OCS Study
MMS 99-0060

Coastal Marine Institute

Effect of Produced-Water Discharge on Bottom Sediment Chemistry

Final Report

U.S. Department of the Interior
Minerals Management Service
Gulf of Mexico OCS Region

Cooperative Agreement
Coastal Marine Institute
Louisiana State University

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Final Report

Editors

Ronald D. DeLaune
Charles W. Lindau
and
Robert P. Gambrell

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EXECUTIVE SUMMARY

Petroleum hydrocarbons, metals and radionuclides can enter the environment as the result of petroleum extraction and recovery operations. Produced water discharge associated with oil recovery has in the past introduced these compounds into Louisiana aquatic environment, including the sediment column. Investigations were conducted to determine the factors determining solubility and mobility of these pollutants in sediment.

The effect of sediment redox conditions on the solubility of Fe, Pb, Ni, Ba, and Cu in bottom sediment collected from a produce water discharge site was invested using kinetics and chemical fractionation procedures. Under oxidizing sediment conditions, the behavior of Fe, Pb and Ni were governed by Fe(III) and Mn(IV) oxides; Ba by insoluble complexation with humic compounds, Cu by carbonates and humic complexation. Under reducing sediment condition, the behaviors of Fe and Cu were controlled by the formation of insoluble sulfides, carbonates and humic complexes.

Kinetics and chemical fractionation procedures were also used in quantifying the effects of sediment redox (Eh) condition on the behaviors of As, Cd, Cr and Zn in the bottom sediment. Under oxidizing conditions, As, Zn and Cr behavior were governed by redox chemistry of Fe(III) and Mn(IV) oxides. Cd transformations were controlled by both Fe(III), Mn(IV) oxides and carbonates. Under reducing condition, the behaviors of Zn and Cr was controlled primarily by insoluble large molecular humic material and sulfides; the behavior of Cd was controlled by carbonates. When sediment redox potential increased, the affinity between Fe(III), Mn(IV) oxides and As, Cd, Cr, and Zn increased. Results suggest reducing conditions in bottom sediment sites of produced water discharge would limit heavy metal availability.

Sediment collected from a produced water discharge site and in waste pit was extracted into various chemical fractions and analyzed for radium-226 (fractions included water-soluble, exchangeable, forms associated with carbonates, reducible, or organic/sulfide). It was determined that 95 percent of the radium present was tied up in an unavailable form that could be extracted only with very strong acids. Radium in this fraction would be released very slowly into the environment. Results showed that less than 5% of the radium in sediment was in potentially available forms.

Petroleum hydrocarbon degradation in sediment collected from a low energy brackish wetland site which had been exposed for a number of years to produced water discharge was also studied. Recalcitrant or higher molecular weight compounds were the primary hydrocarbon fractions found in the sediment. Oxidized sediment conditions resulted in a higher rate of degradation for most hydrocarbons fractions as compared to degradation in reduced sediment following addition of South Louisiana Crude oil. Nutrient amendments to contaminated sediments significantly increased rate of hydrocarbon degradation.

The effect of chromium (Cr) and lead (Pb) on degradation added South Louisiana Crude oil in sediment showed that metal concentration normally found at produced water discharge sites would not influence degradation of hydrocarbon in the sediment profile.

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EFFECTS OF PRODUCED WATER DISCHARGE ON BOTTOM SEDIMENT CHEMISTRY

Project Personnel:
T.Z. Guo, B.C. Banker, I. Devai, R.D. DeLaune, C.W. Lindau, C. Mulbah and R.P. Gambrell

Louisiana State University
Wetland Biogeochemistry Institute

1.0 INTRODUCTION

During the production of crude oil, condensates or natural gas and water may also be brought to the surface. This water is called formation water, produced water or oil field brine. Produced waters are one of a variety of wastes generated from oil and gas production wells (Neff et al. 1987). The volume of water produced may be quite large (Neff et al. 1989). It has been estimated that a total of 2 million barrels of oil and gas produced waters are discharged into the State waters of Louisiana per day from nearly 700 sites among the 70 oil and gas fields. At the time of the study, 23%, 22% and 17% were discharged into fresh, brackish and saline wetland environments, respectively, with the remainder discharged into open embayments or nearshore Gulf waters (Boesch and Rabalais 1989). Petroleum production and recovery activity in Louisiana coastal zone can discharge a considerable amount of produced waters (Boesch and Rabalais 1989). The produced waters can contain elevated concentrations of toxic metals radium and petroleum hydrocarbons as compared to the receiving water (St. Pe 1990). It is estimated that annually 1.7 to 8.8 million metric tons of petroleum hydrocarbons are released into the environment (Leahy and Colwell 1990). Metals in produced water can include barium, cadmium, chromium, iron, mercury, manganese, strontium and thallium (Tillery et al. 1981; Koons et al. 1977; Lyssj 1981). As the produced water enters wetland environments, toxic metals can enter the sediment column.

Produced water discharge can lead to contamination of sediments, streams and wetlands. Production waters from oil recovery process are passed through pits for an indeterminate time until being discharged into the environment. Petroleum hydrocarbons, metals, and radionuclides are prevalent pollutants in produced waters and sediments (Neff et al. 1989; St. Pe' 1990). Petroleum components, specifically polycyclic aromatic hydrocarbons, can contain numerous carcinogenic and mutagenic compounds. Substantial contamination of fine-grained sediments with petroleum hydrocarbons of produced water origin has been observed with distance from produced water sites in coastal Louisiana (Rabalais et al. 1991).

Analysis of total metal concentration in sediment quantifies the degree of trace metal enrichment. Total metal content does not provide information on transformation and mobilization of trace metals. Speciation studies can: 1) provide an insight into metal distribution patterns, 2) identify metal bioavailability and toxicity in ecosystems, and 3) explain transformation and mobility of metal species. Metal species distribution has been studied in various ways (Gambrell et al. 1991a; Giblin et al. 1986; Giesy et al. 1977; Keller and Vedy 1994). These techniques have included multistep extractions in which a chemical solution removes various metal forms. Such fractionation schemes can provide information on the general behavior of metals in sediment and provides an estimate of their potential mobility (Keller and Vedy 1994). Metals in sediment are generally considered to be present in the following forms: water soluble, exchangeable, carbonate bound, ferric and manganic oxide bound, organic matter and sulfide bound, silicate bound and residual.

The oxidation/reduction state (redox potential) of sediment is an important parameter affecting heavy metal transformation and hydrocarbon degradation. The redox conditions (Eh) of estuarine sediment varies widely from approximately +500 mV (surface sediments) to approximately -300 mV (strongly reducing sediments). Sediment redox levels can greatly affect toxic metal uptake by plants (Gambrell and Patrick 1988; Giblin et al. 1986), leaching losses of toxic metals by runoff or ground water (Folson et al. 1988; Palermo et al. 1989), but there is little information on redox chemistry of toxic metals in different geochemistry forms in sediment.

Heavy element species kinetics in wetland soil kinetics are influenced by many factors. These factors include temperature, organic matter, surface activity of Fe and Mn compounds, microorganism activity and other sediment characteristics. Since it is difficult to study these factors individually, the factors were combined in this study into one parameter, the rate constant of the assumed zero-order reaction. This pseudo-zero-order reaction model was used in this study. When the rate constant is positive, the metal content increases in the specific fraction. When the rate constant is negative, the metals are removed from the specific fraction. When considering trace elements bound to the organic matter and sulfide phase, it was assumed that the formation of insoluble organic matter (complexation of insoluble, large molecular weight humic fraction) and sulfides was independent (Gambrell and Patrick 1978; Gambrell et al. 1980). At sediment Eh = -130 mV or Eh> -130 mV, the changes in heavy elements in this fraction were due to insoluble, large molecular weight humic substances.

Surface of clays, organic matter, and iron oxides in sediment will absorb or desorb heavy elements when the ionic composition or Eh-pH changes (Keller and Vedy 1994; Khalid et al. 1981; Gambrell et al. 1980). Significant heavy element content is also associated with sediment carbonates (Ramos et al. 1994; Gambrell 1994). This fraction would be susceptible to pH change. Iron and manganese oxides existing as nodules and concretions, cemented between particles or on particle coatings in sediment are excellent scavengers for heavy elements and are affected by sediment Eh and pH change (Feijtel et al. 1988; Levy et al. 1992). Heavy elements are also bound to various insoluble organic forms such as living organisms, detritus, and humic material (Gambrell et al. 1980; Ramos et al. 1994). Sediment redox conditions can affect the degradation and solubility of such organic material and then influence the release of heavy elements. Heavy elements can also exist as sulfides under anaerobic conditions (Gambrell et al. 1980; 1991b) which are susceptible to Eh and pH changes. Heavy elements found in primary and secondary minerals are relatively stable in a natural sediment environment (Gambrell 1994).

Radionuclides in produced waters include naturally occurring radium-226. Produced water and drilling muds are commonly stored in waste pits created at the production site. In Louisiana alone, an estimated 20,000 oil-production sites are known to have radioactive contamination significant enough to require permitting. Produced water brines in the Gulf of Mexico region can contain up to 37 Bq L^{-1} of Radium 226 (Kraemer and Reid 1984), an amount ten times the levels found in natural water. Little is known about the fate of radium in sediment and waste pits. In order to improve our ability to predict its migration into aquatic environments and the food chain, we must understand the physical and chemical processes controlling solubility and movement.

Cocontaminants (e.g., heavy metals) at sites contaminated with petroleum hydrocarbon has raised the question of the reliability of natural detoxification and engineered remediation processes in these complex mixtures. Interactions between the contaminants may inhibit biodegradation processes occurring in the site. One example is the inhibition of biodegradation in contaminated sediments by the presence of toxic heavy metals such as Cd, Cr, Zn, and Hg. Studies have documented the toxicity of metals to microorganisms in culture (Farrell et al., 1990) and in soils and sediments (Capone et al., 1980). However, few studies have concentrated on non-lethal effects of heavy metals on microbial functions (e.g., biodegradation of organic chemicals), particularly in sediments.

Studies which have been performed on these processes indicate that effects of metals on biodegradation processes are complex and dependent on the type, concentration, and speciation of the metals added (Said and Lewis 1991). Understanding metal impact on petroleum hydrocarbon degradation is important in the implementation of remediation at waste or spill sites.

Hydrocarbon biodegradation is influenced by both physicochemical and biological properties of the environment. Extensive research has been carried out on the biodegradation of sludge (Boyd and Shelton, 1984; Bossert et al., 1984) and other hydrocarbon compounds (Zhang and Miller, 1992; Miller and Bartha, 1989; Oberbremer et al., 1990). There is little information on degradation of petroleum hydrocarbon in sediment receiving produced water discharge.

In this study, the kinetics and transformations of heavy metals, radium, and petroleum hydrocarbon degradation in estuarine sediment at a site in Coastal Louisiana receiving produced water discharge were examined. The effects of sediment redox potential (Eh) on the kinetics of transformation of toxic metals and radium in sediments are detailed. Petroleum hydrocarbon degradation was also studied.

2.0 MATERIALS AND METHODS

2.1 Effect of Sediment Redox Conditions on Heavy Metal Chemistry

Studies were designed to determine the speciation and solubility of heavy metals in sediment receiving produced water discharge. Sediment was collected from a canal (Humble Canal) from a waste pit at the point of discharge associated with a petroleum recovery operation in the Lirette Oil and Gas field in Terebonne parish (Fig. 1). The effluent or produced water was discharged from the secondary compartment of the pit into the canal (St. Pe, 1990). Five active wells contributed produced water to the pit. Average discharge has been reported to be 482 barrels per day (St. Pe, 1990). The sediment had a pH=7.0 and contained 0.1% Ba, 0.04% Mn and 2% Fe. The heavy metal content of the sediment was determined using wet ashing and ICP procedures.

Two hundred grams of sediment (dry weight equivalent, amended with 0.3% (W/W) ground dried plant material) was added to 1.8 L of 5% salinity sea water in laboratory microcosms used to control sediment Eh-pH conditions. The microcosm originally described by Patrick et al. (1973), equipped with a combination pH electrode, Pt-electrodes and reference electrodes, allows for the continuous recording Eh and pH.

The sediment suspensions were kept stirring with a magnetic stirrer. The suspensions were preincubated at 26 ^{o}C under aerobic condition (+430 mV) for 25 days. After the initial preincubation, the suspensions were purged with nitrogen gas and maintained under anaerobic

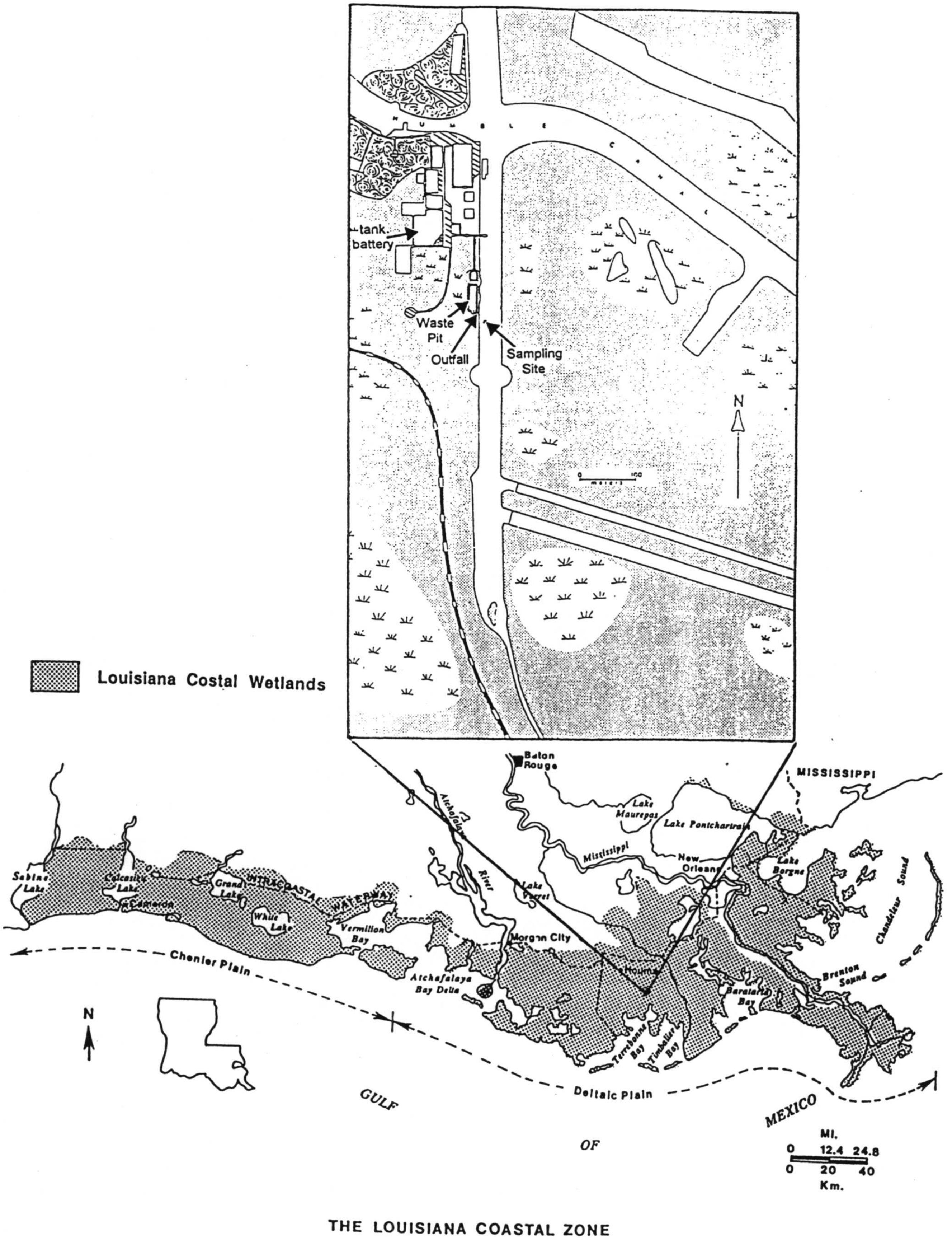


Figure 1. Location of Lirette (LRT) site from which sediment samples were collected (from Guo et al. 1997a, 1997b).

condition (-170 mV). The suspensions were maintained at pH=7.0, (the normal pH of sediments under flooded conditions), by addition of diluted HCl or NaOH solution as needed during the preincubation and anaerobic incubation periods.

Metal was added to the sediment suspension at a rate four times of the original heavy metal contents of the sediment. The heavy metal contents of the sediment with added metals were: Cu=610 mg/kg, Pb=300 mg/kg, Cd=21 mg/kg, Zn=800 mg/kg, Cr=210 mg/kg, As=370 mg/kg, and Ni=580 mg/kg. No barium was added to the sediment.

Samples from the sediment suspensions were taken at selected intervals. The suspension samples were centrifuged and the supernatant filtered through a 0.45 μm membrane filter. This supernatant was assumed to be water soluble. The remaining sediment was extracted sequentially as described below. The sediment sample was kept under nitrogen or oxygen free atmosphere during extraction. Following removal of the water soluble phase, the sediment was sequentially extracted into fine fractions (F1 to F5) described below.

F1-Exchangeable Phase. The solid phase from the water soluble fraction was extracted at room temperature for 30 min. with 8 ml 0.5 M $Mg(NO_3)_2$/g dry weight sediment, adjusted to pH 7.0 with nitric acid. The samples were agitated continuously.

F2-Bound to Carbonate Phase. The sediment residue from F1 was leached at room temperature for five hours with 8 ml, 1M NaOAc, adjusted to pH 5.0 with acetic acid for 1 g dry weight sediment. These samples were also agitated continuously.

