Hourly and Daily Variation of Sediment Redox Potential in Tidal Wetland Sediments

Biological Science Report
USGS/BRD/BSR–1999-0001

U.S. Department of the Interior
U.S. Geological Survey

USGS
science for a changing world

Technical Report Series

The Biological Resources Division publishes scientific and technical articles and reports resulting from the research performed by our scientists and partners. These articles appear in professional journals around the world. Reports are published in two report series: Biological Science Reports and Information and Technology Reports.

Series Descriptions

Biological Science Reports ISSN 1081-292X

This series records the significant findings resulting from sponsored and co-sponsored research programs. They may include extensive data or theoretical analyses. Papers in this series are held to the same peer-review and high quality standards as their journal counterparts.

Information and Technology Reports ISSN 1081-2911

These reports are intended for publication of book-length monographs; synthesis documents; compilations of conference and workshop papers; important planning and reference materials such as strategic plans, standard operating procedures, protocols, handbooks, and manuals; and data compilations such as tables and bibliographies. Papers in this series are held to the same peer-review and high quality standards as their journal counterparts.

Copies of this publication are available from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161 (1-800-553-6847 or 703-487-4650). Copies also are available to registered users from the Defense Technical Information Center, Attn.: Help Desk, 8725 Kingman Road, Suite 0944, Fort Belvoir, Virginia 22060-6218 (1-800-225-3842 or 703-767-9050).

Printed on recycled paper

Hourly and Daily Variation of Sediment Redox Potential in Tidal Wetland Sediments

Biological Science Report
USGS/BRD/BSR–1999-0001
March 1999

By

W. James Catallo

U.S. Department of the Interior
U.S. Geological Survey
National Wetlands Research Center
700 Cajundome Blvd.
Lafayette, LA 70506

Suggested citation
Catallo, W.J. 1999. Hourly and daily variation of sediment redox potential in tidal wetland sediments. U.S. Geological Survey, Biological Resources Division Biological Science Report USGS/BRD/BSR-1999-0001. 10 pp.

Contents

Page

Introduction 1
Methods 3
  Platinum (Pt) Electrodes 3
  Redox Potential Data Loggers 3
  Sediments and Plants 3
  Static Microcosms 3
  Tidal Mesocosms 3
  Field Site 4
  System Checks 4
Results 5
  Static Microcosms 5
  Tidal Mesocosms 5
  Reproducibility of Redox Potential Measurements 6
Discussion 7
Acknowledgements 7
References 8

Figures

Figure *Page*

1 Effect of equilibration time after placement on redox potential readings from electrodes 2
2 Schematic diagram of the tidal mesocosms 4
3 The water profile resulting from flooding of the tidal mesocosms 4
4 Time series of redox potential data from the static microcosms upon cessation of aeration (96 h) 5
5 Time series redox potential and pH data in surface sediments of a tidal mesocosm, and redox potential from an identical electrode placed in a drained, nontidal mesocosm 5
6 In-phase redox potential oscillations from two tidal mesocosms running synchronously 6
7 Reproducibility of redox potential time series measurements using calibrated electrodes 6
8 Redox potential time series from ORP electrodes in tidal and back marsh (flooded nontidal) zones of a saline coastal marsh in Louisiana; spectral analysis of the redox potential time series 7

Hourly and Daily Variation of Sediment Redox Potential in Tidal Wetland Sediments

W. James Catallo
Laboratory for Ecological Chemistry
Toxicology Department, School of Veterinary Medicine
Louisiana State University
Baton Rouge, Louisiana 70803

Abstract: Variation of electrochemical oxidation-reduction (redox) potential was examined in surface salt marsh sediments under conditions of flooding and tidal simulation in mesocosms and field sites. Time series were generated of redox potential measured in sediment profiles at 2-10 cm depth using combination Pt-Ag/AgCl (ORP) electrodes. Redox potential data were acquired at rapid rates (1-55 samples/h) over extended periods (3-104 days) along with similar times series of temperature (water, air, soil) and pH. It was found that redox potential varied as a result of water level changes and was unrelated to diurnal changes in temperature or pH, the latter of which changed by <0.5 units over the tide cycles. In closed, hydrostatic microcosms isolated from atmospheric oxygen, development of negative redox potentials proceeded rapidly (>370 mV redox potential decrease in under 48 h). Attenuation of microbial activity by γ-radiation and toxic chemicals eliminated this response. In tidal salt marsh mesocosms where the sediment-plant assemblages were exposed to a simulated diurnal tide, redox potential oscillations of 40-300 mV amplitude were recorded that had the same periodicity as the flood-drain cycle. Periodic redox potential time series were observed repeatedly in sediments receiving tidal pulsing but not in those sediments exposed to static hydrological conditions. Data collected over 12 days from a coastal marsh site experiencing diurnal tides showed similar fluctuations in redox potential. Data from these experiments indicated that (a) redox potential can be a dynamic, nonlinear variable in coastal and estuarine wetland sediments over hourly and daily scales, and the designs of biogeochemical experiments should reflect this, (b) redox potential can change rapidly and significantly in coastal wetland sediments in response to flooding and draining, (c) microbial community processes are primary determinants of the time course of redox potential in wetland sediments, and elimination or inhibition of microbial activity (e.g., by pollutants) can significantly alter that behavior, and (d) fast redox potential dynamics appear to be characteristic of sediments that experience changes in hydrology. The rapid redox potential changes observed in these systems indicated dynamic metabolic and biogeochemical conditions in the field, and confirmed that hourly and daily redox potential variations should be resolved in studies of sediment functioning.

