Actinide Migration Studies at the Rocky Flats Environmental Technology Site
The Effect of Soil-Water Redox Potential on $^{239,240}Pu$ Solubility

P.I.: Bruce D Honeyman, Ph D , Associate Professor, Environmental Science and Engineering Division, Colorado School of Mines, Golden, CO 80401

Collaborators: Richard Harnish (CSM), Terry McKibben (CSM), John Spear (U Colorado), Scott Winkler (CSM)

Contractor· Kaiser-Hill, LLC

Contract: KH800022MW

Fiscal Year 1999

Date: 7 October 1999

Final Report

SEP 2002
RECEIVED

ADMIN RECORD

SW-A-004597

DOCUMENT CLASSIFICATION
REVIEW WAIVER PER
CLASSIFICATION OFFICE

List of Tables

Table 1 Pond B4 In-situ physical and chemical parameters measured in the field on the day of sampling (10 March, 1999)
Table 2 Thermodynamic properties of redox indicators
Table 3 Chemical composition of the nutrient media used in the nutrient-amended samples and controls Nutrient solutions were autoclaved before introduction into the reaction chambers
Table 4 Chain of custody identification numbers of cores and water samples used in the sediment incubation experiments
Table 5 Sediment incubation experiment protocols
Table 6 Experimental trial characteristics
Table 7 Tabulation of ^{239,240}Pu and ^{241}Am experimental results
Table 8 Comparison of pre-experiment E_H measurement of Pond B4 sediment taken in-situ on the day of core acquisition (3-10-99) and post-experiment E_H measurements of post-incubation cores
Table 9 Post-experiment E_H measurements of post-incubation SED029 cores
Table 10 Iron oxidation-state distribution at the cessation of the incubation experiments
Table 11 Results of 'dissolved' (< 0 45 μm) manganese analysis of Pond B4 incubation experiment water column samples
Table 12 Results of 'dissolved' (< 0 45 μm) analysis of iron in Pond B4 incubation experiment water column samples
Table 13 Results of 'dissolved' (< 0 45 μm) manganese analysis of SED029 incubation experiment water column samples
Table 14 Results of 'dissolved' (< 0 45 μm) iron analysis of SED029 incubation experiment water column samples
Table 15 Results of 'dissolved' (< 0 45 μm) total organic carbon (TOC) analysis of Pond B4 incubation experiment water column samples
Table 16 Results of 'dissolved' (< 0 45 μm) Total Organic Carbon (TOC) analysis of SID 029 incubation experiment water column samples
Table 17 ^{239,240}Pu activities measured post-experiment in the water columns of the Pond B4 and SED029 incubation suites MDA signifies minimum detection limit, expressed as pCi/L
Table 18 Summary of core material digestions

2

List of Figures

Figure 1 Schematic illustration of postulated Pu release to the solution phase through the reductive dissolution of host soil constituents (a, b) or change in Pu oxidation state (c, d)
Figure 2 Site map showing the locations of incubation core sample acquisition
Figure 3 Diagram of the glovebox arrangement developed to maintain reducing conditions
Figure 4 Detail of the cell constructed to regulate system E_H
Figure 5 Log fractional distribution (α) of the redox indicator 2,6-dichloro-indo-phenol as a function of pe
Figure 6 Comparison of three indicators used to ascertain system E_H
Figure 7 Schematic illustration of the tangential-flow ultrafiltration system
Figure 8 Illustration of the incubation chambers used in the core experiments
Figure 9 Schematic illustration of the sample matrix
Figure 10 a) $^{239,240}Pu$ or ^{241}Am activity (pCi L^{-1}) as a function of E_H b) The Pu data presented as concentration (1 fM = 10^{-15} M) Error bars are based on a relative error of 20%
Figure 11 Comparison of Pu solubility from thermodynamic calculations and measured values from the E_H cell
Figure 12 a) Cross-flow ultrafiltration of 10 g/L soil (97L1879-002) at –90mV Sample volume was 400 mL b) System open to the atmosphere (E_H ca +800mV) Sample volume was 400 mL
Figure 13 Iron oxidation-state distribution at the cessation of the incubation experiments
Figure 14 a) 'Dissolved' iron and b) manganese as a function of date for Pond B4 incubation experiments
Figure 15 a) 'Dissolved' iron and b) manganese as a function of date for Pond B4 incubation experiments
Figure 16 Total organic carbon (TOC) as a function of date for the Pond B4 (16a) and SED029 (16b) incubation experiments
Figure 17 Location of data sets in E_H/pH 'space' and their relationship to selected environmental 'systems'

3

Actinide Migration Studies at the Rocky Flats Environmental Technology Site
The Effect of Soil-Water Redox Potential on ^{239,240}Pu Solubility

Significant results of the FY 1999 study

Overall:
Results of electrochemical cell and core incubation experiments do not provide support for the hypothesis that reducing conditions in soil/water systems at Rocky Flats Environmental Technology Site yield enhanced ^{239,240}Pu solubility

Terminology:
Throughout this report, placing the word dissolved in quotes (i e , 'dissolved') indicates that an operational definition of dissolved is used, i e , those constituents that pass a 0 45 µm filter

Water quality criteria are listed in terms of activity (e g , pCi L^{-1}), discussion of chemical processes require concentration (e g , M or m) The following conversions can be used ^{239,240}Pu (1 pCi L^{-1} = 67 64 fM), ^{241}Am (1 2 fM) 1 fM = 10^{-15} M 1 pCi = 10^{-12} Ci

Specific results:

1 Fiscal Year 1999 redox cell results confirm FY 1998 findings

- ^{239,240}Pu solubility (defined as the activity of ^{239,240}Pu released from the soil phase upon suspension of soil particles in an aqueous solution, and which passes a 0 45 µm filter) over a range of redox conditions (-90 mV < E_H < +800 mV) is relatively limited for these experiments The maximum fractional ^{239,240}Pu solubility observed for the experimental conditions was 0 18% of total Pu soil activity For the conditions of the experiment (10 g L^{-1} soil suspension = 3 1 x 10^3 pCi, Pu_T = 2 1 x 10^5 fM), the highest observed 'dissolved' ^{239,240}Pu concentration was 6 17 pCi L^{-1} (4 16 x 10^2 fM)
- Although Pu and Am 'dissolved' activities in the analyses reported here are low, they are generally at or above Site surface water action levels
- ^{239,240}Pu solubility decreases under moderately-reducing conditions (E_H < 200 mV) by about 2/3 relative to oxidizing conditions (+800 mV)
- The decrease in Pu solubility with a lowering in system E_H is consistent with a reduction of Pu(V) to Pu(IV)
- ^{241}Am solubility is, within experimental error, independent of system E_H This result is consistent with the redox independence of Am(III)

2 Tangential flow ultrafiltration of solutions in equilibrium with soil isolates indicated that colloidal (10K Dalton to 0 4 µm) Pu accounts for approximately 75 percent of the 'dissolved' Pu at E_H values of both +800 and –90 mV

3 Redox cell analysis of Pond B4 sediments also produced limited ^{239,240}Pu solubility (ca 0 1 to 0 6 pCi/L = 6 7 to 40 1 fM) over the E_H range evaluated (-90 mV < E_H < +800 mV)

4 Laboratory incubations of sediment cores collected at Pond B4 and SED029 were accomplished under conditions designed to accelerate microbial processes and encourage reducing conditions in sediments Strongly reducing (-234 mV < E_H < -387 mV SED029, -247

mV < E_H < –353 mV Pond B4) conditions were achieved in the incubated sample sediments along with evidence of enhanced microbial activity in the sediment/water incubation systems

5 A decline in the sediment-core redox level was significantly enhanced by tandem amendment of carbon and nutrients to the sediment/water system

6 Under the reducing conditions achieved in the sediment incubation chambers, significant solubilization of iron and manganese from the sediments to the overlying water column was achieved

7 The extent of reductive dissolution of iron and manganese was maximally enhanced by singular amendment of microbially-utilizable carbon (lactate) as compared to other amendment combinations used in this experiment

8 Loss of the sterile integrity of irradiated control samples precludes any definitive conclusion regarding the potential role of *microbially-induced-redox* conditions on potential solubilization of plutonium However, limited conclusions regarding *redox-driven* potential solubilization can be made by comparison of matrix controls and samples

9 Based on post-incubation analysis of 'dissolved' (<0 45 μm) $^{239,240}Pu$ in the Pond B4 matrix water control and Pond B4 experimental samples, there was no measurable evidence of enhanced $^{239,240}Pu$ dissolution from sediments to the water column under the reducing conditions established in the incubation experiment

10 Based on post-incubation analysis of 'dissolved' (<0 45 μm) $^{239,240}Pu$ in laboratory Nanopure water (SED029 matrix water control) and SED029 experimental samples, there was no substantive evidence of enhanced $^{239,240}Pu$ dissolution from sediments to the water column under the strongly reducing conditions established in the incubation experiment

1. Introduction

The chemical behavior of plutonium in response to changing soil environmental conditions at Rocky Flats may have a significant impact on approaches to remediation and strategies for long-term closure of the Site Work preformed at the Colorado School of Mines during Fiscal Year 1998 (Honeyman, 1998) initiated an examination of $^{239,240}Pu$ and ^{241}Am solubility over a range of E_H values through the use of an electrochemical cell Fiscal Year 1998 results led to the preliminary conclusion that $^{239,240}Pu$ solubility in soil (soil isolate # 97L1879-002)/water slurries does not increase with decreasing E_H (+800 to –90 mV), indeed, $^{239,240}Pu$ solubility significantly decreased below ca +200 mV relative to more oxidizing (+800) electrode potentials

Work during this fiscal year (FY 1999) focussed on evaluating our ability to generalize the results of the FY 1998 work Results described in this report follow from two experimental strategies

1) continued analysis of $^{239,240}Pu$ solubility using the E_H cell,
2) a laboratory incubation experiment designed to address issues of the potential response of extant plutonium forms and host soil sediment phase constituents (iron and manganese oxyhydroxides, and natural organic matter) in intact sediment cores exposed to conditions favoring microbially-mediated reductive conditions (by native microbial populations), and the potential for subsequent release of Pu from the host phases

In the first approach, system E_H was regulated through an imposed potential using platinum (Pt) electrodes connected to a potentiometer In the second approach, system E_H was likely the consequence of microbial activity rather than an externally-imposed potential

5

Figure 1 presents conceptual models illustrating potential effects of changing system redox on Pu solubility Figure 1a shows a section of a hypothetical soil/water system Soil particles are represented as a suite of irregular shapes surrounded by an aqueous phase In this figure, Pu is shown as sorbed to an iron oxyhydroxide particle Under certain circumstances, a decrease in system redox (i e , a lowering in E_H) may result in the reductive dissolution of the iron hydroxide, e g

$$Fe(OH)_3(s) + 3H^+ + e^- = Fe^{2+} + 3H_2O \qquad [1]$$

A loss of the sorbent (i e , the $Fe(OH)_3$) may result in a release of the Pu to the aqueous phase Typically, plutonium has a limited solubility (10^{14} to 10^{-17} M) and is not expected to be transported to any appreciable extent as a soluble species (e g , Graf, 1994) However, contaminants of low solubility may be transported through porous media through association with a mobile, non-aqueous phase (McCarthy and Wobber, 1993, and references therein, Honeyman, 1999) This mobile phase may consist of micro-particles or colloids

Another scenario with respect to Figures 1a and 1b is that the Pu, rather than sorbed to the iron oxide particle, is in the form of micrometer-sized $PuO_2(s)$[1] particles which are aggregated with the immobile iron oxide soil phase The reductive dissolution of the iron oxide could result in the release of the colloidal Pu species to the fluid stream Considerable research has been conducted on the transport of contaminants by colloidal materials (e g , Ryan and Elemelich, 1996) and evidence supports the limited transport of colloid-associated Pu through Rocky Flats soil macropores (e g , Ryan *et al*, 1998) Alternatively, the Pu may be present in a relatively insoluble form (Figure 1c) and subsequently transformed into a more soluble species through changes in system redox status (Figure 1d)

Under certain conditions, sediment microbiota are capable of influencing the rate and extent of redox transformations of redox-sensitive elements in sediments At RFETS, conditions for such transformations may be expected to be especially pertinent to areas of permanent or ephemeral water cover (e g , interceptor ponds/interceptor ditches) with microbially active sediment-water interfaces that are relatively nutrient and carbon-rich and that contain sediments with active established microbial populations It has been noted (U S DOE, 1997), for example, that at Pond C-2, the annual spring "turnover" coincided temporally with concurrent, elevated 'dissolved' manganese and plutonium concentrations in pond surface waters, suggesting potential microbial effects on plutonium solubility The spring "turnover" in ponds, and surface water influx to interceptor ditches, may be reasonably assumed to be accompanied by increased sediment/water column temperatures, influx of carbon and nutrients from spring snowmelt, runoff, and rain events, with accelerated microbiotic activity resulting from these factors

[1] $PuO_2(s)$ is used here as a convention. The exact form of Pu continues to be subject discussion.

6

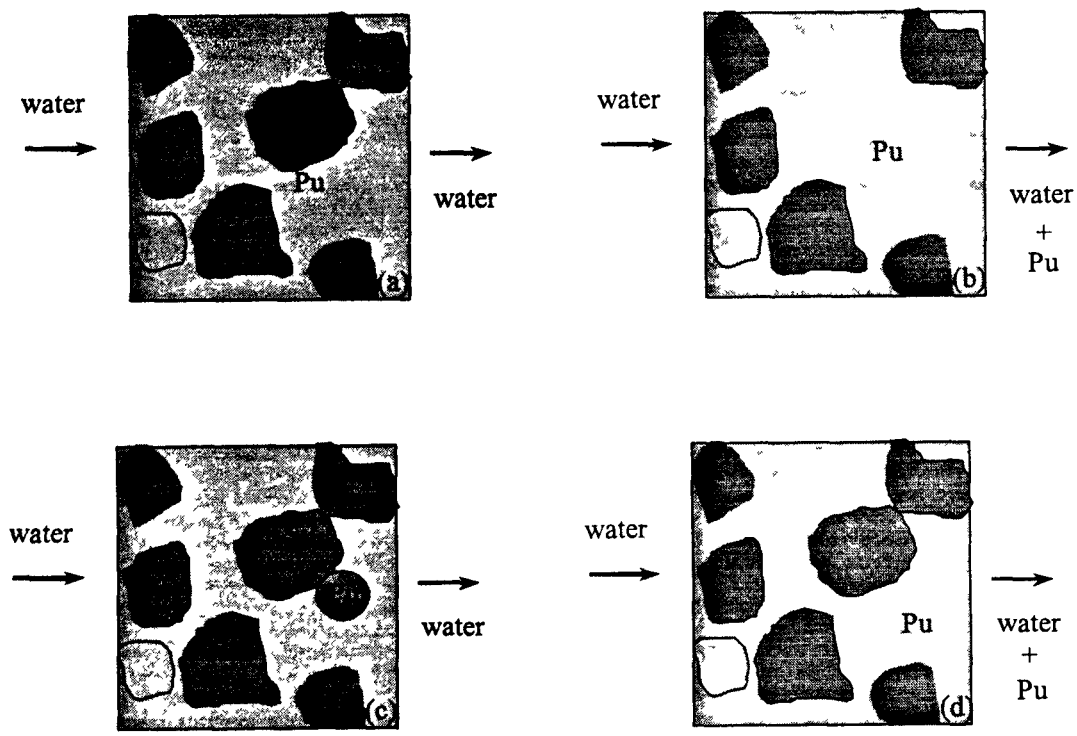


Figure 1 Schematic illustration of postulated, potential Pu release to the solution phase through the reductive dissolution of host soil constituents (a, b) or change in Pu oxidation state (c, d) Refer to the text for a detailed explanation Work concluding this fiscal year indicates that significant transport of Pu though the 'dissolved' pathway, as delineated in the Site Conceptual Model, is not extant Similarly, work concluded this fiscal year demonstrates that soil reducing conditions do not enhance Pu 'solubility' relative to oxidizing conditions

2. Materials and Methods.

2 1 Sample locations and form

Environmental samples from three locations were used in the FY 1999 work

Soil isolate 97L1879-002 This sample was provided to CSM by Rocky Mountain Remediation Services for the FY 1997 work, from a location SW of the 903 Pad in the 'lip' area The soil sample consisted of a 'box core' (ca 10 cm x 10 cm x 10 cm) from which rocks and debris greater than approximately one-half centimeter were removed Six hundred and forty two grams remained of the original sample This portion was split using a Humboldt Model H3973 Riffle Splitter by passing the sample through, collecting one-half, passing it through, until eighty grams remained Thus, three passes were required The eighty grams were then used as the stock from which individual sample aliquots were taken for analysis

Pond B4 and SED029 *Field sampling for core acquisition and in-situ physico-chemical parameters* Field sampling for core acquisition and measurement of in-situ physico-chemical parameters was accomplished on March 10, 1999, by Andy Carpenter and Bob Henceman (Commodore Advanced Sciences), and witnessed by Richard Harnish (Colorado School of Mines), Greg Wetherbee (Wright Water Engineers, Inc) and Win Chromec (RMRS) Sampling and analysis conformed to protocols outlined in the Sampling and Analysis Plan for this project

Core samples were collected at two sites 1) *Pond B4*, at the southwest edge of the pond adjacent to tall marsh habitat Pond B4 is located in the South Walnut Creek watershed downstream of the B-Series Bypass, which routes South Walnut Creek to Pond B3 (Figure 2), and 2) approximately 200 feet upstream of *SED029*, near the center of the SID transect SED029 is a tall marsh habitat located in the SID (South Interceptor Ditch) just downstream of the 903 Lip Area (Figure 2)

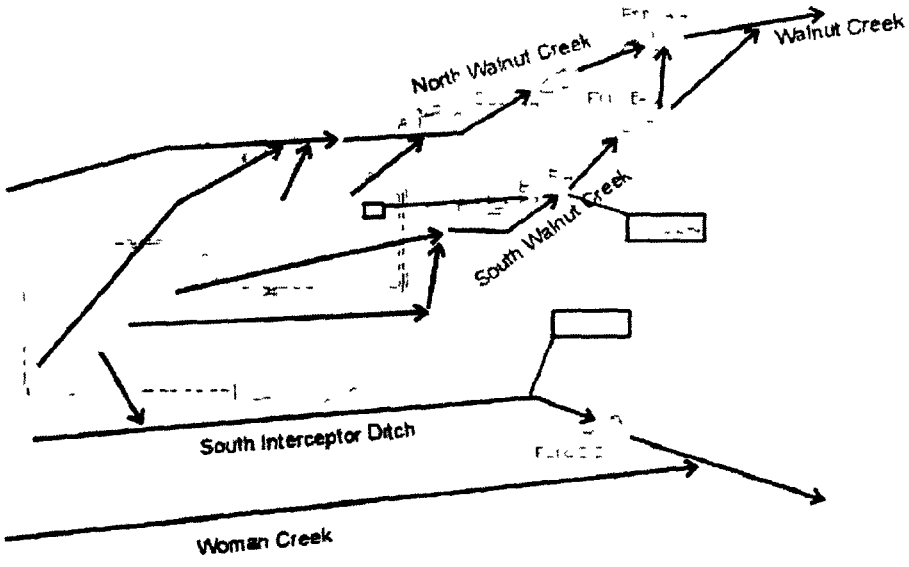


Figure 2 Site map showing the locations of incubation core sample acquisition

8

On the day of sampling, the weather was clear, cool, with moderate winds Sampling took place from approximately 9 AM to 4 PM Pond B4 was ice-free, and SED029 surface soil was moist, but with no standing water in the immediate sampling area

2 1 1 Pond B4 Physiochemical parameters of the sediments and water column were measured before core acquisition began pH, E_H and the temperature of the sediments at the sediment-water interface were measured by inserting pH, E_H, and thermistor electrodes into the sediment and recording responses at 1, 2, 3 and 4 in depth into the sediments (Table 1) Measurements of pH, alkalinity, 'dissolved' oxygen were performed on Pond B4 water, and samples were field-processed for Fe(II)/total Fe analysis

Table 1 Pond B4 *In-situ* physical and chemical parameters measured in the field on the day of sampling (10 March, 1999)

Depth Below the Sediment/Water Interface (Inches)	Temperature (°C)	pH	E_H (mV)	Dissolved Oxygen (mg/l)
Interface	3 8	8 05	96	8 9[1], 9 3[2]
1	4 3	7 8	-39 6	
2	4 5	7 8	-69 3	
3	4 7	7 8	-158	
4	5 0	7 8	-190 5	

Notes Temperature, pH, and E_H were measured at depth in the sediment using calibrated electrodes Dissolved oxygen was measured in the water column near the sediment-water interface [1]Dissolved oxygen concentration as measured using a YSI probe, [2]Dissolved oxygen concentration as measured using a Hach kit method.