F3-Bound to Iron and Manganese Oxides Phase. The sediment residue from F2 was extracted at 96 °C for six hours with 20 ml 0.08 M NH_2OH HCl in 25% (v/v) acetic acid for 1 g dry weight sediment. These samples were occasionally agitated.

F4-Bound to Organic Matter and Sulfides Phase. For 1 g of dry weight sediment, the sediment residue from F3 was extracted at 85 °C for 2 hrs. with 3 ml 0.02 M HNO_3 and 5 ml 30% H_2O_2 (adjusted to pH = 2.0 with HNO_3) was added, and extraction continued at 85 °C for another 3h. The sample was then cooled, 5 ml 3.2 M NH_4OAc in 2% (V/V) HNO_3 was added, and the sample was diluted to 20 ml with deionized water. The samples were agitated continuously for 30 min. NH_4OAc was added to prevent adsorption of extracted metals onto the oxidized sediment.

F5-Mineral Matrix Phase. The sediment residue from F4 was extracted with 25 ml concentrated HNO_3 for 1 g of dry weight sediment at 105 °C, the sediment was digested until 5 ml solution was left, and the sample was diluted to 25 ml with deionized water.

The above sequential extractions were conducted in 250 ml centrifuge tubes which prevented any loss of sediment between the successive extractions. Separation was conducted by centrifuging at 5000 rpm for 30 min. Supernatants were filtered using 0.45 μm millipore filters and then analyzed for metals. The residues were rinsed with 8 ml deionized water for 1 g dry weight sediment and centrifuged at 5000 rpm for 30 min. These second supernatants were discarded.

Metal concentrations in the water soluble phase and the chemical extracts were determined by ICP. Quality assurance was conducted by spiking extracts with certified element standards.

2.2 Radium Chemistry

Another set of experiments were conducted to determine the speciation and solubility of radium. The primary study site from which sediment was collected was also located in the Lirette Oil and Gas field (Humble Canal located in a tidally influenced brackish marsh environment). Additional sediment samples were collected from waste pits located in Quarantine Bay. Sediment at both sites had been exposed to produced water. Microcosm studies were initiated for studying the partitioning of radium as influenced by either oxidized and reduced sediment conditions at the two sites.

Sediment was incubated in the microcosms in a similar manner as heavy metal studies. Two hundred grams of sediment on a dry weight basis (amended with 0.2% (W/W) ground dried plant material) was added to 1.8 L deionized water in laboratory microcosms under controlled Eh-pH condition. The microcosm described by Patrick et al. (1973) originally, equipped with a combination pH electrode, Pt-electrodes and reference electrodes, allowed for the continuous recording or controlling sediment Eh and pH.

The sediment suspensions were kept suspended with a magnetic stirrer. The suspensions were preincubated at 26^0C under aerobic conditions for 25 days. After the initial preincubation, the suspensions were purged with nitrogen gas and maintained in anaerobic condition. The suspensions were maintained at pH=7.0, the natural pH of the sediments, by addition of diluted HCl or NaOH solution as needed during the preincubation and anaerobic incubation periods. Eh was maintained at preset conditions ranging from +600 mV (oxidized) to -250 mV (reducing).

After incubation and equilibration of sediment under oxidized (+600 mV) and reduced (-250 mV) conditions aliquots were removed from each microcosm and chemically extracted. The sequential extraction procedures adopted from R.D. Shannon (1991) as described previously (in the metal section) with a minor modification of the residue fraction was used for determining the partitioning phase of the radium over time under various sediment redox conditions.

Direct γ-ray spectrometry of daughter products using a shielded, Ge(Li) detector interfaced with a multichannel analyzer was used for determining ^{226}Ra activity in the fractions (Michel et al., 1981). Primary quantification of ^{226}Ra was made by analysis of ^{214}Bi daughter product (energy 609 keV, 43•0 γ per 100 disintegrations). The instrument was calibrated using a ^{226}Ra standard from the National Bureau of Standards (NBS), Washington, DC. Extract samples were placed in polycarbonate bottles and sealed for daughter in-growth for 1 month. Samples were counted until at least 1000 counts were detected.

2.3 Effect of Heavy Metal Content of Sediment on Petroleum Hydrocarbon Degradation

Sediment used in this study was also collected from a stream in the Lirette Oil and Gas field in Terebonne Parish (Fig. 1). Five hundred grams of homogenized wet sediment was placed into each of eight 2 L flask microcosms and water added to produce a sediment: water ratio of 1:10 (on weight basis). Each suspension was kept continuously stirred with a magnetic stirrer. The soil pH and temperature were maintained at 6.5 and 25^0C, respectively. Breathing air was continuously bubbled through the suspensions for oxidation (redox potentials ranging from +500 mV to +600 mV). Nitrogen was bubbled through the reduced microcosms. Two milliliters of South Louisiana Crude oil (API Gravity 36.0) was added to each flask and allowed to homogenize for two weeks. South

Louisiana Crude was weathered in shallow open pans for four days (for removal of volatile hydrocarbons) prior to addition. Weathered loss was 11 percent. The addition of weathered oil and allowing two weeks of equilibration in microcosms was to eliminate volatilization losses from the study which is directed at determining effects of heavy metal concentrations on hydrocarbon degradation. Twenty milliliters of each suspension was then removed and placed in Teflon tubes for extraction and analysis of hydrocarbons.

Next, 50 ml of Cr solution equivalent to 0, 250, 1000 and 5000 μg Cr per gram of sediment (dry weight) were added to separate flasks. Similarly, 50 ml of Pb solution equivalent to 0, 100, 500 and 2500 μg added Pb per gram of dry sediment were added to an additional four flasks. Twenty milliliters of suspension were removed from the flask two days after metal additions for ICP analysis. Ten milliliters were taken for dry matter determinations. Subsequent aliquots were removed over a period of 91 days to determine changes in petroleum hydrocarbon levels.

Extraction for petroleum hydrocarbons (alkane fractions) was conducted by the addition of a solvent (1:1 hexane:acetone) to each 20 ml portion of suspension taken from the microcosms. This mixture was shaken for 7 hours to facilitate extraction. The mixture was then centrifuged at 10,000 rpm for 13 min. to separate the solvent, microbial mat, water and sediment fractions. The top three fractions were decanted off into a separatory funnel and the sediment particulates washed with solvent. The microbial mat was rinsed three times and the hydrocarbon laden solvent decanted off. The decanted solvent was passed through pre-dried anhydrous sodium sulfate to remove water. The final solvent-hydrocarbon mix was evaporated down to 10 ml under the fume hood. One ml sample was placed into a vial and 20 μg ml^{-1} of internal standard added for GC/MS analysis.

The hydrocarbon analysis will be performed on a gas chromatograph (Hewlett Packard 5890 Series II Plus) equipped with an HP-5 high resolution capillary column (30 m, 0.25 μm film thickness, 0.25 mm i.d.) which will be directly interfaced to a quadrupole mass spectrometer (Hewlett Packard 5972 Mass Selective Detector). The carrier gas helium of ultra high purity) flow-rate will be 1.0 ml/min, the injector temperature will be 300 ^{0}C, the column temperature will be programed from 50 ^{0}C to 310 at 8^{0}C/min rate with initial 3.0 min delay and 15.0 min hold at the end. The interface to the mass selective detector will be maintained at 280 ^{0}C. Injections will be made using a Hewlett Packard 7673 automatic liquid sampler into a splitless injection port.

Hewlett Packard Vectra 486/66XM computer system and Hewlett Packard G1034C Software for the MS ChemStation (DOS Series) was used in collecting and analyzing data. G1033A NIST PBM Library was used for the peak identification. ASTM Crude Oil Quantitative Standard (Supelco, Inc., Bellefonte, PA) was used for the quantification and Semivolative Internal Standard Mix (Supelco, Inc., Bellefonte, PA) was used as internal standard.

At the end of incubation, subsamples of sediment (oxidized and reduced) were removed from the microcosms with a syringe. The samples were extracted with $NaOA_c$ (pH 4.5) and the extracts were analyzed for metals using ICP procedures.

All data was subjected to analysis of variance and Duncan's Multiple Range Test (SAS 1995). Comparisons were made between two or more regression functions describing changes in percent hydrocarbon with time at Cr and Pb rates of 0, 250, 1000, 5000 and 0, 100, 500 and 2500 μg/g, respectively. This analysis used the method of comparison of two or more linear functions (Neter et al., 1990).

2.4 Degradation of Petroleum Hydrocarbons in Sediment Receiving Produced Water Discharge

Studies were also designed to determine (1) residual petroleum degradation, (2) degradation of applied South Louisiana Crude and (3) fertilizer effect on hydrocarbon degradation in sediment (oxidized and reduced) collected from a produced water discharge site. Sediment samples collected were homogenized and air-dried for 3 days. Total salts were calculated from electrical conductivity measurements and pH was measured with a combination electrode. Cation exchange capacity (CEC) measured the sum of exchangeable K, Na, Ca and Mg. Oil percent was determined by gravimetric methods following extraction with petroleum ether. Total petroleum hydrocarbon content (TPH) was determined by Freon-113 (1, 1, 2-trichloro-1, 2, 2-trifluoroethane) extraction. Twenty grams of wet sediment was extracted with 90 ml of Freon-113 and compared with a calibrated standard to obtain total concentration. Sediment parameters and concentrations are summarized in Table 1.

Microcosms were also employed to study effects of sediment redox conditions on hydrocarbon degradation in sediment suspension (Patrick, et al., 1973). Wet sediment from the point of discharge (0 m) was used in all microcosm experiments. Sediment suspensions were prepared in 2,000 ml Erlenmeyer flasks by mixing 85 grams of wet homogenized sediment with 1700 ml distilled water. Suspensions were constantly stirred using a magnetic stirrer and purged with oxygen free nitrogen gas. A period of about two weeks was needed for microcosms to attain the desired reduced redox level before petroleum additions. Oxidized conditions were maintained by pumping air through the microcosms.

The redox control systems maintained sediment redox level within ±20 mV of the desired potential. This was accomplished with platinum electrodes and a calomel reference electrode connected to a millivolt meter which monitored sediment redox potential. The output of the millivolt meter was connected to a meter relay which activated an air pump. When sediment redox dropped below the set point, a small amount of air was pumped into the apparatus in order to maintain the desired potential.

2.4.1 Experiment I - Degradation of Residual Hydrocarbons

A microcosm study was designed to determine rate of residual hydrocarbon loss from sediment collected from the discharge site. Six redox controlled microcosms were set up and divided into oxidizing (+450 mV) and reducing (-150 mV) sets. Sediment samples were removed at 1, 14, 30, 60 and 103 days and extracted for hydrocarbon components.

2.4.2 Experiment II - Effect of Oxidizing Sediment Conditions on Degradation of South Louisiana Crude

Based upon the results from Exp. I, a second laboratory study was initiated to determine degradation rates of hydrocarbon components of South Louisiana Crude oil added to oxidized sediment suspensions. Redox potential was controlled (+450 mV) in three microcosms followed by addition of 20 ml of South Louisiana Crude. At 1, 4, 7, 16 and 28 days after oil addition, sediment samples were removed and analyzed for hydrocarbon fractions and concentrations.

The oil used for this experiment was a low sulfur oil rich in light aromatics, paraffins and olefins. It is moderately toxic and has been shown to be degraded by indigenous microorganisms under aerobic sediment conditions.

2.4.3 Experiment III - Nutrient Influence on Hydrocarbon Degradation

This experiment determined the effects fertilizer and redox conditions had on hydrocarbon degradation. Nitrogen and phosphorus were added to the 1700 ml sediment slurries in the controlled redox microcosms. Four grams of NH_4NO_3 and 2 g of K_2HPO_4 was the high treatment and 2 g of NH_4NO_3 and 1 g of K_2HPO_4 was the low treatment. Twenty ml of South Louisiana Crude oil was added to the controlled redox microcosms (+450 mV and -150 mV) and samples were removed at 1, 6, 10, 14, 28 and 42 days after fertilization. Sediment samples were analyzed for concentration of C-10 (decane) through C-17 (heptadecane) hydrocarbons. Treatments consisted of reduced and oxidized sediment conditions with two levels of fertilizer amendment and reduced and oxidized controls (oil only). Treatments were not replicated due to the limited number of available microcosm apparatus.

Extraction techniques followed EPA Method 8270 and were used for all three petroleum degradation experiments. A 20 ml sediment sample was removed from the redox controlled microcosm and pipetted into a Teflon tube. Ten ml of 1:1 hexane:acetone solvent was added and tubes were shaken for 7 hours followed by centrifugation at 10,000 rpm for 13 minutes. The petroleum laden solvent layer was transferred into a separatory funnel and the Teflon tube rinsed several times with the hexane:acetone solvent. Anhydrous sodium sulfate removed trace amounts of water and the petroleum laden solvent was evaporated to 10 ml using dry nitrogen. Samples were stored at 5^0C until GC/MS analysis could be performed. One ml of each sample was transferred into a LoVial and 0.4 µl of an internal standard added. A Hewlett Packard 5890 Series II plus GC/MS was used for analyzing the samples for selected petroleum hydrocarbons. A HP-5 high resolution capillary column (30 m x .250 mm i.d., 0.25 µm film thickness) was used and directly interfaced with a quadrapole mass spectrometer (HP 5972 Mass Selective Detector). The carrier gas (ultra high pure He) flow rate was 1.0 ml min^{-1}, injection temperature 300^0C, column temperature programmed from 50^0C to 310^0C at 8^0C min^{-1} with an initial 3 minute delay and 15 minute hold time at the end. Sample injections were made using a HP 7673 automatic liquid sampler into a splitless injection port. A HP Vectra 486/66 computer system equipped with HP G1034C software and G1033A NIST PBM Library for the MS ChemStation was used for collecting and analyzing mass spectrometer results. Table 2 displays the hydrocarbons analyzed in this study. Not all fractions are discussed for each of the three laboratory experiments.

Hydrocarbon data were analyzed using the Statistical Analysis System (SAS 1995) to fit the simple linear regression model:

$$Y = B_0 + B_{1X} + E$$

where Y and X represent the dependent and independent variables respectively (Freund and Wilson 1993). E is the random error term and slope is change in Y(hydrocarbon concentration) with respect to change in X(days), which is the degradation rate of selected petroleum hydrocarbons. Comparison between redox levels and other treatments utilized the General Linear Model and Post-Anova Duncan's Techniques of the SAS programs.

Table 1

Sediment Characterization

Location	P	Na	K	Ca	Mg	Al	S	B
	mg/kg							
Outfall	208	24938	423	3217	584	0.4	171	28
15 m	335	2905	520	2843	1644	1.5	286	3

	Salts	TPH	Oil	CEC	pH
	mg kg^{-1}		(%)	meq 100 g^{-1}	
Outfall	95260	66510	9.3	130	6.9
15m	8300	2010	1.7	42	6.7

Table 2

Hydrocarbon Compounds Analyzed

n-alkane	**C#**	**Polycyclic aromatic hydrocarbons (PAH)**
decane	10	Naphthalene
undecane	11	Acenaphthene
dodecane	12	Fluorene
tridecane	13	Phenanthrene
tetradecane	14	Pyrene
pentadecane	15	Benzo(a)anthracene
hexadecane	16	Chrysene
heptadecane	17	Benzo(b)fluoranthene
octadecane	18	Benzo(a)pyrene
eicosane	20	Benzo(k)fluoranthene
tetracosane	24	Dibenzo(a,h)anthracene
octacosane	28	Benzo(g,h,i)perylene
dotriacotane	32	**Isoprenoids**
hexatriacotane	36	2, 6, 10 c-trimethyldodecane
		2, 6, 10, 14-tetramethylheptadecane-pristane
		2, 6, 10, 14-tetramethylpentadecane-pristane

3.0 RESULTS AND DISCUSSION

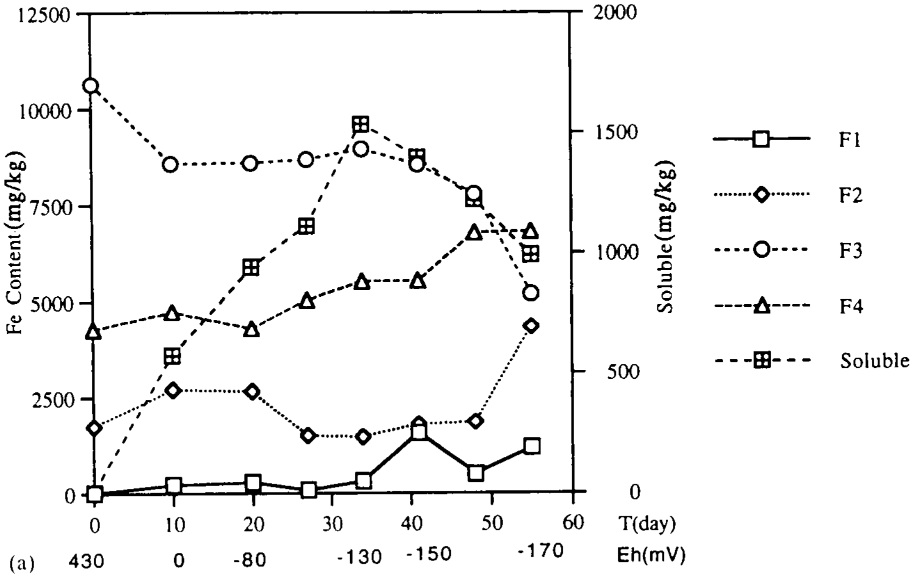
3.1 Effect of Sediment Redox Conditions on Heavy Metal Chemistry

Metal kinetics are influenced by many factors. These factors include temperature, organic matter, surface activity of Fe and Mn compounds, microorganism species and other sediment characteristics. Since it is difficult to individually quantify the variables, in this investigation the factors were combined into one parameter - the rate constant of the assumed zero-order reaction, the so called pseudo-zero-order reaction model. In our discussion below, the pseudo-zero-order reaction model was used. When the rate constant was positive, the reaction released constituents of metals into solution. When the rate constant was negative, the metals are removed from solution. When considering metals bound to organic matter and sulfide phase, we assumed that the formation of insoluble organic matter (complexation of insoluble, large molecular weight humic) (Gambrell and Patrick 1978, 1980) and sulfides were independent. At sediment Eh=-130 mV, (the Eh where sulfate is reduced) and above the changes in metals in this fraction was attributed to insoluble, large molecular weight humic substances.

