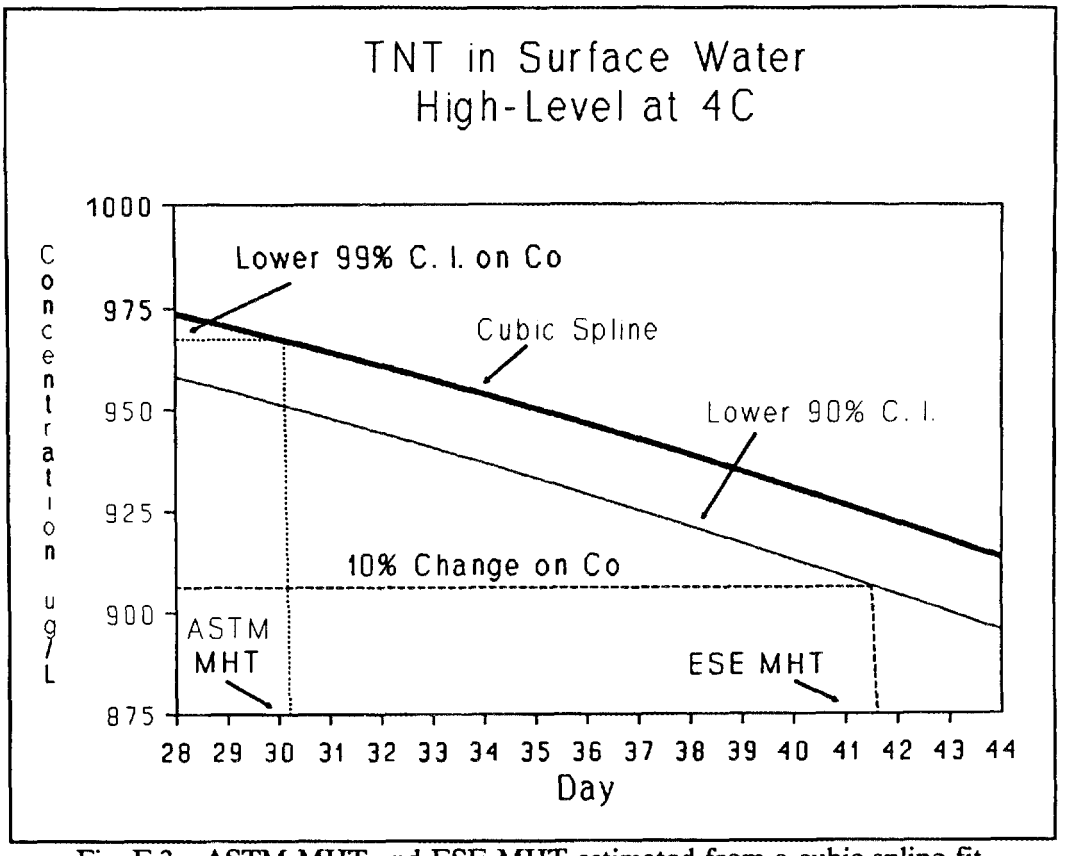

Fig. E.3 ASTM MHT and ESE MHT estimated from a cubic spline fit. high-level concentrations of TNT in surface water stored at 4°C.

Table E.2 Alternative models for explosives in water samples.

Conc Level	Explosive Compound	Water Type	Storage Condition	Model	C_0	C_1	B	A	D_0	D_1
Low	RDX	Ground	Room	Cubic	50.1	0.0			120.0	150.0
	TNT	Ground	Room	Log	51.8		-0.0119	-8.3424		
	TNT	Surface	4°C	Cubic	53.5	0.0			15.0	32.1
	TNT	Surface	Room	Cubic	48.1	0.0			0.7	4.0
	DNT	Distilled	4°C	Log	53.2		-0.0078	-2.0751		
	DNT	Distilled	Room	Cubic	51.4	32.3			0.0	104.8
	DNT	Ground	4°C	Log	53.7		0.0078	-2.4537		
	DNT	Ground	Room	Log	53.4		0.0078	-2.6743		
	DNT	Surface	Room	Log	47.6		0.0543	-11.510		
High	HMX	Distilled	4°C	Cubic	975	545			20.0	44.5
	HMX	Distilled	Room	Cubic	979	531			30.0	50.0
	RDX	Distilled	Extract	Log	797		-2.5197	77.919		
	TNT	Distilled	Extract	Log	777		-1.8232	68.357		
	TNT	Ground	Room	Cubic	999	9			0.0	79.4
	TNT	Surface	4°C	Cubic	1007	590			7.1	127.5
	TNT	Surface	Room	Log	929		1.3032	-225.18		
	DNT	Distilled	Extract	Log	810		-1.4185	55.494		
	DNT	Ground	Extract	Log	862		-1.4729	41.578		
	DNT	Surface	Extract	Cubic	946	338			60.0	140.1

Table E.3 Alternative Models for Explosives in Soil Samples.

Conc Level	Explosive Compound	Soil Type	Storage Condition	Model	C_0	C_1	B	A	D_0	D_1
Low	RDX	USATHAMA	Room	Cubic	9.9	0.0			10.3	68.6
	RDX	Tennessee	Room	Cubic	9.0	0.5			4.2	64.1
	TNT	USATHAMA	Room	Cubic	8.9	0.0			0.5	3.0
	TNT	Tennessee	Room	Inverse	-0.30		0.0016	4.7250		
	TNT	Mississippi	4°C	Inverse	3.48		-0.0052	3.7720		
	TNT	Mississippi	Room	Inverse	-0.26		0.0009	5.5228		
	DNT	USATHAMA	Room	Cubic	9.0	0.0			0.0	9.3
	DNT	Tennessee	Room	Cubic	9.1	0.2			0.0	21.2
High	TNT	USATHAMA	Room	Log	83.3		-0.0421	-11.921		

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