Bulk water samples were taken (ca 16 L of pond water) Eighteen sediment cores were acquired from a boat by manually pushing 6 in long x 2 in diameter core tubes into the sediment and capping them before retrieval above the water surface Effort was made to minimize disturbance of the sediment-water interface and exposure to atmospheric gases during sampling The cores were kept in an upright position at all times The water column overlying the sediments at the sampling location was approximately 6 to 8 in deep On retrieval, cores were labeled, caps taped, and cores stored in a vertical position Following rad-screening at RFETS, the cores were delivered to CSM on 15 March 1999 and were immediately frozen at –4 °C Delays necessitated by rad-screening precluded analysis of time-sensitive (4 to 6 hours) Fe(II)/total Fe samples at CSM

2 1 2 SED029 Eighteen sediment cores were acquired using a core driver assembly and 6 in x 2 in diameter core liners On retrieval, cores were immediately capped, sealed, labeled, and stored in a vertical position Following rad-screening, the cores were delivered to CSM on 15 March, 1999 and were immediately frozen at –4 °C No surface water was evident in the vicinity of the sampling site No *in-situ* physico-chemical measurements were made at the site

9

2 2 Sample disposition Of the 18 sediment cores and 16 L of pond water collected at Pond B4, and the 18 sediment cores collected at SED029, one-half of all samples (9 B4 cores, 8 L of B4 water and 9 SED029 cores) were sent to Peter Santschi (Texas A&M University at Galveston) for related research

2 3 Tracers *^{242}Pu yield tracer* The ^{242}Pu used by CSM was NIST standard solution NIST SRM 4334F at 28 26 Bq g^{-1} with a relative expanded uncertainty (k = 2) of 0 74% *^{243}Am yield tracer* The ^{243}Am used by CSM was NIST standard solution NIST SRM 4332D at 36 27 Bq g^{-1} with a relative expanded uncertainty (k=2) of 0 78%

2 4 ^{239,240}Pu radiochemistry

Aqueous solutions were generally acidified with nitric acid, ^{242}Pu and ^{241}Am yield tracers were added, and the acidified solutions were taken to dryness on a hotplate [Note the water column samples for the incubation experiments were acidified but taken directly to the Fe precipitation step] Residues from drying were re-dissolved in nitric acid and treated with sodium nitrite for valence adjustment Fe carrier was used to co-precipitate the actinides as an iron oxyhydroxide pH adjustment was made with ammonium hydroxide The precipitate was removed from solution through centrifugation, re-dissolved with 9 M hydrochloric acid and the solution passed through an anion exchange resin. Pu was then eluted and co-precipitated with neodymium as a fluoride Finally the microprecipitate was mounted on a filter and assayed using alpha pulse height analysis Details of the radiochemical separations for Pu can be found in Appendix 2

2 5 ^{241}Am radiochemistry

The Am fraction was dried on a hotplate then re-dissolved in a nitric acid/methanol solution and further purified using an anion exchange resin to separate the Am from other actinides and matrix elements The Am was then put through a TEVA Resin™ column using ammonium thiocyanate as a complexing agent to separate the Am from lanthanides and actinium The Am was then co-precipitated with neodymium as a fluoride Finally the microprecipitate is mounted on a filter and assayed using alpha pulse height analysis Details of the radiochemical separations for Am can be found in Appendix 2

2 6 Experimental apparatus for regulating system E_H (or pe)

An environmental isolation system was developed (*qq v*, Honeyman, 1998) to study the effects of reducing environments on the release of metals and radionuclides from a soil matrix to solution at specified E_H values The system as utilized

1 provides a controlled redox environment,
2 allows for the containment a soil/water slurry with constant mixing,
3 allows for periodic spectrophotometric measurements without exposure of samples to oxidizing conditions,
4 provides a variable electrical potential and electron current across the slurry,
5 allows for the relatively rapid determination of system redox potential (E_H),
6 provides the means for rapid separation of the liquid and solid phases, thereby effectively halting further reaction,
7 provides the means to easily monitor and adjust the pH at periodic intervals,
8 allows the removal of samples and the introduce new material and equipment into the isolation chamber without compromising the redox status of the experimental environment

10

The following equipment was utilized in the creation of the redox control system (Figure 3)

1 Coy Laboratory Products, Inc Anaerobic Chamber and associated Manual Airlock (collectively referred to as the glovebox),
2 IBM Instruments, Inc EC/225 Voltammetric Analyzer (Potentiometer),
3 GeoFilter large diameter filtering apparatus,
4 Orion Model 720 pH meter and electrode,
5 Roy Milton Co Spectronic 20,
6 110 volt low RPM stirring motor,
7 An electrochemical cell of in-house design for the regulation of electrochemical potential and sample manipulation (Figure 4)

In addition to the equipment listed above, the following materials were also utilized

1 A suite of redox indicators (Section 2 7),
2 0 45 µm large diameter membrane filters,
3 0 45 µm syringe filters and syringes,
4 a Zeolite O_2 scrubber,
5 O_2 - free nitrogen (<0 5 ppm)

2 6 1 Analysis procedure All equipment and materials were introduced into the chamber prior to the evacuation of ambient air and subsequent purging and filling with nitrogen The equipment internal to the glovebox was disassembled to allow glovebox evacuation to the greatest extent possible Equipment external to the chamber included the potentiometer, the nitrogen cylinders and the zeolite oxygen trap Figure 3 is a schematic illustration of the glovebox and associated instrumentation A pump attached to the airlock was used to purge the glovebox of gas The chamber was filled with oxygen-free nitrogen and purged for three cycles before the final inflation

Two sources of nitrogen were used throughout the experimental period The nitrogen entering through the airlock was not further purified of oxygen from the manufacturer's specification of <0 5 ppm This N_2 source was used to refill the chamber and airlock after evacuation of ambient air The second source of <0 5 ppm nitrogen was further scrubbed of O_2 by passing it through a zeolite trap prior to entering the chamber This second source was fed into the bottom of the cell through the 5 µm pre-filter/ sparging system that was mounted in the base of the cell apparatus (Figure 4) The filters acted as sparging devices to disperse the nitrogen into the slurry Throughout the duration of an experiment, a constant flow of nitrogen passed through the cell, over-pressuring the cell and the glove box relative to ambient pressures thereby preventing glovebox gas (< 0 5 ppm O_2) from entering the cell and ambient room air from entering the glovebox Experience with the cell and glovebox system demonstrated that a tiered gas isolation system is requisite for achieving low E_H values

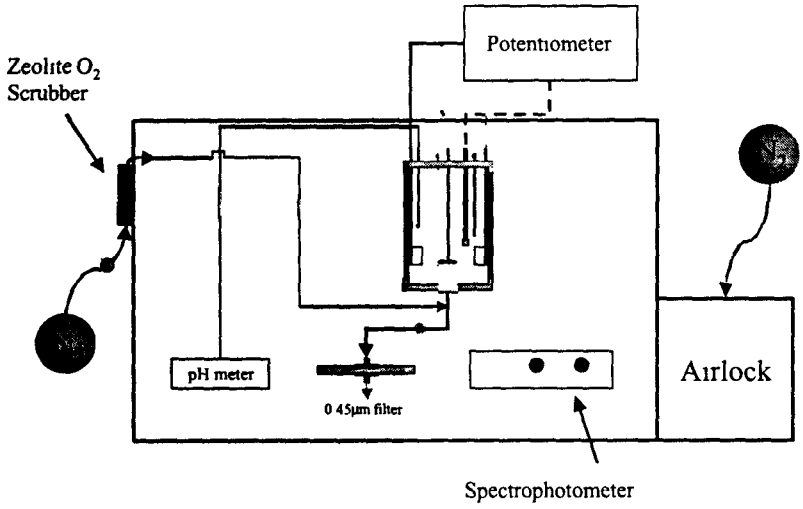


Figure 3 Diagram of the glovebox arrangement developed to maintain reducing conditions Two sources of N_2 are used to isolate the glovebox interior from ambient O_2 1) high purity N_2 (<0 5 ppm O_2) is the primary gas for glovebox inflation, 2) high purity N_2 which has been scrubbed of O_2 by a zeolite O_2 trap is used directly for cell sparging A series of valve manipulations allows *in situ* separation of suspended soil particles from the solution phase through the use of two filters in series 1) a 5 0 μm stainless-steel prefilter at the cell base (Figure 4), a 0 45 μm Nuclepore filter Additional equipment includes an IBM EC/225 Voltammetric Analyzer, an Orion Model 720 pH meter and a Roy Milton Co Spectronic 20

A four gram sample was weighed out to the nearest milligram and placed in the cell Four hundred milliliters of 1 0 mM potassium chloride aqueous solution was also added to the cell A Teflon-coated impeller attached to a stirring motor kept the slurry well mixed throughout the experimental period Sufficient redox indicator was then added to the soil/electrolyte slurry such that the initial percent transmittance reading from the spectrophotometer was between 10 and 50 (approximately 1 mM in total indicator) Readings were taken as soon as the indicator was well mixed in order to establish the initial indicator concentration

Initially, a three electrode system was used to apply a potential to the cell (Figure 4) A silver/silver chloride reference electrode was immersed in the slurry Two platinum mesh electrodes were sealed in position with their leads protruding upward through the top of the cell The mesh electrodes were completely immersed in the slurry at diametrically opposed positions near the wall of the cylindrical cell Eventually, the three electrode system was abandoned in favor of the two electrode system Since the potential established in the slurry was determined by the indicators, the applied potential had little relevance except in affecting the rate and the stability of the redox process (It was found that applying a potential of negative two volts over a period of time could have a destructive effect on one or more of the indicators) Other types of studies

12

may warrant the use of the three electrode system For the purposes of this study, the two electrode system was found to be simpler and sufficient to provide a stable potential

2 6 2 Reduction of NR04 The following paragraphs describe the procedure followed for the reduction of sample NR04 All samples were reduced using slight variations on the NR04 procedure

After the NR04/KCl slurry containing the indicator was thoroughly mixed, no potential was applied during the first several hours Spectrophotometric measurements were taken every few hours to determine if the indicator would be stable in the slurry with no bias applied A disposable pipette was used to remove several milliliters of slurry from the cell into a clean vessel A syringe fitted with a 0 45 µm filter was used to remove approximately 4 mL of solution from the settled slurry, leaving as much of the NR04 solids in the vessel as possible

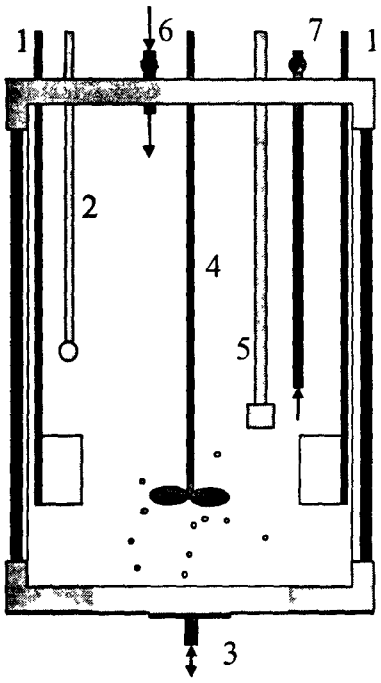


Figure 4 Detail of the cell constructed to regulate system E_H 1 Platinum electrodes, 2 combination pH electrode, 3 N_2 gas sparger/filtration port with 5 0 µm stainless steel pre-filter and hose bib for connection of the fluid stream to a downstream 0 45 µm Nuclepore filter (Figure 3), 4 Teflon stirrer, 5 reference electrode, 6 N_2 inlet port for cell pressurization, 7 port for slurry extraction

Since every measurement of this type removed a small amount of solids from the slurry, estimates of the total solids removed were made and corrections for a changing solid/solution ratio were included in data concentration calculations Solids loss determinations were made by weighing ten dried filters containing filtered solids and comparing to the weight of ten unused filters In the

13

study of sample NR04, approximately 0 8 grams of solids were removed throughout the 24 day experiment

Indicator analysis (*qq v*, Section 2 7) After sample filtration, the separated aqueous phase was immediately put into a photometry cell and measured for percent transmittance at a wavelength of 600 nm The separated solution was then returned to the cell Occasionally, the filtered aqueous portion was removed from the glove box to test for reversibility of the reduction reaction As indicated as part of the indicator selection criteria, indicator reversibility is critical to ensure that loss of the oxidized species color is due to indicator reduction and not loss through processes such as degradation or sorption Sample oxidation was carried out by bubbling air through the solution for several minutes On at least two occasions (NR02B and NR03, data not reported), this reversibility was not demonstrated and the experimental data were determined to be invalid

Sample NR04 showed a fairly immediate drop in color intensity (9 2 to 18 9 % transmittance) prior to applying a potential Such a reduction may be due to the presence of electron donors in the soil or some other process removing the indicator from solution Over the course of the NR04 study, nearly thirty indicator/E_H measurements were made Of these, five, at intervals throughout the study, were taken to demonstrate reversibility For all five samples, sparging with ambient air returned the indicator to a percent transmittance value very near the value obtained near the beginning of the study

The slurry was maintained at a pH of 7 2 throughout the study though step-wise addition of a weak solution of HCl as the solution pH tended to increase as the experiment progressed Note that the reduction of the oxidized form of the pe indicator (eq 2) contributes to the consumption of protons and an increase in solution pH

Sparging the electrochemical cell with N_2 resulted in a small, continuous loss in water This lost water was periodically replaced when the water level decline was noticeable, that is on the order of 10 milliliters or 2-3% of the total volume This evaporative loss and water reintroduction introduces a small uncertainty in the measurements

Once the target E_H and reaction time were obtained, the aqueous phase was quickly separated from the solid phase by pressure filtration 1) the stirring motor was turned off, the shaft of the propeller disconnected from the motor shaft collar and the propeller shaft allowed to drop below the top of the guide tube through which it spins during operation, 2) the top of the guide tube was sealed off using a connector and plug threaded to match the threads on the connector tube All other ports were sealed with plugs, 3) the nitrogen sparging line was closed and a connection was made to a second valve at the top of the cell (Figure 4 #6), 4) a third valve was opened at the bottom of the cell allowing the solution to leave the cell and travel through a tube to the filtering device (Figure 3 #3), 5) pressure to the cell was increased to 80 psi and the solution was forced out of the cell through the 5 μm prefilter and 0 45μm Nuclepore filter, and into a receiving vessel, 6) the aqueous solution was then removed from the chamber and the volume measured In the case of NR04, approximately 66 mL remained in the cell after pressure evacuation A correction factor (0 835 for NR04) was used in subsequent activity calculations

After phase separation the aqueous phase was re-oxidized by bubbling ambient air into the solution for a period of several minutes An aliquot of the solution was then tested in a final check

14

of indicator reversibility In the case of NR04, the solution was re-oxidized to a final percent transmittance value of 27 9, at 600 nm The sample was then submitted for $^{239,240}Pu$, ^{241}Am by alpha pulse height analysis and stable elements by inductively coupled plasma analysis

2 7 Redox indicators

Electrode measurements of soil and sediment E_H values are relatively easy to make but their interpretation is hindered as a consequence of practical and theoretical limitations (e g , Thorstenson, 1984) More accurate methods of redox determination involve the measurement of *in-situ* oxidized and reduced forms of target indicator elements, e g , Fe(II)/Fe(III) Problems with this approach include the concentration of indicator elements at or near the detection limit of routine analytical methods and redox-active species that may not be in equilibrium An additional method of assessing system redox is the addition of colored redox indicators to the system under consideration Selection criteria for indicators include (after Tratnyak and Wolfe, 1990) 1) the reversibility of the redox couple, 2) that the colors of the indicator must be easily distinguishable in sediment suspensions, 3) that the color of the oxidized and reduced forms of the indicators must not be strongly affected by pH, 4) that the oxidized and reduced forms of the indicators must have a negligible tendency to sorb, and 5) that the indicators must have a moderate water solubility

Tratnyak and Wolfe (1990) evaluated a suite of indicators for use in evaluating the redox status of anaerobic sediments Table 2 lists the properties (Wurmser and Banerjee, 1964) of the redox indicators used in this study

Table 2 Thermodynamic properties of redox indicators

Indicator	$E_H^o(w)$ (volts)	$pe^o(w)$	pe^o	log K
2,6-dichloro-indo-phenol	0 217	3 67	10 67	21 3
indigo-5,5',7,7'-tetrasulfonate	-0 046	-0 78	6 22	12 4
Indigo-5,5'-disulfonate	-0 125	-2 11	4 89	9 78

$E_H^o(w)$ is the standard electrode potential at pH =7, $pe^o = -\log\{e\}$ at pH = 0 under standard conditions In general, E_H and pe are related as follows $pe = \frac{F}{2\ 3RT}E_H = 16\ 9E_H$ in volts at 25 °C Similarly

$$pe^o(w) = \frac{F}{2\ 3RT}E_H^o(w) = 16\ 9E_H^o(w) \text{ and } pe^o = pe^o(w) + \frac{n_H}{n_e}7 \text{ and } n_H pe^o = \log K$$

where n_H and n_e are the stoichiometric coefficients (eq 1) for the transfer of protons (H) and electrons (e)

The redox reactions of all three indicators can be described by the following general reaction

$$Ox + 2H^+ + 2e^- = Red \qquad [2]$$

where Ox and Red represent the oxidized and reduced forms of the indicators, respectively The concentrations of the oxidized forms were followed through analysis of solution absorbance, relative to a blank, at ~600 nm, the approximate absorbance maxima The pe corresponding to a

15

calculated loss in the oxidized form was determined from a log α_0 *versus* pe diagram (Figure 5) The fractional reduction of the indicator is defined as

$$\alpha_0 = \frac{[Ox]}{[Ox]+[Red]} \qquad [3]$$

The indicators are blue in color when in their oxidized form and are colorless or yellow in their reduced form

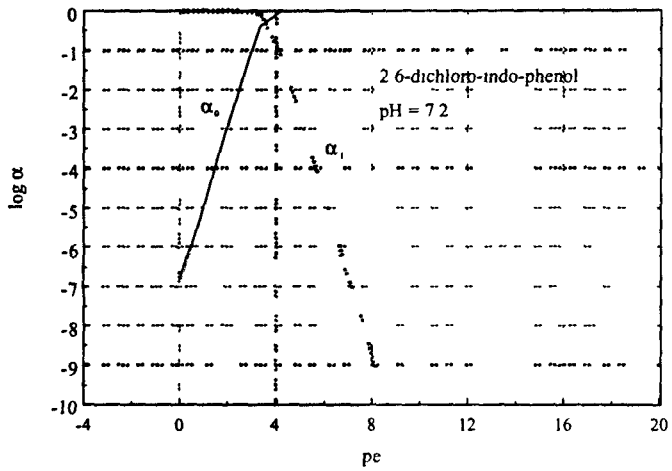


Figure 5 Log fractional distribution (α) of the redox indicator 2,6-dichloro-indo-phenol as a function of pe See Table 2 for indicator characteristics α_0 is the fraction of the indicator in the oxidized (colored) form, α_1 is the fraction in the reduced form pe values can be converted to E_H as described in the footnotes to Table 2

16

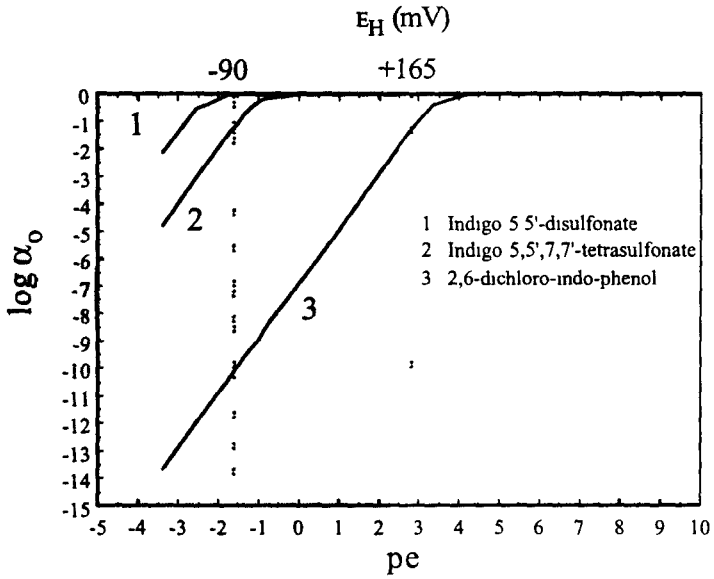


Figure 6 Comparison of three indicators used to ascertain system E_H α_o is the fraction of the indicator in the oxidized form The vertical reference lines indicate the target E_H values for the experimental runs Each indicator is optimal for a particular E_H value