Iron

Figure 2.1 shows the effect of sediment Eh (redox potential) on the content of Fe in the various chemical fractions. As Eh decreased, Fe(III) oxides were microbialy reduced to soluble Fe(II), therefore increasing the soluble Fe concentration (K=42.5 mg/kg/d) in solution. When Eh further decreased to -130 mV, a reduction in exchangeable iron was observed which was attributed to sulfide formed as a result of sulfate reduction, precipitating dissolved Fe(II) to form insoluble FeS. Based on the fractionation data at all redox levels studied, dissolved Fe(II) was also removed through Fe becoming associated with insoluble organic matter (primarily as a result of complexation of Fe with insoluble, large molecular humic material). The above two factors result in the reduction of soluble Fe concentration in solution (K=-25.8 mg/kg/d). The rate constants of the removal reactions for dissolved Fe(II) are 40.7 mg/kg/d and 31.4 mg/kg/d for the formation of sulfides and complexation of insoluble, large molecular humic, respectively.

Fe(III) oxides in the sediment were reduced to the more soluble Fe(II) during anaerobic incubation. Under reducing condition (Eh > -130 mV), the reduction of Fe(III) oxides occurred only by direct microbial reduction (K=-42.6 mg/kg/d) involving organic carbon turnover. This part of Fe(III) reduction was equivalent to approximately 2071 mg/kg (20% of total reducible Fe(III)). At sediment (Eh < -130 mV), Fe(III) reducing microorganisms can inhibit sulfate reduction by out competing sulfate reducers for electron donors (Lovley and Phillips, 1987). We assume that a portion of Fe(III) reduction occurred by sulfides reducing Fe(III) oxides. Only a small amount of the Fe(III) reduction at this redox level can occur by direct bacteria reduction involving organic carbon turnover (Jacobson, 1994). Accordingly, almost 8571 mg/kg (80% of total reducible Fe(III)) was reduced by the sulfide oxidation pathway (K=-171.5 mg/kg/d). The rate constant of indirected Fe(III) oxide reduction by sulfides is significantly greater than that by direct bacteria reduction. The rate constants of the pseudo-zero-order reaction are listed in Table 3.



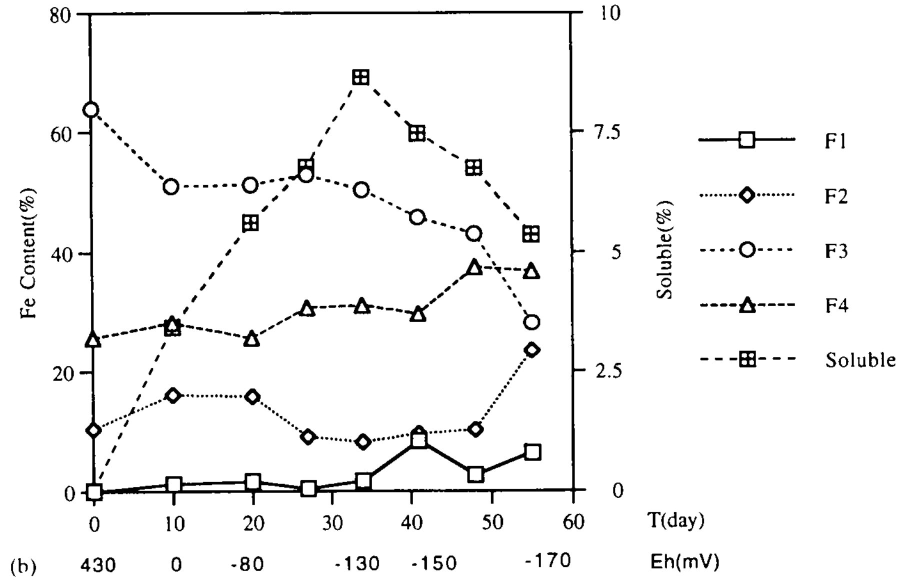


Figure 2.1 The effect of Eh on the distribution of Fe in the chemical fractions (from Guo et al. 1997a).

Figure 2.2 The effect of Eh on the percentage of Fe in the various chemical fractions (from Guo et al. 1997a).

Table 3

The Rate Constants K (mg/kg/d) of the Pseudo-Zero-Order Reaction Involving Fe

	soluble	F2	F3	F4
K_1 (direct microbial reduction)	42.5	-17.5	-42.6	31.4
K_2 (indirect reduction by sulfide)	-25.8	124.1	-171.5	72.1

Figure 2.2 shows percentage distribution of Fe found in the various chemical fractions. During anaerobic incubation approximately half of the reduced Fe(III) was converted to sulfide bound Fe(II). The remaining half of the reduced Fe(III) was converted to carbonate bound Fe(II). Under oxidizing sediment condition Fe(III) oxide predominated with Fe behavior was controlled by Fe(III) oxides. Under reducing sediment conditions, sulfide and insoluble large molecular humic bound Fe(II) was the dominant fraction controlling iron behavior.

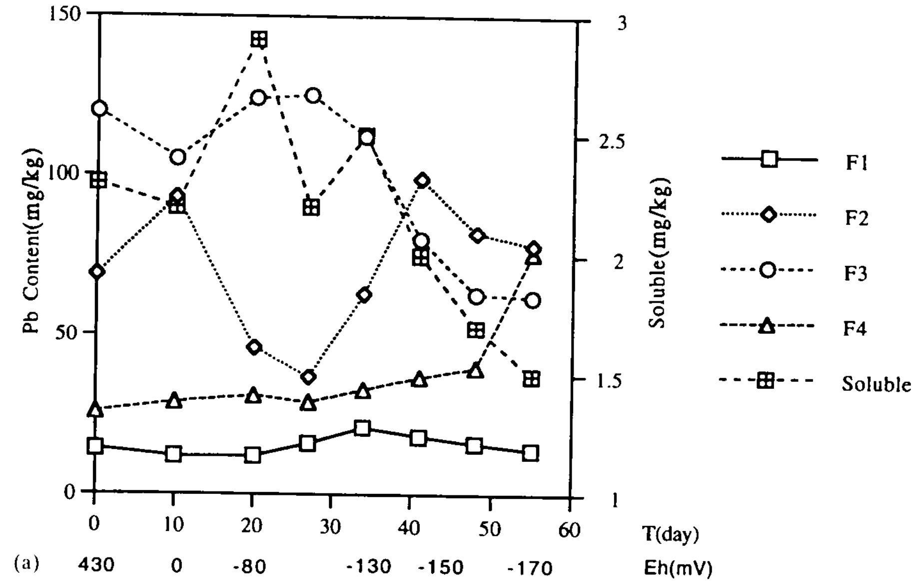
Lead

Figure 3.1 shows the effect of sediment Eh on the actual distribution content of Pb in the various chemical fractions. As Eh decreased Fe(III) and Mn(IV) oxides were reduced and released into solution. Adsorbed Pb decreased (K=-1.1 mg/kg/d) with a significant portion of the released Pb going into solution (K=17 mg/kg/d). Continued decrease in Eh resulted in dissolved Pb concentration decreases (K=-47 mg/kg/d) as a result of the formation of insoluble lead associated with sulfides (K=1.72 mg/kg/d), insoluble complexes of insoluble large molecular humic material (K=0.17 mg/kg/d) and carbonates. As a result of the above processes, most of the Pb released by Fe(III) and Mn(IV) reduction was apparently converted to lead sulfide.

Figure 3.2 shows the effect of Eh on the percentage of Pb in the various chemical fractions. Under oxidizing conditions, Pb was bound to Fe(III) and Mn(IV) oxides. Pb behavior in the sediment was apparently controlled by chemical adsorption on Fe(III) and Mn(IV) oxides. Under reducing sediment conditions, Pb behavior was also governed by sediment carbonate and sulfide since lead was found in both the carbonate and sulfide fractions.

Nickel

Figure 4.1 shows the effect of Eh on the content of Ni in solution and changes among the fraction over the redox range studied. When sediment Eh decreased, Fe(III) and Mn(IV) oxides were reduced to soluble Fe(II) and Mn(II). The Ni adsorbed on Fe(III) and Mn(IV) oxides decreased (K=-3.2 mg/kg/d) resulting in the release of Ni into solution (K=1.5 mg/kg/d). When sediment Eh decreased further, dissolved Ni concentration decreases (K=-1.6 mg/kg/d) may be attributed to the formation of nickel bound to carbonates (K=3.2 mg/kg/d), sulfides



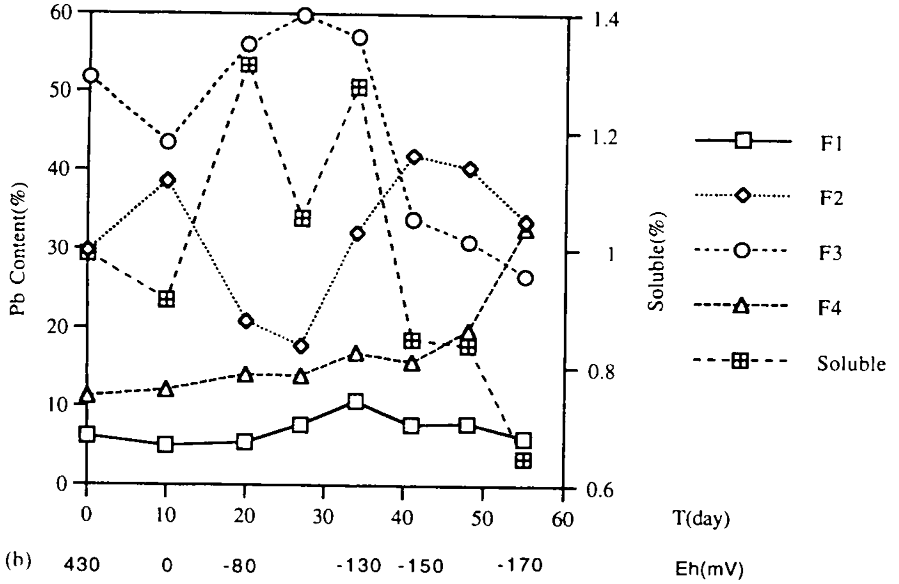
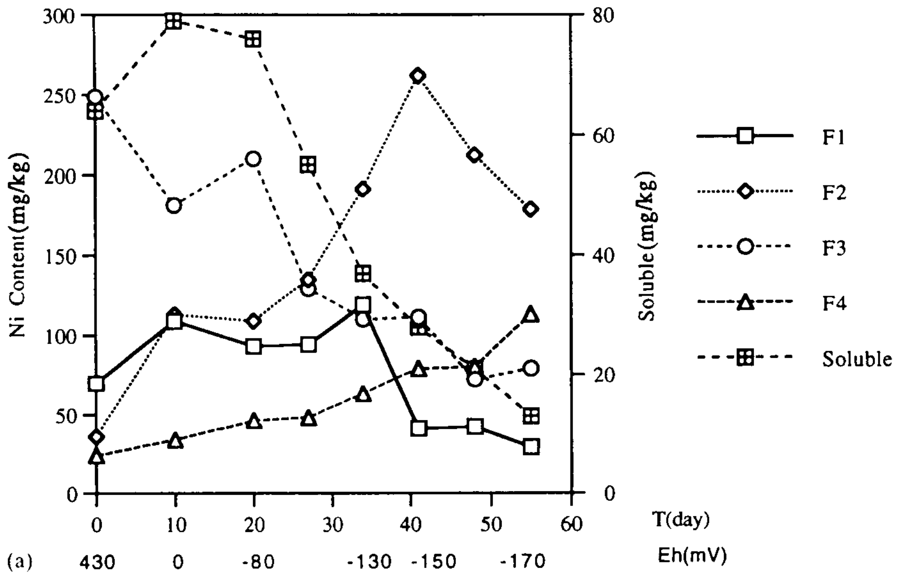


Figure 3.1 The effect of Eh on the distribution of Pb in the chemical fractions (from Guo et al. 1997a).

Figure 3.2 The effect of Eh on the percentage of Pb in the various chemical fractions (from Guo et al. 1997a).



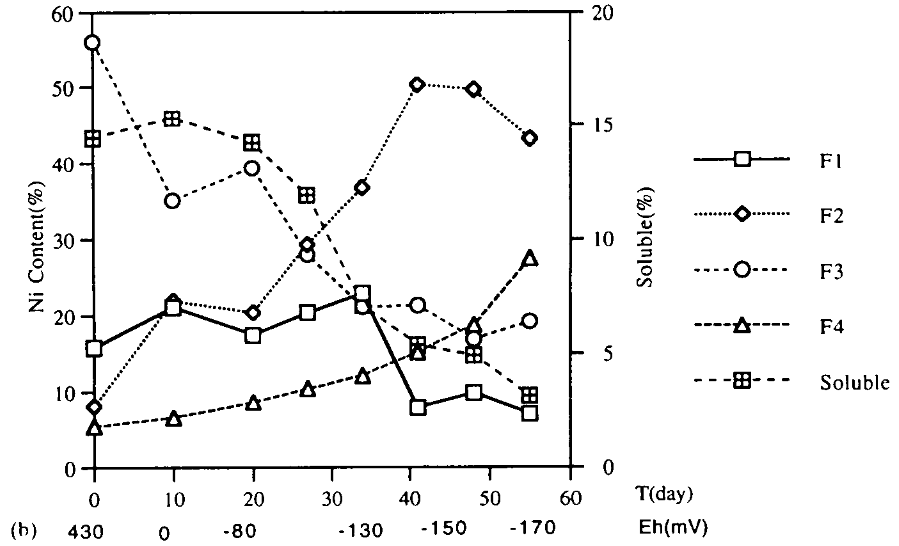


Figure 4.1 The effect of Eh on the distribution of Ni in the chemical fractions (from Guo et al. 1997a).

Figure 4.2 The effect of Eh on the percentage of Ni in the various chemical fractions (from Guo et al. 1997a).

(K=1.1 mg/kg/d) and insoluble large molecular humic (K=1.1 mg/kg/d). Most of the nickel released is transformed into nickel bound to carbonates. A small percentage of the nickel released was bound to sulfides and large molecular weight humic compounds, making nickel less soluble.

Figure 4.2 shows the effect of Eh on the percentage of Ni in the various chemical fractions. Under oxidized sediment condition, Ni was bound to Fe(III) and Mn(IV) oxides. Under reducing sediment conditions, the Ni was mainly bound to carbonates. The Ni bound to insoluble sulfides only increased slowly as Eh sediment decreased to low levels suggesting that Ni was not strongly influenced by sulfide. Similar results have been reported by Griffin et al. (1989) for reducing sediment conditions. Ni behavior in sediment in this study was controlled primarily by the formation of nickel bound to carbonates.

Barium

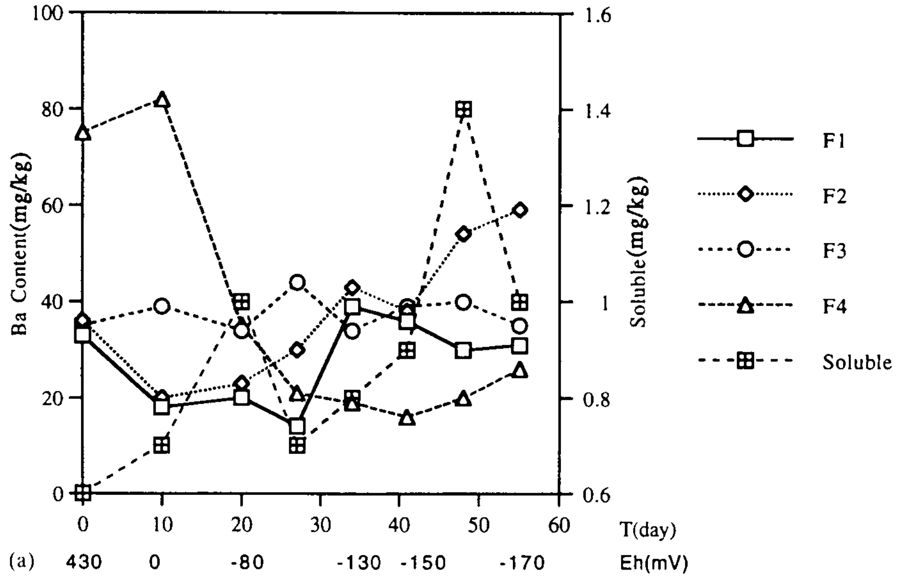
Figure 5.1 shows the effect of sediment Eh on levels of Ba in the various chemically active fractions. Sediment Eh had little effect on dissolved Ba levels in the sediment, since Ba has only one valence state and Ba(II) has lower affinity to ferric and manganic oxides than other metals. Sediment Eh had little effect on dissolved Ba levels in the sediment since Ba has only one valence state. Ba(II) has a lower affinity than other metals to ferric and manganic oxides. As sediment Eh decreased the Ba bound to sulfides and insoluble large molecular humic fraction did decrease. We know that at Eh>-130 mV no sulfide exists. The only possible explanation is that as Eh decreased, the Ba bound to insoluble, large molecular humic material also decreased. This decreased Ba is converted to Ba bound to carbonates. The rate constant of the formation of barium bound to carbonates is 0.91 mg/kg/d.