Key Words: redox potential, coastal sediments, time series, ecological function

---

"The ecologist, then, . . . must endeavor to discover the laws which govern panoramic changes. Ecology, therefore, is a study in dynamics" (Cowles 1899).

Introduction

A central variable of interest in aquatic and wetland ecosystems is the sediment redox potential, or "Eh" (Baas-Becking et al. 1960; Ponnamperuma 1972; DeLaune et al. 1976; Gleason and Zieman 1981). In practice, the redox potential is measured by comparing voltmeter readings from platinum or other solid electrodes to a reference electrode (Bohn 1968, 1969, 1971). The measured potential values (typically + 350 mV to -500 mV vs. the saturated calomel electrode [SCE]) correspond to the electrochemical status of the sediment and can be related to important soil properties and processes. Relationships have been confirmed between measured or inferred redox potentials in sediments and (a) biogeochemical cycling of C, H, O, N, S, P and numerous trace metals (Ponnamperuma 1972; DeLaune et al. 1976), (b) wetland plant distributions, productivity, and physiological status (Howes et al. 1981; DeLaune and Pezeshki 1991), (c) microbial and meiofaunal distributions and ecology (Fenchel 1978), (d) transformation and transport of hydrophobic pollutants (Hambrick et al. 1980; DeLaune et al. 1981; Catallo and Gambrell 1994) and trace metals (Khalid 1980; Masscheleyn et al. 1990; Lindsay 1991; Gambrell 1994), (e) sediment exchange of radioisotopes (Pardue et al. 1989), and (f) preservation of "chemical fossils" used in organic chemical source and diagenetic studies (Meyers and Ishiwatari 1993; Catallo et

al. 1995). Other studies have related redox potential to wetland soil function and taxonomy (Faulkner et al. 1989), groundwater chemistry (Grenthe et al. 1992), and ecotoxicology of sediment microbes (Koepfler and Kator 1986; Catallo and Gambrell 1987). In many cases the redox potential can be considered a "master variable" in sediment-water systems, and its behavior in response to natural and anthropogenic perturbation is of continuing interest (Lindsay 1991). The behavior of redox potential and related variables in different sediments under conditions of environmental stress and natural change have global ecological significance (Coleman et al. 1992).

The redox potential measured in the field reflects interactions between hydrology (e.g., flood duration and periodicity), microbiological activity, plant root processes, sediment factors (e.g., clay content, chemical equilibria), and budgets of organic matter and nutrients (Ponnamperuma 1972; Armstrong 1975; Cogger and Kennedy 1992; Cogger et al. 1992, DeLaune et al. 1983). Several studies have shown that fluctuating redox potentials arising from alternate wetting and drying of sediments are conducive to faster rates of C and N transformations than are more static conditions (i.e., those that are constantly drained or flooded; Patrick and Wyatt 1964; Sorensen 1974; Reddy et al. 1978; Smith and Patrick 1983; Odum 1983a; Odum 1983b). In some work, strong associations between wetland hydrologic conditions, sediment redox potentials, and biogeochemical-ecological processes have been described (Burdick et al. 1989; Nyman and DeLaune 1991).

Generally, redox potential is measured infrequently in natural settings and microcosms, that is, with sample intervals on the order of days to weeks. This frequently results from inaccessibility of field sites (Faulkner et al. 1989) and technological inadequacies (i.e., lack of field deployable automated samplers). Ongoing work has shown that, even in cases of static hydrological conditions (continuous flooding) and feedback-control of redox potential in microcosms (Patrick 1966; Patrick et al. 1973), structured changes in redox potential can be large in natural sediments and in microcosms and mesocosms over hourly and daily scales (Catallo unpublished data, 1996).