2 8 Tangential flow ultrafiltration

Post 0 45 µm filtration was accomplished using a Millipore Minitan filtration system (Figure 7) with 10,000 NLMW (nominal molecular weight) filter plates guided by protocols described in the manufacturers user guide (Millipore, 1995) Filter plates used were type PLGC (Millipore catalogue number PLGCCOMP04) 10K low-protein-binding regenerated cellulose (Lot number RGEM72608) Four filter plates were used, for a total filtration surface area of 240 cm^2 Prior to filtration, filters and filtration apparatus (acrylic filter holder, filter separators, silicone pump tubing, polypropylene apparatus tubing) were cleaned using a sequence of soak and rinse steps 1) 20 minutes exposure to 0 05% detergent solution for metal removal, 2) 10 liter rinse with Nanopure water, 3) 20 minutes exposure to 0 1 M NaOH for organic removal, and 4) a final rinse with 10 liters of Nanopure water A filter integrity test was run at an inlet pressure of 5 psi prior to filtration

Sample filtration was done in the concentration mode, at an average transmembrane pressure of 8 psi Filtration was accomplished in a glove box under positive UHP (ultra high purity) nitrogen atmosphere As an additional step to preserve anoxic conditions during filtration, the headspace of sample containers were purged with UHP argon for the duration of the filtration

17

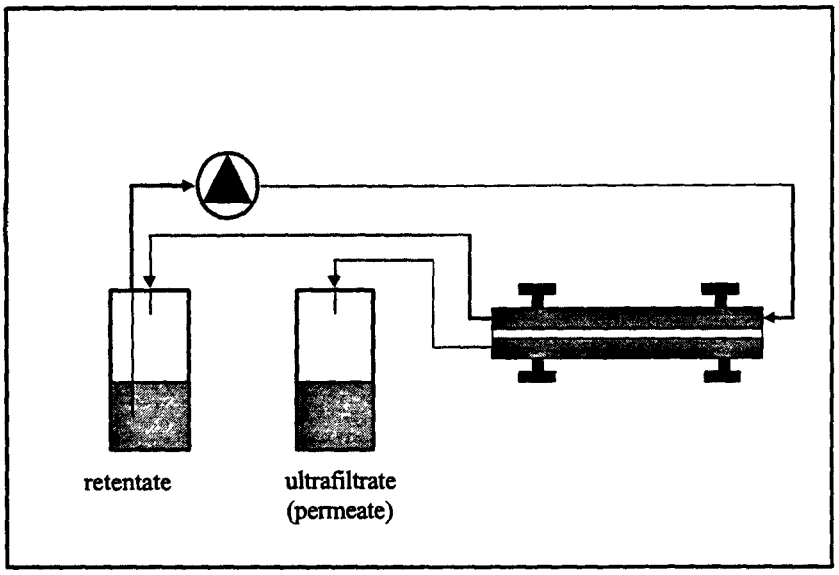


Figure 7 Schematic illustration of the tangential-flow ultrafiltration system

2 9 Incubation experiments

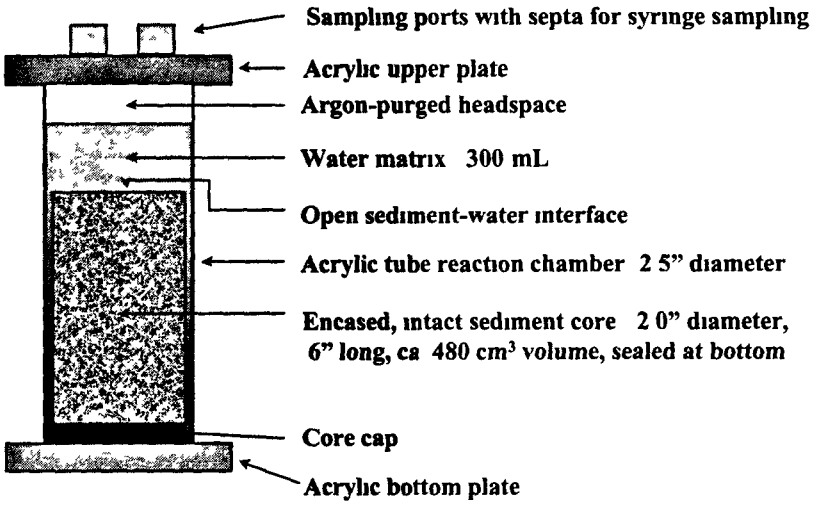
2 9 1 Experimental apparatus for sediment core incubation An apparatus of in-house design was developed and fabricated for sediment core incubations, based on the following criteria to

1 Provide minimal disturbance of core and sediment/water column interface during handling,
2 Maintain extant microbial colonies at depth by maintaining intact core (i e no homogenization of sediments),
3 Delimit exposure of core, so that only the sediment/water column interface is exposed to the water column,
4 Design a system that is relatively gas-impermeable and capable of maintaining sub-oxic conditions over the period (several weeks) of the incubation,
5 Allow for periodic sampling of the water column (sample withdrawals) and equal volume water additions (sample additions), while maintaining an inert atmosphere (argon) in incubator headspaces

The design of the incubation chamber is detailed in Figure 8 Chambers were constructed of $2^1/_2$ inch O D ($2^1/_4$" I D) acrylic tube, 10" long, with ¼" thick acrylic sheetstock used for the upper and lower plates Upper plates were drilled and tapped to accommodate two ½" plastic or brass compression fittings, which held in place 11mm silicon-based septa The internal diameter of the acrylic reaction chamber allowed undisturbed, core-liner encased cores to be inserted in the chambers with minimum perturbation Fabrication of the chambers was completed 3 weeks before initiation of the incubation experiment to allow for complete curing and degassing of solvent based adhesives and sealers used in fabrication in order to avoid potential toxic effects on microbiota Pre-experiment, the reaction chambers were leached with several changes of 10% nitric acid (4 hours exposure) followed by distilled water (20 hours exposure) and further repeated rinses with

18

distilled water Sterilization of the chambers by immersion in isopropyl alcohol was performed before the experiment was begun



Reaction Chamber

Figure 8 Illustration of the incubation chambers used in the core experiments The chambers were designed to minimized handling of the cores prior to the incubation experiments The encased core is the sediment sample in the original core liner

2 9 2 Synopsis of experimental approach

1 Intact cores were collected from Pond B4 and the SID (SED029) before Spring turnover (10 March, 1999)
2 Gamma-sterilized (^{60}Co) sediment cores were established as microbial activity controls, 'duplicate' cores (cores from the same site) were procured for the incubation analyses
3 Sediment cores were placed in sealed reactor vessels with 300 mL Pond B4 water (de-ionized, Nanopure grade water for SED029) Supernatant water was amended with carbon alone (C+, NO), nutrients alone (C0, N+), carbon and nutrients (C+, N+), or remained unamended (C0, N0)
4 Controls and samples were incubated at 35 ^{0}C, water column samples were taken every several days for analysis (e g , Fe, Mn) or archived for later analysis
5 'Dissolved' (<0 45 µm) Mn and Fe were measured for evaluation of system redox status
6 The incubations were terminated when Fe and Mn data suggested that system E_h might be increasing
7 Post-experiment, water columns from the incubation chambers were analyzed for $^{239,240}Pu$, metals (ICP), iron redox state, and total organic carbon

2 9 3 Gamma sterilization of cores Prior to beginning the incubation experiment, 3 frozen cores from each site were sent to the Radiation Center at Oregon State University for gamma sterilization in a Gammacell 220 irradiation chamber Cores were gamma-irradiated (^{60}Co) for a

19

period of 20 7 hours at an irradiation intensity of 1 2 E +5 rad/hour (Pratt, 1999) The cores were irradiated on 4 May 1999, then frozen at –4 °C until the beginning of the incubation period These cores served as irradiated controls on microbial activity in the sediment/water column during incubation The remaining cores (samples) were not irradiated, but kept frozen at -4 °C until the initiation of the incubation experiment

2 9 4 Sample Matrix and amendment protocol A schematic illustration of the experimental control and sample matrix is shown in Figure 9 Cores from each site were assigned as either irradiated controls (3 each) or samples (4 each), along with a matrix control consisting of matrix water alone Controls and samples were treated with 4 combinations of water matrix amendments 1) carbon alone (6 grams/L lactate as sodium lactate), 2) nutrients alone (Table 3), 3) carbon and nutrients, or 4) matrix water with no amendments Practical issues of scope of effort precluded replicate samples and controls only single representatives of controls and samples were established for the incubations Matrix water for the Pond B4 experiments was Pond B4 water collected on the day of core acquisition, then autoclaved before introduction to the reaction chambers Matrix water for the SED029 experiment was laboratory Nanopure water, autoclaved before introduction to the reaction chambers The chemical composition of the nutrient amendments is shown in Table 3 Lactate added in the sodium form at 6 g/L served as the carbon source in the carbon-amended samples and controls Solutions were autoclaved before their introduction into the reaction chambers

Table 3 Chemical composition of the nutrient media used in the nutrient-amended samples and controls Nutrient solutions were autoclaved before introduction into the reaction chambers

Compound	Concentration (g/L)
KH_2PO_4	0 5
NH_4Cl	1 0
Na_2SO_4	2 0
$CaCl_2$-$2H_2O$	1 0
$MgCl_2$-$7H_20$	1 0
Yeast Extract	0 4
$FeSO_4$-$7H_2O$	5 0 x 10^{-6}

20

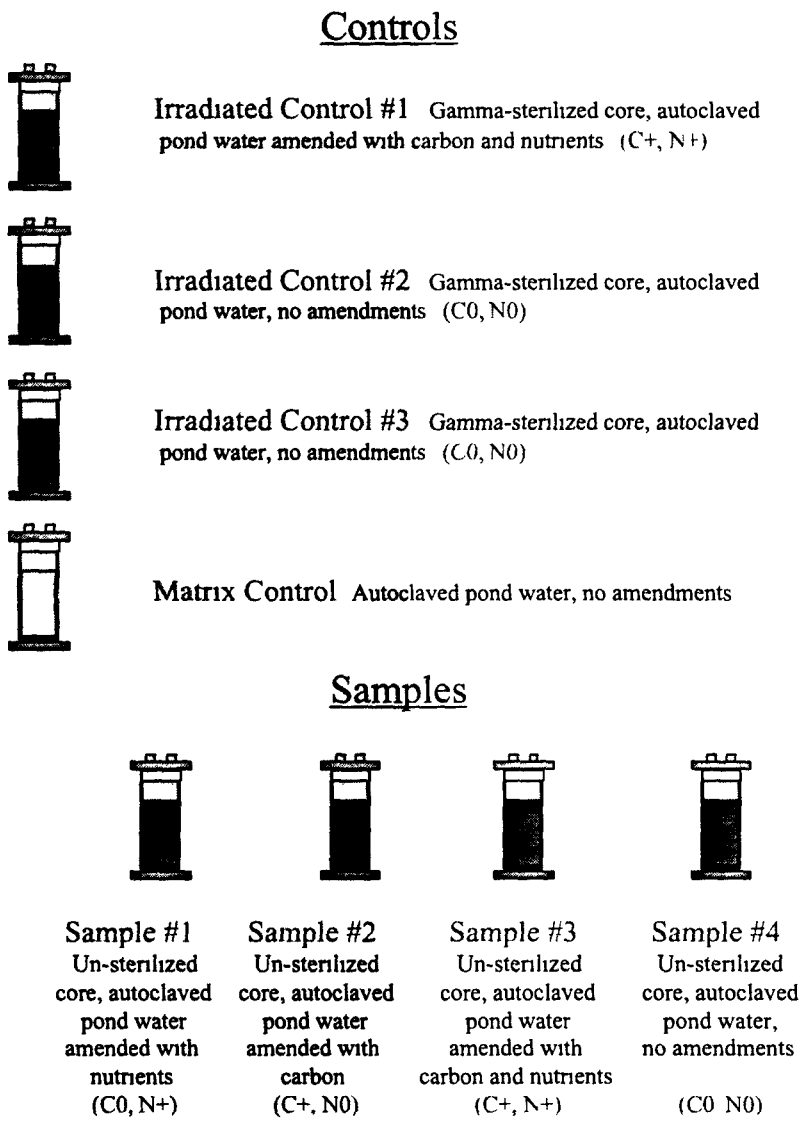


Figure 9 Schematic illustration of the sample matrix '+' indicates that the incubation chamber was amended with either carbon (6 g/L lactate) or the nutrient media (Table 3) 'o' denotes an unamended core with respect to either C or nutrients

2 9 5 Incubation protocols Prior to introduction of cores into the incubation chambers, the incubation chambers were immersed in isopropyl alcohol for four hours, then allowed to air dry This sterilization technique was used in lieu of autoclaving to prevent autoclaving damage to the reaction chambers Re-used sampling equipment (i e , needles and syringes), was soaked in 10 HNO3 solution to prevent cross contamination during sampling) All amendment solutions were autoclaved for 30 minutes Prior to the experiment, samples were taken from all amendment solutions for chemical analysis

21

Incubations were done in a constant temperature environmental chamber at CSM Incubation temperature was held at 35 degrees C (+/- 1 ^{0}C) for the duration of the incubation period The experimental incubation chambers remained physically undisturbed for the duration of the incubation except during periodic withdrawal of water column samples for analysis or archival purposes To avoid potential photoreductive reactions, samples and controls were maintained in complete darkness for the duration of the experiment, with the exception of brief periods of fluorescent light exposure (several hours per sampling) during periodic water sample extraction Sediment incubation protocols are shown in Table 5

Incubation of the control and sample suites for Pond B4 and SED029 were begun at 4 00 PM on 20 May, 1999 Incubation of Pond B4 samples and controls was terminated at 11 00 AM, 11 June, 1999 after 22 days of incubation Incubation of SED029 samples and controls was terminated at 9 00 AM, 14 June, 1999 after 25 days of incubation

2 9 6 Sample identification The chain of custody identification numbers of collected cores, and the corresponding incubation experiment sample designations are shown in Table 4

Table 4 Chain of custody identification numbers of cores and water samples used in the sediment incubation experiments Laboratory Nanopure grade water was used as the water matrix for SED029 incubations

Incubation experiment Sample Designation	Chain of custody Sample number (core)	Chain of custody Sample number (water)
Pond B4 Irradiated Control #1 (C+, N+)	99D5920 012	99D5920 023/024
Pond B4 Irradiated Control #2 (C0, N0)	99D5920 013	99D5920 023/024
Pond B4 Irradiated Control #3 (C0, N0)	99D5920 014	99D5920 023/024
Pond B4 Matrix Control	none	99D5920 023/024
Pond B4 Sample #1 (C0, N+)	99D5920 015	99D5920 023/024
Pond B4 Sample #2 (C+, N0)	99D5920 016	99D5920 023/024
Pond B4 Sample #3 (C+, N+)	99D5920 017	99D5920 023/024
Pond B4 Sample #4 (C0, N0)	99D5920 019	99D5920 023/024
SED029 Irradiated Control #1 (C+, N+)	99D5920 035	none
SED029 Irradiated Control #2 (C0, N0)	99D5920 036	none
SED029 Irradiated Control #3 (C0, N0)	99D5920 037	none
SED029 Matrix Control	none	none
SED029 Sample #1 (C0, N+)	99D5920 038	none
SED029 Sample #2 (C+, N0)	99D5920 039	none
SED029 Sample #3 (C+, N+)	99D5920 040	none
SED029 Sample #4 (C0, N0)	99D5920 041	none

22

Table 5 Sediment incubation experiment protocols + designates that the incubation matrix water was amended with either carbon or nutrients '0' designates no amendment

Sample Designation	Amendment Protocol	Incubation Start Date	Incubation End Date	Duration Of Incubation (days)	Incubation Temp (°C)	Water Matrix
Pond B4 Irradiated Control #1	C+, N+	5/20/99	6/11/99	22	35 +/- 1	Pond B4 water
Pond B4 Irradiated Control #2	C0, N0	5/20/99	6/11/99	22	35 +/- 1	Pond B4 water
Pond B4 Irradiated Control #3	C0, N0	5/20/99	6/11/99	22	35 +/- 1	Pond B4 water
Pond B4 Matrix Control	C0, N0	5/20/99	6/11/99	22	35 +/- 1	Pond B4 water
Pond B4 Sample #1	C0, N+	5/20/99	6/11/99	22	35 +/- 1	Pond B4 water
Pond B4 Sample #2	C+, N0	5/20/99	6/11/99	22	35 +/- 1	Pond B4 water
Pond B4 Sample #3	C+, N+	5/20/99	6/11/99	22	35 +/- 1	Pond B4 water
Pond B4 Sample #4	C0, N0	5/20/99	6/11/99	22	35 +/- 1	Pond B4 water
SED029 Irradiated Control #1	C+, N+	5/20/99	6/14/99	25	35 +/- 1	Nanopure grade de-ionized
SED029 Irradiated Control #2	C0, N0	5/20/99	6/14/99	25	35 +/- 1	Nanopure grade de-ionized
SED029 Irradiated Control #3	C0, N0	5/20/99	6/14/99	25	35 +/- 1	Nanopure grade de-ionized
SED029 Matrix Control	C0, N0	5/20/99	6/14/99	25	35 +/- 1	Nanopure grade de-ionized
SED029 Sample #1	C0, N+	5/20/99	6/14/99	25	35 +/- 1	Nanopure grade de-ionized
SED029 Sample #2	C+, N0	5/20/99	6/14/99	25	35 +/- 1	Nanopure grade de-ionized
SED029 Sample #3	C+, N+	5/20/99	6/14/99	25	35 +/- 1	Nanopure grade de-ionized
SED029 Sample #4	C0, N0	5/20/99	6/14/99	25	35 +/- 1	Nanopure grade de-ionized

23

Frozen core samples were refrigerated for 24 hours before incubation to initiate thawing Cores were placed intact (core liner remaining in place) in the reaction chambers with the bottom cap remaining in place The top cap was removed to expose the sediment-water interface 300 mL of appropriate water phase was added, then the reaction vessels were sealed at the joint between the top and bottom segments with vinyl tape Once sealed, the reaction vessels were removed from the glove box and moved to the 35 °C incubation chamber for the duration of the experiment

2 9 7 Sampling protocols
Samples of the water columns from the Pond B4 experimental suite were taken every several days for chemical analysis The experimental suite from SED029 was sampled less frequently For each sample and control, 6 mL was withdrawn for metals analysis, 15 mL was withdrawn for anion and total organic carbon analysis, and 10 ml was withdrawn for archival freezing at each sampling event All samples were 0 45 um filtered using disposable 25-mm syringe filters before preservation Samples for metals analysis were collected in 25 mL polypropylene bottles, preserved with ultrapure nitric acid to pH <2, and stored at room temperature Anion samples were collected in amber glass vials and immediately refrigerated, Archival samples were collected in 25 mL polypropylene bottles and immediately frozen All samples were taken from mid-depth in the water column using a 20 mL polypropylene syringe with a 6" long stainless steel sampling needle through the septa of one of the sampling ports During sampling, grade 5 0 UHP (ultra-high purity) argon purged the gas headspace through a needle inserted into the second sampling port to preserve anoxia in the headspace Following sampling, the volume of water withdrawn from each sample/control during sampling was replaced with the same volume (31 mL) of appropriate original liquid phase (i e , amended or unamended) to match the original water sample matrix and to maintain a total 300 mL of water matrix in each of the reaction chambers Care was taken to avoid perturbation of the sediment-water interface during sampling To avoid cross-contamination during sampling, separate syringes and needles were used for each sample/control If reused, sampling equipment was soaked in 10% HNO_3 and rinsed with Nanopure water between samplings Over the course of the incubation, 8 samplings were made on the Pond B4 experimental suite, 5 samplings were made on the SED029 experimental suite

2 9 8 Incubation experiment termination protocols The decision to terminate the incubations was based on temporal measurements of 'dissolved' (<0 45 μm) iron and manganese concentrations in the water columns The goal was to terminate the experiment on or near indication of maximum dissolution of (oxy)hydroxides of these elements to achieve an end point indicative of maximally intensive reducing conditions in the sediments/water column, and of active microbially-mediated redox state transformations

2 9 9 Post incubation sample processing Initial post incubation experiment sample processing was done under nitrogen atmosphere in the glove box Reaction chambers were disassembled and the water matrix phases decanted into 250-mL conical polypropylene centrifuge tubes which were capped under N_2 atmosphere Sediment cores were capped and immediately frozen for archival purposes Sealed water matrix phases were then removed from the glove box and centrifuged at 3000 rpm for 30 minutes to separate particulates from the aqueous phase as a preclude to final filtration Final filtration (0 45 μm syringe filtration) was accomplished with continual purging of centrifuged samples with UHP nitrogen during the filtration process Immediately following filtration, 20 mL samples were taken and processed for iron speciation (Fe(II)/Fe(III)) Bulk

24

filtered water samples (ca 250 mL/sample) were acidified to < pH2 with ultrapure HNO_3, then refrigerated in preparation for actinide analysis

29 10 Analytical Methods All analytical procedures (with the exception of day-of-sediment acquisition measurements made by RFETS personnel) were accomplished by qualified CSM personnel using CSM instrumentation All analyses were guided by published and generally accepted analytical and quality assurance protocols

