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Picric Acid Degradation in Sterilized Sediments from the Louisiana Army Ammunition Plant, Minden, Louisiana

Stephanie Kimberly Rice

PICRIC ACID DEGRADATION IN STERILIZED SEDIMENTS FROM THE LOUISIANA ARMY AMMUNITION PLANT, MINDEN, LA

by
Stephanie K. Rice

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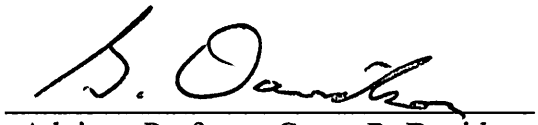
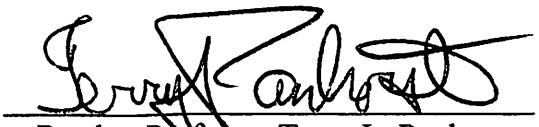


Advisor: Professor Gregg R. Davidson



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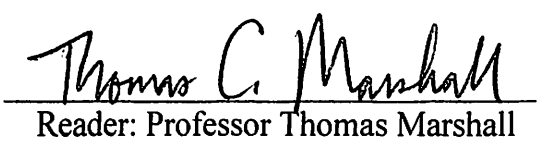

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ABSTRACT

STEPHANIE K. RICE: Picric Acid Degradation in Sterilized Sediments from the Louisiana Army Ammunition Plant, Minden, LA
(Under the direction of Gregg R. Davidson)

Picric acid is an explosive historically produced and disposed of at the Louisiana Army Ammunitions Plant (LAAP). The potential for natural degradation was investigated in two studies by creating picric acid slurries with four LAAP samples of sediment of variable composition. While the first study combined the sediment with picric acid without alteration to the sediment, the second study sterilized the sediment before the slurries were created. The purpose of the soil sterilization was to quantify the role of microbes in the degradation process. In the first study, picric acid concentrations decreased 10 to 18% the first day, attributed to adsorption, followed by slower decreases attributed to degradation. Near complete degradation was observed in two of the slurries within eight weeks. No correlation was found between degradation and grain size, clay or organic content, or element concentrations in the sediment. The only exception was manganese, which was higher in the two samples which exhibited high degradation. In the second study, initial concentration decreases ranged from 5 to 25%, which can be attributed to adsorption, and minimal degradation was observed for the remainder of the 100-day study. The difference in the degradation between the two studies is attributed to the removal of the microbial communities by sterilization.

Key words: picric acid, degradation, natural attenuation, LAAP

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Introduction

The Louisiana Army Ammunitions Plant (LAAP) is a 14,974-acre government-owned contractor-operated facility located in Minden, Louisiana, approximately 22 miles east of Shreveport, Louisiana. Constructed in 1941-42, the plant closed in 1994 after over 50 years of operation. LAAP assembled and packaged ammunition items, manufactured metal ammunition parts, and provided support functions for ammunitions production (Harrelson et al., 2001). The plant is located within the North Louisiana Syncline, which has anomalous thickening and thinning lithologic units. Pleistocene units are exposed at the surface and are underlain by Eocene, Cretaceous, and Jurassic formations. Small uplifts in the area modify the structural geology and groundwater flow directions, which could influence flow of subsurface contaminants in the groundwater.

The primary waste products detected in the subsurface are TNT and RDX (2,4,6-trinitrotoluene and hexahydro-1,3,5-trinitro-1,3,5-triazine, respectively), with lesser concentrations of other nitro-organic compounds including picric acid (2,4,6-trinitrophenol), HMX (octahydro- 1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetraxocine), and N, 2, 4, 6-tetranitro-n-methylanine. A study conducted by Beller and Tiemeier (2002) investigated contaminants at LAAP using liquid chromatography with UV spectrophotometric detection and identified traces of the ammunition wastes MNX and TNX in the groundwater. The detection suggests potential difficulties with the techniques because the MNX and TNX only occurred on the last sampling date despite regular testing (five times in 11 months) (Beller and Tiemeier, 2002).

The picric acid at LAAP was mainly produced during 1944 and 1945 and was deposited into 16 unlined ponds and ditches, causing contamination of underlying sediments and groundwater. The plant was placed on the National Priorities List in 1989 because of contamination caused by the disposal of waste-laden water into the surface ponds (Harrelson et al., 2001). Beginning in 1988 and continuing until 1994, remediation techniques, including the draining of wastewater and incineration of soils, were conducted to reduce contamination (Harrelson et al., 2001). During the 1980's, remediation and long-term monitoring was begun to determine if the contaminants would naturally degrade over time.

When harm to humans or ecosystems is not imminent, monitored natural attenuation is an attractive option because of its lower cost. Most of the studies investigating natural attenuation at LAAP have focused on TNT and RDX and their degradation products (Beller and Tiemeier, 2002, and Ringelberg et al., 2003). Picric acid has been relatively unstudied in the literature, in part because of its low concentration in most explosives contamination.

If introduced into groundwater systems, picric acid has the potential to become highly mobile. A low octanol-water partition coefficient ($K_{ow} = 40$) suggests that picric acid is not readily absorbed onto mineral or organic particles (Goodfellow et al., 1983), and a 30-day degradation study reported resistance to hydrolysis, biodegradation, and photolysis (Dave et al., 2000). Different degradation pathways have been studied recently (Joshi et al., 2003 and Ksibi et al., 2003). Kisibi et al. (2003) used UV irradiation with ZnO and TiO_2 as catalysts and suggested that degradation occurs by substituting hydroxyl radicals for hydrogen and nitro groups and by forming NO_3^- and

NH_4^+. Although the investigations in the literature provide important information regarding degradation, the studies were performed in laboratories under different conditions than found in natural groundwater systems. The current study simulates subsurface conditions in an attempt to create groundwater conditions in a controlled environment.

Subsurface contamination of explosives and related compounds at former ammunition production sites has been a world-wide problem since World War II. Sites in Germany, East Europe, and the United States have undergone testing to determine soil and groundwater contamination from ammunition production (Steuckart et al., 1994). High Performance Liquid Chromatography (HPLC) has been integrated into the determination of nitroaromatics, nitramines, and other explosives using reversed-phase chromatography and UV detection. (Steuckart et al., 1994).

The current work is following up on previous studies by G.R. Davidson at The University of Mississippi. In these initial studies (not yet published), picric acid was added to slurries made with four different sediments and placed on a roller table in the dark for 14 weeks. During this time, nearly complete degradation was observed in two of the slurries, and only minor degradation in the remaining two. No significant correlations were found between degradation and grain size, clay content, organic content, solution composition or solid-phase element concentration, with the exception of Mn. Manganese may have acted as a catalyst to facilitate degradation in the two slurries where degradation was nearly complete. However, there could also have been significant differences in the microbial populations in the different sediments. In an effort to

simulate natural conditions, these sediments were not sterilized prior to creation of the slurries.