From a signal analysis perspective (Chen 1989; Benedetto and Frazier 1994), these studies showed that experimental and analytical variables interact to determine the magnitude and response of redox potentials measured in the field. Important factors included electrode type (size, configuration, composition, junctions), potentiometric cell construction (distance between working and reference electrodes, use of salt bridges), physicochemical effects on reference electrodes or salt bridge behavior (e.g., colloidal organic matter, temperature), electrode placement (permanent vs. temporary; zone of placement), and electrode equilibration and passivation rates after placement. A limited example of the effect of electrode equilibration on redox potential measurement indicates that variation in measured redox potential may result from experimental manipulation rather than from changes in natural conditions (Fig. 1). The data are from a redox potential time series from a combination electrode inserted approximately 10 cm into saturated, anaerobic, salt marsh mud. The introduction of the electrode (accompanied by outgassing of sulfides) apparently caused relative oxidation of the sampling zone which resulted in artificially high potential values for many hours after placement.

After nearly 24 h, the measurement zone equilibrated with the bulk phase and stable redox potential values were obtained. The exponential character of this equilibration was close to what was predicted using a simple model of aqueous sulfide diffusion across the sediment volume sampled by the electrode (Armstrong 1975). Thus, discrete potential values measured for many hours after electrode placement reflected conditions resulting from experimental manipulation of the system rather than the true system properties of interest. This problem would be compounded if the experimental design featured repeated use of temporary electrodes after insufficient equilibration times, or if the equilibration times were different in different parts of the system (e.g., streamside vs. marsh interior) or at different times of the day or year (morning vs. noon, winter vs. summer).

These and other data suggested that rapid, periodic forcing (e.g., diurnal tides) could elicit significant variation in redox potentials at hourly or daily scales. While there has been substantial effort devoted to providing data on biogeochemical process variability in sediments and organic mats (Patrick and Wyatt 1964; Bailey and Beauchamp 1971; Sorensen 1974; Whisler et al. 1974; Gleason and Zieman 1981; Howes et al. 1981; Smith and Patrick 1983;

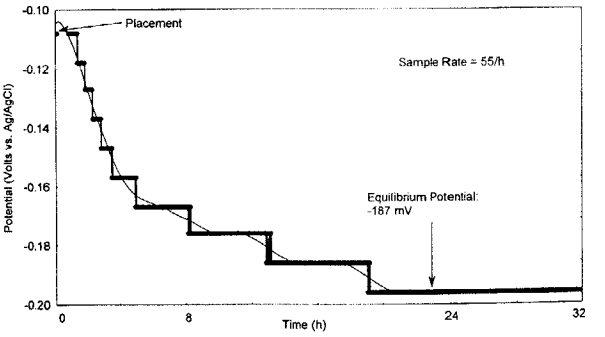


Fig. 1. Effect of equilibration time after placement on redox potential readings from electrodes. Samples were logged at 56 samples/h and 1800 data points are shown (thick line). Also given is a negative exponential fit of the data points (thin line). The electrode was a calibrated ORP electrode (combination Pt-Ag/AgCl reference). Sampling in our studies was begun after a 24 (or 48) h equilibration period.

Giblin and Howarth 1984; Cogger and Kennedy 1992; Fessel 1994, Haraguchi 1995; Anisfeld and Benoit 1997), comparatively little work has been devoted to temporal variations in a range of processes. The purpose of this work was to examine the hourly and daily responses of sediment redox potential under constantly flooded and tidally pulsed conditions and relate these data to sampling and analytical design for ecological process monitoring in microcosms and field settings.

Methods

Platinum (Pt) Electrodes

Combination Pt-Ag/AgCl reference electrodes (Sensorex, Stanton CA) were calibrated prior to use with 0.05 g quinhydrone in 50 mL of pH 7.0 and pH 4.0 buffer solutions (Bohn 1968, 1969). Calibration was checked at the end of each experiment, and agreement between beginning and ending values was required to be within 15% for data acceptance.

Electrodes placed in flooded soils require substantial equilibration times in order to provide reliable, stable readings (Fig. 1). Hence, redox electrodes used in the tidal mesocosms were equilibrated on site for 48 h before sampling. Electrodes used in the field experiments were equilibrated for 24 h.