Figure 5.2 shows the effect of Eh on the percentage of Ba in the various chemical fractions. It is obvious that under oxidizing conditions, Ba behavior was controlled by complexation of Ba with insoluble, large molecular humic compounds. Under reducing conditions, Ba behavior was controlled primarily by Ba bound to carbonates.

Copper

Figure 6.1 shows the effect of sediment Eh on the solubility and distribution of Cu in the various chemical fractions. As Eh decreased to 0 mV, dissolved Cu content increased (K=70 mg/kg/d) apparently as the result of the dissolution of copper associated with Fe(III) and Mn(IV) oxides and carbonates. Continued decrease in sediment Eh resulted further reduction in dissolved Cu level (K=-0.16 mg/kg/d) attributed to the formation of the insoluble complexation of Cu with large molecular humic compounds (K=4.3 mg/kg/d) and copper bound to sulfides (K=0.6 mg/kg/d) . Griffin et al. (1989) also reported that under reducing conditions, Cu behavior was controlled by sulfides. Under very reducing sediment conditions, Cu bound to carbonates was apparently converted to Cu bound to insoluble sulfides and large molecular humic compounds. Paralleling this sediment reduction, Cu bound to Fe(III) and Mn(IV) oxides also decreased slightly. The rate constants of the pseudo-zero-order reaction are -2.1 mg/kg/d and -0.67 mg/kg/d for the dissolution of copper bound to carbonates and Fe(III), Mn(IV) oxides respectively. Upon sediment reduction, Cu solubility decreased, thus reducing Cu toxicity.

Figure 6.2 shows the effect of sediment Eh on the percentage distribution of Cu in the various chemical fraction. Under oxidizing sediment conditions, copper was bound primarily to



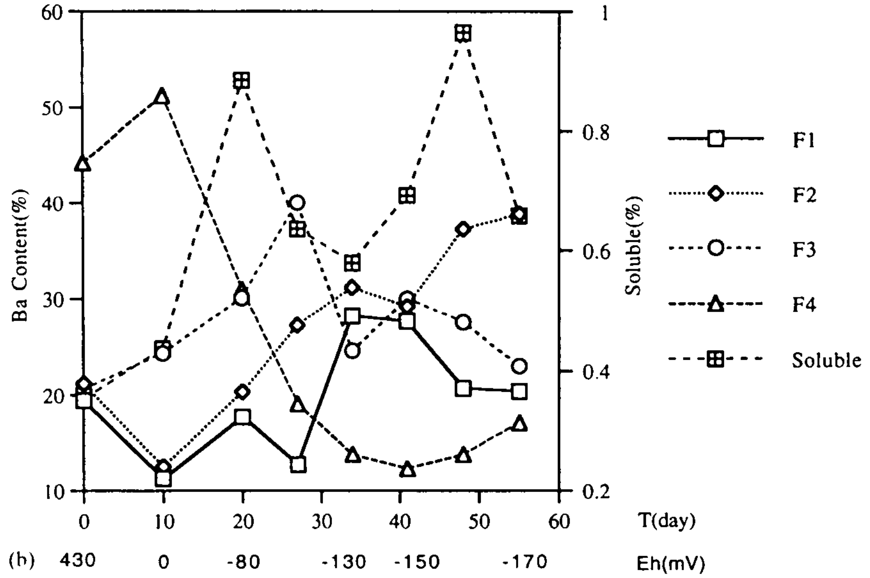
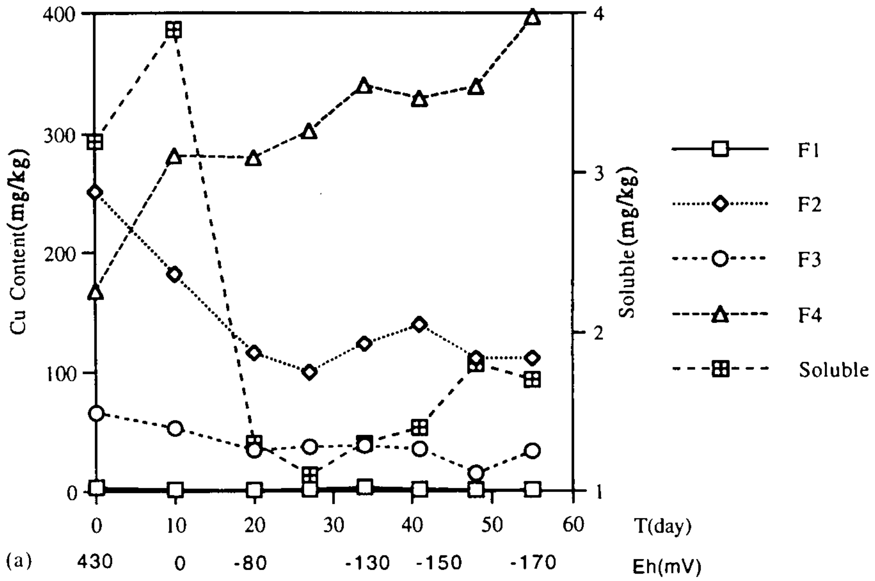


Figure 5.1 The effect of Eh on the distribution of Ba in the chemical fractions (from Guo et al. 1997a).

Figure 5.2 The effect of Eh on the percentage of Ba in the various chemical fractions (from Guo et al. 1997a).



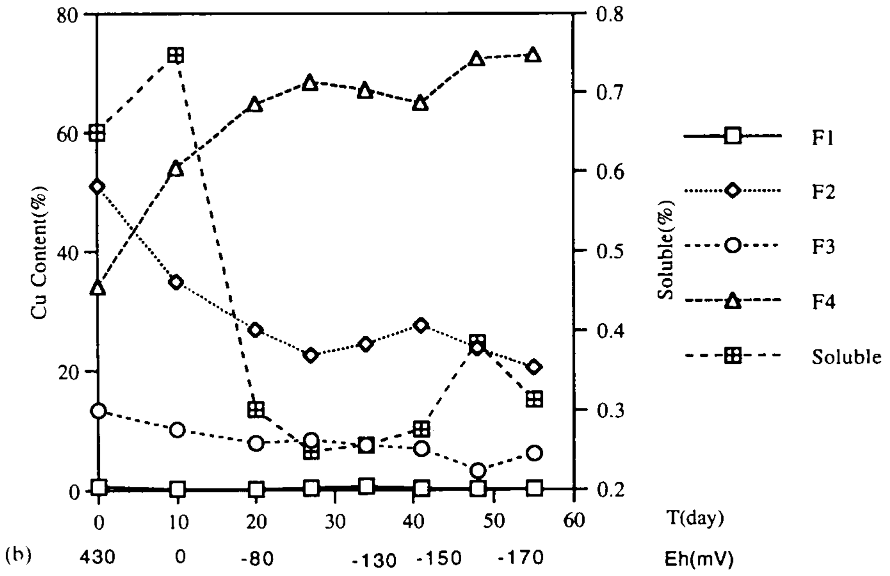


Figure 6.1 The effect of Eh on the distribution of Cu in the chemical fractions (from Guo et al. 1997a).

Figure 6.2 The effect of Eh on the percentage of Cu in the various chemical fractions (from Guo et al. 1997a).

carbonates and large molecular humic material. Under reducing sediment condition, Cu was found to be bound to a insoluble sulfides and to some extent humic compounds.

Arsenic

Figure 7 shows the effect of Eh on the level of As in the water soluble chemical fraction. When Eh decreased to 0 mV, As(V) was reduced to As(III) (K=-0.21 mg/kg/d). At sediment Eh=0 to -100 mV, dissolved arsenic concentration was essentially zero. This may be due to the fact that the fresh As(III) which was formed from As(V) reduction became insoluble.

Following manganic oxide and ferric oxide reduction, the As bound with these oxides decreased (K=-0.88 mg/kg/d). Similar results have been reported by McGeehan and Naylor, (1994). Parallel increases in As bound to insoluble large molecular humic compounds correlated with reduction of manganese and iron oxide. The rate constant of pseudo-zero-order reaction for the formation of As with insoluble large molecular humic substances was 0.97 mg/kg/d. There was no evidence to show that As associated with sulfides was formed.

At Eh levels between 430 mV to -130 mV, As bound to carbonates decreased (K=-0.51 mg/kg/d). Further decreases in Eh (< -130 mV) caused the As bound to carbonates to increase (K=0.59 mg/kg/d).

Figure 8 shows the effect of Eh on the percentage of As in the various chemical fractions. The dominant active As fraction is As bound to Fe(III) and Mn(IV) oxides.

Chromium

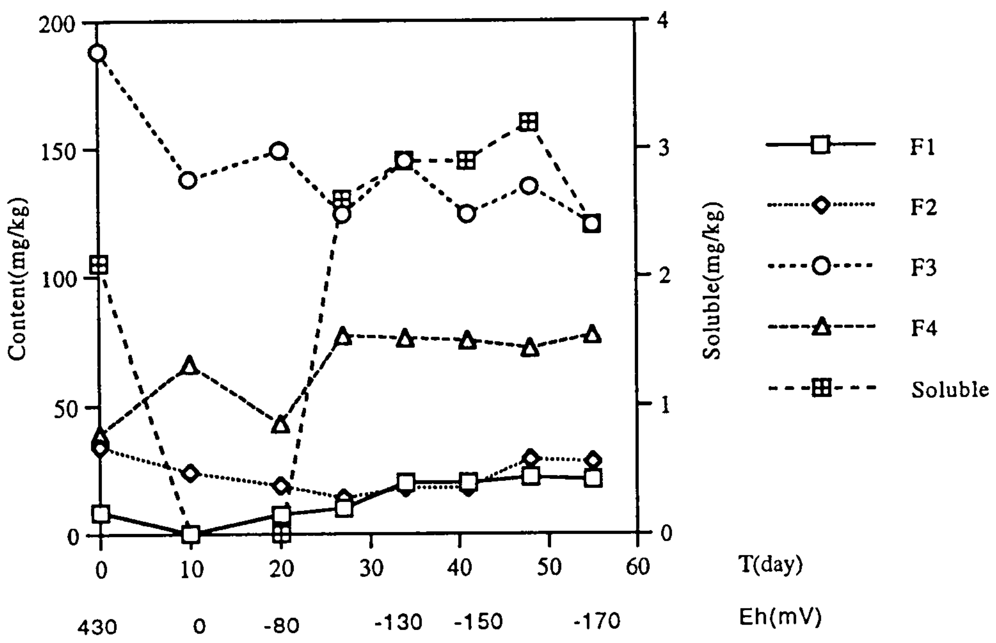
Cr fractions were also affected by sediment redox conditions (Figures 9 and 10). As Eh decreased to 0 mV, Fe(III) and Mn(IV) oxides in the sediment were reduced to more soluble Fe(II) and Mn(II) and the Cr adsorbed on Fe(III) and Mn(IV) oxides was apparently released increasing dissolved Cr concentration. At Eh<100 mV, soluble Cr(VI) was apparently reduced to insoluble Cr(III) (mostly as $Cr(OH)_3$) (Masscheleyn et al. 1992). Cr(III) also apparently reacted with organic matter to form dissolved Cr(IV)-organic complexes (Masscheleyn et al. 1992). The above three reactions controlled dissolved Cr concentration in the sediment. The combination of these three reactions resulted in little difference in dissolved Cr content being measured under the various redox conditions studied.

As sediment Eh decreased, Cr associated with Fe(III), Mn(IV) oxides decreased (K=-0.32 mg/kg/d), while Cr associated with insoluble large molecular humic material increased (K=0.81 mg/kg/d). There was no evidence to show that any Cr associated with sulfides was formed.

Figure 10 shows the effect of Eh on the percentage of Cr in the various chemical fractions. Under oxidizing conditions, Cr associated primarily with Fe(III) and Mn(IV) oxides, with Cr activity being controlled by chemical adsorption of Cr on Fe(III) and Mn(IV) oxides. Under reducing soil conditions, Cr was bound to insoluble large molecular humic substances.

Cadmium

Fig. 11 shows the effect of Eh on the levels of water soluble Cd and Cd in the various chemical fractions. As sediment Eh decreased, dissolved Cd decreased from 4.6 mg/kg to 0.3 mg/kg (K=-0.09 mg/kg/d), and Cd associated with Fe(III) and Mn(IV) oxides also decreased (K=-0.01 mg/kg/d).



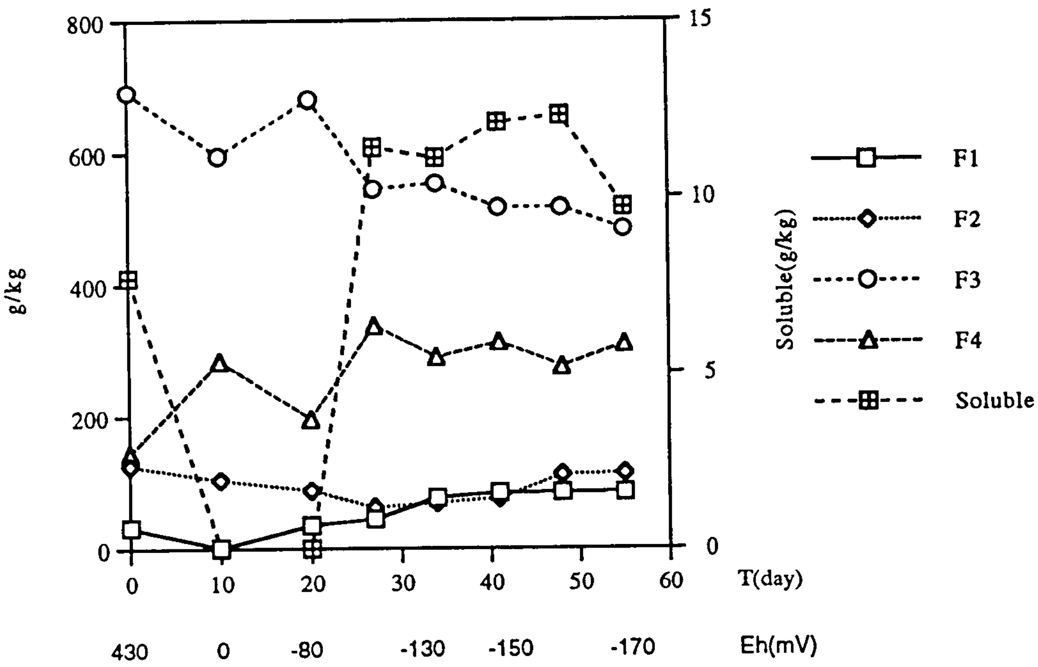
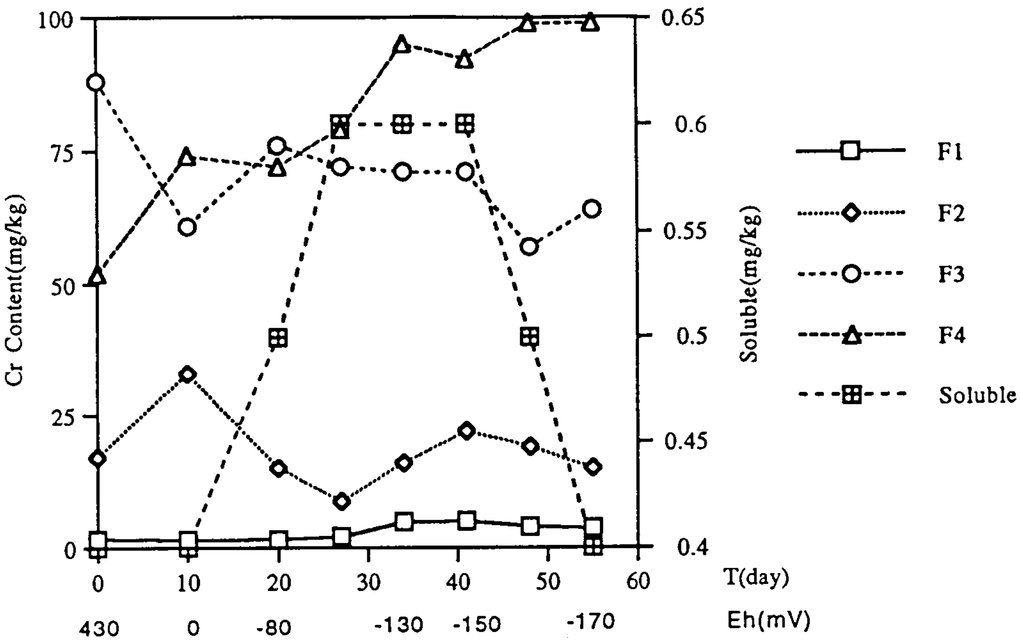


Figure 7. The effect of Eh on the distribution of As in the chemical fractions (from Guo et al. 1997b).

Figure 8. The effect of Eh on the percentage (expressed as g/kg) of As in the various chemical fractions (from Guo et al. 1997b).