Procedures from the previous investigation were followed after the sterilization of the sediments to investigate the influence of microbial activity on degradation. If degradation is greatly reduced after sterilization, this will suggest microbial action as the principle mechanism for degradation and additional studies can characterize the microbial differences found in the different sediments. If residual picric acid is not detected in the sediment, then the area of LAAP from which the samples were gathered is probably not contaminated.

History of HPLC

Chromatography was first used in 1905 by Michael S. Tswett (Ettre, 1980). As a botanist, Tswett studied the adsorption of plant pigments. He proposed that non-polar solvents cannot extract the plant pigments from the plant material while polar solvents can, because the polar solvents can break down the original adsorption complex within the plant. Tswett conducted model experiments showing that plant pigment mixtures adsorbed onto artificial material just as they do in the natural leaf. Using these models, Tswett developed the first column chromatography (Ettre, 1980). He filtered an ether solution through a column of an adsorbent, which resolved the pigments into colored zones according to their adsorption sequence. The pigment solution then flowed through a stream of solvent, which resolved the different components of the pigments mixture on the column, which were later quantitatively and qualitatively described. He realized that separation of the components occurred because of different affinities of substances for the adsorbent packed in the column (Done et al., 1974). Tswett continued to improve his methods, however, chemists during this time did not recognize the significance of chromatography, and the method and techniques became dormant in the scientific community.

In 1930, Edgar Lederer resumed work with Tswett's under-utilized technique by performing the first chromatographic experiment. He collected a pure sample of calcium carbonate by separating lutein and zeaxanthine in a carbon disulfide solution (Ettre, 1980). Other scientists began using the same techniques because liquid

adsorption chromatography was simple and could be carried out in most labs. The technology further developed so that readings could be carried out on separations that were outside of the visible spectrum. A. Winterstein and P. Karrer used UV fluorescence to describe the relationship between separated colors, light adsorption, and the chemical structure of compounds invisible in visible light (Ettre, 1980). In 1937 G.M. Schwab further developed the technique so that inorganic compounds could be used.

During the 1940's techniques with continuous feed of the components were developed. A. Tiselius began using frontal analysis and continuously fed the component into the column so that a pure component would elute from it once the absorbent in the column was saturated and the front had passed through the column (Ettre, 1980). Displacement development was soon created. The mixture of components were followed by a continuous supply of a displacer liquid which was adsorbed more on the column material than the sample components, which pushes the sample components off the adsorbent and forces them ahead in the column, which displaces components of the sample into individual zones.

Reverse-Phase Chromatography was developed by A.J.P. Martin and G.A. Howard at the Lister Institute in London. The separation of long-chain fatty acids was not possible with traditional chromatography because the components would favor the less polar mobile phase and not adsorb into the column, thereby not separating. Martin and Howard changed the system by making the mobile phase more polar than the stationary phase of the column (Ettre, 1980).

High Performance Liquid Chromatography was developed in the 1970's . Prior to its development, HPLC functions were performed inadequately by open-column chromatography, paper chromatography, and thin-layer chromatography. These early methods were inadequate for quantifying compounds and identifying resolution between similar compounds. Pressure liquid chromatography developed as a result of studies of each component of the chromatography setup. Studies were conducted on porosity and small-diameter particles, stationary phases, high inlet pressures, pump systems, small-volume detectors, and reversed phase and gradient-elution chromatography (Ettre, 1980). However, the flow and pressure could not both remain stable and it was debated as to which was more important.

High Performance Liquid Chromatography, first introduced as High Pressure Liquid Chromatography, is capable of controlling both the flow rate and the pressure, and quickly improved throughout the 1970s as column packing materials and on-line detectors were developed.

HPLC Operation

The HPLC operates by injecting a sample into an eluent and then pumping the fluid through a column which separates the components. The separated compounds are read using UV wavelengths through a detector before being flushed into a waste container.

The eluents enter the pump (Figure 1) and are forced into an injector where they are mixed with the sample. The eluent/sample mix is then pumped through the guard column into the separator column. Next the separated components are read in the optical detector, which is labeled in Figure 1 as DS3. The mixture flows through the backpressure tubing before exiting the system into the waste container.

The eluent, referred to as the mobile phase, is a solvent which is continuously applied to the column. The separation occurs in the column, which is packed with the stationary phase. The adsorbent packing material in the column is composed of micrometer-sized porous particles. Since the stationary phase is composed of tiny particles, a pump is required to efficiently move the mobile phase through the column (Kazakevich and McNair, 2003).

The sample is injected into the mobile phase, which acts as the carrier of the compound as it travels though the column. A guard column is often used before the separator column in order to filter particles from the mixture and prevent deterioration to the more expensive separator column. As the sample flows through the column,