Redox Potential Data Loggers

Redox potential was measured by using a data logger developed for this study. Development of a new data logger was necessary because available commercial potential loggers were limited by one or more of the following factors: (a) inappropriate potential ranges (e.g., 0-2 V absolute) for sampling oxidized and reduced sediments, (b) inability to stand alone, that is, without computers and AC power, and (c) expense and restrictions on field deployability (size, sensitivity to heat, moisture, etc.). The unit developed for this work consists of a 12.5 x 10.5 cm printed circuit board (Precision Etching Inc., Odenton, MD), seven input channels with single or individual reference capabilities, auxiliary battery, solar panel, computer interface, and status LED. The system and electrode leads were protected from external signals by Faraday cages. With sampling rates set at 1/h, this unit was capable of standalone monitoring of seven independent channels for 30 days.

Sediments and Plants

Sediments for use in mesocosms were collected from a *Spartina alterniflora* marsh in Terrebonne Parish, Louisiana (salinity 16-25 g/L; pH 6.6-7.4 ± 0.2 wet measurement). The sediment was wet sieved (1 mm), mixed with quartz sand (5% w/w) and ground *S. alterniflora* matter (5% w/w), and wet with sterile artificial seawater (13-15 g/l). Readily oxidizable organic matter (OM) contents in both sediments were on the order of 9%, as measured by using standard methods (Catallo and Gambrell 1987).

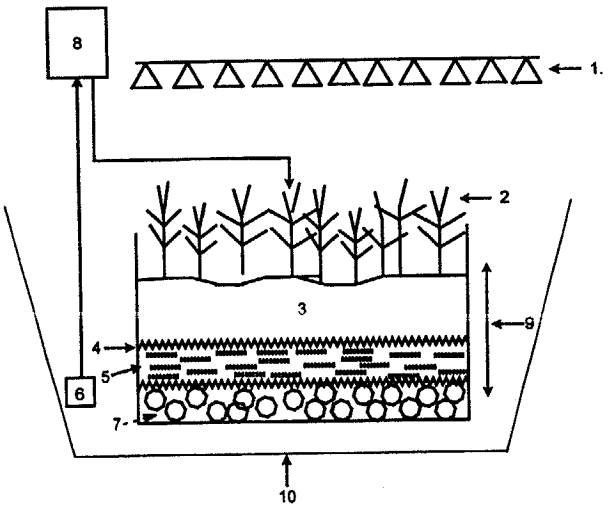
Spartina alterniflora was grown from seed obtained commercially (Environmental Concern, Inc., St. Michaels, Maryland) in greenhouses and in the laboratory under artificial sunlight. Plants were germinated in commercial seed starter and then transplanted to the salt marsh soil. When the plants had attained heights of 6-10 inches, they were transplanted into mesocosm enclosures and maintained under artificial sunlight and simulated diurnal tides.

Static Microcosms

The flooding of well-drained, oxidized sediments attenuates gaseous oxygen diffusion to the system and promotes the development of reducing conditions by microbial respiration and accumulation of chemical reductants (Ponnamperuma 1972; DeLaune et al. 1976). It was of interest to examine the time dynamics of this process and the effects of "damping" variables, such as biocidal chemicals and γ radiation, on redox potential time series. The salt marsh sediments were aerated for 96 h and placed in 1-l glass flasks which were then sealed. The flasks were equipped with vacuum-tight feed troughs for two calibrated electrodes. Three treatments were established: (a) clean salt marsh sediment-water, (b) salt marsh sediment-water contaminated with 1% (w/w) coal carbon black, and (c) clean sediment-water exposed to γ radiation (2 MRad) using a submerged Co^{60} source. The coal carbon black contained polycyclic aromatic hydrocarbons and heterocycles known to be toxic to sediment microbes (Catallo and Gambrell 1987; Catallo 1996). Settling of particulates after 24 h in each microcosm gave approximately a 1:1 sediment to water ratio (v/v), with an electrode sampling the water and the sediment phases. Redox potential values in the water and sediment of the treatments were sampled at a rate of 1/h for periods of 180-530 h. The pH was measured at the beginning and end of the experiments. The level of microbial respiration in each treatment was determined at the beginning and end of the experiments using iodonitrotetratzolium (INT) reduction (Catallo et al. 1990). The systems were maintained at room temperature (21 ± 2° C) throughout the experiments. Reproducibility of redox potential measurements in these systems was evaluated by establishing duplicate microcosms, each with their own calibrated electrode and logger.