2 9 10 1 Iron and Manganese analysis Iron and manganese analyses were performed using a Perkin-Elmer Optima 3000 inductively-coupled plasma emission spectrometer with a Perkin-Elmer AS-91 autosampler The system software provides two techniques for minimizing spectral interferences inter-element correction and multi-component spectral fitting Sample preparation and analysis were performed per Perkin-Elmer specifications and were guided by protocols outlined in EPA Method 6010B (EPA 1996) Detection limits measured on this instrument in May, 1999 were iron 5 ppb , manganese 1 ppb Acidified samples were analyzed without dilution Scandium at 1 ppm was added to each sample before analysis as an internal standard to access instrument stability

2 9 10 2 Iron redox state analysis Immediately following sediment/water phase separation by centrifugation and 0 45 um filtration at the end of the experiment, water column samples were analyzed for iron redox state using modified colorometric bipyridine methods for ferrous (Skougstad *et al* , 1979a) and total iron (Skougstad, et al , 1979b) Ferric iron concentration was calculated as the difference between measured total iron concentration and measured ferrous iron concentration

Summary of Method Iron, total recoverable, bipyridine This method is based on the reaction between ferrous iron and 2,2-bipyridine that yields a red complex Hydroxylamine hydrochloride reduces ferric iron to ferrous iron The color develops immediately and is stable for several hours The color intensity is independent of pH in the range 3-10

Summary of Method Iron, ferrous, dissolved, colorometric, bipyridine This method is identical to the iron, total recoverable, bipyridine method, except that no reductant is added to reduce ferric iron in solution

Apparatus Milton Roy Company Spectronic 20 spectrophotometer, wavelength 520 nm , 10 mm cell

2 9 10 3 Total organic carbon analysis Total organic carbon analysis of water column samples by catalytic combustion-non-dispersive infrared gas analysis was accomplished on a Shimadzu Total Organic Carbon Analyzer, Model TOC-500, according to manufacturers instructions (Shimadzu Corporation, 1990) and Standard Method 5310B, Total Organic Carbon, Combustion-Infrared Method (American Public Health Association, 1989)

2 9 10 4 Metals analysis Fractions of the actinide-containing solutions were taken from the digested and/or extracted samples for metals analyses The fractions were diluted with 1 M nitric acid to approximately 15 mL and then submitted for direct aspiration and quantification by inductively coupled plasma emission spectrometry

25

All metals analyses under this study were performed by personnel of the Colorado School of Mines Chemistry Department on a Perkin Elmer Optima 3000 inductively coupled plasma emission spectrometer with a Perkin Elmer AS 91 Auto Sampler The system software provides two techniques for minimizing spectral interferences inter-element correction and multi-component spectral fitting Metals were analyzed per Perkin Elmer specifications using standard protocols

Quality Assurance measures for these analyses include initial calibration with NIST traceable standards, continuing calibration verification throughout the analytical run time Scandium is utilized as an internal spike for assessing performance parameters Data review is performed by qualified ICP operators and the ICP laboratory supervisor prior to final reporting

2 9 10 5 pH and E_H measurements Measurement of pH and E_H were accomplished using an Orion Model 720 pH meter, and calibrated pH and E_H electrodes

3. Results and Discussion: redox cell experiments

3 1 Analysis of $^{239,240}Pu$ and ^{241}Am solubilities over a range of redox conditions

The release of $^{239,240}Pu$ and ^{241}Am from fractions of RFETS soil isolate 97L1879-002 suspended in aqueous solution, to solution, was examined as a function of suspension E_H Details of the experimental system are described in Sections 2 6 and 2 7 Experimental trial characteristics are summarized in Table 6 A complete tabulation of experimental results (FY 1998 and 1999) can be found in Table 7 Figure 10a shows $^{239,240}Pu$ and ^{241}Am aqueous-phase activities (pCi/L) as a function of slurry E_H For these experiments, the 'solution' phase was operationally-defined as the portion of the system passing 0 45μm filters Figure 10b contains a plot of Pu concentration as a function of E_H

^{241}Am solution phase activities over the range of E_H values studied were, within experimental error, independent of slurry E_H, with an average value of 1 2 ± 0 8 pCi L^{-1} (1 44 fM) For the conditions of the experiment (a 10 g L^{-1} soil/water slurry 438 pCi L^{-1} $^{241}Am_{total}$), approximately 0 27% of the soil ^{241}Am was released to solution Paired t-tests showed no significant correlation (at the 95% confidence level) for ^{241}Am activity and 1) E_H, or 2) length of equilibration time

Analysis of $^{239,240}Pu$ solution-phase activity was conducted as a function of 1) E_H, 2) soil/water contact time, at a set E_H, and 3) molecular weight separation using tangential flow ultrafiltration $^{239,240}Pu$ solution-phase activities (Figures 10a, Table 7) are considerably more variable than in the case of ^{241}Am Furthermore, examination of Figure 10a shows the broad characteristics of the experimental results $^{239,240}Pu$ solution-phase activity decreases with E_H

- *E_H = -90 mV* The average $^{239,240}Pu$ activity at –90 mV is 1 96 ±0 46 pCi/L (1 30 x 10^{13} ±0 30 x 10^{-13} M) for the three experimental trials at that E_H (NR02, NR04 and NR07)

- *E_H = +165 mV* Three experimental trails were also conducted at an E_H value of ca +165 mV (NR01, NR06 and NR08) The trials at ca 24 days produced $^{239,240}Pu$ activities of 2 1 and1 15 pCi/L, the trial at 2 days (NR01) yielded 6 17 pCi/L It is yet to be determined whether NR01 reflects a kinetic component to reduction or that the data is an experimental 'outlier'

26

- $E_H = +800\ mV$ Four experimental trails were conduced under conditions open to the atmosphere (NO02, NO03, NO04 and NO06) Three trials (-02, -03 and –06) were grouped, yielding an average $^{239,240}Pu$ value of 4 85 ± 0 32 pCi/L (328 ± 22 x 10^{-13} M) A fourth trial, NO04, produced a $^{239,240}Pu$ activity of 2 32 pCi/L Three (-03, -04 and –06) of the four trials were conducted at prolonged contact time of 24 days Paired t-tests of the data indicate that NO04 (2 32 pCi/L) can be rejected at part of the population consisting of NO02, NO03 and NO06 at the 95% confidence level

[Note Fiscal Year 1998 work (Honeyman, 1998) evaluated removal of Pu and Am by the Pt electrodes Honeyman (1998) concluded that because the Pu and Am associated with the electrodes was statistically indistinguishable from the bulk soil $^{239,240}Pu/^{241}Am$ ratio that the electrode buildup is the consequence of the entrapment of fine soil particles that could not be removed by scrubbing]

Table 6 Experimental trial characteristics

Experiment	Sample ID[1]	Equilibration time (days)	Final E_H (mV)	Indicator
NO02	97L1879-02	1 5	+800	None[2]
NO03	97L1879-02	24	+800	None
NO04	97L1879-02	24	+800	2,6-dichloro-indo-phenol
NO06	97L1879-02	24	+800	2,6-dichloro-indo-phenol
NR01	97L1879-02	1 5	+164	2,6-dichloro-indo-phenol
NR02	97L1879-02	1 5	-90	indigo-5,5',7,7'-tetrasulfonate
NR04	97L1879-02	24	-90	indigo-5,5',7,7'-tetrasulfonate
NR06	97L1879-02	22	+165	2,6-dichloro-indo-phenol
NR07	97L1879-02	2	-90	indigo-5,5',7,7'-tetrasulfonate
NR08	97L1879-02	22	+165	2,6-dichloro-indo-phenol
NR10	Hematite (α-Fe_2O_3)	24	-90	indigo-5,5',7,7'-tetrasulfonate
NO05	99D5920 011	2	+800	None
NR11	99D5920 011	2	+165	2,6-dichloro-indo-phenol
NR12	99D5920 011	2	-90	indigo-5,5',7,7'-tetrasulfonate
NRB01	Blank	2	+165	None
NRB02	Blank	2	+165	2,6-dichloro-indo-phenol

[1]97L1879-02 903 Pad lip area soil, 99D5920 011 Pond B4
[2]NO02 was open to the atmosphere The E_H was calculated from the stability of H_2O with respect to oxidation at pH 7 2 and P_{O_2} = 0 17 atm

21

Table 7 Tabulation of ^{239,240}Pu and ^{241}Am experimental results for FY 1998 and 1999 work Sample #97L1879 is a soil sample from the 903 Pad 'Lip' area, 99D5920 is from the Pond B-4 soil core cluster

RFETS Sample ID #	Sample name	Sample Mass (g)	V_E (mL)	Tracer Added (Bq)	Tracer Cnts	Pu-239/240 Cnts	Pu-239/240 In tracer	Count time (m)	Scaling factor	Sample Act (pCi/g)	% of total	Sample Act (Bq/L)	Counting Uncertan (1σ)(Bq/L)	Sample Act (pCi/L)	Counting Uncertan (1σ)(pCi/L)	Detec Effic	Yield (%)	Sample MDA pCi/g
97L1879-02	NR01	4 0594	400	5 1594	73271	1231		1000	0 95	0 607	0 37	0 2281	0 0066	6 17	0 18	0 3152	75 1	0 0065
	BLK 01	4 0226	400	0 3072	5955	74		1000	1	0 026		0 0095	0 0011	0 258	0 030	0 3152	102 5	0 0045
	BLK-12	4	400	0 306	5819	3		1000	1	0 001		0 0004	0 0002	0 0107	0 0062	0 3152	100 6	0 0047
97L1879-02	NR02	4 0392	400	0 9216	13217	337		1000	0 95	0 166	0 10	0 0618	0 0034	1 671	0 092	0 3152	75 8	0 0064
97L1879-02	NO02	4 001	400	0 6154	9599	1133		1000	0 95	0 516	0 32	0 1912	0 0060	5 17	0 16	0 3152	82 5	0 0060
	BLK-13	4	400	0 306	5301	55		1000	1	0 021		0 0079	0 0011	0 215	0 029	0 3152	91 6	0 0051
97L1879-02	NR04	4 1371	400	2 594	144952	1152		4000	0 835	0 161	0 10	0 0617	0 0018	1 668	0 049	0 3152	73 9	0 0018
97L1879-02	NR04 EL SM	4 1371	400	0 3067	6630	6711		1500	1	2 028	1 24	0 776	0 013	20 98	0 36	0 3152	76 2	0 0040
97L1879-02	NR04 EL LG	4 1371	400	0 3054	8144	3503		1500	1	0 858	0 52	0 328	0 0066	8 88	0 18	0 3152	94 0	0 0032
	BLK-14	4	400	2 6025	137698	165		4000	1	0 021		0 00780	0 00061	0 211	0 016	0 3152	69 9	0 0017
97L1879-02	NO03 (0 45μm)	25 0	2486	0 3025	7588	7841		1500	1	0 338	0 21	0 12574	0 0020	3 398	0 055	0 3152	88 4	0 00056
97L1879-02	NO03 (10K MW)	25 0	2514	0 3067	8206	2793		1500	1	0 113	0 069	0 04152	0 00091	1 122	0 025	0 3152	94 3	0 00053
	BLK-15	25	2500	0 3084	13167	13		2500	1	0 00033		0 00012	0 000034	0 00329	0 00091	0 3152	90 3	0 00033

Table 7, Continued

RFETS Sample ID #	Sample name	Sample Mass (g)	V_E (mL)	Tracer Added (Bq)	Tracer Cnts	Pu-239/240 Cnts	Pu-239/240 In tracer	Count time (m)	Scaling factor	Sample Act (pCi/g)	% of total	Sample Act (Bq/L)	Counting Uncertan (1σ)(Bq/L)	Sample Act (pCi/L)	Counting Uncertan (1σ)(pCi/L)	Detec Effic	Yield (%)	Sample MDA pCi/g
97L1879-02	NR06	4 0	400	0 301	17478	1795		3000	1	0 209	0 127	0 07728	0 00192	2 089	0 052	0 3152	102 3	0 00153
	BLK-17	4	400	0 2979	13220	17		2500	1	0 00259		0 00096	0 000232	0 02588	0 00628	0 3152	93 9	0 00200
97L1879-02	NR07-(0 45μm)	4	400	0 1437	2019	81		1000	0.2052	0 190	0 12	0 0702	0 0080	1 898	0 215	0 3512	66 7	0 0307
	NR07-10K	4	400	0 1437	2433	120		1000	0 7948	0 060	0 04	0 022	0 0021	0 603	0 056	0 3512	80 3	0 0066
97L1879-02	NR08-0 45	4	400	0 1437	4074	96		1000	0.2847	0 080	0 05	0 030	0 0031	0 804	0 083	0 3512	134 5	0 0110
	NR08-10K	4	400	0 1437	2186	56		1000	0 7153	0 035	0 02	0 01287	0 0017	0 348	0 047	0 3512	72 2	0 0081
97L1879-02	NO04	4	400	0 1437	2507	521		1000	0 8728	0 231	0 14	0 08554	0 0041	2 312	0 111	0 3512	82 8	0 0058
Blank	NRB01	4	400	0 1417	1473	399	18 8544	1000	0 95	0 260	0 16	0 10101	0 0057	2 730	0 154	0 3512	49 3	0 0090
Indicator	NRB02	4	400	0 1417	2407	129	30 8096	1000	0 95	0 041	0 03	0 01998	0 0018	0 540	0 049	0 3512	80 6	0 0055
99D5920 0 11	NO0 5	4 0063	400	0 1417	2330	40	29 824	1000	1	0 004	0 00	0 00608	0 0010	0 164	0 026	0 3512	78 0	0 0054
97L1879-02	NO06	4 0046	400	0 1417	2353	1192	30 1184	1000	1	0 472	0 29	0 17946	0 0064	4 850	0 172	0 3512	78 8	0 0053
99D5920 0 11	NR11	4 0041	400	0 1417	2165	43	27 712	1000	0 95	0 007	0 00	0 00741	0 0011	0 200	0 031	0 3512	72 5	0 0061
99D5920 0 11	NR12	4 0022	400	0 1417	2368	158	30 3104	1000	0 95	0 054	0 03	0 02488	0 0020	0 672	0 055	0 3512	79 3	0 0056

29

Table 7, Continued

RFETS Sample ID #	Sample name	Sample Mass (g)	V_E (mL)	Tracer Added (Bq)	Tracer Cnts	Am-241 Cnts	Am-241 In tracer	Count time (m)	Scaling factor	Sample Act (pCi/g)	% of total	Sample Act (Bq/L)	Counting Uncertan (1σ)(Bq/L)	Sample Act (pCi/L)	Counting Uncertan (1σ)(pCi/L)	Detec Effic	Yield (%)	Sample MDA pCi/g
97L1879-02	NR01	4 0594	400	7 056	99022	364	163	1000	0 95	0 100	0 23	0 0683	0 0036	1 84	0 10	0 3152	74 2	0 0065
	BLK 01	4 0226	400	0 1844	3016	22	5	1000	1	0 007	0 016	0 00336	0 00072	0 091	0 019	0 3152	86 5	0 0054
	BLK-12	4	400	0 1835	3256	10	5	1000	1	0 002	0 0040	0 00141	0 00045	0 038	0 012	0 3152	93 8	0 0050
97L1879-02	NR04	4 0594	400	3 5378	180232	832	297	4000	0 835	0 084	0 19	0 0489	0 0017	1 322	0 046	0 3152	67 3	0 0021
97L1879-02	NR04 EL SM	4 1371	400	0 09210	566	400	1	1500	1	0 424	1 0	0 1627	0 0106	4 398	0 287	0 3152	21 7	0 014
97L1879-02	NR04 EL LG	4 1371	400	0 09104	2333	615	4	1500	1	0 156	0 36	0 0600	0 0027	1 622	0 074	0 3152	90 3	0 0033
	BLK-14	4	400	3 5371	170803	510	282	4000	1	0 032	0 07	0 0264	0 0012	0 714	0 032	0 3152	63 8	0 0018
97L1879-02	NO03 (0 45um)	25 0	2486	0 09084	2035	574	3	1500	1	0 028	0 063	0 01031	0 00049	0 279	0 013	0 3152	79 0	0 00063
97L1879-02	NO03 (10K MW)	25 0	2514	0 09108	1693	158	3	1500	1	0 009	0 021	0 00338	0 00028	0 091	0 008	0 3152	65 5	0 00076
	BLK-15	25	2500	0 09012	3415	24	6	2500	1	0 001	0 0012	0 00025	0 000052	0 007	0 001	0 3152	80 1	0 00037
97L1879-02	NR06	4 0	400	0 2024	3298	136	5	1000	1	0 054	0 124	0 02087	0 00183	0 564	0 049	0 3152	86 2	0 00544
	BLK-17	4	400	0 2011	3499	37	6	1000	1	0 012	0 0277	0 00532	0 000879	0 144	0 024	0 3152	92 0	0 00509

30

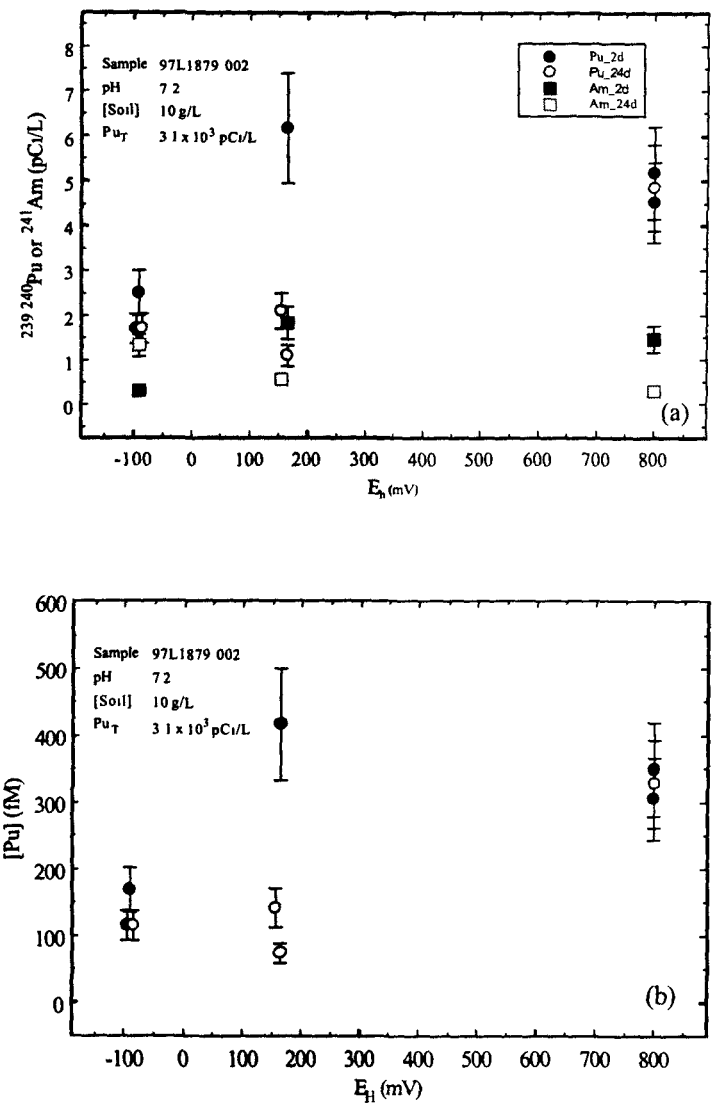


Figure 10 a) $^{239,240}Pu$ or ^{241}Am activity (pCi L^{-1}) as a function of E_H The experimental apparatus for the actinide solubility experiments is shown in Figures 4 and 4 In all cases, the soil concentration was 10 g L^{-1} and the initial solution composition was 17 M ohm Nanopure water made 10^{-3} M in KCl System E_H was determined through the method described in Section 2 7 Table 7 provide details on the individual experiments The $^{239,240}Pu$ and ^{241}Am soil activities for the soil isolate are 310 ± 55 7 and 43 8 ± 7 4 pCi g^{-1}, respectively b) The Pu data presented as concentration (1 fM = 10^{-15} M) Error bars are based on a relative error of 20% Pu_T = 2 1 x 10^{-10} M (3 1 x 10^3 pCi L^{-1})

31

Figure 11 shows $^{239,240}Pu$ concentration (M) is shown as a function of E_H (mV) and represents the data set with the greatest reproducibility The total 'dissolved' Pu data have been 'corrected' to include only the fraction of Pu that passed the 10K Da ultrafilter Pu species considered in the construction of the diagram are $Pu(OH)_4^o(aq)$, which is the dominant soluble Pu(IV) species at pH 7 2 in the region -200 mV $< E_H <$ +600 mV, and $PuO_2CO_3^-$ which is the primary Pu(V) species at ca +800 mV, for the conditions of the experiment (i e , $C_T = 10^{3\,5}$ M) The chemical identity of the Pu species in the system, both solid phase and 'dissolved' are not known at this time, the diagram has been constructed only to provide a reference frame for discussions concerning Pu solubility It is not even certain, for example, if the Pu data represent equilibrium conditions