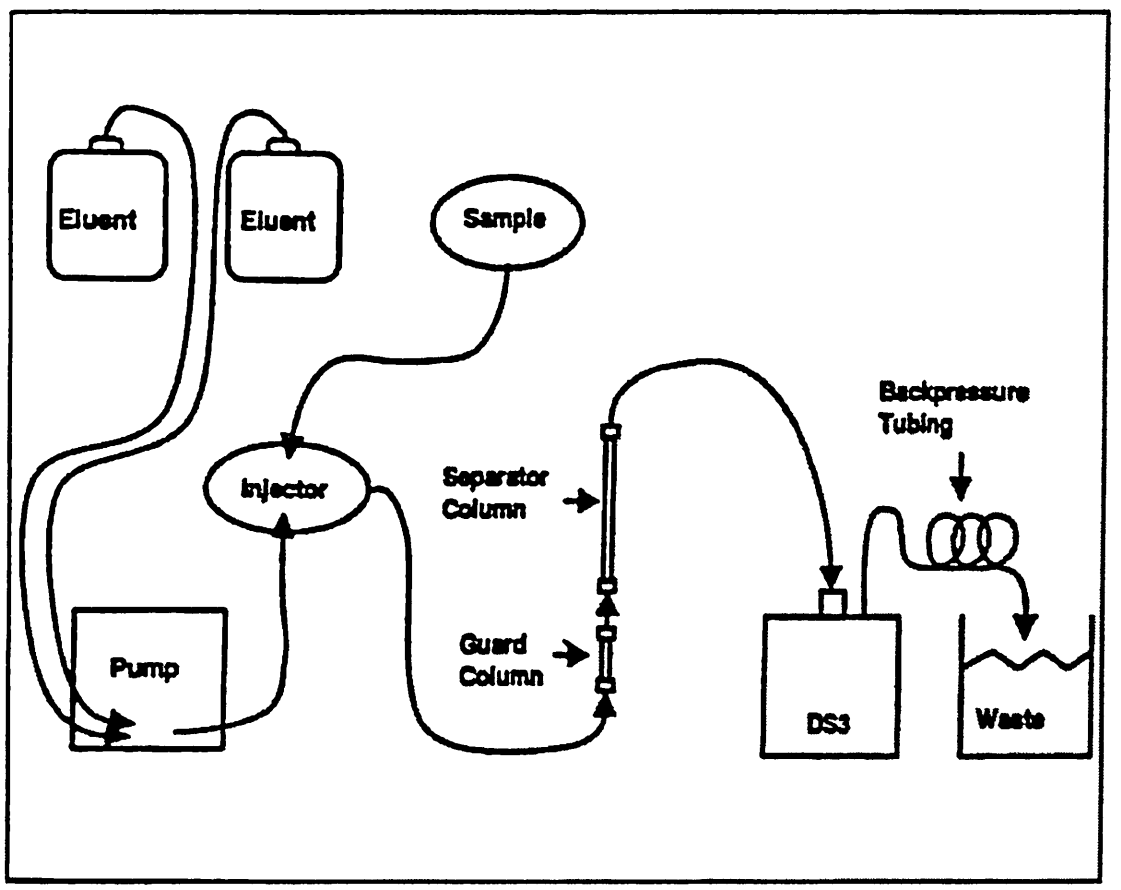

Figure 1—HPLC Flow Diagram. Diagram outlines the progression of the sample through the High Performance Liquid Chromatography.

_____, DX 500 Operational Techniques and Maintenance: Training Course Manual, Dionex Corporation, Sunnyvale, CA (1995), pp. 253.

the components of the sample separate according to non-covalent interactions with the column. The samples which have stronger relations to the mobile phase will travel through the column faster, while the samples which interact with the stationary phase will elute more slowly through the column.

Columns have been developed to contain different types of stationary phases, including liquid-solid (adsorption) and liquid-liquid phases (Majors, 1980). Liquid-solid uses polarity to separate samples. Polar compounds which are capable of hydrogen bonding will adhere to the stationary phase, while non-polar compounds will elute faster from the column. Liquid-liquid columns also use polarity, however, these columns are better for samples of medium polarity. The separation occurs by matching the polarities of the sample and stationary phases while using a mobile phase which has a different polarity.

After the compound is separated, an optical detector is used to quantitatively describe the sample. A beam of light is passed through the effluent as it flows through the detector. The most commonly used light detector is ultraviolet light, however, other common detectors include fluorescence and mass spectrometry. The variations in light intensity caused by UV absorption are recorded as the sample components pass through the detector. A computer is used to resolve these data and display the retention time and peak area data (Kazakevich and McNair, 2003).

After the separation process has occurred and the data have been plotted, the sample can be interpreted. The data is charted on a chromatograph and provides the retention time of the sample, the peak height, and the peak area. The retention time is a measure of the time between the injection of the sample into the eluent and the

maximum detection response. The retention time is a function of the column, mobile phase, and flow rate and is inversely proportional to the eluent flow rate (Kazakevich and McNair, 2003). In order to quantitatively read data, however, peak area is the preferred data result because it is less affected by minor changes in temperature, flow rate, or retention time than the peak height (Dionex, 1995). Peak height is useful when complete separation of peaks of several compounds is not possible.

After the separated compound passes through the optical detector, it passes through backpressure tubing and is deposited into a waste container. The back pressure tubing reduces ambient pressure and allows the fluid to drip from the system.

Procedure

The subsurface of LAAP consists of unconsolidated Pleistocene-age, terraced fluvial sediment, deposited in a fining-upwards sequence. Four subsurface sediment samples from two previously identified fluvial terraces have been collected at LAAP, which represent the possible contaminated sediment in the area. The lower terrace is composed of fine sands and trace gravels, and the upper terrace is composed of fine-grained silts, clays, and silty clays. Brief sample descriptions are given in Table 1. Samples were collected from an uncontaminated site at LAAP from pits dug by a backhoe. Three of the samples were taken from different depths in the Upper Terrace (identified as U1, U2, and U3), and one was taken from the Lower Terrace deposits (L1).

The initial experiment conditions were developed to simulate natural underground conditions at LAAP. The samples of the sediment were mixed, and the top layer of the sediment was selected for the sub-sample. The sub-samples of each sediment were disaggregated and dried in an oven for three days. Roller bottles were then filled with 600 g of the dried sediment and dried in a 110°C oven overnight. The second, higher-temperature drying was included to kill microbial organisms. One slurry of each type of sediment was made using the 1.8 L glass roller bottles filled with the 600 g dried, sterilized sediment and 800 mL of 100 mg/L picric acid solution. The picric acid solution was made from 98% purity solid picric acid solution and boiled, distilled water. A blank slurry was prepared for each sediment

Zone	Sample ID	Depth	Visual description
Upper Terrace	U1	1.2 m	sandy silt
	U2	2.4 m	silt
	U3	3.4 m	clayey silt
Lower Terrace	L1	5.5 m	sand

Table 1—Sediment Descriptions. Stratigraphic zone, depth and visual description of sediment collected at LAAP.

with 600 g of sediment and 800 mL boiled, distilled water. Water used in blanks and picric acid solutions was boiled to ensure sterilization. Samples were placed on rollers to ensure good contact between the sediment and solutions. The four picric acid and sediment slurries and the four blank slurries were kept in the dark and rolled continuously at approximately 2 rpm at room temperature for 100 days. A ninth bottle was prepared with only the picric acid solution and stored in the dark in order to compare the acid degradation with and without sediment.

Samples of the picric acid and blank solutions were collected daily for the first week, and weekly for the remainder of the project. For analysis, each slurry was removed from the rollers and allowed to settle for 6 hours before sampling. Picric acid concentration and pH were determined from each sample. The pH of each solution was measured using a VWR SympHony Series pH Electrode with Ag/AgCl Internal Reference System, model 8000. Approximately 1.5 mL of the solution from each of the eight roller bottles and the pure solution bottle was collected at each sampling time, filtered, and transferred into 1.8 mL autosampler vials, which were sealed and stored under refrigeration until analysis.

Picric acid concentration was measured using High Performance Liquid Chromatography (HPLC) equipped with a 250x4.6 mm Adsorbosphere XL-C18 column and a UV detector operated at 365 nm. The method was 1.5 mL/min of 40/60 methanol/buffer solution passed through the column for 25 minutes. The buffer was 6.8 g/L KH_2PO_4, acidified to pH 3.5 with acetic acid. The effluent was passed through the column for 25 minutes to adequately flush the 25 cm column between samples.

For data interpretation, a concentration curve was created using the HPLC readings for the 100 mg/L, 10 mg/L, and 1 mg/L picric acid. The concentrations follow a liner association, and r^2 equaled 0.9998 (Figure 2). The area under the peak curve for each sample was interpolated with the curve to yield a concentration of the acid.