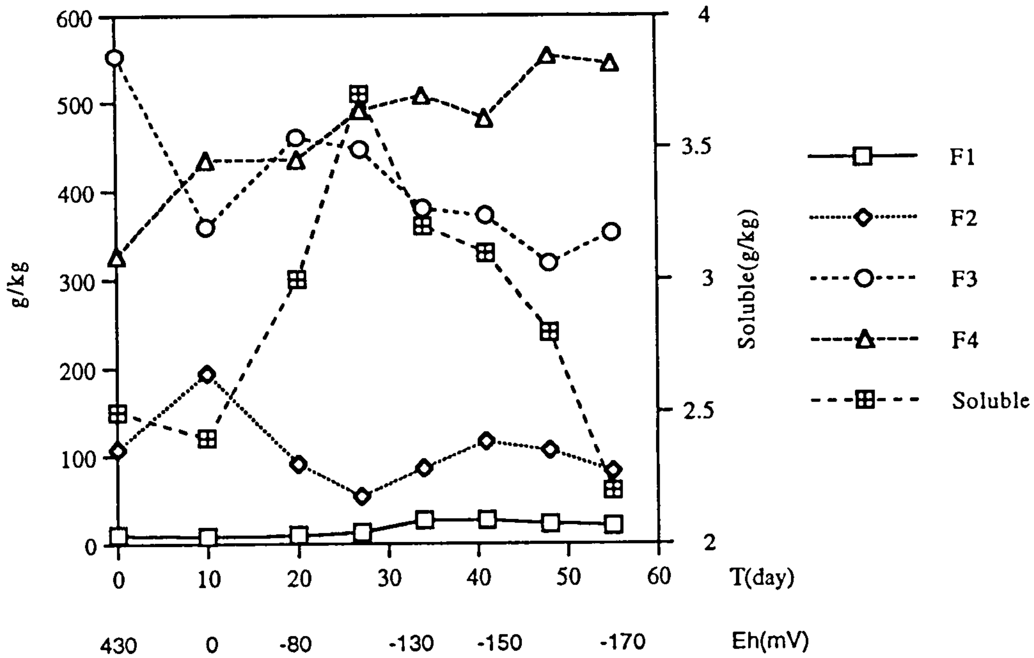
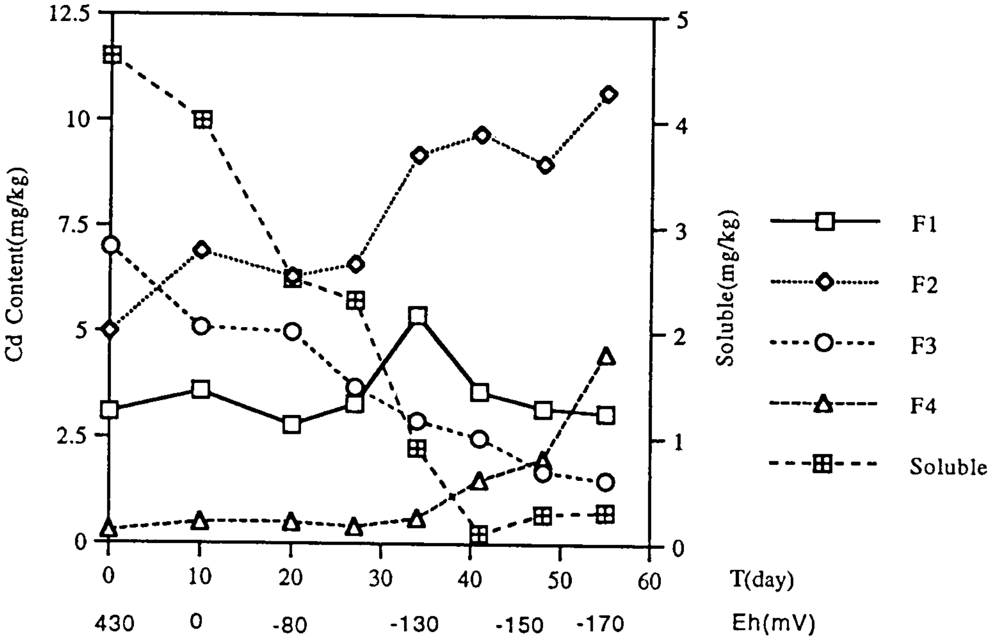


Figure 9. The effect of Eh on the distribution of Cr in the chemical fractions (from Guo et al. 1997b).

Figure 10. The effect of Eh on the percentage (expressed as g/kg) of Cr in the various chemical fractions (from Guo et al. 1997b).



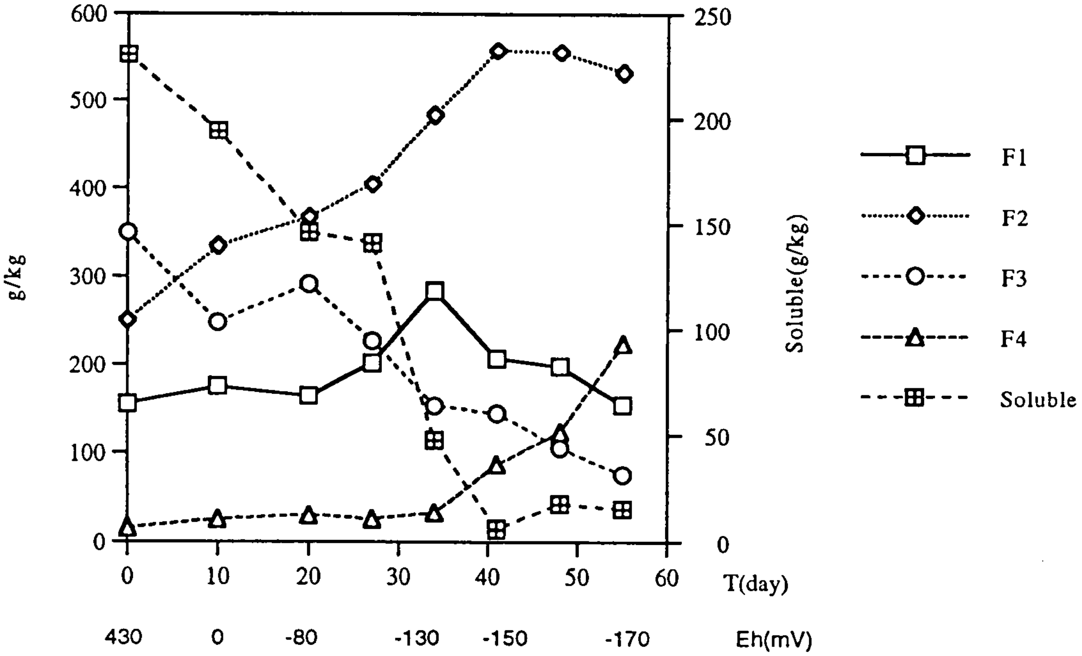


Figure 11. The effect of Eh on the distribution of Cd in the chemical fractions (from Guo et al. 1997b).

Figure 12. The effect of Eh on the percentage (expressed as g/kg) of Cd in the various chemical fractions (from Guo et al. 1997b).

In contrast Cd associated with carbonates (K=0.01 mg/kg/d), and Cd associated with insoluble large molecular humic substances and sulfides increased as Eh decreased. The rate constants of pseudo-zero-order reaction on the formation of Cd associated with insoluble sulfides and large molecular humic material were 0.16 mg/kg/d and 0.01 mg/kg/d respectively. These results are similar to the findings of Kerner and Wallman (1992) for Cd associated with dissolved and sulfide forms.

Fig. 12 shows the effect of Eh on the percentage of Cd in the water soluble and chemical fractions. Under oxidizing sediment conditions, Cd was associated with Fe(III) and Mn(IV) oxides, carbonates, and soluble phase Cd. Soluble Cd accounted for 230 g/kg of the total concentration under oxidized conditions. Under reducing sediment conditions, Cd bound to the carbonates fraction accounted for most of the Cd while water soluble Cd accounted for only 15 g/kg of total Cd concentration. As Eh decreased, the decreased Cd associated with Fe(III) and Mn(IV) oxides and soluble phases was transformed into Cd associated with insoluble carbonates and sulfides.

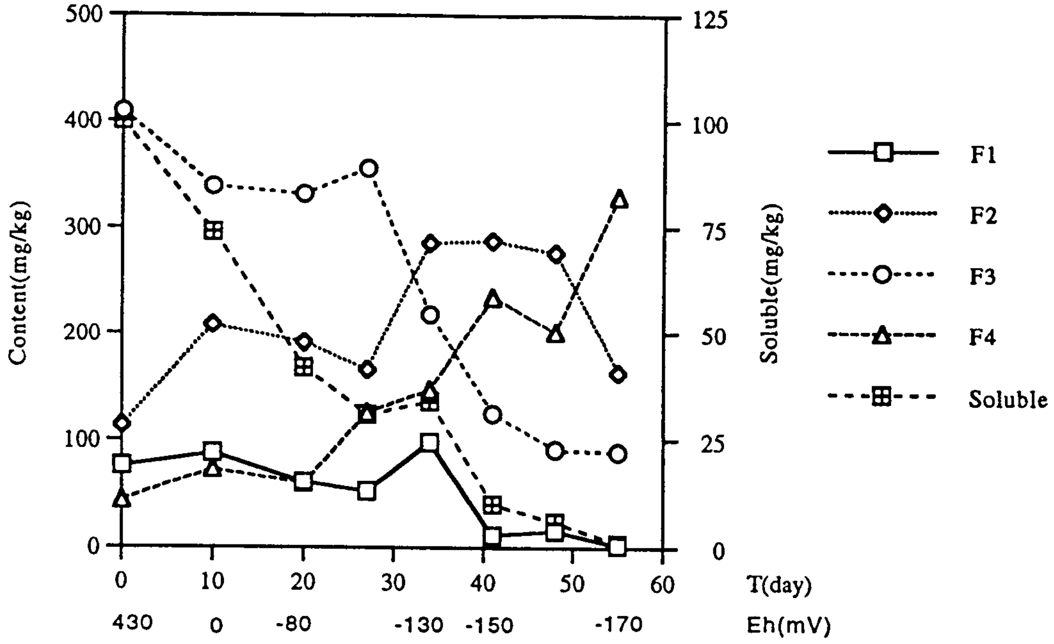
Zinc

Fig. 13 shows the effect of sediment Eh on the distribution of Zn in the water soluble and chemical fractions. As Eh decreased, dissolved Zn decreased from 100 mg/kg to 0.8 mg/kg (K=-1.78 mg/kg/d, Fig. 14), Zn associated with Fe(III) and Mn(IV) oxides also decreased (K=-6.5 mg/kg/d). In contrast, Zn associated with carbonates (K=3.3 mg/kg/d) and Zn associated with insoluble large molecular humic substances and sulfides increased as sediment Eh decreased. The rate constants of the pseudo-zero-order reaction for the formation of Zn associated with insoluble sulfides and large molecular humic material were 5.4 mg/kg/d and 2.9 mg/kg/d respectively. These results are similar to that reported by Kerner and Wallman (1992) who determined Zn existed primarily in dissolved and sulfide forms.

Fig. 14 shows the effect of sediment Eh on the percentage distribution of Zn in the various fractions. Under oxidizing conditions, Zn was associated with Fe(III) and Mn(IV) oxides and soluble phases. Soluble Zn accounted for 140 g/kg of total content of all fractions. Under reducing conditions, Zn was found to be associated with insoluble sulfide, large molecular humic compounds and carbonates. Soluble Zn accounted for 1 g/kg of the total content found in the fractions. As sediment Eh decreased, the Zn associated with Fe(III) and Mn(IV) oxides and soluble phases was transformed into Zn fractions associated with insoluble carbonates, sulfide and large molecular humic compounds. The data collected show that Zn becomes less mobile under reducing sediment conditions.

3.2 Radium Chemistry

Selective extraction of wastepit and Humble Canal sediment exposed to produced water showed that greater than 95% of the ^{226}Ra could be detected only in the residual fractions (Figure 15 and 16). Only a small amount of ^{226}Ra activity was detected in exchangeable or carbonate fractions that would indicate the presence of more readily available forms of radium. The extraction data suggest that ^{226}Ra solubility may be controlled by the mineral phase. Due to the large ionic radius of radium, it is unlikely that ^{226}Ra is incorporated within the clay lattice of the sediment.



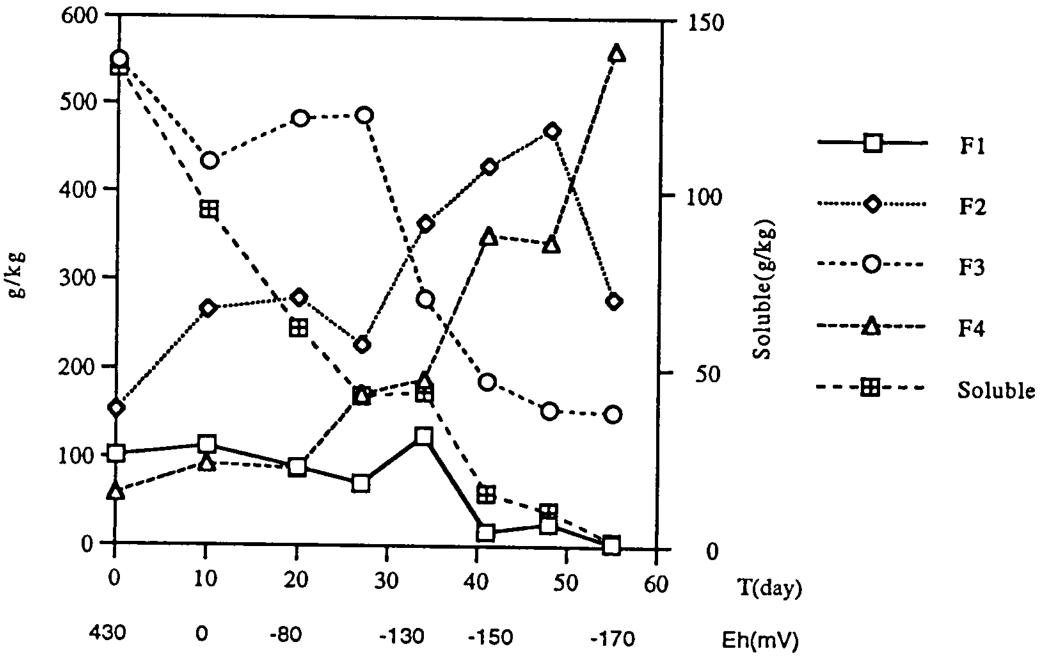
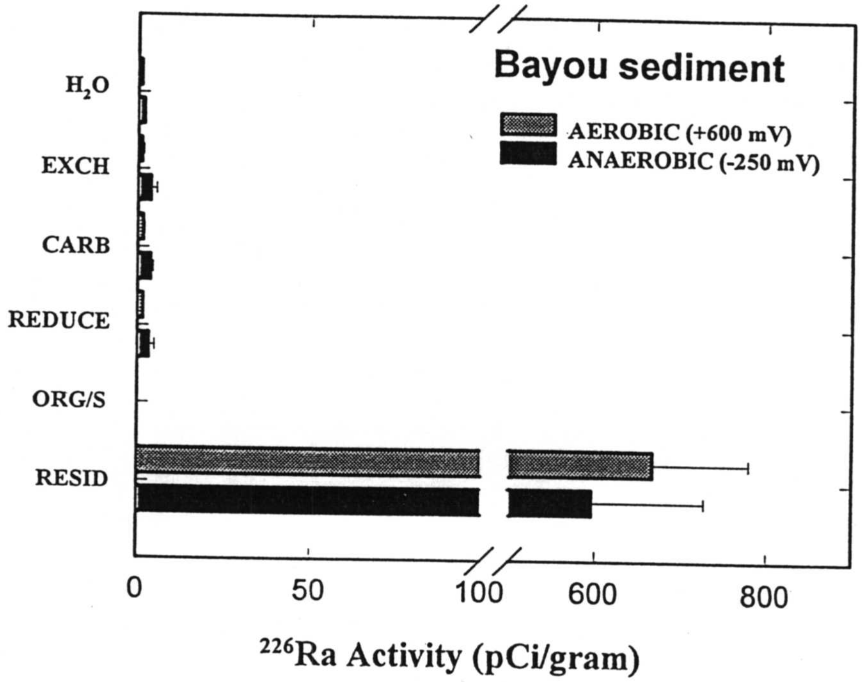


Figure 13. The effect of Eh on the distribution of Zn in the chemical fractions (from Guo et al. 1997b).

Figure 14. The effect of Eh on the percentage (expressed as g/kg) of Zn in the various chemical fractions (from Guo et al. 1997b).



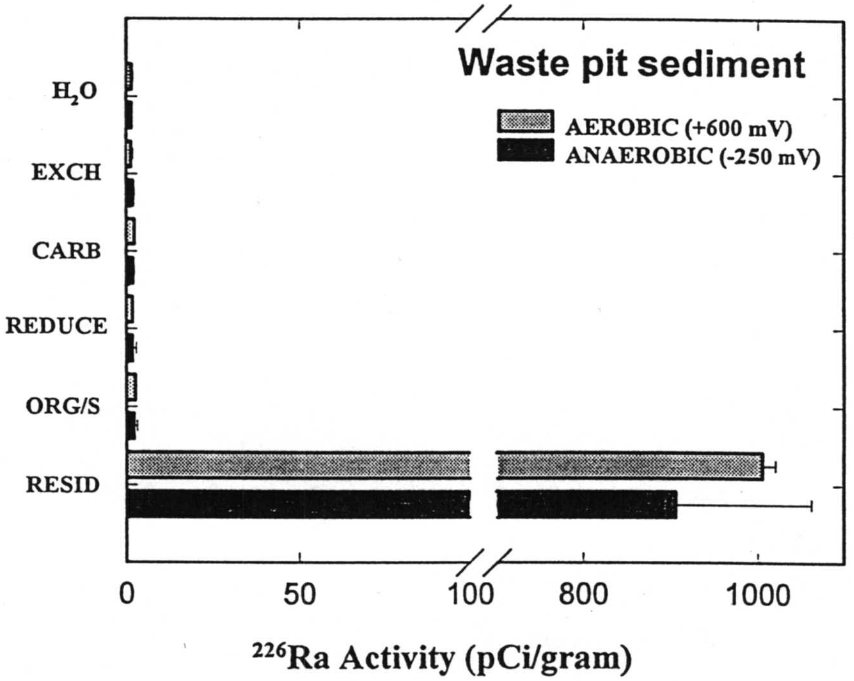


Figure 15. ^{226}Ra activity in various chemical fractions in Humble Canal sediment incubated under aerobic and anaerobic conditions.