Tidal Mesocosms

Salt marsh sediments were loaded into 64-cm high PVC cages (32 x 68 cm) encased in plastic mesh (1 cm^2) and fine landscaping mesh (ca. 0.5 mm^2) to a height of 60 cm (Fig. 2). All sides and the bottoms of these enclosures were permeable to water, but not to sediments. These enclosures were situated in 300-gallon injection molded plastic containers. A diurnal tide was simulated by moving 230-250 gallons of artificial sea water (salinity of 13-15 g/l; pH = 7.0-7.4) into and out of the mesocosms once daily. The flood tide was delivered via siphon from water reservoirs



1. Light banks with timers
2. Plants
3. Sediment
4. Agricultural mesh and burlap
5. Oyster shell
6. Pumps
7. Cobblestones
8. Reservoirs
9. Simulated tide range
10. 300-gallon enclosure

Fig. 2. Schematic diagram of the tidal mesocosms.

at flow rates sufficient to flood the sediment columns after 10 h. After 3 h at full flood, the water was withdrawn using a remotely timed sputter pump. The resulting water level profile resulted is shown in Fig. 3.

The seawater reservoir was continuously aerated and the systems were maintained at room temperature. At "high tide," the sediment columns were covered with about 2 cm of water, while at "low tide" the columns were completely drained, with about 5 cm of water remaining at the bottom of the system. Electrodes were positioned in the top 3-10 cm of sediments and care was taken to avoid positioning the electrode directly in the root mass of the plants.

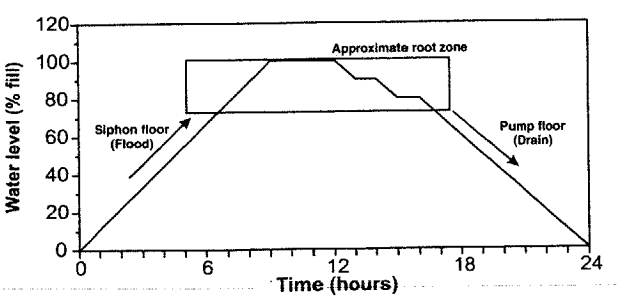


Fig. 3. The water profile resulting from flooding of the tidal mesocosms.

Duplicate tidal mesocosms were established and potentials were recorded at rates of at least 1 sample/h. Other data logged at the same or higher rates were water temperature, air temperature, light levels, relative humidity, pH, and soil temperature. Discrete data were compiled on output properties, including trace gases leaving sediments and salinity. System checks included monitoring redox potential while (a) the system was turned off at high or low water and (b) the water lines were disconnected but the pumps and timers were allowed to cycle as usual. "Dummy" electrodes and grounded leads not in contact with the tidal system also were monitored during the experiments. These tests were designed to account for extraneous signals that might be detected by the system and mistaken for sediment potential variations.

Field Site

The field measurements were taken in a semi-impounded tidal saline marsh (salinity16 g/l) in southern St. Charles Parish, Louisiana. Two calibrated combination redox potential electrodes (Sensorex) were placed at 4-cm depth in (a) an intertidal flood zone and (b) a nearby flooded back marsh area. Each electrode had an independent logger sampling at 1/h, and samples were acquired synchronously for 12 days. The electrodes and loggers were recovered at the end of the sampling and the electrode calibration was again checked.

System Checks

The possibility of signal aliasing (Box and Jenkins 1976; Chen 1989; Brockwell and Davis 1991) was examined by sampling the tidal and static mesocosms and microcosms at higher frequencies than were used in the experiments (e.g., sample rates between 2 Hz and 15/min). The goal was to detect any contaminating signals with frequencies above the Nyquist frequency (i.e., 1/2 the sample frequency) and amplitudes >5 mV.

As with all instrumental potential measurements, the process of redox potential data acquisition involved the transfer of a small amount of current in the sample loop of the logger (Bohn 1971). In the automated (stand alone) sampling mode, these currents and associated potential transients at the electrode surface were small—on the order of pA and nV, respectively. Nevertheless, it was important to determine whether repeated measurement caused chemical changes, for example, redox reactions, in the vicinity of the electrode being sampled (cf. Zhi-Guang and Tian-Ren 1984). This determination was made by rapidly sampling an electrode (2 Hz-4/min for 10 min) equilibrated in a standard solution of quinhydrone at 25° C. Changes or drift in the potential readings in the system being rapidly sampled were taken as evidence of chemical changes near the electrode resulting from the process of measurement.