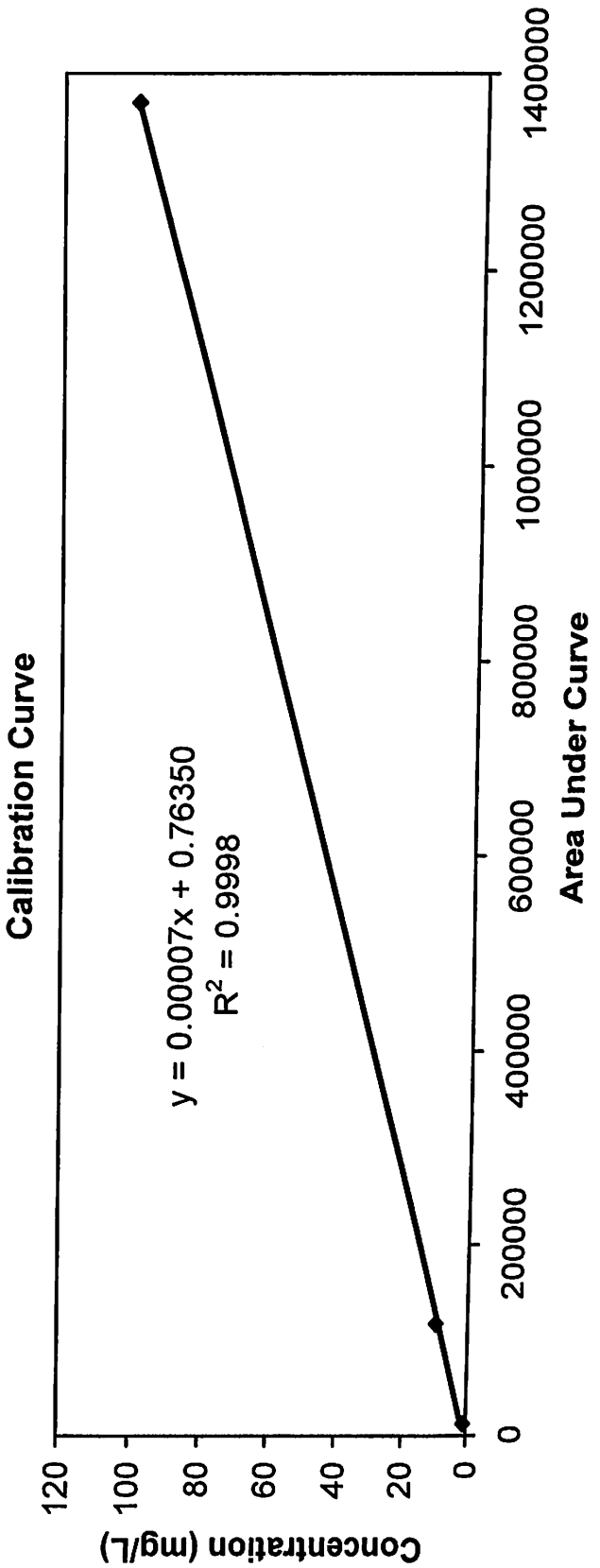

Figure 2—Calibration Curve. The picric acid follows a linear degradation. The curve was created using samples of 100 mg/L, 10 mg/L, and 1 mg/L concentrations

Results of Previous Study

The samples for this study were collected from LAAP at different depths in order to represent a range in grain size. Particle size determinations on the three samples from the Upper Terrace (U1, U2, and U3) were found to have similar grain size distributions (Figure 3). The grain size distributions for these samples were 53-63% fine sand, 35-44% silt, and 3-4% clay. Sediment from the Lower Terrace (L1) was 88% fine sand, 11% silt, and less than 1% clay. The sample from the greatest depth in the Upper Terrace (U3) contained the highest fraction of combined silt and clay (47%), followed by U2, U1, and L1.

The organic content and carbonate content were higher in the finer-grained sediments (U3> U1> U2 > L1) (Figure 4). The organic content ranged from 1.2 to 3.2 %, and the carbonate content from 0.07% to 0.15% by weight. The elemental composition of the sediments did not show a consistent trend with grain size (Table 2). Of the elements found above 10ppm, only iron, aluminum, manganese, and barium stand out as being significantly lower for the more coarse-grained, Lower Terrace sediments.

In the previous study conducted by G.R. Davidson, the blank slurries contained no measurable picric acid throughout the 98-day sampling period. The picric acid concentrations in the slurries decreased by 10 to 18% the first day, attributed to adsorption, followed by slower decreases attributed to degradation. The blank slurries contained no measurable picric acid (detection limit of 0.01 mg/L)