Figure 16. ^{226}Ra activity in various chemical of waste pit sediment incubation under aerobic and anaerobic conditions.

The co-precipitation with other minerals such as barite, gypsum and anhydrite has been reported (Langmuir and Melchior 1985). The presence of elevated levels of barite in the sediment would suggest that precipitation with barite would be the most likely sink for ^{226}Ra as indicated by the detection of ^{226}Ra only in the residue.

3.3 Effect of Heavy Metal on Petroleum Hydrocarbon Degradation

Water soluble plus exchangeable Cr and Pb concentrations are shown in Table 4. The majority of the added metal was sequestered or precipitated by other sediment fractions. Only under reducing sediment conditions were significant water soluble plus exchangeable metal concentrations observed. At 5,000 mg/kg added Cr only 145 mg/kg remained in the water soluble plus extractable phase. At 2,500 mg/kg added Pb, 183 mg/kg remained in the more bioavailable water soluble plus exchangeable fraction.

Figure 17 depicts changes in total hydrocarbon concentration (alkane fractions) under oxidized and reduced conditions. The data shows that total hydrocarbon concentration decreased with time in all treatments. Total hydrocarbons were greater in suspensions treated with 1000 mg/kg Cr compared to suspensions receiving no Cr. Sediment suspensions treated with 5000 mg/kg Cr had higher hydrocarbon concentrations remaining than suspensions that received 1000 mg/kg Cr. Since the actual amounts of hydrocarbons varied for the oxidized and reduced suspensions, comparisons are difficult to make. It was evident that total hydrocarbon concentration measured at the end of the anaerobic incubation of suspensions treated with higher Cr levels was greater than the lower Cr treatments.

Table 4

Water Soluble Plus Exchangeable Chromium and
Lead Concentrations in Oxidized and Reduced Suspensions

Treatment (mg/kg)	Amount found (mg/kg)	
Cr		
	Oxidized	Reduced
0	0.59	0.99
250	1.50	22.60
1000	2.44	61.60
5000	32.52	145.40
Pb		
0	3.85	5.90
100	4.08	16.40
500	4.40	40.30
2500	11.46	183.20

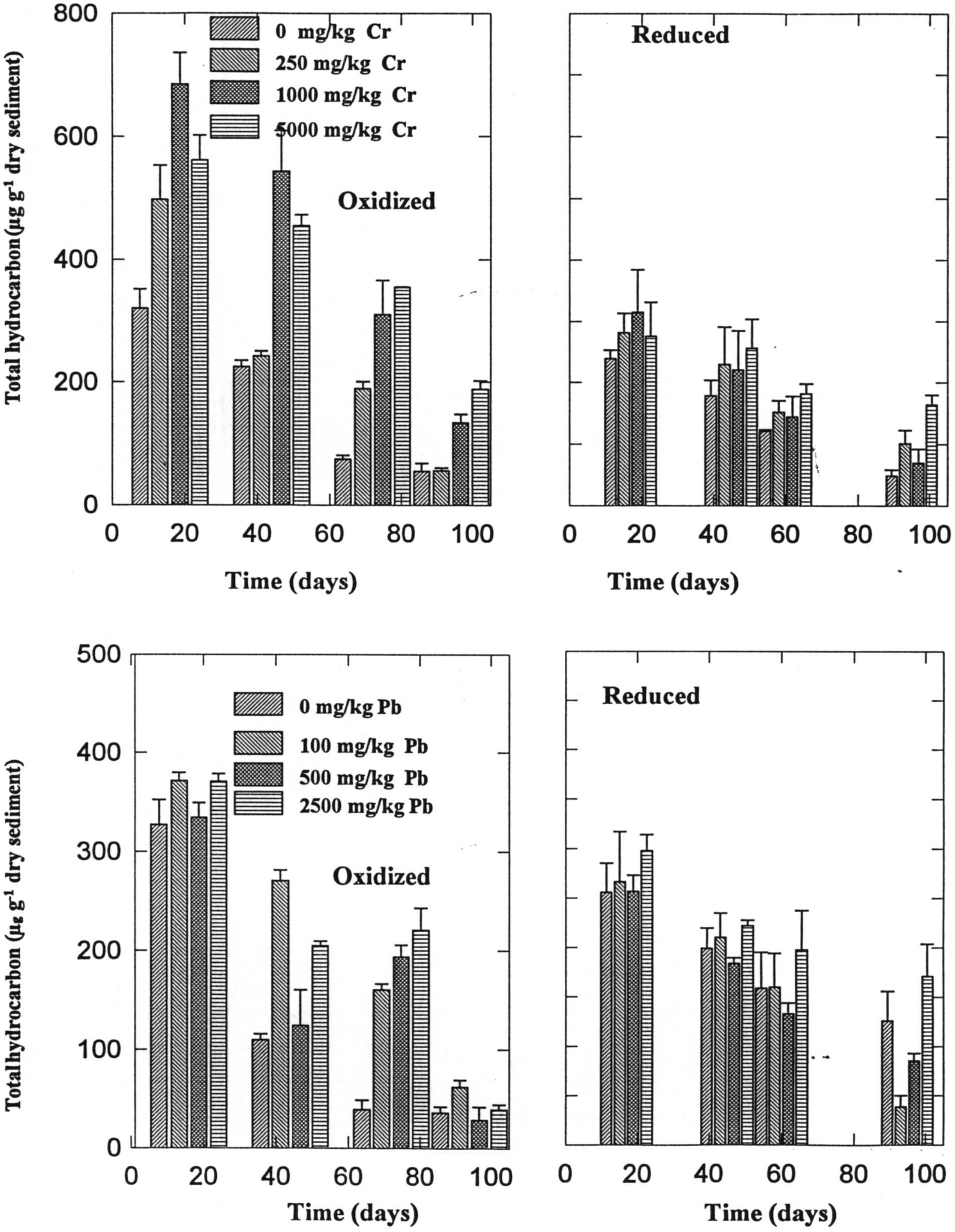


Figure 17. Chromium and lead effects on total hydrocarbon degradation in oxidized and reduced sediment suspensions (from DeLaune et al. 1998).

The change in total hydrocarbon degraded (percent) provides some information on treatment effects (Figure 18, Table 5). Little difference in petroleum hydrocarbon degradation existed between 0 and the 1000 mg/kg Cr treatment levels. However at 5000 mg/kg Cr, percent total hydrocarbon remaining was higher compared to the other treatments, thus showing reduced degradation of the total hydrocarbon fractions. The difference was not statistically significant.

In the case of the Pb treated sediment suspensions, data (Figure 18, Table 6) shows that under oxidized conditions 50 to 60% of the added hydrocarbons were still present for the 500 and 2500 mg/kg Pb rates after the third sampling. However, under reducing conditions, remaining hydrocarbons were even higher (50-80%) after the third sampling date. This shows that total hydrocarbon degradation rates were slower compared to oxidized treatments. At the end of the oxidation incubation the highest total remaining hydrocarbon percentage in the Pb treatments was around 10%. Total remaining hydrocarbons measured in the Pb treated suspensions under reduced conditions ranged from 10 to 55%. The percent degraded (Table 6) shows very little treatment effect. However, unlike the Cr treatments, there was a much larger difference between the percent degraded during the oxidation and reduction phases for all Pb treatment levels.

Table 5

Chromium and Lead Effect on Total Hydrocarbon Degradation (total of all alkane fractions) as Affected by Oxidized and Reduced Soil Suspensions (91 days of incubation)

Degradation Rate (mg/kg soil/day) Treatment (mg/kg)	Oxidized	Duncan Grouping	Reduced	Duncan Grouping
Chromium				
0	3.65	A	2.49	A
250	5.28	A	2.40	A
1000	7.18	A	3.20	A
5000	4.62	A	1.54	A
Lead				
0	3.68	A	1.68	A
100	3.69	A	2.96	A
500	3.20	A	2.22	A
2500	3.69	A	1.60	A

Note: Means in columns followed by the same letter are not significantly different.

The differences observed may be explained by examining the observed degradation rates (Table 5). Petroleum hydrocarbon degradation in the oxidized suspensions was faster than that measured under reducing conditions. The disparity was observed in all concentration rates in the individual flasks.

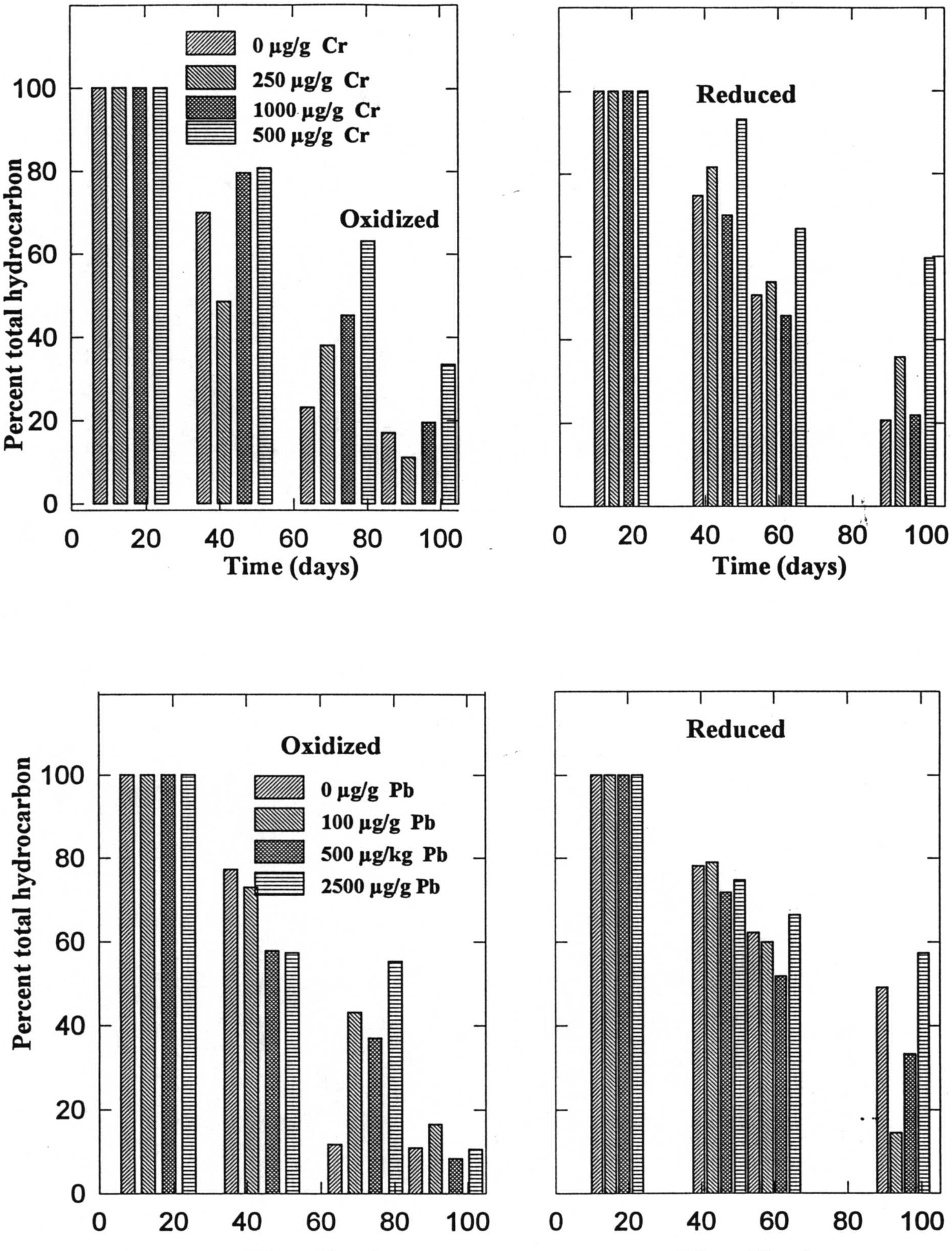


Figure 18. Chromium and lead treatments effects on changes in total petroleum hydrocarbon (percent) in oxidized and reduced sediment suspensions during 91 days of incubation (from DeLaune et al. 1998).

Effect of Cr and Pb on Degradation of Individual Hydrocarbon Fractions in Oxidized and Reduced Sediment Suspensions

Eleven hydrocarbon fractions were quantified but three (pentadecane, hexadecane and octadecane) were individually graphed for analysis of degradation under both oxidized and reduced conditions. Since the effects of treatments on the total hydrocarbon degradation result from the degradation rates of its individual components, the percent of each fraction is graphically presented in Figure 19.

The results show that under both oxidized and reduced environments the low molecular weight hydrocarbons tend to disappear much faster than heavier hydrocarbons. In general, the degradation of the three hydrocarbon fractions decreased as Cr treatment increased.

Under oxidized conditions, the percent of the three individual hydrocarbons in Pb treated suspensions decreased quite rapidly with time (Figure 20). Under reduced conditions, less than 20% of the original hydrocarbon fraction remained. But there were no visible treatment trends observed from this set of data. However, it must be noted that much larger fractions of the original concentrations were present at the termination of the study.

Table 6

Effect of Chromium and Lead Treatments on the Percent Total Petroleum Hydrocarbons Degraded (after 91 days) in Oxidized and Reduced Sediment Suspensions

Compound	Treatment Rate (mg/kg)	Oxidized		Reduced
		----------	%	---------
Chromium	0	82.88		79.83
	250	88.84		64.17
	1000	80.48		78.12
	5000	66.56		40.43
Lead	0	89.20		50.85
	100	83.48		85.51
	500	91.69		66.74
	2500	89.52		42.68

Following a statistical analysis of Cr and Pb on the degradation (percent) of three selected hydrocarbon fractions (pentadecane, hexadecane and octadecane), we could only show a significant difference of Cr on octadecane degradation. Chromium only showed degradation under reducing

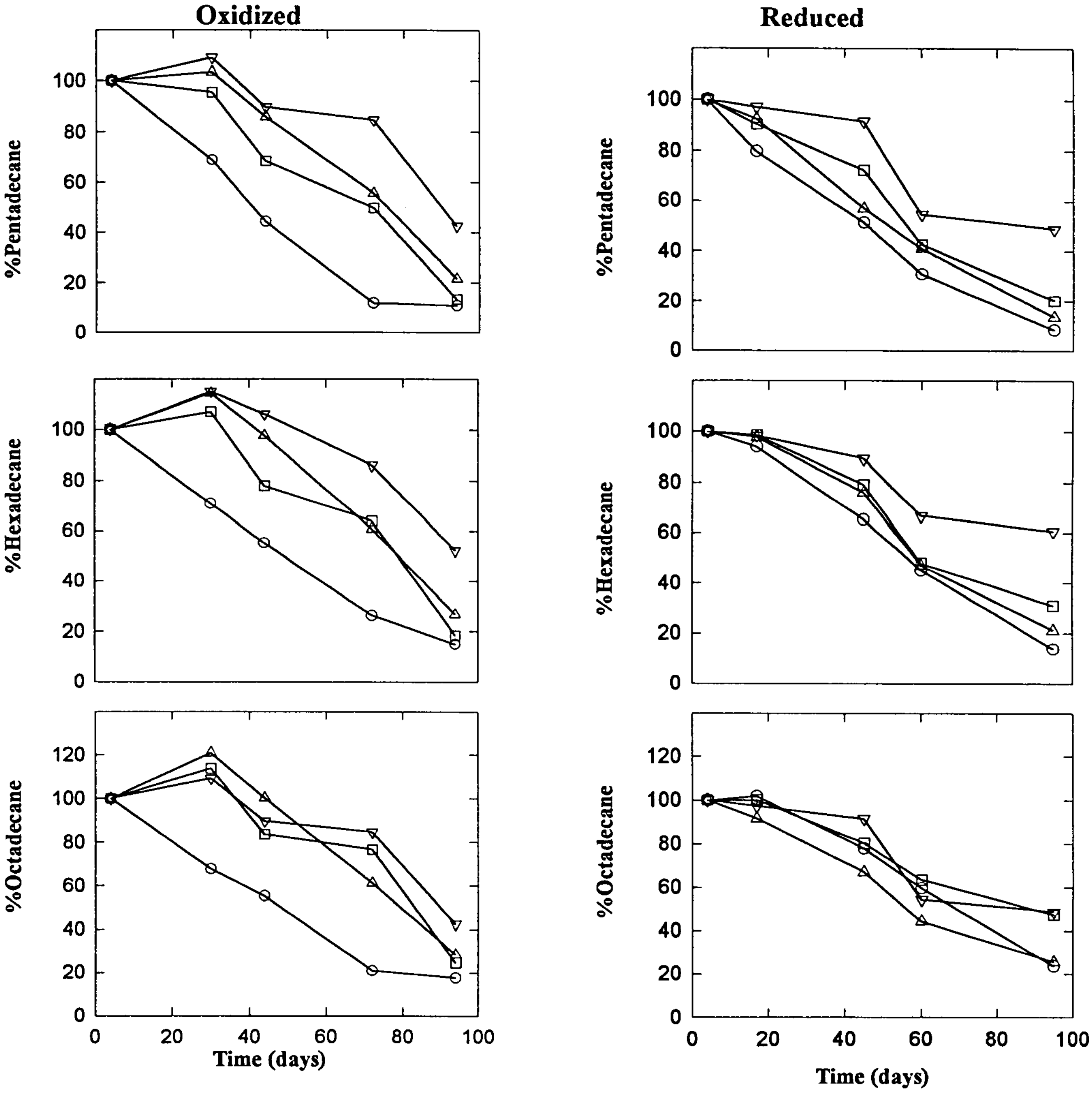


Figure 19. Effect of chromium on changes in percent of hydrocarbon degraded in oxidized and reduced sediment suspensions receiving 0 mg/kg (O), 250 mg/kg (□), 1000 mg/kg (V) and 5000 mg/kg (Δ) Cr added (from DeLaune et al. 1998).