Results

Static Microcosms

The purpose of these systems was to simulate conditions of aerobic sediment being flooded or a flooded sediment being deprived of regular flushing with oxygenated water. The goal was to observe the rate and nature of the redox potential response versus systems that had been contaminated or sterilized, thus inhibiting microbial respiration. Fig. 4 shows the redox potential versus time profile for clean, coal tar-contaminated, and γ-irradiated salt marsh sediment slurries in static microcosms. Upon elimination of oxygen supply to these systems (i.e., cessation of aeration), the clean, untreated sediments developed rapidly reducing redox potentials (>370 mV/48 h). The overlying water remained more oxidized until about 300 h, after which the potential decreased to the same level as the sediment. At this point, the sediment and water darkened, and sulfides were detected in head space samples. By the end of the test, the pH had dropped from 6.6 to 5.9. Conversely, the coal tar-contaminated and γ-ray-sterilized sediments did not display rapid redox potential decreases, color changes, pH decreases, or evolution of sulfides. The contaminated sediment remained electrochemically unchanged until minor redox potential decreases were observed after 400 h. It was found that INT reduction (proportional to microbial respiratory electron transport) was approximately tenfold greater in the clean sediments than in the contaminated sediments at the end of incubation (530 h). The γ-irradiated sediments showed no pH changes or INT reduction, that is, there was no evidence of microbial respiration.

Tidal Mesocosms

The tidal mesocosms were used to examine the effects of periodic water level fluctuations on redox potential time dynamics in sediment-plant systems. It was clear from the static microcosm results that measured redox potential values could change dramatically in short periods; assuming that the electrochemical processes at the electrode were reversible or nearly so, regular variations on the order of >75 mV were expected to be realized within a tide period (based on the linear part of data shown in Fig. 4). Previous sampling studies had shown that (a) there were no signals in the tidal simulation (or static microcosms) with frequencies higher than, or close to, the sampling frequency (i.e., 1/h), and (b) the process of automated sampling did not perturb the chemical environment around the electrode so as to stabilize subsequent potential readings. Fig. 5 shows the high resolution redox potential and pH time series from a surface electrode in salt marsh sediment enclosures containing *S. alterniflora* in a tidal mesocosm. It was clear that the redox potential electrode registered potential fluctuations that followed the simulated tides and that measured pH changes were too small to account for this variation (Fig. 5). Fast Fourier transform (FFT) and multiresolution "wavelet" analyses (Benedetto and Frazier 1994) confirmed the presence of strong diurnal variations in the redox potential series from the tidal systems, with the wavelet transform providing a mean value period of 23.78 ± 2.10 h.

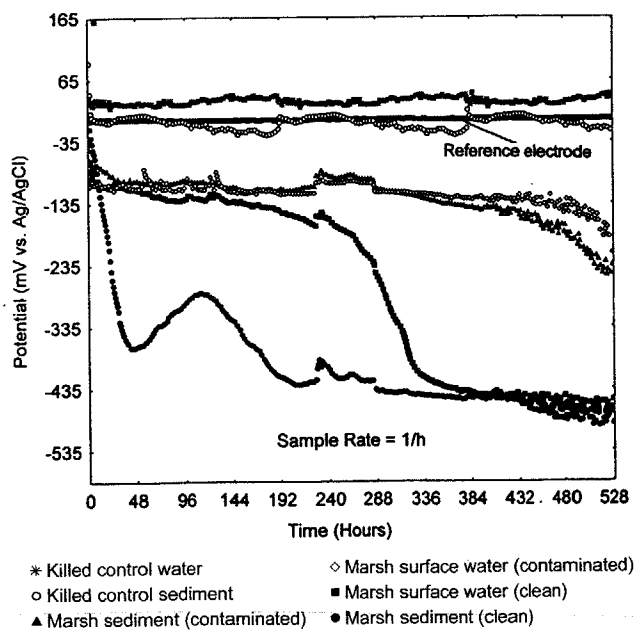


Fig. 4. Time series of redox potential data from the static microcosms upon cessation of aeration (96 h). "Contaminated" sediments received 1% coal carbon black, and "killed control" slurries were sterilized with 2Mrad γ radiation prior to the run.

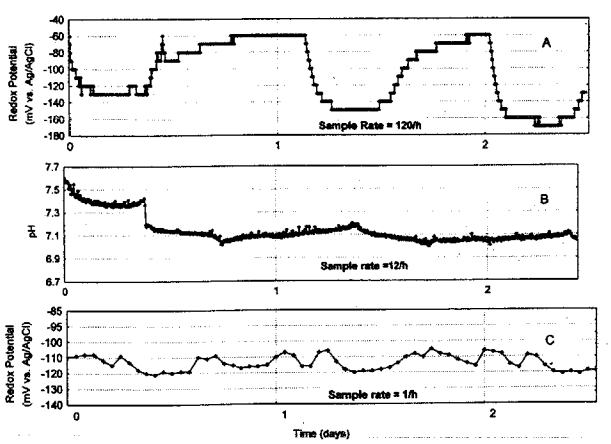


Fig. 5. Time series redox potential (**A**) and pH (**B**) data in surface sediments (7 cm) of a tidal mesocosm, and redox potential from an identical electrode placed in a drained, nontidal mesocosm (**C**).