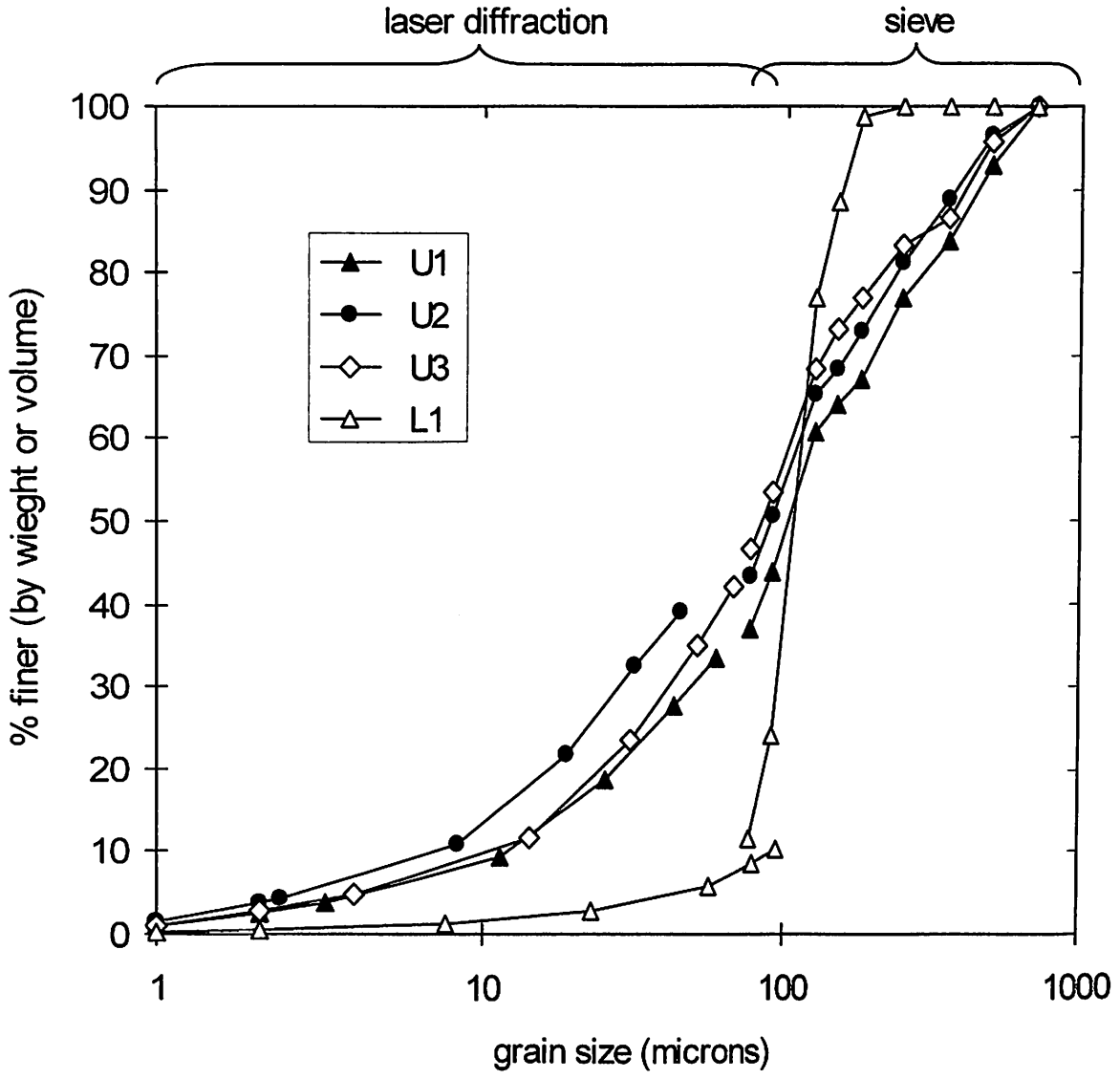

Figure 3—Grain Size Distribution. Silt and clay sizes determined by laser diffraction method (% by volume). Sand sizes determined by wet sieving (% by weight). Sediments with high picric acid degradation in initial study (U1 and U2) are shown with solid data markers.

	High degradation		Low degradation	
	U1	U2	U3	L1
Fe	9009	7251	9793	2249
Al	5717	5330	6720	2041
Ca	1104	857	823	722
Mg	509	311	729	320
K	385	339	474	249
Na	262	233	332	235
Mn	172	180	74	39
Ba	55	67	58	16
Zn	33	12	18	17
V	16	15	14	2.8
Cu	15	6.4	9.7	6.2
Pb	14	8.3	6.8	2.3
Cr	8.9	8.1	7.6	2.5
Sr	7.6	6.7	7.8	5.4
Ti	7.0	5.0	6.3	3.9
As	4.6	4.5	2.6	0.6
Ni	4.4	3.3	5.4	3.3
Co	3.9	3.6	3.9	3.1
Li	3.2	3.0	4.1	2.0
Sb	1.6	0.7	1.1	1.3
Cd	1.2	1.0	0.7	1.0
Be	0.4	0.4	0.4	0.1
Mo	0.3	1.4	0.2	0.5

Table 2—Elemental Concentration. Concentrations are in mg/L. *High* and *Low degradation* refers to the degree of picric acid removal in the initial experiment. Elements are ordered from high to low concentration in U1.

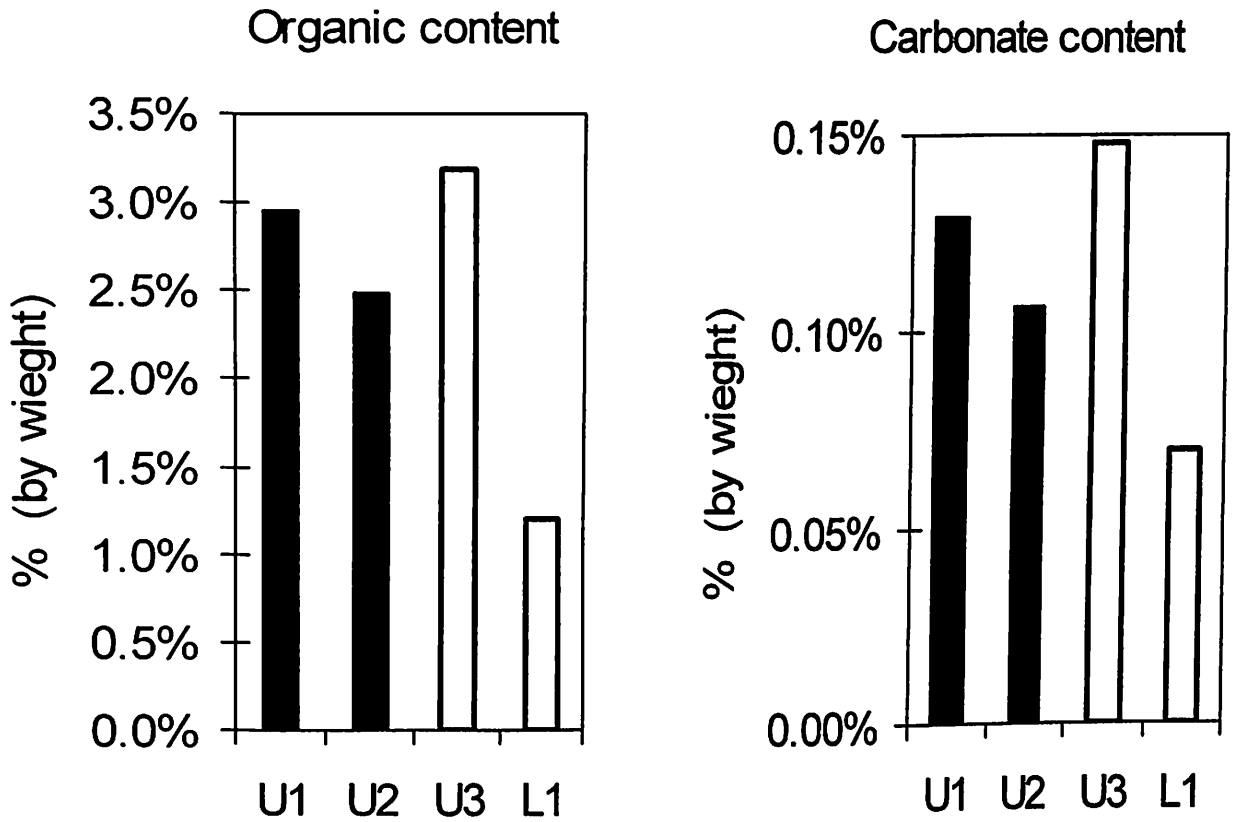

Figure 4—Organic and Carbonate Content. Sediments with high picric acid degradation in initial study are shown as solid bars.

throughout the investigation (which lasted 98 days). A blank sample of 100 mg/L picric acid with no sediment, which was also stored in the dark at ambient temperature, was analyzed at the start and at the end of the investigation, and the concentration was found to have decreased by 7.5% to 92.5 mg/L after 98 days. The changes in the picric acid concentrations in the four sediment/picric acid slurries are shown in Figure 5. Initial decreases in concentration were observed the first day in all four samples, and ranged from 10 to 18%. These concentration decreases may be attributed to adsorption on mineral and organic surfaces. The largest decrease observed on the first day occurred in the bottle with sediment U2, which has the second highest concentration of clays and silts.