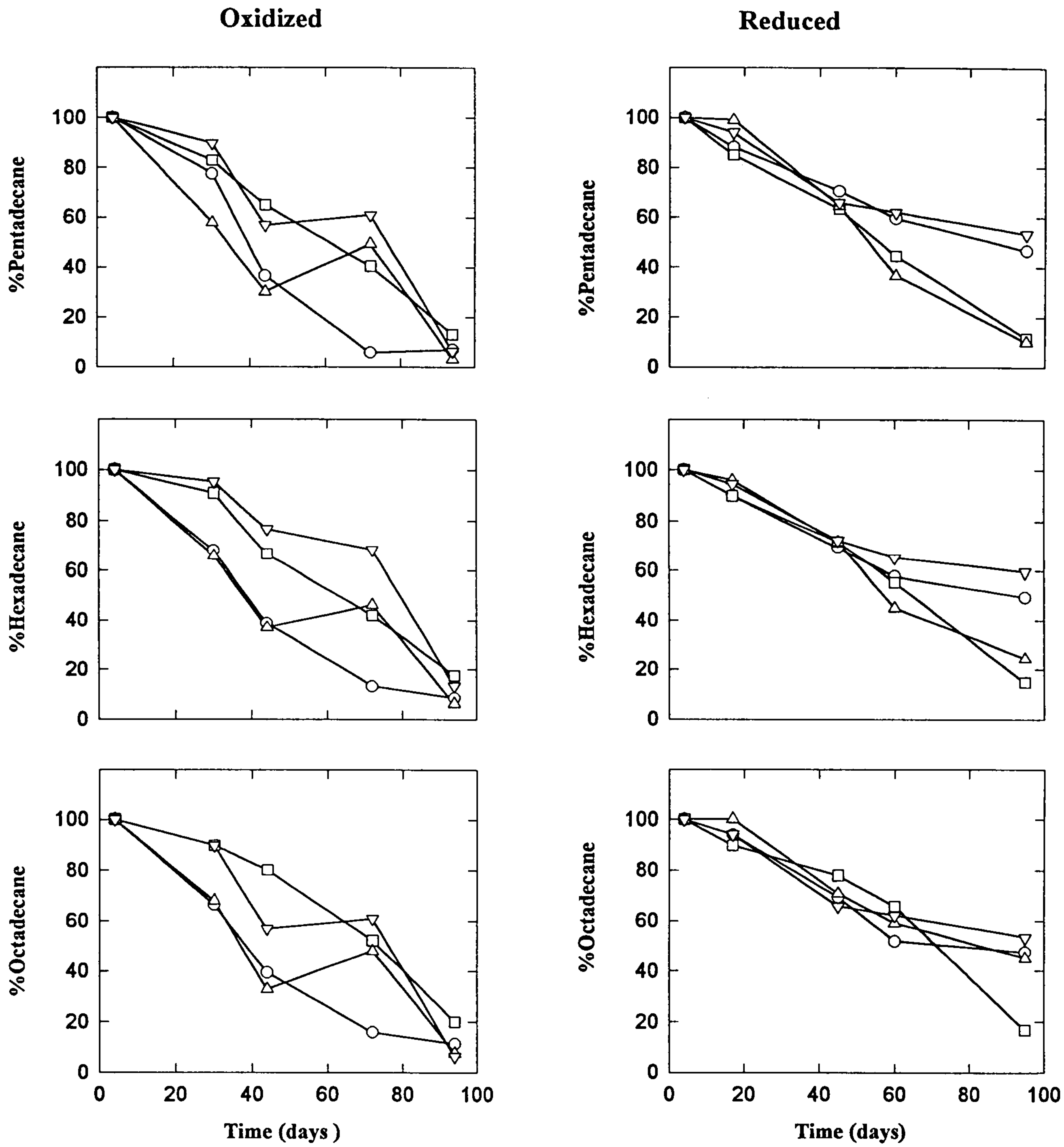


Figure 20. Effect of lead on changes in percent of hydrocarbon degraded in oxidized and reduced sediment suspensions receiving 0 mg/kg (O), 100 mg/kg (□), 500 mg/kg (V) and 2500 mg/kg (Δ) Cr added (from DeLaune et al. 1998).

conditions at 5,000 mg/kg added Cr. There were no significant differences in degradation as influenced by metal content for the oxidized treatments ($\alpha = 0.05$). The slope of octadecane degradation of the reduced 5000 mg/kg Cr treatment was significantly different than the 0 and 250 mg/kg Cr treatments ($\alpha = 0.05$). There was no statistical influence of Cr and Pb on degradation of pentadecane and hexadecane.

Chromium and Pb at the levels used in this study had no significant impact on degradation of South Louisiana Crude oil. The Cr and Pb added was bound by the sediment into insoluble or unavailable forms. Results suggest that heavy metals would not influence degradation of petroleum hydrocarbon in sediment at the produced water discharge site. Data presented should not be extrapoled to sites containing sandy substrates in which heavy metals were not sequestered or removed from the solution or exchangeable fractions.

3.4 Degradation of Petroleum Hydrocarbons in Sediment Receiving Produced Water Discharge

3.4.1 Degradation of Residual Hydrocarbons (Exp. I)

Initial residual sediment concentrations of hexadecane, heptadecane, eicosane, tetradecane, tridecane and hexatriacotane in the oxidized and reduced microcosms were similar and averaged (6 replications) 88.4, 87.5, 65.5, 50.3, 28.6, 1.6 µg/g dry sediment, respectively (Figs. 21 and 22). High concentrations (day 1) of octadecane (82.1), pentadecane (78.0) and 2, 6, 10, 14 tetramethylpentadecane (70.5 µg/g) were also measured but not graphed. Initial concentrations of tetracosane and the remaining isoprenoids ranged from about 20 to 35 µg/g and decane, undecane, dodecane and dotriacotane concentrations were less than 10 µg/g. At the end of the study (103 days), initial concentrations of residual hexadecane, heptadecane, eicosane, tetradecane and tridecane were reduced an average of 87% under oxidized sediment conditions compared to only 54% reduction under reducing conditions. Hexatricotane concentrations were reduced only 41% under oxidizing conditions and no change in concentration was measured under reduced sediment conditions. Remaining hydrocarbons investigated (not graphed) averaged 77% reduction under oxidizing conditions and 44% reduction under reducing conditions over the 103 day experiment.

Degradation rates were faster under oxidizing conditions (Fig. 21) compared to a reducing environment (Fig. 22). All other alkanes analyzed (see Table 2) displayed similar rates of degradation. Degradation rates under oxidized sediment conditions ranged from a low of 0.029 (decane) to a high of 0.721 µg/g/d for hexadecane. Higher degradation rates (oxidized conditions) were also observed for tetradecane, pentadecane, heptadecane, octadecane, eicosane and 2, 6, 10, 14 tetramethyl pentadecane (Table 7). Degradation of residual hydrocarbons under controlled reducing conditions was slower. Rates ranged from 0.012 (decane) to 0.351 (hexadecane) µg/g/d. Degradation rates (reducing conditions) of all investigated hydrocarbon fractions averaged 58% (ranged from 30 to 96%) slower compared to corresponding rates measured under oxidizing conditions (Table 7).

Significant differences in degradation rates of hydrocarbon fractions were observed as affected by sediment redox conditions. All petroleum fractions displayed a significantly ($P<0.05$) greater loss from the oxidized treatment compared to the reduced treatment.

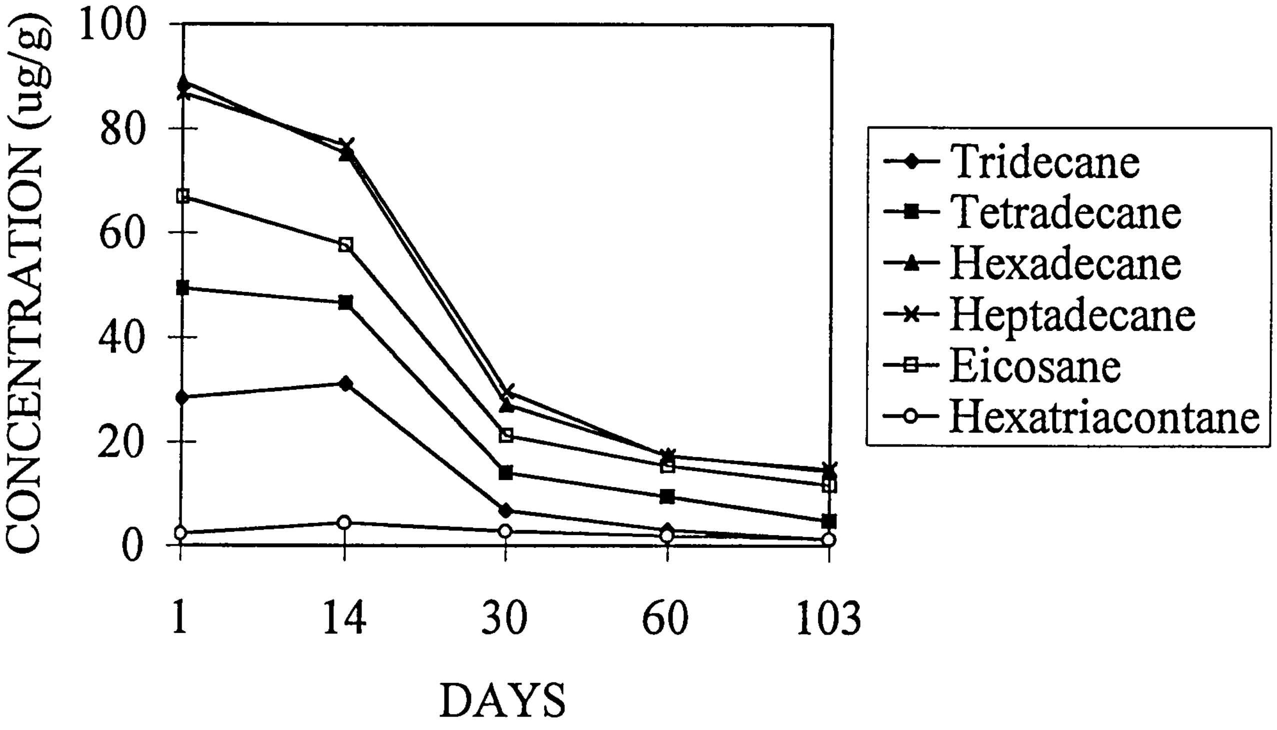


Figure 21. Change in selected hydrocarbon fraction with time under oxidized conditions.

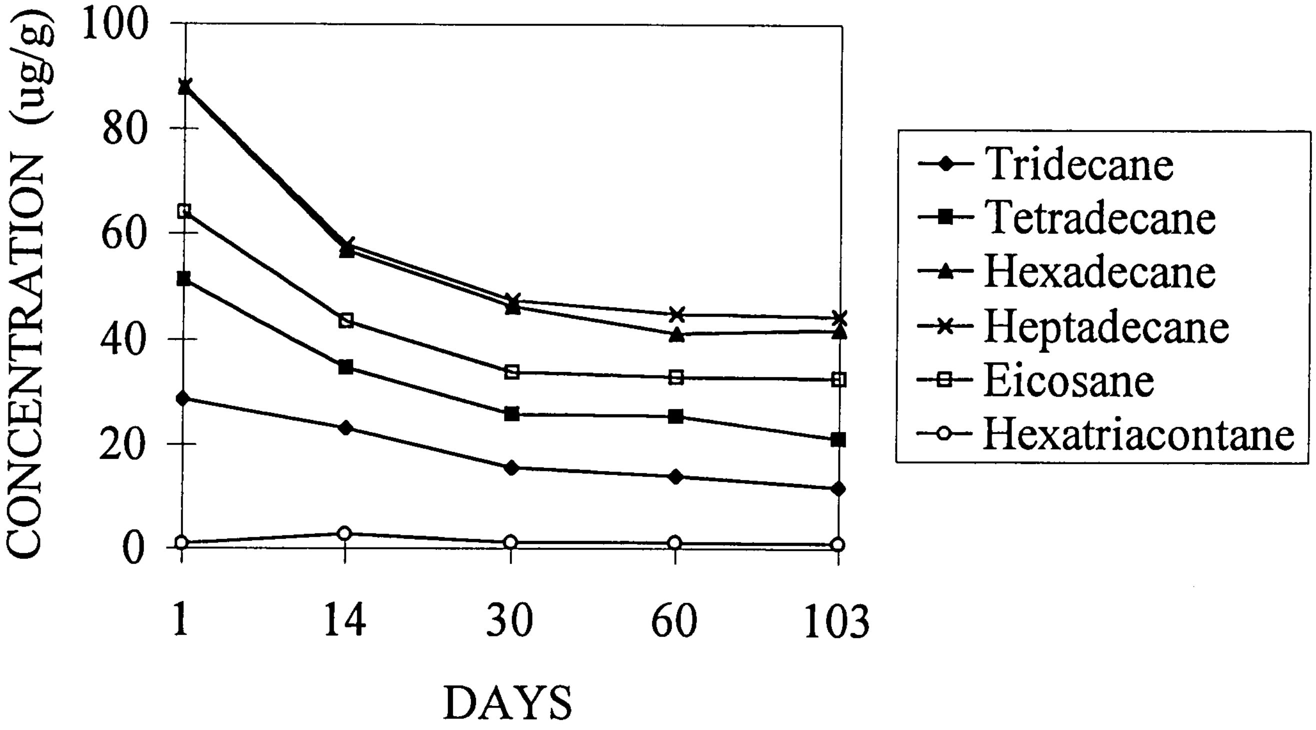


Figure 22. Change in selected hydrocarbon fractions with time under reduced conditions.

Table 7

Degradation of Residual Hydrocarbons in Produced Water Sediment

Compound	**Oxidized Rate (µg/g/d)**	**Reduced Rate (µg/g/d)**
decane	0.029	0.012
undecane	0.050	0.022
dodecane	0.128	0.070
tridecane	0.294	0.150
tetradecane	0.449	0.235
pentadecane	0.649	0.340
hexadecane	0.721	0.351
heptadecane	0.715	0.326
octadecane	0.620	0.175
eicosane	0.533	0.237
tetracosane	0.279	0.058
octacosane	0.106	0.014
dotriacontane	0.067	0.022
Hexatriacontane	0.18	0.006
2, 6, 10trimethyl-dodcane	0.153	0.075
2, 6, 10, 14tetramethyl heptadecane	0.253	0.149
2, 6, 10, 14tetramethyl pentadecane	0.400	0.281

3.4.2 Effect of Oxidized Sediment Conditions on Degradation of South Louisiana Crude (Exp. II)

Degradation of selected South Louisiana Crude hydrocarbons under controlled redox conditions (+450 mV) is graphed in Figure 23. Initial concentrations (day 1) of tridecane, dodecane, undecane, dotricotane, phenanthrene and pyrene were 299.4, 292.6, 182.7, 25.0, 9.3 and 0.6 µg/g, respectively. Initial concentrations of remaining hydrocarbons analyzed (not graphed) ranged from 66.9 (octacosane) to a high of 240.5 µg/g for octadecane. Starting concentrations of heptadecane, hexadecane and pentadecane averaged 195.1 µg/g dry sediment. After 28 days of laboratory incubation, initial concentrations of undecane, dodecane and tridecane were reduced an average of 81% with the largest reduction (96%) observed for the shortest n-alkane (undecane, C-11). Dotriacotane and phenanthrene concentrations were reduced 51.5% and pyrene 28% under oxidizing conditions.

Degradation rates of shorter n-alkanes; undecane (3.01), dodecane (4.41) and tridecane (3.58 µg/g/d) were much faster than the longer n-alkane; dotriacotane (0.20) and polycyclic aromatic hydrocarbons; phenanthrene (0.09) and pyrene (0.002 µg/g/d). Degradation of tetradecane (2.62), pentadecane (2.12), hexadecane (1.71), heptadecane (0.89), octadecane (2.18), eisocane (1.80), tetracosane (0.86), octacosane (0.61) and naphthalene (0.22 µg/g/d) are not graphed in Figure 23. All compounds investigated showed significant ($P<0.05$) degradation over the 28 day study except pyrene ($P=0.233$).

3.4.3 Nutrient Influence on Hydrocarbon Degradation (Exp. III).

Linear regression degradation rates for undecane, tridecane, pentadecane and heptadecane as affected by redox and fertilizer are graphed in Figure 24. A general overview shows degradation rates in oxidized sediments amended with fertilizer were much higher (except undecane) compared to the reducing sediment treatments. Highest degradation rates were observed for tridecane, pentadecane and heptadecane (4.4 to 5.1 µg/g/d) in sediments amended with the high rate of fertilizer. Undecane's highest degradation rate occurred in reduced sediment plus high fertilizer (3.9 µg/g/d). In most cases, hydrocarbon degradation rates decreased as level of fertilizer decreased and lowest rates were observed for the control treatments (oil only). Under reducing conditions, many treatments showed an increase (production) in tridecane, pentadecane and heptadecane over the 42 day experiment (Fig. 24). Net production rates ranged from 0.1 (tridecane) to 0.6 (pentadecane) µg/g/d. An increase in sediment heptadecane concentration was also observed for the oxidized control (0.2 µg/g/d). The observed net increases were thought to be due to faster production rates from higher molecular weight compounds compared to slower degradation rates of the hydrocarbons.