The position of the data relative to solubility control by a Pu (oxy)hydroxide is highly dependent on the identity of the solid phase (and the quality of the thermodynamic data) For example, if the controlling solid phase is postulated to be $Pu(OH)_4$(am), rather than PuO_2 (c), the solution-phase concentration of $Pu(OH)_{4(aq)}^o$ and $PuO_2CO_3^-$ become 1 02 x 10^{-10} and 8 5 x 10^{-8} M, respectively In addition, the identity of the solution-phase Pu species also remains uncertain For example, tangential-flow ultrafiltration analysis of the solution-phase indicates that a significant fraction of the 'dissolved' Pu is associated with material of colloidal size (Section 3 4, below) and of unknown composition

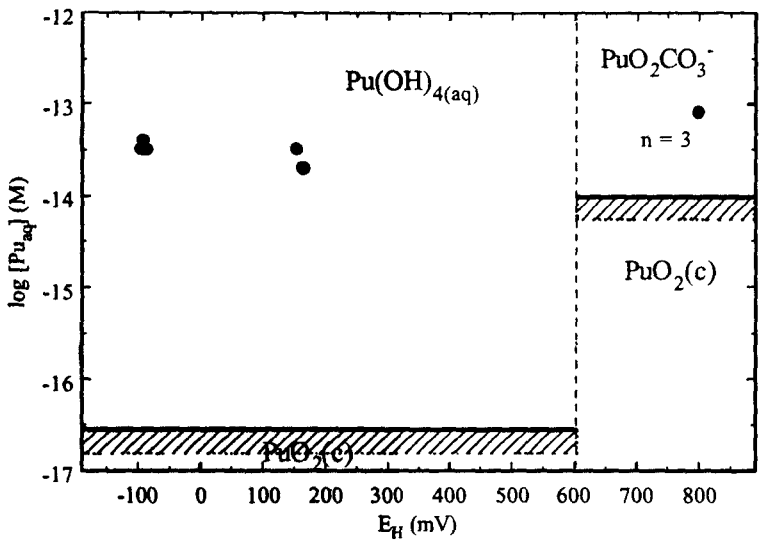


Figure 11 Comparison of Pu solubility from thermodynamic calculations and measured values from the E_H cell, as corrected for the < 10K Da fraction pH 7 2 $^{239,240}Pu$ solubility was calculated from ΔG_f^o (kcal/mole) data compiled by Puigdomenech and Bruno (1991) $Pu(OH)_{4(aq)}^o$ (-329 35), $PuO_2CO_3^-$ (-336 28), PuO_2(c) (-238 53)

32

3 2 Electrochemical cell analysis of Pond B4 sediments

The results of redox cell analysis of Pond B4 sediments is provided in Table 7 As with the soil isolate, reduction of B4 sediments suspended in Pond B4 water produced limited $^{239,240}Pu$ solubility (ca 0 1 to 0 6 pCi/L) over the E_H range evaluated (-90 mV < E_H < +800 mV)

3 3 Reduction of hematite (α-Fe_2O_3) using the E_H cell

Fiscal Year 1998 work (Honeyman, 1998) indicated that only a small fraction of the soil isolate Fe and Mn was solubilized during the reduction experiments Fe and Mn soil concentrations were, for isolate 97L1879-02, 18 and 0 37 ppt, respectively For all E_H values, less than 1‰ of the Fe was solubilized in the electrochemical cell indicating that the system

An experimental trial was undertaken this fiscal year to evaluate the ability of the E_H cell to reductively-dissolve Fe(III) The trial conditions were 3 4 x 10^2 mg/L of hematite (α-Fe_2O_3), which was prepared as described by Matijevic and Scheiner (1978), at pH 7 2 The hematite was suspended in a 0 01 M $NaClO_4$ electrolyte solution, the system E_H was –90 mV, the hematite/solution contact time was 24 days, the pH was 7 2 and the system was free of atmospheric CO_2 The total Fe in the system (hematite + soluble Fe) was 1 06 x 10^{-3} M

ICP analysis of 'dissolved' Fe at the conclusion of the experiment yielded 0 056 ppm Fe (= 1 02 x 10^{-6} M) The detection limit of the ICP for iron under the operating conditions of the analysis is 5 ppb

The solubility of hematite is describe by the following reaction (Morel and Hering, 1993)

$$\tfrac{1}{2}Fe_2O_3(s) + \tfrac{1}{2}H_2O + H^+ = Fe(OH)_2^+ \qquad [4]$$

where $Fe(OH)_2^+$ is the dominant Fe(III) species at pH 7 2 in the absence of other iron-complexing ligands Log K for reaction [4] is –6 4 which yields a $Fe(OH)_2^+$ concentration of 2 5 x 10^{-14} M at pH 7 2 This result indicates that the electrochemical cell has aided in the partial dissolution of the hematite

3 4 Ultrafiltration experiments

Figure 12 shows the results of tangential flow ultrafiltration (TFUF) analysis of 'solution-phase' $^{239,240}Pu$ activities for experimental runs at –90 (12a) and +800 mV (12b) A schematic illustration of the ultrafiltration system is presented in Figure 7

Separation of the post-0 45 µm solutions for NO03 (+800 mV) was carried out at ambient atmospheric conditions The separation protocol for NR07 (-90 mV) was considerably more elaborate In this latter case, a separate N_2-filled glove bag was set up near the primary glovebox system shown in Figure 3 A transfer container was constructed to take the post-0 45 µm solution O_2-free environment of the primary chamber to the glovebag housing the tangential flow system (Figure 7) The general redox status of transfer was monitored visually by the indicator color development

33

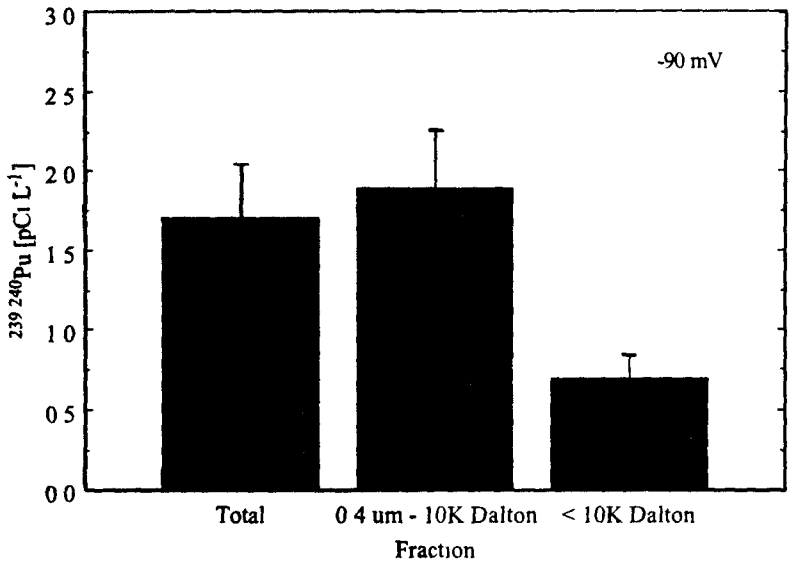
Mass balances for the ultrafiltration analyses were fair and excellent for the –90 and +800 mV analyses, respectively The error bars on the data shown in Figure 12 are an estimated propagation of errors of 20 % Mass balances were determined by replicate experiments one for total 'dissolved' $^{239,240}Pu$ and the second for the TFUF

$$\text{Mass Balance} = \frac{^{239,240}Pu_{0.45\mu m-10K\ Dalton} + {}^{239,240}Pu_{<10K\ Dalton}}{^{239,240}Pu_{total}} \qquad [5]$$

The total $^{239,240}Pu$ activity used for the mass balance for the +800 mV system is the average value of 4 85 pCi/L as discussed in Section 3 1

Results from both E_H values indicate that about 75% of the 'dissolved' $^{239,240}Pu$ is in the colloidal size range The chemical speciation of the Pu is not known

34



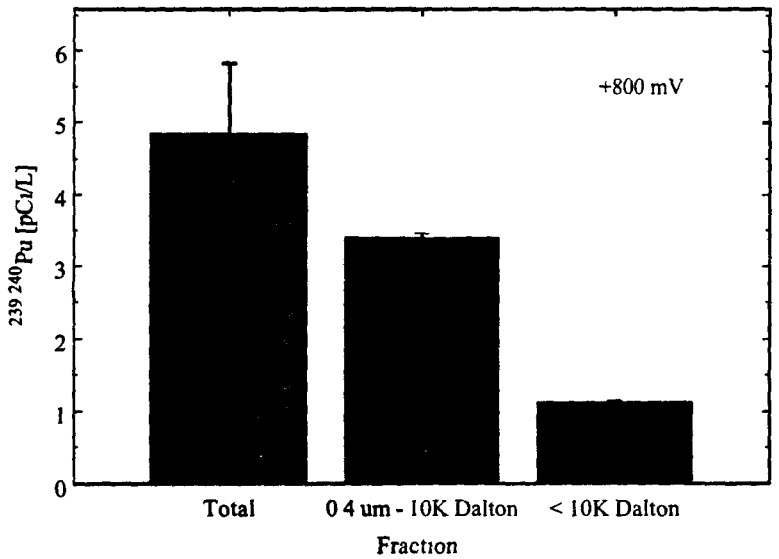


Figure 12 Comparison of total 'dissolved' $^{239,240}Pu$ (i e , 0 45μm filter passing) with its component colloidal (0 45μm to 10K Da) and < 10K Da fractions a) Cross-flow ultrafiltration of 10 g/L soil (97L1879-002) at –90mV, sample volume was 400 mL The mass balance is 1 47 ± 0 51 b) System open to the atmosphere (E_H ca +800mV), sample volume was 5 L The mass balance is 0 94 ± 0 35

35

4 0 Results and discussion: Incubation experiments

4 1 Comparison of redox values

Tables 8 and 9 compare pre-experiment E_H values determined using an E_H electrode with post-experiment E_H values for both Pond B4 and SED029 sediments For samples from Pond B4, post-experiment-measured E_H values at 2 inches depth in the sediments ranged from -171 1 to -353 4 mV The most reducing sediment condition (maximum negative E_H value) was noted in the carbon and nutrient-amended sample (Sample #3 C+, N+) For samples from SED029, measured E_H values ranged from -65 5 to -386 8 mV As with the Pond B4 experimental suite, the most reducing sediment condition for the SED029 experimental suite was noted in the carbon and nutrient-amended sample (Sample #3 C+, N+) Post-experiment E_H values for the C+, N+ amended samples for both Pond B4 and SED029 were significantly more negative in intensity (by approximately -90 to -120 mV) than those measured in other samples of the sample suites This observation suggests that reducing sediment E_H condition is markedly enhanced by combined carbon-nutrient input (C+,N+) and that the introduction of carbon and nutrients in tandem was more effective than carbon alone (C+, N0), nutrients alone (C0, N+), or no amendments (C0, N0) in establishment of reducing conditions in the sediment columns

E_H measurements of post-experiment Pond B4 incubated sample cores demonstrate significantly enhanced reducing conditions in the incubated cores as compared to E_H measurements taken at the same depth below the sediment-water interface in-situ in the field on the day of collection of the cores (Table 1) The E_H value measured at 2 in depth *in-situ* in Pond B4 on the date of sediment core acquisition was -69 3 mV, compared to -246 6 mV measured at 2 in depth for unamended Sample #4 (C0, N0) at the conclusion of the incubation experiment

Microbial mediation of enhanced reducing conditions under the conditions of the incubation experiment protocol was evidenced by 1) visual observations of increased water column turbidity in undisturbed sample incubation chambers as compared to initial conditions, 2) visual evidence of gas production (gas bubble production at the sediment-water interface) not evident under initial conditions, and 3) pronounced sulfide odor in the water columns, indicative of hydrogen sulfide production, not evident in pre-incubation samples

4 2 Water column redox condition

As inferred from iron speciation (Table 10 and Figure 13), [Fe(II)]/[Fe(III)] measurements performed on water columns post-experiment (6-11-99 for Pond B4 samples), and (6-14-99 for SED029 samples), reducing conditions were evident in the water columns (predominance of Fe(II) species), with the exception of Sample #2 (C+, N0) in which, for both the Pond B4 and SED029, the oxidized form (Fe(III)) predominated Minimum detection limits of the bipyridine method precluded assessment of the iron redox state of Matrix Controls from the Pond B4 and SED029, and of Sample #3 (C+, N+) of Pond B4

The E_H values shown in the last column of Table 10 were calculated using the following stoichiometry

$$Fe(OH)_2^+ + H^+ + e^- = FeOH^+ + H_2O \qquad [6]$$

36

Table 8 Comparison of pre-experiment E_H measurement of Pond B4 sediment taken in-situ on the day of core acquisition (3-10-99) and post-experiment E_H measurements of post-incubation cores All measurements were made at 2 inches depth in the sediment column relative to the sediment-water interface using calibrated platinum E_H electrodes

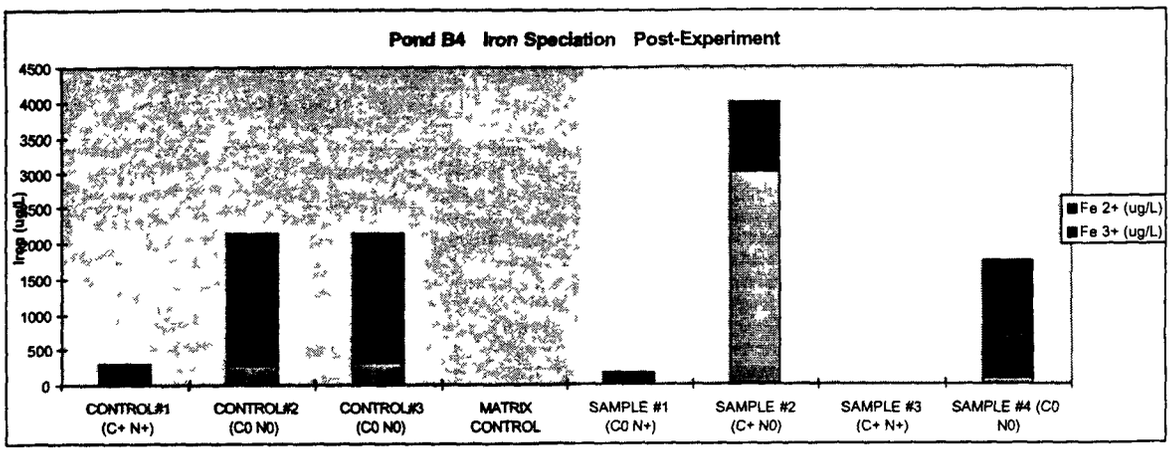
Sample	Date of E_H measurement	Depth below sediment/water interface	E_h (mV)
Pond B4 Irradiated Control #1 (C+, N+)	6-11-99, Post-Experiment	2 inches	-171 1
Pond B4 Irradiated Control #2 (C0, N0)	6-11-99, Post-Experiment	2 inches	-208 2
Pond B4 Irradiated Control #3 (C0, N0)	6-11-99, Post-Experiment	2 inches	-227 2
Pond B4 Sample #1 (C0, N+)	6-11-99, Post-Experiment	2 inches	-267 9
Pond B4 Sample #2 (C+, N0)	6-11-99, Post-Experiment	2 inches	-263 1
Pond B4 Sample #3 (C+, N+)	6-11-99, Post-Experiment	2 inches	-353 4
Pond B4 Sample #4 (C0, N0)	6-11-99, Post-Experiment	2 inches	-246 6
Pond B4 In-situ sample	3-10-99, Pre-experiment in-situ measurement taken on day-of-core acquisition	2 inches	-69 3

Table 9 Post-experiment E_H measurements of post-incubation SED029 cores No in-situ E_h measurements were made in the field on the day of core acquisition All measurements were made at 2 inches depth in the sediment column relative to the sediment-water inter face using calibrated platinum E_H electrodes

Sample	Date of E_H measurement	Depth below sediment/water interface	E_h (mV)
SED029 Irradiated Control #1 (C+, N+)	6-14-99, Post-Experiment	2 inches	-144 3
SED029 Irradiated Control #2 (C0, N0)	6-14-99, Post-Experiment	2 inches	-65 5
SED029 Irradiated Control #3 (C0, N0)	6-14-99, Post-Experiment	2 inches	-94 6
SED029 Sample #1 (C0, N+)	6-14-99, Post-Experiment	2 inches	-246 1
SED029 Sample #2 (C+, N0)	6-14-99, Post-Experiment	2 inches	-267 7
SED029 Sample #3 (C+, N+)	6-14-99, Post-Experiment	2 inches	-386 8
SED029 Sample #4 (C0, N0)	6-14-99, Post-Experiment	2 inches	-233 6

37

coupled to the assumption that, for the pH values of interest, $Fe(III)_T \approx [Fe(OH)_2^+]$ and $Fe(II)_T \approx [FeOH^+]$ Note that water-column E_H values are considerably less reducing than are the sediment values determined with the E_H electrode



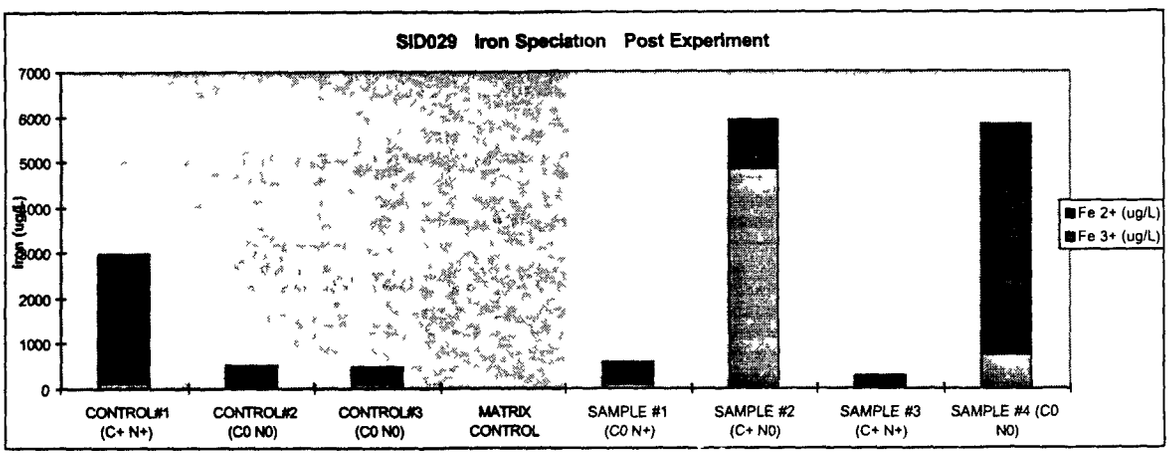


Figure 13 Iron oxidation-state distribution at the cessation of the incubation experiments Fe(II) was determined by the bi-pyridine method and Fe(III) by difference ($Fe_T - Fe(II)$)

38

Table 10 Iron oxidation-state distribution at the cessation of the incubation experiments (6-11-99 for the Pond B4 experimental suite, 6-14-99 for the SED029 experimental suite) Fe total and Fe (II) were determined by the colorometric bipyridine method and Fe(III) by difference between Fe total and Fe(II)

Incubation experiment sample designation	Total Iron (µg/L)	Iron (II) (µg/L)	Iron (III) (µg/L)	pH	Fe(II)/Fe(total)	E_H[1] (mV)
Pond B4 Irradiated Control #1 (C+, N+)	295	295	0	6 82	1 00	141
Pond B4 Irradiated Control #2 (C0, N0)	2155	1865	290	6 8	0 87	146
Pond B4 Irradiated Control #3 (C0, N0)	2155	1845	310	6 83	0 86	144
Pond B4 Matrix Control	0	0	0	7 58	-	
Pond B4 Sample #1 (C0, N+)	168	120	48	6 78	0 71	152
Pond B4 Sample #2 (C+, N0)	3997	993	3004	6 93	0 25	170
Pond B4 Sample #3 (C+, N+)	0	0	0	7 15	-	
Pond B4 Sample #4 (C0, N0)	1758	1670	88	6 78	0 95	144
SED029 Irradiated Control #1 (C+, N+)	2980	2832	148	6 2	0 95	179
SED029 Irradiated Control #2 (C0, N0)	538	538	0	6 26	1 00	174
SED029 Irradiated Control #3 (C0, N0)	488	353	135	6 31	0 72	179
SED029 Matrix Control	0	0	0	7 3	-	
SED029 Sample #1 (C0, N+)	558	488	110	6 42	0 87	168
SED029 Sample #2 (C+, N0)	5910	1075	4835	6 61	0 18	197
SED029 Sample #3 (C+, N+)	323	293	30	6 82	0 91	143
SED029 Sample #4 (C0, N0)	5812	5047	765	6 23	0 87	179