As seen in figure 5, significant degradation of picric acid following the first day was observed in only two of the four sediments (U1 and U2). An approximately linear decrease in picric acid concentration was observed in near surface sediments (U1 and U2) to less than 1 mg/L within 8 to 9 weeks. The yellow color of the solution faded over time as picric acid concentrations decreased. In contrast, the picric acid concentration in the deeper Upper Terrace sample (U3) and Lower Terrace sediments (L1) experienced a modest decrease after the initial decrease in the first day to approximately 15% over a 3 to 6 week period before degradation appeared to cease. The yellow color of these solutions remained vivid throughout the entire 98 day study.

The filtered aqueous samples which were removed from the slurries during each sampling period were reanalyzed after six months to determine if degradation would continue under refrigeration. No significant changes were observed.

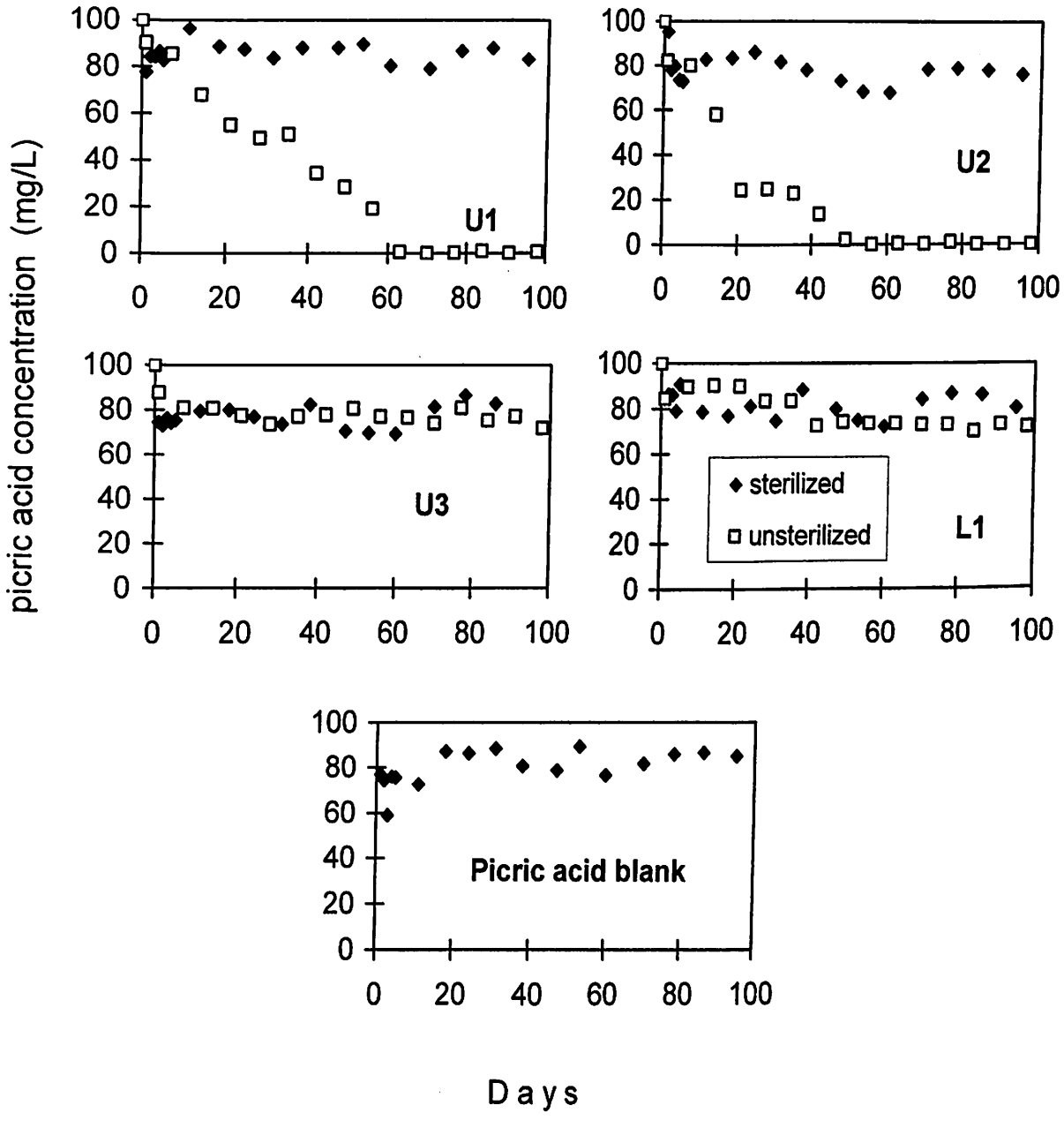

Figure 5—Picric Acid Concentrations. *Sterilized* refers to the current experiment, in which sediment was sterilized, and *unsterilized* refers to the initial study in which sediment was used without sterilization.

The pH of all four sediment-picric acid slurries began approximately 0.2 to 0.3 pH units lower than the corresponding blank slurries (Figure 6). In the two slurries with minimal degradation (U3 and L1), the pH remained lower than the blank throughout the experimental period. In the two slurries with nearly complete degradation (U1 and U2), the pH of the blank and picric acid slurries approached the same value as the picric acid concentration approached zero. Once the picric acid concentration dropped below 1 mg/L (>99% degradation), the pH of the spiked slurries remained higher than the corresponding blanks.