Degradation and production rates of decane, dodecane, tetradecane and hexadecane (not graphed) followed the same general distribution as undecane, tridecane, pentadecane and heptadecane. High degradation rates were calculated for dodecane, tetradecane and hexadecane (4.6 to 5.0 µg/g/d) in oxidized sediment amended with high fertilization. Net production of dodecane, tetradecane and hexadecane (0.3 to 0.5 µg/g/d) was observed in some reduced sediment treatments.

Averaged over the eight hydrocarbons (C-10 through C-17) degradation rates (net production included) for the control, low and high fertilization (oxidizing conditions) were 1.0,

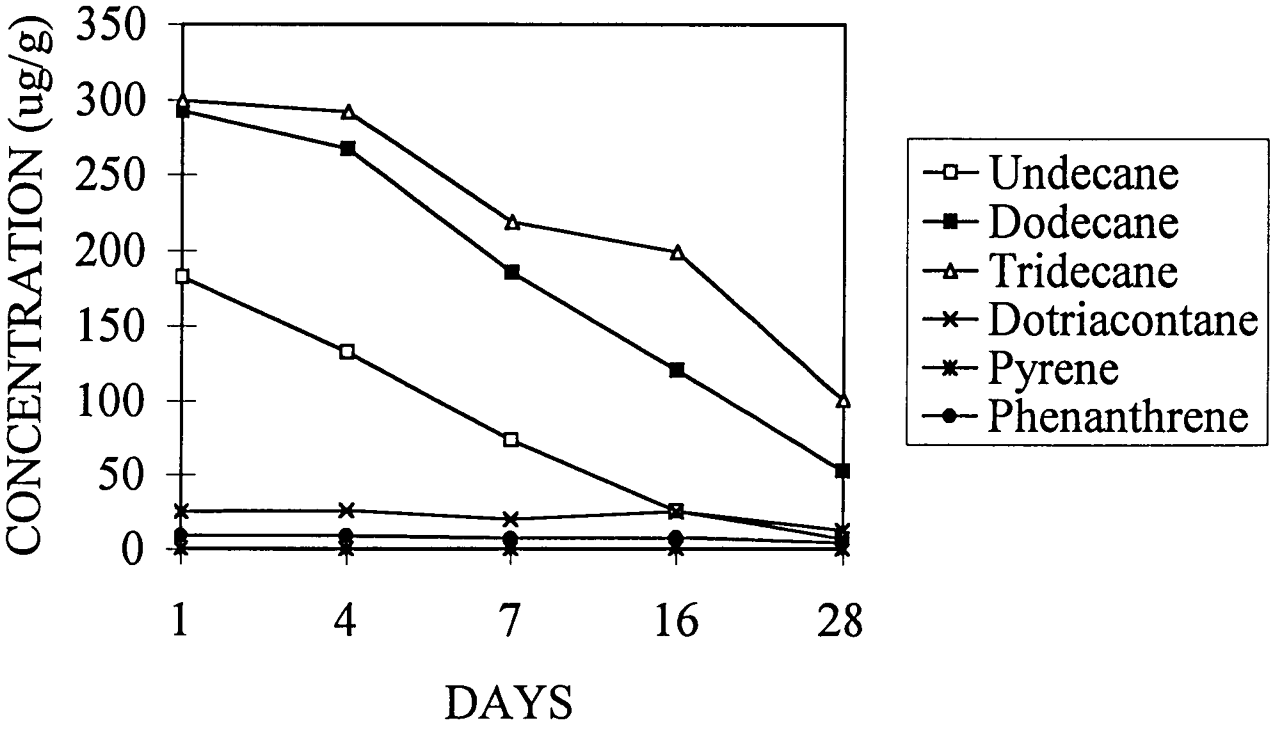


Figure 23. Degradation of selected fractions of South Louisiana Crude under oxidized conditions (+450 mV).

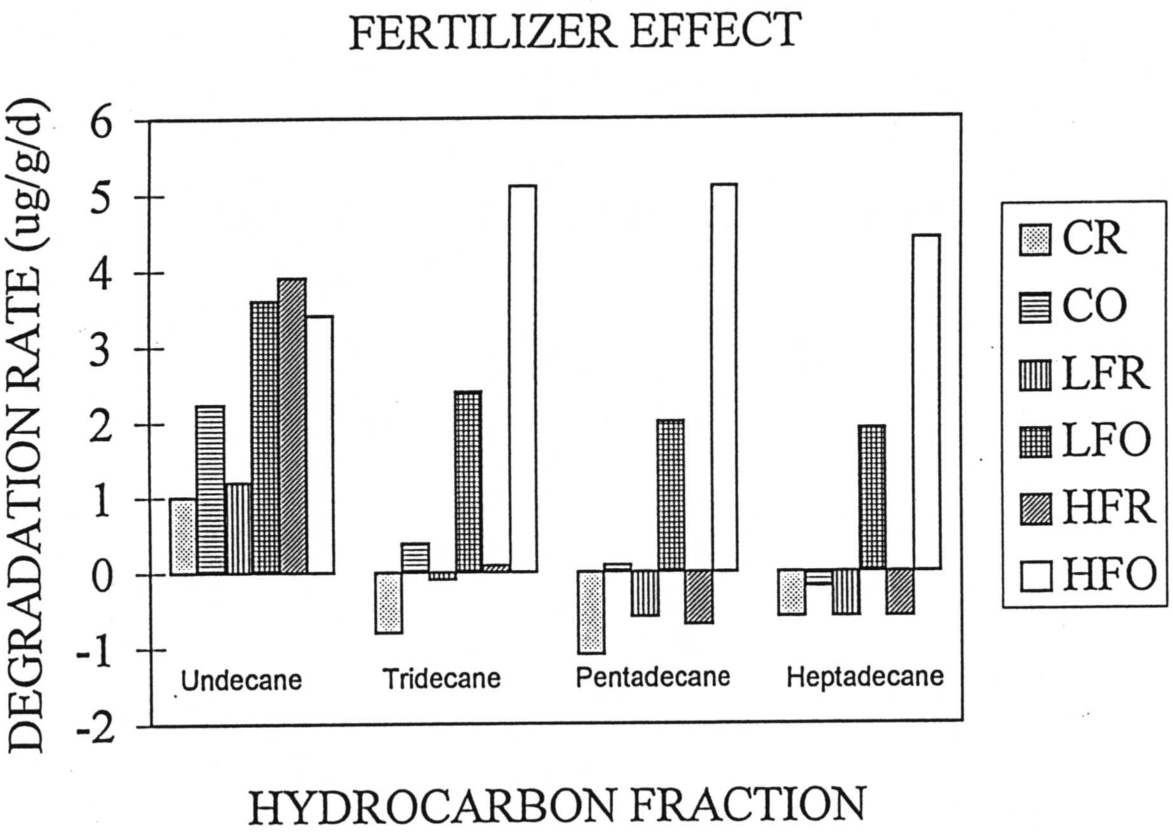


Figure 24. Linear regression degradation rates of selected hydrocarbon fractions as affected by redox and fertilizer addition (C = Control, R = Reduced, O = Oxidized, LF = Low Fertilization, HF = High Fertilization).

2.7 and 4.3 µg degraded g^{-1} dry sediment d^{-1}, respectively. Under controlled reducing conditions, degradation rates averaged 0.3, 0.8 and 1.1 µg g^{-1} d^{-1}, respectively. Initial concentrations of the eight n-alkanes investigated were reduced approximately 25, 67 and 99% over 42 days for the control, low fertilizer and high fertilizer treatments, respectively, under oxidized sediment conditions. Reducing conditions reduced initial concentrations approximately (production included) 27, 3 and 13%, respectively.

A general linear statistical model was used to test the interaction of the main effects (redox and fertilization), sorted by individual hydrocarbon compound. Additional analysis used the entire model, grouping all hydrocarbon fractions (C-10 through C-17) together. Analysis revealed fertilizer amendment had a greater effect on degradation rates of decane, undecane, tridecane and tetradecane than sediment redox. A post-analysis of variance technique was used to check for significant differences between redox and fertilizer effects. Duncan's Multiple Range Test for variable concentration of petroleum hydrocarbons found redox effects produced significant differences ($P<0.05$) in degradation rates. The two fertilizer treatments and control were also significantly different. These studies support previously published research showing fertilization can be used as a method for enhancing degradation of crude oil (Wright et al. 1997).

Multiple regression was performed with both main effects and interactions. The interaction of fertilizer and redox had the greatest effect on change in hydrocarbon concentration over time. The most significant main effect was time followed by redox and fertilization. None of the main effects or interactions were found to be insignificant compared to controls.

Oxygen concentration has been reported to be a critical rate limiting factor in biodegradation of hydrocarbons (Atlas and Cerniglia 1995). In this study, oxidation status or sediment redox condition was also shown to govern hydrocarbon degradation at the wetland site impacted by produced water discharge. High concentrations of recalcitrant isoprenoids were encountered in sediment gathered at the outfall from a produced water pit. Degradation of these more resistant hydrocarbons was slow but showed a response to sediment redox condition. Oxidized sediment conditions showed a significant increase in the degradation rate for all compounds studied at the site compared to reducing sediment conditions. Even the recalcitrant isoprenoids showed appreciable degradation rates under oxidizing conditions.

South Louisiana Crude oil was added to sediment to determine rate of degradation of lighter hydrocarbon crude oil fractions. Oxidizing conditions resulted in an increased degradation rate of added South Louisiana Crude. This was especially true for the shorter n-alkane (<C-14). Concentration of some of the longer n-alkanes showed an increase with time, apparently caused by stripping of methyl groups during biodegradation, resulting in formation of n-alkanes. The oxidizing conditions increased the susceptibility of the branched long-chained hydrocarbons (isoprenoids), that are more difficult to degrade than the n-alkanes.

4.0 SUMMARY

The effect of sediment redox conditions on the solubility behavior of Fe, Pb, Ni, Ba, and Cu in bottom sediment collected from a produced water discharge site was investigated using kinetics and chemical fractionation procedures. Sediment collected was composited and subsamples incubated in laboratory microcosm's under controlled Eh-pH conditions. Sediment was sequentially extracted for determining metals in five fractions (exchangeable, carbonate, bound to iron and manganese oxide, bound to organic matter and sulfide, mineral matrix or residue). Metal distribution in the fractions indicate that under oxidizing sediment conditions, the behavior of Fe, Pb and Ni were governed by Fe(III) and Mn(IV) oxides; Ba by insoluble complexation with humic compounds, Cu by carbonates and humic complexation. Under reducing sediment condition, the behaviors of Fe and Cu were controlled by the formation of insoluble sulfides and humic complexes; the behaviors of Ni and Ba by carbonate and Pb behavior by sulfides, carbonates and humic complexes. With increases in sediment redox potential, the affinity between Fe(III), Mn(IV) oxides and Fe, Pb, Ni, Cu increased, affinity between insoluble large molecular humic and Ba increased, and the affinity between carbonates and Cu increased. With decreasing sediment redox potential, the affinity between carbonates and Fe, Ni, Ba increased, affinity between sulfides, humic substances and Fe, Pb, Ni, Cu also increased. Upon Fe(III) oxide reduction, it is estimated 20% of total reducible Fe(III) oxide were reduced by direct bacterial reduction (k=-42.6 mg/kg/d), 80% of total reducible Fe(III) oxides was associated with chemical fractions attributed to sulfide oxidation (K=-171.5 mg/kg/d). The rate constants (mg/kg/d) for dissolved Ni ($Eh < 0$ mV), Pb ($Eh < -80$ mV) and Cu ($-80 \text{ mV} < Eh < 0$ mV) are -1.6, -0.047 and -0.16 respectively. In our incubation period, the rate constants (mg/kg/d) for Ni bound to Fe(III) and Mn(IV) oxides, Ba bound to carbonates and Cu bound to insoluble large molecular humic are –3.2, 0.91 and 4.3 respectively.

Kinetics and chemical fractionation procedures were also used in quantifying the effects of sediment redox (Eh) condition on the behaviors of As, Cd, Cr and Zn in the bottom sediment collected from a Louisiana Coastal site receiving produced water discharge. Sediment samples were incubated in microcosms in which Eh-pH conditions were controlled. Sediment was sequentially extracted for determining metals in various chemical fractions (water soluble, exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to insoluble organic and sulfides) and chemical inactive fraction (mineral residue). Under oxidizing conditions, As, Zn and Cr behavior were governed by redox chemistry of Fe(III) and Mn(IV) oxides. Cd transformations were controlled by both Fe(III), Mn(IV) oxides and carbonates. Under reducing condition, the behaviors of Zn and Cr was controlled primarily by insoluble large molecular humic material and sulfides; the behavior of Cd was controlled by carbonates. When sediment redox potential increased, the affinity between Fe(III), Mn(IV) oxides and As, Cd, Cr, and Zn increased. When sediment redox potential decreased, the affinity between carbonates and Cd and Zn increased; the affinity between insoluble sulfides, large molecular humic matter and As, Cd, Cr, Zn increased; the soluble Cd and Zn decreased; the soluble As and Cr remained constant. Results suggest reducing sediment conditions would reduce Cd and Zn toxicity. Under reducing or anaerobic conditions, the solibilization rate constants (mg/kg/d) for As, Cr, Cd, Zn bound to Fe(III) and Mn(IV) oxides were –0.88, -0.32, -0.01, -6.5 respectively; the rate constants (mg/kg/d) for dissolved Cd and Zn were –0.09 and –1.78 respectively.

Sediment from oil recovery pit and stream bottom sediment receiving produced water discharge were incubated in laboratory microcosm under oxidized and reduced sediment conditions.

The sediment was then extracted into various fractions and analyzed for radium-226. The results indicated that very little (5 percent) of the total radium in the sediment material was present in a form that was extractable or otherwise available from the waste-pit material and/or bottom sediment (such forms include water-soluble, exchangeable, associated with carbonates, reducible, or organic/sulfide). Approximately 95 percent of the radium present was tied up in a residual form that could be extracted only with very strong acids. Radium in this fraction would be released very slowly into the environment from the contaminated sediment.

Rate of petroleum hydrocarbon degradation was measured in sediment collected from a low energy brackish wetland site which had been exposed for a number of years to produced water discharge. Recalcitrant or higher molecular weight compounds were the primary hydrocarbon fractions found in the sediment. Degradation rates were determined by measuring loss of selected petroleum hydrocarbons components with time in laboratory incubation. South Louisiana Crude oil was added to the sediment to measure degradation rates of soluble hydrocarbons which were too low in concentration in the original sediment. Oxidized sediment conditions resulted in a higher rate of degradation for most hydrocarbon fractions as compared to reduced sediment. Fertilizer or nutrient amendments to contaminated sediments significantly increased the rate of hydrocarbon degradation. Fertilizer enhanced the degradation of the lower and more soluble molecular weight fractions as compared to the higher molecular weight fractions.

The effect of chromium (Cr) and lead (Pb) on degradation of South Louisiana Crude oil in sediment collected from a produced water discharge site was measured in laboratory microcosms under oxidized and reduced conditions. Metal content had no impact on total hydrocarbon degradation content based on changes in concentration. Even on a percentage basis, which normalizes for differences in hydrocarbon concentrations, no statistical influence of Cr (5,000 μg/g) and Pb (2,500 μg/g) on degradation could be measured under reducing conditions. A more sensitive analysis of metal impact on degradation depicted by an analysis of reduction of selected alkane fractions also showed little effect on degradation. Only degradation of octadecane was shown to be statistically inhibited at 5,000 μg/g of added Cr and only under reducing conditions. The sediment, due to the clay content, sequested much of the added metals. Under reducing conditions, 25 percent of water soluble and exchangeable Cr and Pb remained in solution at the highest Pb (2,500 μg/g) and Cr (5,000 μg/g) levels compared to oxidized sediments. The amount in solution was not great enough to impact hydrocarbon degradation. The study demonstrates that Cr and Pb entering sediment at this produced water site would have minimal impact on petroleum hydrocarbon degradation.

In summary, heavy metal solubility was shown to be low in anaerobic and neutral pH estuarine sediment found at a coastal Louisiana produced water discharge sties. Solubility of Ba found in barite was low under alkaline and either anaerobic or aerobic sediment conditions. Over 95% of radium found in contaminated sediment existed as an unavailable form which could be extracted only with strong acids. Typical heavy metal pollution levels found in the surface sediment environment at produced water discharge sites would not impact microbial degradation of petroleum hydrocarbons in the sediment column. Oxidized sediment conditions resulted in a faster rate of petroleum hydrocarbon degradation as compared to reducing sediment conditions in a produced water impacted sediment column.

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The Department of the Interior Mission

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

The Minerals Management Service Mission

As a bureau of the Department of the Interior, the Minerals Management Service's (MMS) primary responsibilities are to manage the mineral resources located on the Nation's Outer Continental Shelf (OCS), collect revenue from the Federal OCS and onshore Federal and Indian lands, and distribute those revenues.

Moreover, in working to meet its responsibilities, the **Offshore Minerals Management Program** administers the OCS competitive leasing program and oversees the safe and environmentally sound exploration and production of our Nation's offshore natural gas, oil and other mineral resources. The MMS **Royalty Management Program** meets its responsibilities by ensuring the efficient, timely and accurate collection and disbursement of revenue from mineral leasing and production due to Indian tribes and allottees, States and the U.S. Treasury.

The MMS strives to fulfill its responsibilities through the general guiding principles of: (1) being responsive to the public's concerns and interests by maintaining a dialogue with all potentially affected parties and (2) carrying out its programs with an emphasis on working to enhance the quality of life for all Americans by lending MMS assistance and expertise to economic development and environmental protection.