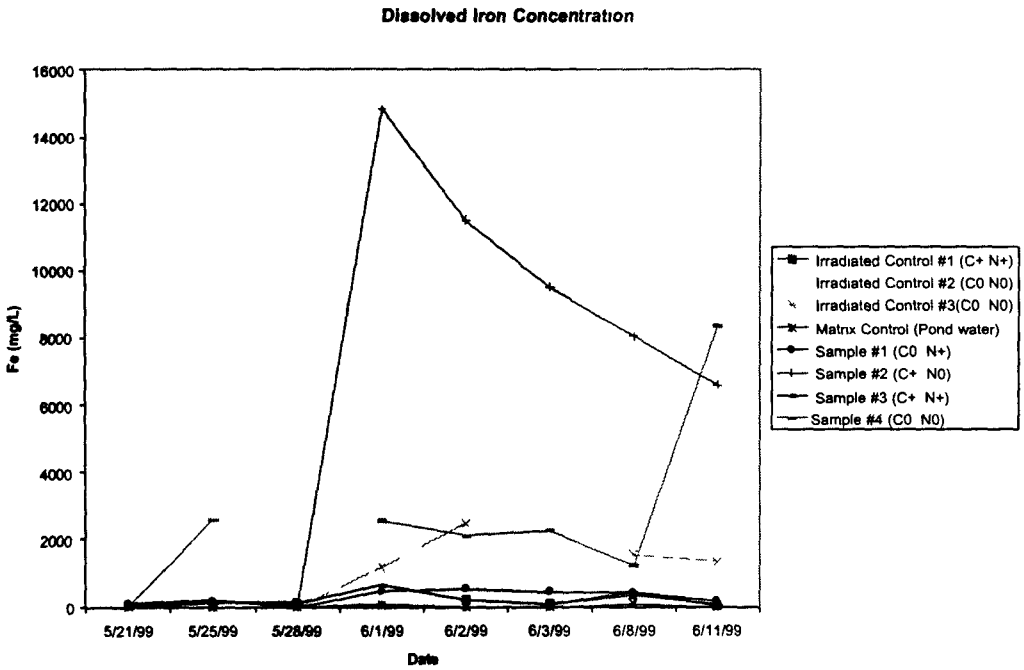
[1]Determined through application of eq 6 using the pH value of column 5

4 3 Irradiated control integrity

Several observations and measurements indicate that the integrity of the sterile controls (Irradiated Control #1, Irradiated Control #2 and Irradiated Control #3) for both the Pond B4 and SED029 experimental suites were compromised at some point during the period 28 May,1999-1 June,1999 (7 days to 10 days after initiation of the experiment)

1 The water columns of the irradiated controls, initially clear visually as compared to the pronounced visual turbidity of the Sample water columns, began to show increasing turbidity on 28 May which increased during the course of the experiment
2 Pronounced sulfide odor (indicative of microbial activity of sulfate reducing bacteria in suboxic conditions), previously not noted, became apparent in all of the irradiated controls in the 1 June sampling
3 'dissolved' iron and manganese concentrations in the water columns of the irradiated controls, initially very low, showed a pronounced increase between the 28 May and 1 June samplings for Pond B4, and between the 21 May and 1 June samplings for SED029 (Figures 14 and 15 for Pond B4 and SED029, respectively, Tables 11 through 14)

39



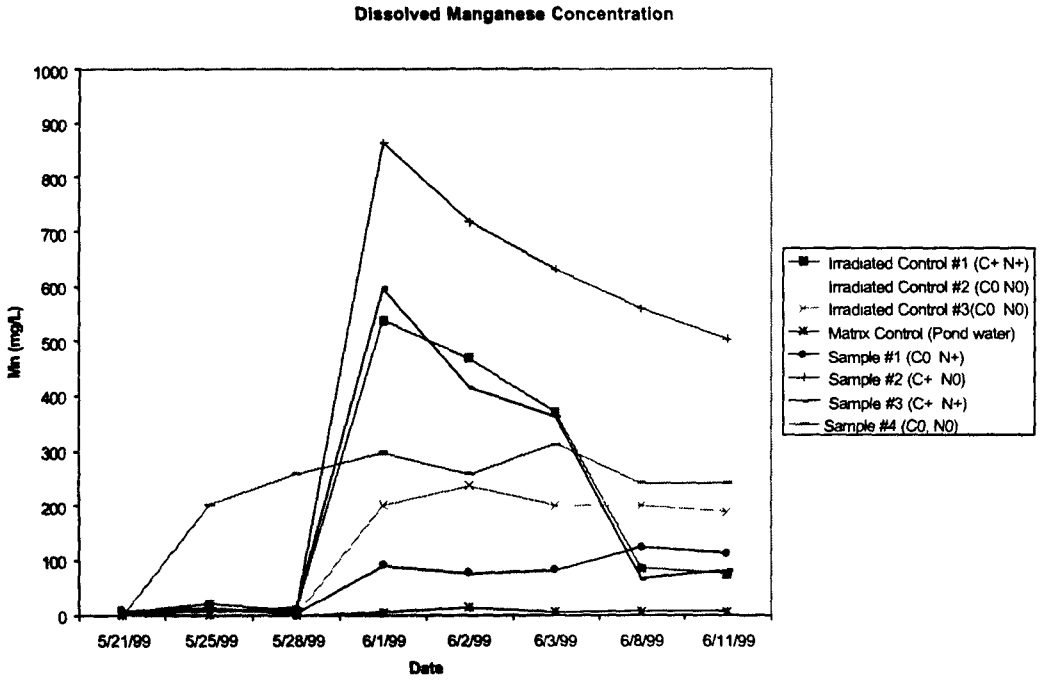
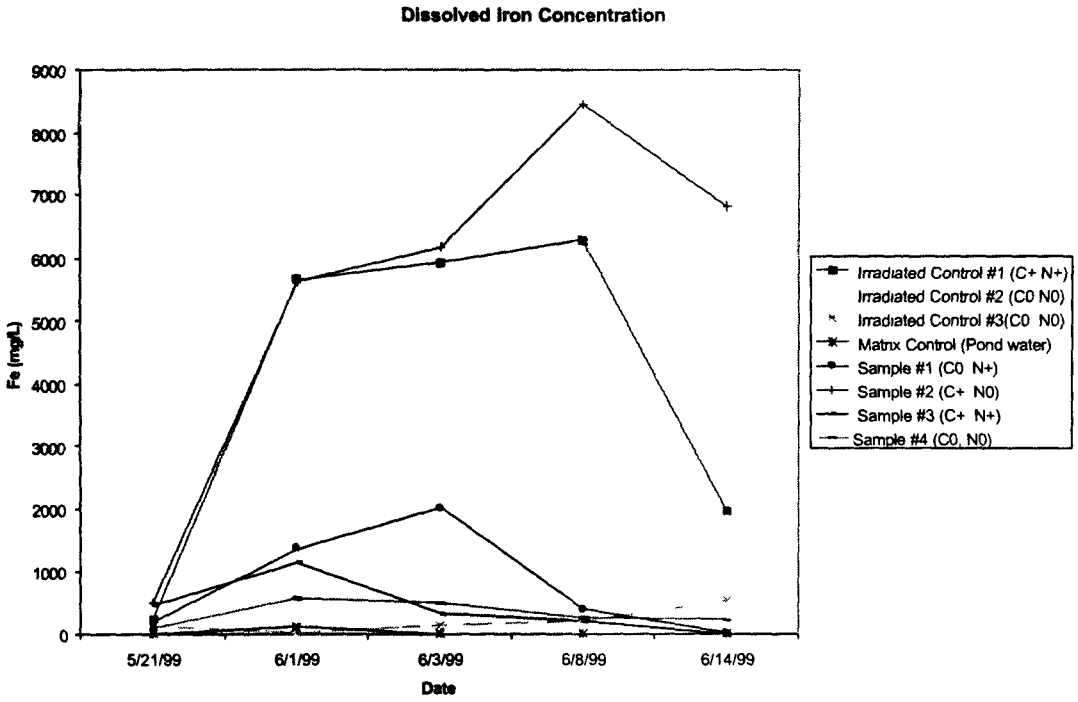


Figure 14 a) 'Dissolved' iron and b) manganese as a function of date for Pond B4 incubation experiments

40



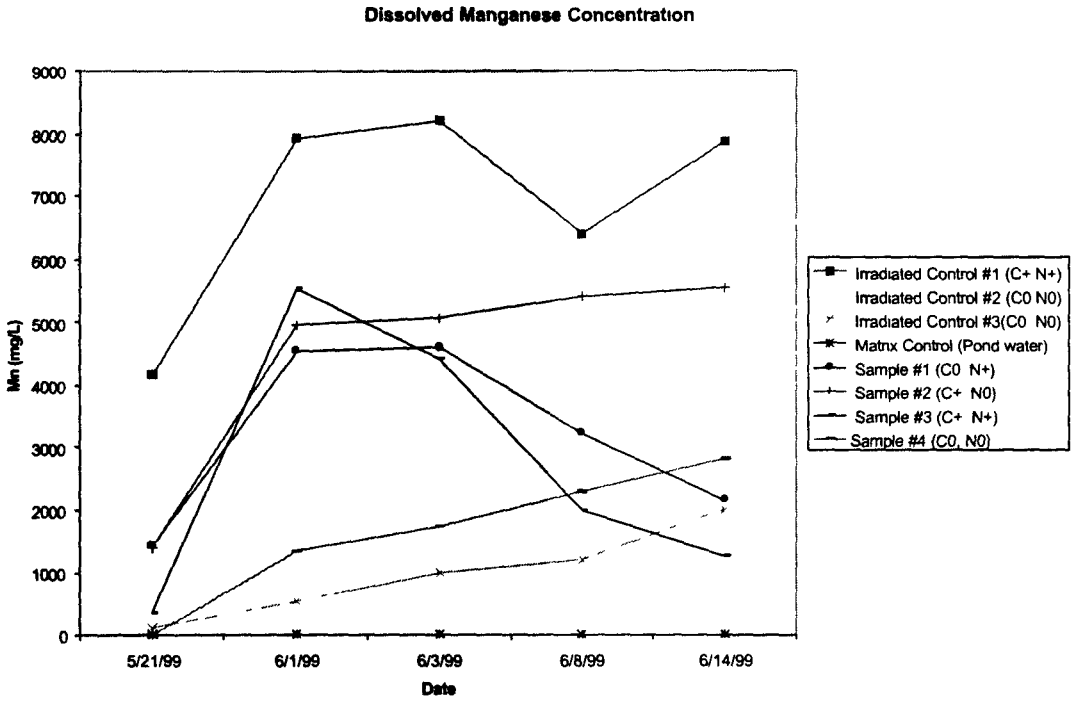


Figure 15 a) 'Dissolved' iron and b) manganese as a function of date for SED029 incubation experiments

41

The source of apparent delayed contamination the irradiated controls is unclear It is conceivable that the original irradiation dose was insufficient to completely sterilize the cores, and left some portion of the microbial population viable, or, it is possible that cross-contamination of microbial populations from active sample cores to sterile irradiated controls occurred during water sample acquisition, or that contamination of irradiated controls occurred at some point during initial core handling steps Given the recognized difficulty of establishing complete sterilization of bulk soil/sediment samples, and the steps taken to avoid cross contamination of samples, it seems probable, although not demonstrable, that incomplete initial sterilization was responsible for the delayed loss in sterile integrity

Given the apparent loss of sterile integrity of the irradiated controls, these samples were dismissed as valid controls for microbial activity in both the Pond B4 and SED029 experimental suites Nevertheless, they continued to be sampled during the remainder of the experiment to ascertain any similarities/differences in chemical/redox behavior between amended and unamended controls, and between the delayed-microbial activity compromised controls and the experimental samples, which exhibited microbial activity earlier in the time course of the experiment

4 4 Manganese and Iron dissolution

Under the strongly reducing sediment conditions established during the incubation, significant solubilization of manganese and iron in the sample water columns were measured as compared to initial conditions and to matrix controls

4 4 1 Pond B4 Manganese and Iron dissolution

'Dissolved' manganese and iron condition of the water columns for the Pond B4 experimental suite are presented in Table 11 (Mn), Figure 14b (Mn) and Table 12 (Fe) and Figure 14a (Fe)

1) Observations regarding the status of manganese and iron dissolution as a function of incubation time course
   a 'Dissolved' Mn and Fe concentrations in the matrix control are generally low compared to concentrations in the sediment-contacted sample matrices, establishing that the source of the 'dissolved' Mn and Fe in the sample water columns was the sediment
   b 'Dissolved' manganese concentrations in the irradiated controls and in Samples 1,2 and 3 remained relatively low until 11 days into the incubation, at which time concentrations increased sharply
   c Elevated 'dissolved' iron concentrations in the irradiated controls and in Samples 1,2 and 3 became apparent earlier in the incubation time course than did elevated manganese concentrations, reflecting dissolution of Fe (oxy)hydroxides at less reducing (less negative E_H) conditions than for Mn (oxy)hydroxides
   d For both manganese and iron, the unamended sample (Sample #4 C0, N0) showed dissolution earlier in the incubation time course, at concentrations that remained relatively more constant over the course of the incubation than those from Samples 1, 2 and 3

42

2) Observations regarding the effect of carbon and nutrient input on manganese and iron dissolution (relative to the unamended sample C0, N0)
   a Nutrient additions alone (C0, N+) appear to inhibit dissolution of manganese and iron
   b Carbon addition alone (C+, N0) appears to facilitate dissolution of manganese and iron
   c Carbon and nutrients, amended in tandem (C+, N+), appear to facilitate dissolution of manganese and iron to a greater extent than carbon addition alone (C+, N0)

4 4 2 SED020 Manganese and Iron dissolution

'Dissolved' manganese and iron condition of the water columns for the SED029 experimental suite are presented in Table 14 (Fe), and Figure 15a (Fe), Table 13 (Mn), Figure 15b (Mn)

1) Observations regarding the status of manganese and iron dissolution as a function of incubation time course
   a As compared to the Pond B4 experimental suite, 'dissolved' Mn and Fe appeared in the water columns of the SED029 samples earlier in the incubation time course 'Dissolved' Mn
   concentrations in the SED029 samples were significantly higher than those measured in the Pond B4 samples
   b 'Dissolved' Mn and Fe concentrations in the matrix control are generally low compared to concentrations in the sediment-contacted Sample matrices, establishing that the source of the 'dissolved' Mn and Fe in the sample water columns was the sediment
2) Observations regarding the effect of carbon and nutrient input on manganese and iron dissolution (relative to the unamended sample C0, N0)
   a Nutrient additions, either alone (C0, N+) or in tandem with carbon additions (C+, N+) appear to facilitate early dissolution of manganese and iron, although the effect diminishes rapidly over the course of the incubation as Mn and Fe concentrations fall
   b Carbon addition alone (C+, N0) appears to facilitate dissolution of manganese and iron, and to maintain dissolved concentrations of these elements at relatively stable levels over the course of the experiment
   c Carbon and nutrients, amended in tandem (C+, N+), appear to facilitate early dissolution of manganese and iron and an accelerated drop in concentration over the course of the incubation

4 5 Total Organic Carbon Analysis

Results of total organic carbon (TOC) analysis performed at intervals on the water columns of the experimental sample suite are presented in Table 15 and Figure 16a for the Pond B4 experiment, and in Table 16 and FIGURE 16b for the SED029 experiment Elevated TOC concentrations in the C+ amended samples reflect lactate additions to these samples TOC concentration in the Pond B4 matrix control reflects native organic carbon content of the Pond B4 water The matrix control for SED029 was laboratory Nanopure grade de-ionized water Pre-experiment measures of TOC in amended and unamended matrix waters were made on 5-20-99, and are included in Tables 15 and 16 as a baseline for initial conditions

43

Table 11 Results of 'dissolved' (< 0 45 µm) manganese analysis of Pond B4 incubation experiment water column samples

Incubation experiment sample designation	5/21/99 Mn (µg/L)	5/25/99 Mn (µg/L)	5/28/99 Mn (µg/L)	6/1/99 Mn (µg/L)	6/2/99 Mn (µg/L)	6/3/99 Mn (µg/L)	6/8/99 Mn (µg/L)	6/11/99 Mn (µg/L)
Pond B4 Irradiated Control #1 (C+, N+)	4	20	9	539	469	371	86	75
Pond B4 Irradiated Control #2 (C0, N0)	1	2	0	180	222	189	225	229
Pond B4 Irradiated Control #3 (C0, N0)	1	2	1	202	238	202	200	189
Pond B4 Matrix Control	1	0	0	3	13	5	7	6
Pond B4 Sample #1 (C0, N+)	9	14	2	89	76	81	123	114
Pond B4 Sample #2 (C+, N0)	6	9	6	862	719	632	561	505
Pond B4 Sample #3 (C+, N+)	4	9	12	596	416	362	66	81
Pond B4 Sample #4 (C0, N0)	0	204	259	297	259	312	243	243

Pre-Incubation experiment matrix water designation	5/20/99 Mn (µg/L)
Pond B4 Pre-experiment sample (C0, N+)	0
Pond B4 Pre-experiment sample (C+, N0)	2
Pond B4 Pre-experiment sample (C+, N+)	1
Pond B4 Pre-experiment sample (C0, N0)	1

44

Table 12 Results of 'dissolved' (< 0 45 µm) analysis of iron in Pond B4 incubation experiment water column samples

Incubation experiment sample designation	5/21/99 Fe (µg/L)	5/25/99 Fe (µg/L)	5/28/99 Fe (µg/L)	6/1/99 Fe (µg/L)	6/2/99 Fe (µg/L)	6/3/99 Fe (µg/L)	6/8/99 Fe (µg/L)	6/11/99 Fe (µg/L)
Pond B4 Irradiated Control #1 (C+, N+)	0	116	148	-	216	70	365	50
Pond B4 Irradiated Control #2 (C0, N0)	0	5	4	1100	1990	1860	2640	3090
Pond B4 Irradiated Control #3 (C0, N0)	1	10	3	1160	2480	-	1540	1321
Pond B4 Matrix Control	0	1	0	64	0	0	91	0
Pond B4 Sample #1 (C0, N+)	107	202	11	463	519	443	409	154
Pond B4 Sample #2 (C+, N0)	73	156	74	14800	11500	9510	8020	6597
Pond B4 Sample #3 (C+, N+)	3	142	122	624	218	50	398	32
Pond B4 Sample #4 (C0, N0)	1	2570	2740	2550	2090	2250	1220	8365

Pre-Incubation experiment matrix water designation	5/20/99 Fe (µg/L)
Pond B4 Pre-experiment sample (C0, N+)	0
Pond B4 Pre-experiment sample (C+, N0)	2
Pond B4 Pre-experiment sample (C+, N+)	4
Pond B4 Pre-experiment sample (C0, N0)	0

45

Table 13 Results of 'dissolved' (< 0 45 μm) Manganese analysis of SED029 incubation experiment water column samples

Incubation experiment sample designation	5/21/99 Mn (mg/L)	6/1/99 Mn (mg/L)	6/3/99 Mn (mg/L)	6/8/99 Mn (mg/L)	6/14/99 Mn (mg/L)
SED029 Irradiated Control #1 (C+, N+)	4160	7920	8210	6410	7864
SED029 Irradiated Control #2 (C0, N0)	66	402	900	1200	1595
SED029 Irradiated Control #3 (C0, N0)	128	548	1000	1200	2010
SED029 Matrix Control	0	0	0	0	0
SED029 Sample #1 (C0, N+)	1440	4550	4600	3240	2163
SED029 Sample #2 (C+, N0)	1390	4950	5080	5410	5557
SED029 Sample #3 (C+, N+)	373	5530	4420	2000	1259
SED029 Sample #4 (C0, N0)	4	1340	1740	2310	2829

Pre-Incubation experiment matrix water designation	5/20/99 Mn (mg/L)
SED029 Pre-experiment sample (C0, N+)	0
SED029 Pre-experiment sample (C+, N0)	1
SED029 Pre-experiment sample (C+, N+)	1
SED029 Pre-experiment sample (C0, N0)	0

46

Table 14 Results of 'dissolved' (< 0 45 um) Iron analysis of SED029 incubation experiment water column samples

Incubation experiment sample designation	5/21/99 Fe (mg/L)	6/1/99 Fe (mg/L)	6/3/99 Fe (mg/L)	6/8/99 Fe (mg/L)	6/14/99 Fe (mg/L)
SED029 Irradiated Control #1 (C+, N+)	229	5660	5930	6280	1974
SED029 Irradiated Control #2 (C0, N0)	6	65	143	278	148
SED029 Irradiated Control #3 (C0, N0)	101	34	144	217	518
SED029 Matrix Control	3	112	0	0	0
SED029 Sample #1 (C0, N+)	177	1350	2020	391	12
SED029 Sample #2 (C+, N0)	510	5630	6180	8450	6822
SED029 Sample #3 (C+, N+)	454	1150	317	217	0
SED029 Sample #4 (C0, N0)	95	558	488	257	229
Pre-Incubation experiment matrix water designation	5/20/99 Fe (mg/L)				
SED029 Pre-experiment sample (C0, N+)	1				
SED029 Pre-experiment sample (C+, N0)	1				
SED029 Pre-experiment sample (C+, N+)	10				
SED029 Pre-experiment sample (C0, N0)	0				