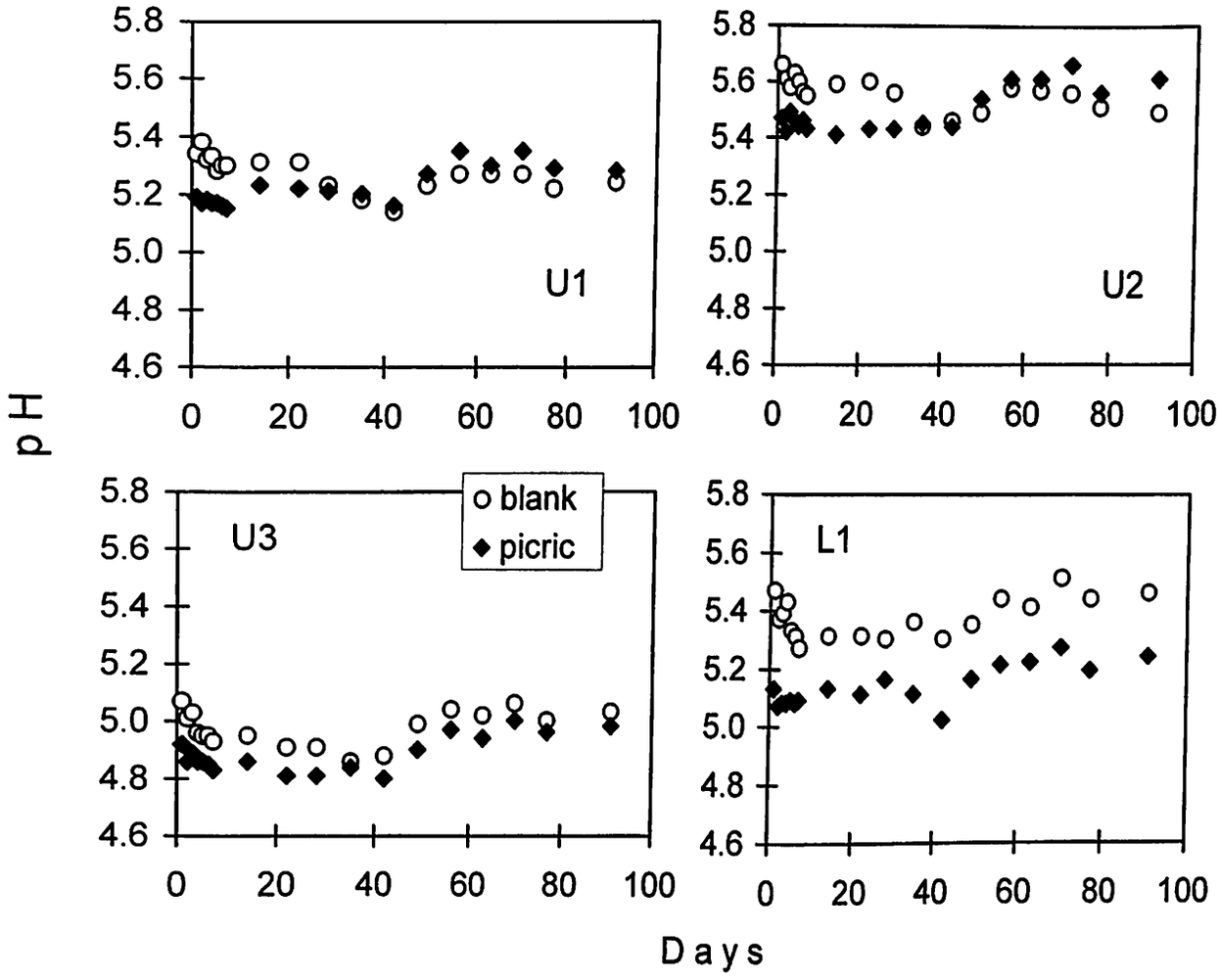

Figure 6— pH of Slurries from Previous Study. The pH of slurries made from picric acid or water mixtures with the unsterilized sediments. *Blank* refers to the water/sediment slurries, while *picric* refers to the picric acid/sediment slurries.

Results of Current Study

The sterilized sediment used in this study was a sub-sample the same sediment used in the previous investigation, so the grain-size distributions, organic and carbonate content, and elemental composition can be assumed to be identical.

The blank slurries contained no measurable picric acid throughout the 100-day investigation period. The concentration of the 100 mg/L picric acid solution with no sediment, which was also stored in the dark at room temperature, was found to have decreased by 23% on the first day, and had degraded an average of 24% after the first 24 days. The changes in the picric acid concentration in the four sediment/picric acid slurries and blank picric acid sample without sediment are shown in Figure 5. Initial decreases in concentration observed on the first day in the sediment/picric acid slurries ranged from 15 to 25% in three of the four sediments (U1, U3, and L1), and initial decrease in concentration was 5% in U2. The largest first day decrease in concentration was observed in the sediment with the highest concentration in clays and silts (U3).

The picric acid concentrations of the four sterilized sediments show virtually no change throughout the total duration of the study. While initial degradation is apparent in all four sediments, the variation can be attributed to noise in the detection. While all four acid slurries showed the same color as each other, the yellow color in all of them dulled slightly.

The pH of the slurries exhibited similar behavior. The pH of all four sediment/picric acid slurries began approximately 0.75 to 1.05 pH units lower than the corresponding blank slurries (Figure 7). Throughout the 100-day study, however, the pH of the picric acid bottles approached the pH of the corresponding blank slurry. The pH of the blank slurries dropped throughout the first 20-30 days and then stabilized. The pH of the picric acid slurries rose throughout this same time period and also stabilized. The pH of the picric acid slurries remained lower than the blank slurries in each of the sediments for the remainder of the study.