For comparison with hydrodynamic situations, an identical electrode-logger system was positioned in moist, well-drained sediments but was not exposed to a simulated tide; this system was monitored synchronously with the tidal system (Fig. 5). Clearly, the significant redox potential variations observed in the tidal system were not observed under static conditions in the nontidal system and could not be attributed to other factors (i.e., external fields, diurnal temperature, measurement artifacts).

Reproducibility of Redox Potential Measurements

It was necessary to evaluate the reproducibility of the redox potential readings in both the static microcosms and the tidal mesocosm systems. In order to do this, replicate static and tide simulation systems were established with independent redox potential sensors and loggers. These replicate systems were tested side by side under identical conditions for several days, with redox potential sampled hourly. Data in Figs. 6 and 7 are representative of results obtained: calibrated ORP electrodes exposed to similar static or dynamic hydraulic conditions in sediments provided reproducible values for redox potential, particularly during periods of rapid change in redox potential (e.g., the first day after flooding). Although there was substantial variance in individual potential measurements (e.g., 10-30%), the time series of the replicates are in close agreement. Measurements from tidal mesocosm replicate sensors also tended to vary when considered on a datum by datum basis (Figs. 6 and 7). Nevertheless, the frequency and amplitude of the extended time series functions were in close agreement (Fig. 6). Divergence in these time series also has been observed, particularly in systems that have been running for extended periods (several months). This divergence reflects the development of redox heterogeneity in the sediments; the development of heterogeneity is an expected part of the evolution of many dynamic systems (Abraham and Shaw 1992). Nevertheless, as shown in Fig. 6, even separate tidal systems tested and sampled synchronously displayed redox potential oscillations that remained in phase for weeks, with good agreement between the time series of the signals over many tide cycles. It is important to point out that the reproducibility of the measurements of redox potential under hydrostatic and dynamic conditions applied to contemporaneous measurements. No attempt was made to determine reproducibility between measurements taken in different systems (e.g., field vs. mesocosms) or measurements made in the same kind of system at different times in the year or between laboratories.

Limited data from a semi-impounded tidal wetland in St. Charles Parish, Louisiana, indicated diurnal fluctuations of redox potential in the surface sediments of an intertidal zone (Fig. 8). Comparison of these data with those collected in a flooded, nontidal area nearby showed no diurnal changes in redox potential, even though the electrode was positioned similarly and would have been equally susceptible to thermal or other possible confuting phenomena. These data agree with those generated in mesocosms, that is, tidal flushing was a major cause of the redox potential fluctuations.

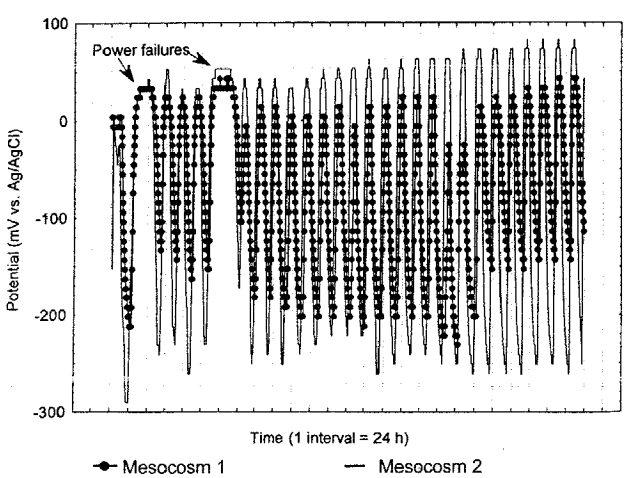


Fig. 6. In-phase redox potential oscillations from two tidal mesocosms running synchronously.