4 5 1 Pond B4 Experimental Suite

Time course TOC analysis of incubated Pond B4 sediment-water columns suggest

1 For the unamended sample (Sample #4 C0, N0), the initial TOC of the matrix water increased from 39 mg/L to 62 mg/L after one day of exposure to the incubated sediment, increased further to 95 mg/L after 4 days incubation, then showed a moderate general increase and stabilization until the conclusion of the experiment This observation is interpreted to reflect initial rapid dissolution of carbon under the elevated temperature conditions established during the incubations, followed by relative steady state, with no evidence of microbial carbon limitation in the native core or measurably accelerated use of native carbon sources by existing microbial populations

2 For the carbon and nutrient-amended sample (Sample #3 C+, N+), the initial amended TOC of the matrix water decreased from 2475 mg/L to 1685 mg/L after one day of exposure to the incubated sediment, then showed a general stabilization of TOC concentration with time until the end of the experiment This observation suggests rapid facultative uptake of introduced carbon (lactate) under the conditions of the incubation, followed by relative steady state of 'dissolved' TOC in the water column. A similar pattern was noted for the carbon-alone-amended sample For the carbon amended sample (Sample #2 C+,N0), the initial amended TOC of the matrix water decreased from 2365 mg/L to 1585 mg/L after one day of exposure to the incubated sediment, then showed relative stabilization of dissolved TOC over the course of the experiment

3 'Dissolved' TOC in the water column of the nutrient-only-amended sample (Sample #1 C0, N+) were relatively constant over the course of the incubation, suggesting that nutrient addition unaccompanied by carbon (lactate) introduction had no measurable effect on native carbon utilization or dissolution

4 5 2 SED029 Experimental Suite

Time course TOC analysis of incubated SED029 sediment-water columns suggest

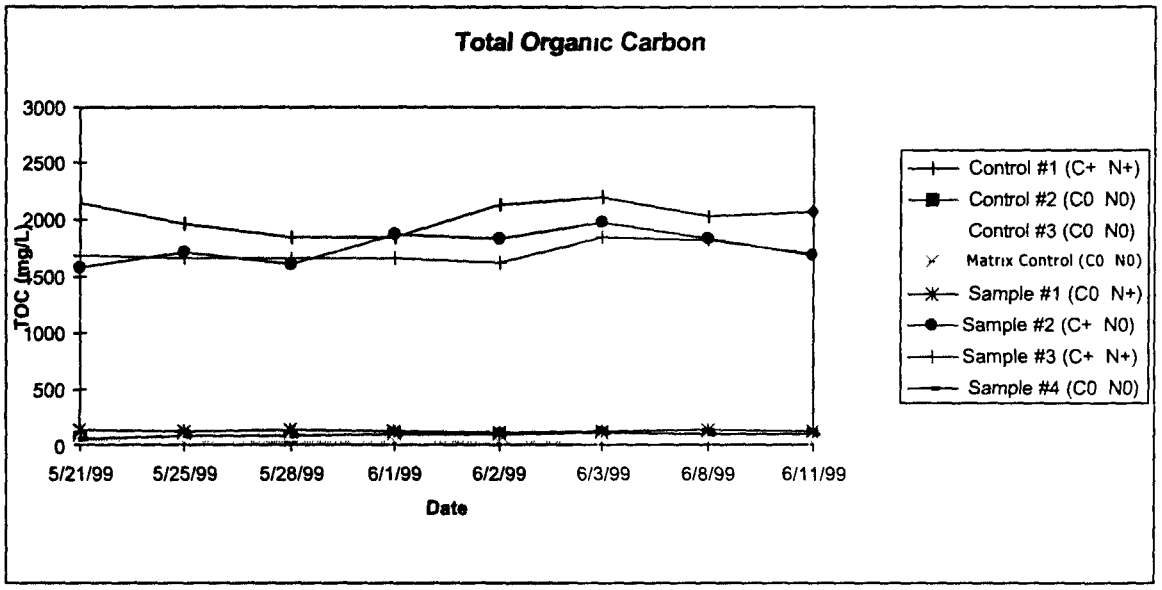
1 For the unamended sample (Sample #4 C0, N0), the initial TOC of the matrix water increased from 0 mg/L to 51 mg/L after one day of exposure to the incubated sediment, remained relatively stable over the first 12 days of the incubation, then showed a moderate increase near conclusion of the experiment This observation is interpreted to reflect initial rapid dissolution of carbon under the elevated temperature conditions established during the incubations, followed by relative steady state, with no evidence of microbial carbon limitation in the native core or measurably accelerated use of native carbon sources by existing microbial populations

2 For the carbon and nutrient-amended sample (Sample #3 C+, N+), the initial amended TOC of the matrix water decreased from 2015 mg/L to 1295 mg/L after one day of exposure to the incubated sediment, followed by a general stabilization of TOC concentration with time until the end of the experiment This observation suggests rapid facultative uptake of introduced carbon (lactate) under the conditions of the incubation, followed by relative steady state of 'dissolved' TOC in the water column A similar pattern was noted for the carbon-alone-amended sample For the carbon amended sample (Sample #2 C+, N0), the initial amended TOC of the matrix water decreased from 2175 mg/L to 1605 mg/L after one day of exposure to

48

the incubated sediment, then showed relative stabilization of 'dissolved' TOC over the course of the experiment

3 'Dissolved' TOC in the water column of the nutrient-only-amended sample (Sample #1 C0, N+) were decreased from 147 mg/L to 64 mg/L over the first day of the incubation, then stabilized, suggesting that nutrient addition stimulated microbial carbon utilization this sample



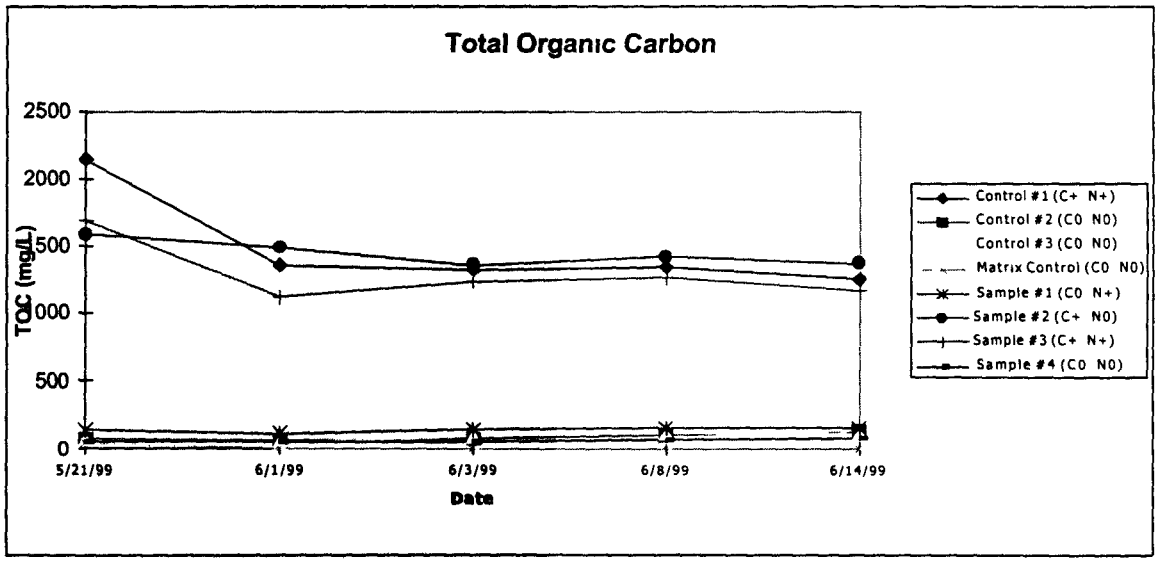


Figure 16 Total organic carbon (TOC) as a function of date for the Pond B4 (16a) and SED029 (16b) incubation experiments

49

Table 15 Results of 'dissolved' (< 0 45 um) Total Organic Carbon (TOC) analysis of Pond B4 incubation experiment water column samples

Incubation experiment sample designation	5/21/99 TOC (mg/L)	5/25/99 TOC (mg/L)	5/28/99 TOC (mg/L)	6/1/99 TOC (mg/L)	6/2/99 TOC (mg/L)	6/3/99 TOC (mg/L)	6/8/99 TOC (mg/L)	6/11/99 TOC (mg/L)
Pond B4 Irradiated Control #1 (C+, N+)	2140	1965	1840	1845	2135	2195	2020	2070
Pond B4 Irradiated Control #2 (C0, N0)	83	90	87	104	101	116	99	101
Pond B4 Irradiated Control #3 (C0, N0)	75	92	100	91	98	93	103	111
Pond B4 Matrix Control	49	46	44	41	44	45	39	46
Pond B4 Sample #1 (C0, N+)	139	137	148	133	114	128	140	138
Pond B4 Sample #2 (C+, N0)	1585	1715	1600	1875	1830	1975	1825	1680
Pond B4 Sample #3 (C+, N+)	1685	1655	1655	1655	1615	1840	1810	1695
Pond B4 Sample #4 (C0, N0)	62	95	96	102	105	114	105	104
Pre-Incubation experiment matrix water designation	5/20/99 TOC (mg/L)							
Pond B4 Pre-experiment sample (C0, N+)	163							
Pond B4 Pre-experiment sample (C+, N0)	2365							
Pond B4 Pre-experiment sample (C+, N+)	2475							
Pond B4 Pre-experiment sample (C0, N0)	39							

50

Table 16 Results of 'dissolved' (< 0 45 um) Total Organic Carbon (TOC) analysis of SID 029 incubation experiment water column samples

Incubation experiment sample designation	5/21/99 TOC (mg/L)	6/1/99 TOC (mg/L)	6/3/99 TOC (mg/L)	6/8/99 TOC (mg/L)	6/14/99 TOC (mg/L)
SED029 Irradiated Control #1 (C+, N+)	1785	1360	1320	1350	1255
SED029 Irradiated Control #2 (C0, N0)	33	68	85	111	127
SED029 Irradiated Control #3 (C0, N0)	37	61	92	115	120
SED029 Matrix Control	0	0	0	0	0
SED029 Sample #1 (C0, N+)	64	117	139	156	158
SED029 Sample #2 (C+, N0)	1605	1485	1355	1420	1370
SED029 Sample #3 (C+, N+)	1295	1115	1240	1265	1170
SED029 Sample #4 (C0, N0)	51	62	63	77	78
Pre-Incubation experiment matrix water designation	5/20/99 TOC (mg/L)				
SED029 Pre-experiment sample (C0, N+)	147				
SED029 Pre-experiment sample (C+, N0)	2175				
SED029 Pre-experiment sample (C+, N+)	2015				
SED029 Pre-experiment sample (C0, N0)	0				

51

4 6 Post-incubation ^{239,240}Pu activities

Results of ^{239,240}Pu analysis performed post-incubation on the water columns of experimental sample suites Pond B4 and SED029 are summarized in Table 17 Table 18 presents the summary data for sediment core digestions Note that the specific ^{239,240}Pu activities are quite low Such low activities may preclude definitive conclusions about the 'solubilization' of Pu from these cores In other words, the Pu source term yielded a bias against solubility enhancement

4 6 1 Pond B4

'Dissolved' ^{239,240}Pu activities measured post-incubation in the water columns of the Pond B4 sample suite reveal no indication of redox-influenced plutonium dissolution from the sediments to the water column under the reducing sediment conditions established in this experiment Measured plutonium activities were uniformly low or not detected, and in no case did reported ^{239,240}Pu activities exceed the sample specific MDA (minimum detection limit)

4 6 2 SED029

'Dissolved' ^{239,240}Pu activities measured post-incubation in the water columns of the Pond B4 sample suite offer no conclusive evidence of plutonium dissolution from the sediments to the water column under the reducing conditions of this experiment With the exception of Sample #4 (C0, N0), 'dissolved' ^{239,240} plutonium activities did not exceed the sample specific MDA In the single sample where measured ^{239,240}Pu activity exceeded the MDA, Sample#4 (C0, N0) water column ^{239,240}Pu activity was low, measured at 0 123 pCi/L, with a counting uncertainty of 0 0185 pCi/L, and a minimum detection activity of 0 0962 pCi/L The lack of a native matrix water control precludes any comparison with initial, ephemeral, water column condition at the SID sampling site However, the inclusion of a Nanopure-grade de-ionized water matrix control allows comparison of the incubated core-contacted aqueous phases with an aqueous phase not influenced by sediment reactions With the exception of Sample #4, results of this experiment demonstrate no measurable difference in post-experiment 'dissolved' ^{239,240}Pu activities between the de-ionized water matrix control and the variously-amended, de-ionized-water-based, sample water columns If the ^{239,240}Pu activity measured in the water column of Sample #4 represents E_H-driven reductive dissolution of sediment plutonium, the effect is negligible and is considered unsubstantive given the counting uncertainty and the proximity of the result to the minimum detection activity

5. Summary.

1) Results of electrochemical cell and core incubation experiments do not provide support for the hypothesis that reducing conditions in soil/water systems at Rocky Flats Environmental Technology Site yield enhanced ^{239,240}Pu solubility

Evidence: The following figure (Figure 17) shows the location of the data sets in E_H/pH 'space' Data for the electrochemical cell are summarized in Figures 10 and 11, Table 7, data for the incubations is presented in Table 17

Table 17 ^{239,240}Pu activities measured post-experiment in the water columns of the Pond B4 and SED029 incubation suites MDA signifies minimum detection limit, expressed as pCi/L Table 5 lists the experimental trail characteristics

Exper Trial Name	Sample mass (g)	QC status	V_E (ml)	Analysis Vol (ml)	Tracer Added Bq	Tracer Cnts	^{239,240}Pu Cnts Counts	^{239,240}Pu in tracer in tracer	Count time (m)	Sample activity pCi L^{-1}	Sample activity (pCi/g)	Percent of total of	Sample activity (Bq/L)	Counting Uncert (1σ)(Bq/L)	Sample Activity (pCi/L)	Count Uncert (1σ)(pCi/L)	Detec Effic	Yield (%)	Sample MDA (pCi L^{-1})
B4 MC	200	matrix blank	300	249	0 2707	4172	41	53	1000	-0 087	-0 00011	-0 006%	-0 0032	0 0034	-0 087	0 092	0 3152	81 5	0 092
B4 S2	200		300	249	0 2707	4061	47	52	1000	-0 036	-0 00004	-0 002%	-0 0013	0 0035	-0 036	0 095	0 3152	79 3	0 095
B4 S3	200		300	249	0 2707	4260	56	55	1000	0 010	0 00001	0 001%	0 0004	0 0033	0 010	0 090	0 3152	83 2	0 090
B4 S4	200		300	249	0 2707	3882	46	50	1000	-0 028	-0 00003	-0 002%	-0 0010	0 0037	-0 03	0 10	0 3152	75 8	0 099
B4 IC 1	200	irrad control	300	249	0 2707	3703	49	47	1000	0 013	0 00002	0 001%	0 0005	0 0038	0 01	0 10	0 3152	72 3	0 10
B4 IC 2	200	irrad. control	300	249	0 2707	212	1	3	1000	-0 237	-0 00030	-0 016%	-0 0088	0 0672	-0 2	1 8	0 3152	4 1	1 8
B4 IC 3	200	irrad control	300	249	0 2707	3335	37	43	1000	-0 050	-0 00006	-0 003%	-0 0019	0 0043	-0 05	0 12	0 3152	65 1	0 12
B4 S1	200		300	249	0 2707	3841	43	49	1000	-0 047	-0 00006	-0 003%	-0 0017	0 0037	-0 05	0 10	0 3152	75 0	0 10
BLK 18	200	reagent blank	300	249	0 2707	3314	39	42	1000	-0 030	-0 00004		-0 0011	0 0043	-0 03	0 12	0 3152	64 7	0 12
SED029 IC1	200	irrad. control	300	249	0 1417	2159	34	28	1000	0 045	0 00006	0 006%	0 0017	0 0035	0 045	0 093	0 3152	80 6	0 093
SED029 IC2	200	irrad control	300	249	0 1417	2204	30	28	1000	0 012	0 00002	0 002%	0 0005	0 0034	0 012	0 091	0 3152	82 2	0 091
SED029 IC3	200	irrad control	300	249	0 1417	2170	34	28	1000	0 044	0 00005	0 006%	0 0016	0 0034	0 044	0 093	0 3152	81 0	0 093
SED029 MC	200	process blank	300	249	0 1417	1776	18	23	1000	-0 041	-0 00005	-0 005%	-0 0015	0 0042	-0 04	0 11	0 3152	66 3	0 11
SED029 S1	200		300	249	0 1417	2325	34	30	1000	0 028	0 00003	0 004%	0 0010	0 0032	0 028	0 087	0 3152	86 8	0 087
SED029 S2	200		300	249	0 1417	2231	28	29	1000	-0 004	0 00000	-0 001%	-0 0001	0 0033	-0 004	0 090	0 3152	83 3	0 090
SED029 S3	200		300	249	0 1417	2209	35	28	1000	0 047	0 00006	0 006%	0 0017	0 0034	0 047	0 091	0 3152	82 4	0 091
SED029 S4	200		300	249	0 1417	2167	45	28	1000	0 123	0 00015	0 016%	0 0045	0 0034	0 123	0 093	0 3152	80 9	0 093
SED029 CC	200	temp control	300	249	0 1417	2618	37	34	1000	0 021	0 00003	0 003%	0 0008	0 0028	0 021	0 077	0 3152	97 7	0 077
B4 CC	200	temp control	300	249	0 1417	2697	30	35	1000	-0 026	-0 00003	-0 002%	-0 0010	0 0028	-0 026	0 075	0 3152	100 6	0 075

MC matrix blank, S_I sample, IC irradiation control, CC temperature control

53

Table 18 Summary of core material digestions

Sample source	Sample ID	Digest Method	Count Date	Sample Mass (g)	Tracer Added (Bq)	Tracer Cnts	$^{239,240}Pu$ Cnts	Count Time (m)	Sample Activity (Bq/g)	Count Uncert (1σ)(Bq/g)	Sample Activity (pCi/g)	Count Uncert (1σ)(pCi/g)	Detect Effic	Yield (%)	Avg Act (pCi/g)	Std Dev (pCi/g)	% Std Dev	Sample MDA (pCi/g)
B4 POND	NR11	total	9/20/99	3 4276	0 2014	1648	2383	1000	0 0850	0 0027	2 296	0 074	0 315	43 3				0 013
B4 POND	NR12	total	9/20/99	3 6224	0 2014	1633	4497	1000	0 1531	0 0044	4 14	0 12	0 315	42 9				0 012
B4 POND	B41	total	10/1/99	1 5114	0 2046	1935	1062	1000	0 0743	0 0028	2 008	0 077	0 315	50 0				0 025
	B4 2	total	10/1/99	1 5619	0 2046	2137	996	1000	0 0611	0 0023	1 650	0 063	0 315	55 2				0 022
	B4 3	total	10/1/99	1 623	0.2046	2330	1199	1000	0 0649	0 0023	1 753	0 062	0 315	60 2				0 019
															1 80	**0 18**	10 2	
SED 029	SED 1	total	10/2/99	1 1881	0 2046	1588	300	1000	0 0325	0 0020	0 879	0 055	0 315	41 0				0 038
	SED 2	total	10/2/99	1 8617	0 2046	2465	986	1000	0 0440	0 0017	1 188	0 045	0 315	63 7				0 016
	SED 3	total	10/2/99	1 7847	0 2046	2408	598	1000	0 0285	0 0013	0 769	0 035	0 315	62 2				0 017
															0 95	**0 22**	23 0	
BLANK	RFETS PB	total	10/1/99	1 5	0 2046	1329	23	1000	0 00236	0 00050	0 064	0 013	0 315	34 3				0 036