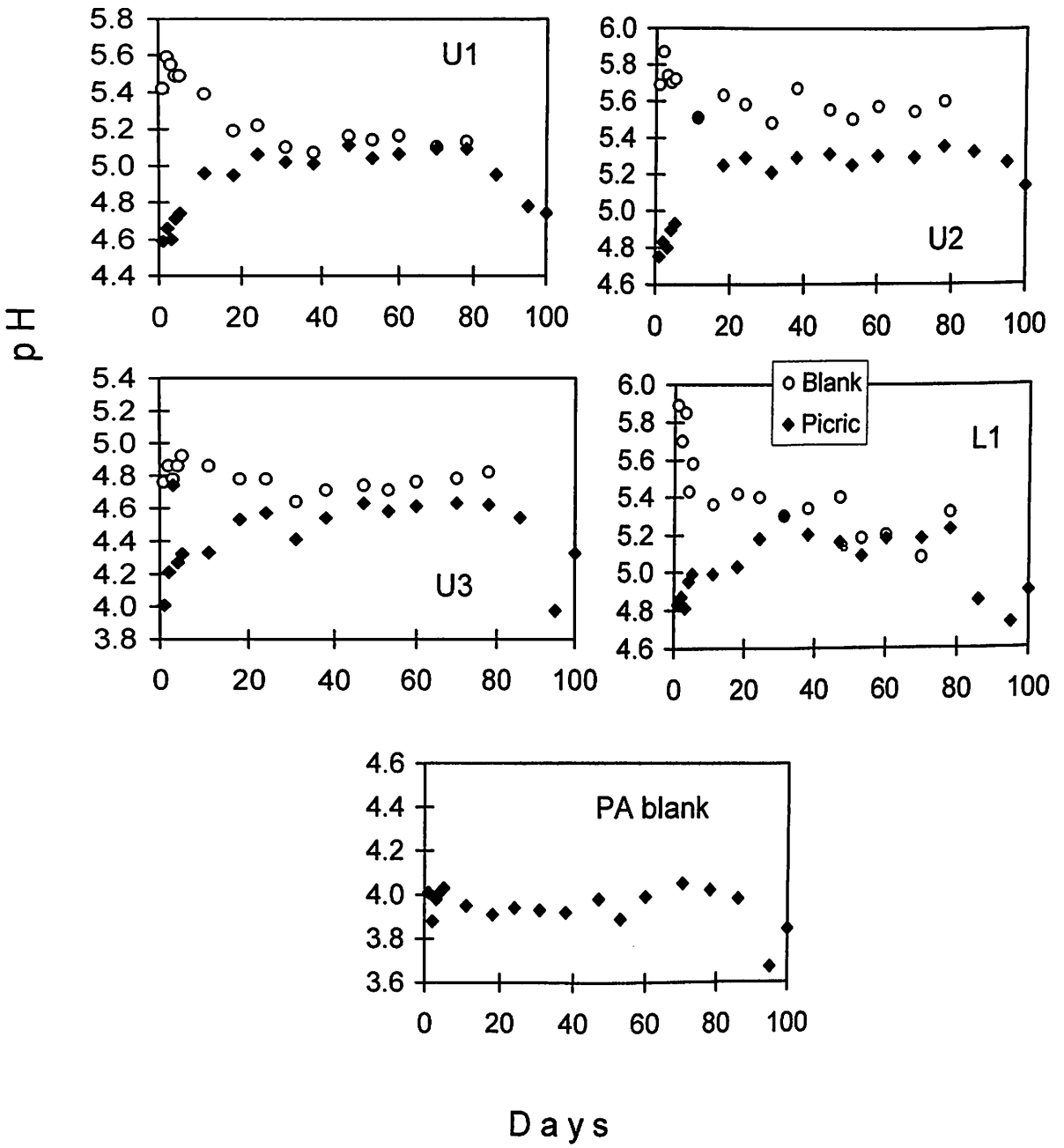

Figure 7— pH of Slurries from Current Study. The pH of slurries made from picric acid or water mixtures with the sterilized sediments. *Picric* refers to picric acid/sediment slurries, while *blank* refers to water/sediment slurries. *PA Blank* refers to the picric acid bottle with no sediment.

Discussion of Results of Previous Study

The results in Figure 5 of the initial unsterilized study suggest that the particle size distribution of the sediment could play an important role in natural degradation of picric acid (G.R. Davidson, personal communication). Picric acid will likely be persistent in the Lower Terrace sands and the lower portion of the Upper Terrace, as evidenced by the lack of degradation of the picric acid in those sediment samples (U3 and L). Picric acid will most likely degrade in the sediment with composition similar to U1 and U2, the upper portion of the Upper Terrace, as the picric acid in those sediments degraded to a composition less than 1 mg/L. Residual and persistent concentrations of picric acid at LAAP have been observed primarily in the deeper observation wells completed in the Lower Terrace sands (G.R. Davidson, personal communication), which is consistent with these laboratory results.

The factors controlling degradation in this initial study were not obvious. Only minor degradation was observed in the sediments containing both the highest (U3) and the lowest (L1) proportion of fine-grained sediment, organic content, and carbonate content. Clays and organic substrates may play some role in the degradation of picric acid, but were apparently not the primary driving force in this study.

At the conclusion of the unsterilized study, Manganese was suggested as a possible catalyst for degradation in the sediments that showed nearly complete degradation of picric acid. Redox sensitive elements such as iron and manganese can

influence decomposition reactions, and, in their oxidized states, Fe and Mn can act as electron acceptors to facilitate the breakdown of complex organic molecules. These elements are much weaker oxidants than O_2, however, so their role in decomposition reactions is generally limited to oxygen-deficient environments. Degradation occurred in the Lower Terrace and lower portion of the Upper Terrace, which could be lower in O_2 than the upper sediments of the Upper Terrace where degradation was not observed. In this investigation, oxygen was not strictly limited, as slurries were opened to the atmosphere each week during sampling.

Under aerobic conditions, Fe or Mn oxides may serve as catalysts in degradation reactions (Nowack and Stone, 2000; Hunter et al., 1999). Iron is abundant in all four sediment samples (Table 2), however, only minor degradation was observed in the sediments with both the highest (U3) and lowest (L1) iron concentrations. Manganese is the only measured variable that correlates with degradation. The Mn concentration is 2.3 to 4.6 times larger in the two sediments with nearly complete degradation of picric acid, suggesting that its elevated concentration in U1 and U2 may influence the acid degradation.

Other elements may also serve to catalyze decomposition reactions. Laboratory investigations have facilitated picric acid degradation using catalysts such as ZnO and TiO_2 (Joshi et al., 2003; Ksibi et al., 2003). Zinc and titanium in the LAAP sediments are low in concentration and do not correlate with the degree of degradation observed in the batch studies (Table 2).

Differences in microbial activity in the different sediments may also have played a role in degradation. In an effort to mimic *in situ* conditions as closely as

possible, the sediments were dried but not sterilized prior to creation of the slurries. Periodic aeration mimicked the passage of oxygenated groundwater, favoring aerobic microbial populations. No efforts were made, however, to characterize the microbial populations. In the second study, the sediments were sterilized prior to creating the slurries in order to eliminate the effects of microbial communities in the picric acid degradation.

Discussion of Results of Current Study

Throughout the study using sterilized sediment, picric acid was not detected in the sediment/water slurries. The absence of residual acid in the blank sediment suggests that the portion of LAAP from which the samples were gathered does not have picric acid contamination.

The results shown in Figure 5 suggest that sediment composition does not play the most important role in picric acid degradation. While the previous study showed two sediment samples (U1 and U2) underwent near complete degradation, results of this second study show no significant variance between the different samples. All four samples show a decrease in concentration on the first day, likely due to adsorption onto the sediment, however, none of the sterilized sediments showed continued degradation after the first week. The variation in the plots of the concentration can be attributed to variable sediment as picric acid adsorbs and is removed from the sediment.

The sediment with the highest fine-grained content (U3) showed the most degradation through the first three days of sampling, however, then began to resemble the other sediments in its picric acid concentration.

Though manganese was suggested as a possible factor in the degradation of sediments U1 and U2 in the previous study, this study does not support that hypothesis. The same two sediment samples do not differ from the other sediment

samples, indicating that the difference in manganese concentrations does not affect the acid degradation.

The difference in the results of the acid concentrations in this study as compared to the previous study is likely due to the sterilization of the sediments prior to use. By exposing the sediments to high heat overnight, the microbial communities were exterminated and not able to biologically degrade the picric acid. Some previous studies have investigated bacteria and fungi that may use picric acid as an energy source (Lenke et al., 1992; Rieger et al., 1999), however, as microbial analysis was not performed on the sediment, the type of biological degradation occurring cannot be characterized.

Conclusion

After sterilization of the sediment in an effort to eliminate microbial degradation, the picric acid degradation in the samples that previously showed degradation was greatly reduced. While the previous study had seen near complete degradation of two of the sediment samples, degradation was not observed in any of the samples in this study. This suggests that the microbial community that was eliminated was integral in the degradation of the acid in the first study. The lack of significant degradation in U3 and L1 between the sterilized and unsterilized sediments suggests that the microbial communities that are present in U1 and U2 are not present in U3 and L1. Additional work can be done to characterize the microbes in the sediment and determine if they are using the acid as an energy source.

In both studies, picric acid was not detected in the blank slurries, composed of sediment and distilled water. The absence of residue from the sediment into the slurry suggests that the sampling site at LAAP does not have contamination.

Additional work is currently being done to duplicate the results of the initial study of unsterilized sediment. The same four sediment samples have been combined with picric acid in an additional eight week study to investigate the degradation. The same sampling schedule will be used. If this duplicate run of the initial study yields similar results to the original study (Figure 5), then the work will be validated and the degradation can be linked to microbial influence.

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