54

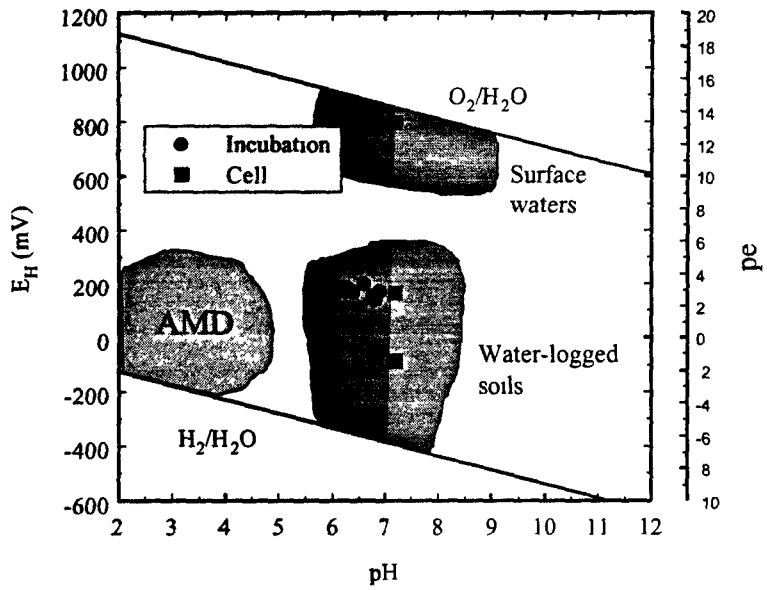


Figure 17 Location of data sets in E_H/pH 'space' and their relationship to selected environmental 'systems' 'AMD' indicates the range of characteristics of acid mine drainage, for comparison The suite of systems evaluated ranged from those characteristic of oxygenated surface waters to deeply water-logged soils Lines labeled 'O_2/H_2O' and 'H_2/H_2O' designate the limits of water stability with respect to oxidation and reduction, respectively

2) Under the conditions of the incubation experiments, with intense reducing conditions established in the Pond B4 sediments, no measurable $^{239,240}Pu$ dissolution was noted in experimental incubated samples as compared to the Pond B4 matrix water control No evidence of redox-driven solubilization of $^{239,240}Pu$ was demonstrated

Evidence: Under reducing sediment conditions ranging from -171 1 to -353 4 mV, $^{239,240}Pu$ activities measured in the Pond B4 matrix water control and in the water columns of experimental reaction chambers post-experiment were uniformly low or not detected, no measurable difference in $^{239,240}Pu$ activities between the matrix water control and the experimental samples was evidenced, and in no case did measured $^{239,240}Pu$ activities exceed the sample specific minimum detection limit

3) Under the conditions of the incubation experiments, with intense reducing conditions established in the SED029 sediments, no substantive evidence of $^{239,240}Pu$ dissolution was

noted in experimental incubated samples as compared to the Nanopure-grade de-ionized water control No evidence of redox-driven solubilization of $^{239,240}Pu$ was demonstrated

Evidence: Under reducing sediment conditions ranging from -65 5 to -386 8 mV, $^{239,240}Pu$ activities measured in the SED029 matrix control water and in the water columns of experimental reaction chambers post-experiment were uniformly low or not detected In one sample only (Sample #4 C0,N0) was $^{239,240}Pu$ activity measured at a level above sample specific minimum detection activity 'Dissolved' $^{239,240}Pu$ measured in the Sample #4 water column was low (0 128 pCi/L), with a counting uncertainty of 0 0192 pCi/L, and a minimum detection activity of 0 0962 pCi/L This result is considered unsubstantive given the counting uncertainty and the proximity of the result to the minimum detection activity

4) Under the conditions of the incubation experiments (elevated temperature and carbon/nutrient input), native cores responded with significantly enhanced reducing conditions in the sediments, and significantly enhanced manganese and iron dissolution, conditions that were not accompanied concurrently by demonstrable $^{239,240}Pu$ dissolution from the sediments to the water column

Evidence: Initial and end-of-experiment measurements of sediment E_H condition showed a marked decrease in E_H intensity Time course measurements of 'dissolved' Mn and Fe over the duration of the experiment, and end-of-experiment 'dissolved' $^{239,240}Pu$ measurements showed no concurrence of elevated 'dissolved' Mn/Fe and $^{239,240}Pu$

56

5. References

American Public Health Association (1989) *5310 Total Organic Carbon, and 5310B Combustion-Infrared Method* In Standard Methods for the Examination of Water and Wastewater, 17th Edition, American Public Health Association, Washington, D C p 5 17-5 23

Graf, W (1994) *Plutonium and the Rio Grande* Oxford University Press (new York) 329p

Guillaumont, R and J P Adolf (1992) Behavior of environmental plutonium at very low concentration *Radiochim Acta,* **58/59**, 53-60

Honeyman, B D (1998) Actinide migration studies at the Rocky Flats Environmental Technology Site Fiscal Year 1998 Final Report to Kaiser-Hill on contract KH800022MW (Fiscal Year 1998) December 8, 1998

Honeyman, B D (1999) Colloidal culprits in contamination *Nature,* **397**, 56-59

Litaor, M I and S A Ibrahim (1996) Plutonium association with selected soil phases in soils of Rocky Flats, Colorado, using sequential extraction technique *J Environ Qual*, **25**, 1144-1152

Matijevic, E and Scheiner (1978) Ferric hydrous oxide sols III Preparation of uniform particles by hydrolysis of Fe(III)-chloride, -nitrate and –perchlorate solutions *J Coll Interf Sci*, **26**, 2357-2364

McCarthy, J F and F J Wobber (1993) *Manipulation of groundwater colloids for environmental restoration* Lewis Publishers (Boca Raton, FL) 371p

Millipore (1995) *Minitan Ultrafiltration User Guide* Millipore Corporation, Bedford, MA

Morel, F M M and J G Hering (1993) *Principles and Applications of Aquatic Chemistry* Wiley-Interscience New York 588p

Pugdomenech, I And J Bruno (1991) *Plutonium solubilities* Swedish Nuclear Fuel and Waste Management Co SKB Tech Rept 91-04

Pratt, D (1999) Personal communication with Dave Pratt, Radiation Center, Oregon State University, August, 1999

Ryan, J N and M Elimelech (1996) Colloid mobilization and transport in groundwater *Colloids and Surfaces,* **107**, 1-56

Ryan J N, T H Illangasekare, M I Litaor and R Shannon (1998) Particle and plutonium mobilization in macroporous soils during rainfall simulations *Environ Sci Technol*, **32**, 475-482

Schierman, M J (1994) *Characterization of Americium and Plutonium Concentrations in Soil Profiles at the Rocky Flats Plant* M S Thesis, Dept of Radiological Health Sciences, Colorado State University

Skougstad, M W, M J Fishman, L C Friedman, D E Erdmann, and S S Duncan, editors (1979b) *Iron, total recoverable, colorimetric, bipyridine, automated (I-4379-78)*, in Techniques of Water-Resources Investigations of the United States Gological Survey, Chapter A1, Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, U S Government Printing Office, Washington, D C

Skougstad, M W, M J Fishman, L C Friedman, D E Erdmann, and S S Duncan, editors (1979a) *Iron, ferrous, dissolved, colorimetric, bipyridine (I-1388-78)*, in Techniques of Water-Resources Investigations of the United States Gological Survey, Chapter A1, Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, U S Government Printing Office, Washington, D C

57

Shimadzu Corporation (1990) Instruction manual, total organic carbon analyzer Model TOC-500 Shimadzu Corporation, Environmental Analyzers Plant, Analytical Instruments Division, Kyoto, Japan

Thorstenson, D C (1984) The concept of electron activity and its relation to redox potential in aqueous geochemical systems Open-file report 84-072, U S Geological Survey, Washington, D C

Tratnyak, P G and N L Wolfe (1990) Characterization of the reducing properties of anaerobic sediment slurries using redox indicators *Environ Toxicol Chem*, **9**, 289-295

U S DOE (1997) *Summary of existing data on actinide migration at the Rocky Flats Environmental Technology Site* RF/RMRS-97-074 UN

U S Environmental Protection Agency (1996) *Method 6010B, Inductively Coupled Plasma-Atomic Emission Spectrometry* In SW-846, CD-ROM version U S Environmental Protection Agency, Office of Solid Waste National Technical Information Service, Springfield, VA pp 6010B-1 - 6010B-25

Wurmser, R and R Banerjee (1964) Oxidation-reduction potentials *Comp Biochem*, **12**, 62-88

58

Appendix 1. SOP Total dissolution of solids for the radiochemical determinations of actinides, other non-volatile radionuclides and metals

Place 1-3 grams of the prepared sample into an appropriate sized Teflon beaker Add approximately 10mL of 1M nitric acid to allow carbonates to react Add the appropriate yield tracers to the samples

To each of the samples add 25 mL of concentrated nitric acid, 5 mL of concentrated hydrochloric acid and 25 mL of 48% hydrofluoric acid Place a Teflon watch glass over each of the beakers

Place the beakers on a hot plate at a temperature setting of 100-150 degrees Centigrade Allow the digestion to proceed for at least twelve hours Remove the samples from the hotplate and allow them to cool

Add 10 mL of 48% hydrofluoric acid and return the samples to the hotplate uncovered Increase the temperature to 200-250 degrees Centigrade Allow the acids to evaporate until there is approximately 10 mL remaining Repeat this sequence until the soil residue is minimal

Add 10 mL of concentrated perchloric acid and 10 mL of hydrofluoric acid to each beaker Turn the hotplate to a temperature of 400-450 degrees Centigrade After the heavy white fumes of perchloric acid have evolved for several minutes, remove the sample from the hotplate to cool Do not allow all of the acid to evaporate away

Dilute the mixture with 2M nitric acid to a volume of approximately 50 mL Transfer the solution to a 250 mL conical bottom centrifuge bottle Rinse the beaker well with 2M nitric acid and transfer to the centrifuge bottle Dilute the sample to approximately 150 mL with 2M nitric acid Add 1 gram of solid boric acid to the samples and mix well Proceed to the separation procedure

Appendix 2 Separation Procedure of Plutonium from Rocky Flats Soils/Sediments Following Redox Treatment

After filtering the solutions (from the redox cell or the microbiological cells) through a 0 45 µm filter, spike the solutions with a known amount of Pu-242 tracer Use approximately one-tenth the expected quantity of Pu-239/240 in the sediment (e g , a sample is 100 pCi/g Pu-239/240 A 3 gram aliquot of soil is taken The Pu-242 tracer used should be 30 pCi for the solution)

Add 1 ml of 20 mg/ml Fe(III) carrier

Add a spatula tip full of sodium nitrite crystals to the solution and mix well

Allow the sample to stand for at least ten minutes

Add conc ammonium hydroxide in excess to precipitate the Fe carrier as iron hydroxide

Centrifuge the sample for 5-10 minutes and discard the supernatant liquid

Estimate the volume of the ferric hydroxide precipitate, add 4 times the volume of conc hydrochloric acid and mix by vortexing Add 9N hydrochloric acid to bring the solution to a final volume of 10-15 ml

Fill a disposal plastic column (approximately 5mm I D , 10 ml capacity) with 2 ml of AG 1X8 anion exchange resin Cover the top of the resin with a small plug of glass wool

Condition the resin with 10 ml of 9N hydrochloric acid Discard the effluent

Filter the solution onto the column if necessary

Load the sample solution onto the column

Rinse the column with 1,2,5,10 ml successive rinses of 9N hydrochloric acid allowing each rinse to pass completely through before adding the next Collect the effluent and combine with the Am fraction

Rinse the column with an additional 40 mL of 9N hydrochloric acid and discard the effluent

Rinse the column with 3 successive 5 ml portions of 0 5 N nitric acid Collect these portions in a plastic test tube as the Pu fraction

Add approximately 0 5 ml 30% hydrogen peroxide to the Pu portion and swirl

Add 100 µg lanthanum carrier Mix well Add 5ml 25% HF Mix well Allow the sample to stand for at least 15 minutes

Place a 25 mm 0 1 µm filter membrane in a filter funnel assembly and wet the membrane with a

60

small amount of methanol or ethanol Vacuum filter the solution then rinse with 10-15 ml of slightly basic water

Remove the filter, dry at low heat and mount on the planchet with double coated tape for APHA (alpha pulse height analysis)

61

Appendix 3: Quality assurance summary.

Precision

Anaerobic Cell/Electrode Redox

THE PRECISION DATA ARE PRESENTED AS STANDARD DEVIATIONS OF POPULATIONS AND ARE THEREFORE A COMBINATION OF ALL OF THE SYSTEMATIC AND RANDOM UNCERTAINTIES ASSOCIATED WITH THE ANALYSES WHEREVER THERE IS BIAS, HOWEVER, SUCH AS IS SUSPECTED WITH THE ANALYSIS OF 0 45 FRACTION OF SAMPLE NR08, THE UNCERTAINTY DOES NOT REFLECT THE SUSPECTED BIAS

Total uncertainties of the analytical data are estimated to be similar to those of the exchangeable fraction in the sequential analysis, which are based upon the standard deviations of the population of results The counting uncertainties are given in percentages as the two sigma (95% confidence interval) uncertainties Where the counting uncertainty is less than the sample specific MDA, due to extremely low count rates, the MDA was used as the default counting uncertainty in the raw data presentation The following table of data represents the 1999 generated data only

TPU Sample	% TPU / %counting Unc Pu-239/240	
NR07 (0 45 um)	47	11
NR07 (10K MW)	47	10
NR08 (0 45 um)	NA	NA (see anomalous occurrences at the end of this section)
NR08 (10K MW)	47	10
NO04	46	5
NR10	47	11
NRB01	46	6
NRB02	47	9
NO05	49	16
NO06	46	4
NR11	48	15
NR12	47	8

DER criteria were not applied to these data since the nature of the process has not been characterized well enough to make a DER value meaningful

62

Core Incubation

BioRedox	% TPU / %counting Unc Pu-239/240	
B4 MC	49	16
B4 S2	48	15
B4 S3	48	14
B4 S4	48	15
B4 IC 1	48	14
B4 IC 2	110	100
B4 IC 3	49	17
B4 S1	49	16
SED029 IC1	49	17
SED029 IC2	49	18
SED029 IC3	49	17
SED029 MC	52	24
SED029 S1	49	17
SED029 S2	50	19
SED029 S3	49	17
SED029 S4	48	15
SED029 CC	49	17
B4 CC	50	19

DER criteria were not applied to these data since the nature of the process has not been characterized well enough to make a DER value meaningful

Accuracy

Anaerobic Cell/Electrode Redox

MDA calculations are performed using the formula given in RFETS Module RC01-B 2 section 5 2 A conservative background count of 5 is utilized in each case The actual backgrounds were monitored to less than this conservative value In every case, activity above the MDA is demonstrated and the analytical uncertainty becomes the value of interest as indicated in ANSI Standard N42 23 MDA as an *a priori* concept is of no value to these *posteriori* data

Count times of 1000 minutes are routine in order to increase the sensitivity of the measurements Count times are recorded in the raw data spreadsheets provided as an appendix

63

Chemical yields are high and within acceptable limits indicating that the chemical separations and analyses are performed correctly Sample number NR08-0 45 has an unacceptably high chemical yield for reasons unknown Possibly it was doubly traced

Blanks are generally a small percentage of the sample activities and are within acceptable limits for these data An exception is sample NRB01 which indicates significant contamination There is no apparent explanation for this contamination NRB01 was taken through the entire apparatus, including the cell with applied voltage It is possible that the contamination is the result of an incompletely cleaned electrode As shown by the data of 1998, the electrodes can retain small but measurable percentages of total Pu in the sample

Laboratory Control Samples are only meaningful in this work if they are processed through the cell as a normal sample Time and equipment constraints led to the decision to not perform spiked sample analyses since the spikes could not represent the binding properties of the normal sample The control for these experiments is found within the experimental design For example, valid control samples for this process is the subjecting of a hematite solution to the cell/electrode system with subsequent analysis of the Iron (II)/Iron (III) couple to verify the accuracy of the indicators as a measurement of the cell Eh

Previous analytical data show that the certified **tracer** utilized in these experiments is reliable as cross-referenced with NIST SRM Pu-239 spikes

Core Incubation /BioRedox

A SMALL AMOUNT OF PU-239 WAS INADVERTENTLY ADMITTED INTO THE TRACER SOLUTION UPON DISCOVERY OF THIS CONTAMINATION, A CORRECTION FOR THE QUANTITY WAS APPLIED AFTER SEVERAL DETERMINATIONS OF THE LEVEL OF CONTAMINATION WITHIN THE TRACER WAS CARRIED OUT A NEW TRACER SOLUTION WAS SUBSEQUENTLY PREPARED FOR THE REMAINDER OF ANALYSES THE SLIGHT NEGATIVE BIAS IN THE DATA INDICATE THAT THERE MAY BE A SMALL OVERESTIMATE OF THE CONTAMINATION, BUT THE EFFECT UPON THE FINAL DATA IS MINIMAL IN ESSENCE, THE PU 239/240 DATA INDICATE NO STATISTICALLY POSITIVE PU RELEASED UNDER EXPERIMENTAL CONDITIONS THE TPU VALUES AS INDICATED IN THE PREVIOUS SECTION MAY BE SLIGHTLY UNDERESTIMATED BUT ARE A REASONABLE ESTIMATE OF THE UNCERTAINTY OF THE MEASUREMENTS ALL EXCEPT ONE RESULT FALLS BELOW THE CALCULATED MDA

MDA calculations are performed using the formula given in RFETS Module RC01-B 2 section 5 2 A conservative background count of 5 is utilized in each case The actual backgrounds were monitored to less than this conservative value In every case, activity above the MDA is demonstrated and the analytical uncertainty becomes the value of interest as indicated in ANSI Standard N42 23 MDA as an *a priori* concept is of no value to these *posteriori* data

Count times of 1000 minutes are routine in order to increase the sensitivity of the measurements Count times are recorded in the raw data spreadsheets provided as an appendix

64

Chemical yields are within acceptable limits indicating that the chemical separations and analyses are performed correctly with the exception of sample number B4 IC 2 which has an unacceptably low chemical yield The lack of this datum does not affect the overall conclusions from the study

Blank values for Pu-239/240 are statistically zero as are the samples

Laboratory Control Samples are only meaningful in this work if they are processed through the incubation procedure as are the samples Time and equipment constraints led to the decision to not perform spiked sample analyses since the spikes could not represent the binding properties found within the normal sample The control for these experiments is found within the experimental design For example, valid control samples for this process are those that were subjected to a radiation field for sterilization (samples indicated with the notation "IC") and whose released Pu quantities are then compared to Pu released from samples which have undergone reductions from microbiological activity

PREVIOUS ANALYTICAL DATA SHOW THAT THE CERTIFIED TRACER UTILIZED IN THESE EXPERIMENTS IS RELIABLE AS CROSS-REFERENCED WITH NIST SRM PU-239 SPIKES

Representativeness

A chain of custody form was received and retained for sample 97L1879-002 during fiscal year 1997 A copy is provided in the raw data package

A chain of custody form was received and retained for samples from the B4 pond and SED 029 Copies are included with the raw data package

Work plans were approved by the Site and followed

Holding times, as they apply to metals analyses and TOC analyses, were met

Preservation of samples is not a criteria that can be addressed in the conventional manner since samples have to be unadulterated in order for the data to be meaningful However, after initial treatment through the cell or incubation, samples were properly preserved with acid prior to analyses

Comparability

Analysis of metals, total organic carbon and iron speciation used for the sediment incubation experiments was guided by established methods referenced in the report and included with the data packages

65

Completeness

The number of samples analyzed (both real and QC) match the work plan except for noted exceptions as documented in the "Anomalous Occurrences" portion of this QA/QC section

Anomalous Occurrences

As discussed in section 2 6 of this document, the configuration, cost, and time (3-4 weeks per sample) for running multiple analyses for the reduction experiments poses serious limitations on the feasibility of performing the usual quality control measures (duplicates, spikes, and matrix spikes) for routine analytical protocol Quality control measures were performed that were feasible under the constraints mentioned and are included for review The primary quality control in these data are the samples which are experimentally designed to demonstrate whether or not there is a statistical difference between samples that have undergone a reduction process and those that have not Within the financial constraints of this study the control objectives have been met, with the exceptions as noted

As indicated in the specific analytical portions of this section, samples with tracer recoveries of less than 50% were not reanalyzed The data quality objectives were not adversely affected by these lower recoveries due to the fact that the individual data were a part of a population of data that supported the individual results The value of reanalysis in these cases was determined to be minimal

The mass of soil particulate removed with each reduction potential measurement introduces a small, immeasurable bias in the final result of the solubilized Pu from the reduction extraction experiments The value of 0 0397 grams of particulate removed per measurement was derived from pre-weighing 10 filter disks prior to sampling and then re-weighing the ten disks after a drying period If twenty measurements are made throughout the course of the reduction phase, approximately 0 8 grams or 20% of particulate will have been removed by the termination of the reduction period The majority of these measurements (>90%) are made after the target reduction potential has been reached Since the kinetics of the Pu release are unknown, the effect of the removal of this material is unknown and unquantifiable There is an upper bound which limits the effect to a Pu value 20% higher than that obtained but is likely a much smaller effect, probably less than 5%

As discussed in Section 4 3 of the report, there occurred an apparent loss of sterile integrity of the irradiated control samples of the sediment incubation experiment at approximately 7 – 10 days following the initiation of the experiment These samples were therefore dismissed as valid controls for microbial activity in the Pond B$ and SED029 samples

Lele/Lele