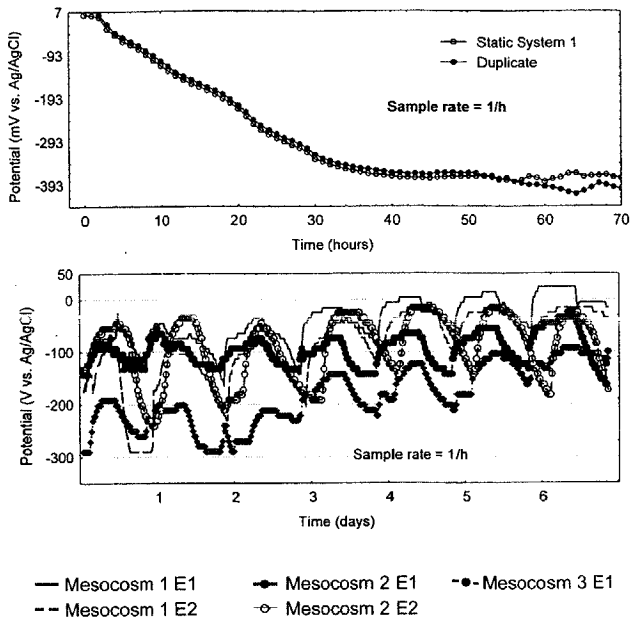


Fig. 7. Reproducibility of redox potential time series measurements using calibrated electrodes. **Top:** Redox potential values from duplicate sealed sediment slurry microcosms (as in Fig. 3). **Bottom:** Redox potential time series data from surface electrodes (7 cm) in triplicate tidal mesocosms. Systems were tested synchronously with respect to all input variables (e.g., tides, light) and sampling times were approximately synchronous. E1 and E2 are duplicate electrodes for each mesocosm. E2 for mesocosm 3 was damaged and therefore data were not acquired.

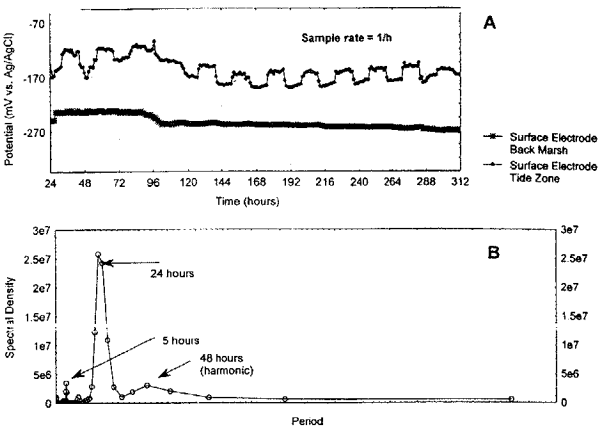


Fig. 8. A. Redox potential time series from ORP electrodes in tidal and back marsh (flooded nontidal) zones of a saline coastal marsh in Louisiana. **B.** Spectral analysis of the redox potential time series shown in part **A**.

Discussion

Data from the experiments summarized above indicated that (a) redox potential can be a dynamic, nonlinear variable in wetland sediments over hour and day time scales, and sampling/data handling strategies should take this variability into account, (b) periodic and other nonlinear changes in redox potential can be detected reproducibly by using the potentiometric systems described here, (c) redox potential can change quickly and significantly in response to tidal flood-drain cycles (e.g., 40-300 mV/12 h) and events that attenuate oxygen supply to the sediment (e.g., static flooding, >350 mV/48 h), and (d) microbial processes and hydrologic variability are primary determinants of the rapid changes in sediment potential, and elimination or inhibition of microbial activity (e.g., by pollutants) or alteration of hydrology can significantly alter that behavior. The importance of microbial respiratory processes to redox potential agrees with previous field work showing significant alteration of potential in contaminated versus pristine sediments resulting from toxicity to sediment microflora and meiofauna (Koepfler and Kator 1986; Catallo and Gambrell 1987).

The rapid potential changes observed in the microcosms and mesocosms were significant from a biogeochemical perspective. For example, the static microcosms were aerobic at the beginning of the runs, but they became anaerobic within several hours, and highly reducing soon thereafter. Thus, the observed potential change corresponded to rapid changes in microbial metabolic status and bioenergetics (i.e., aerobic vs. anaerobic metabolism) and the oxidation states of metabolic endpoints (i.e., H_2O/CO_2 in aerobic processes vs. organic acids and sulfides in anaerobic processes). This transition from aerobic to highly reducing conditions occurred in under 48 h. In tidal mesocosms, the magnitude of change (40-160 mV) was sufficient to alter the biogeochemical processes. Changes of 50 mV can correspond to changes in the processing rate and disposition of organic matter, nutrients, and toxic sulfur species (DeLaune et al. 1976). The equilibration time for these biogeochemical changes can be rapid; for example, upon flooding and development of anaerobic conditions, denitrification half-times for NO_3-N (107-163 mg/g) were on the order of 15-50 h in numerous soils and sediments (Reddy et al. 1978). Thus, the oscillating redox potential profiles observed in the tidal simulation experiments can provide for biogeochemical conditions not observed in more static systems, for example, rapid redox cycles of elements. Clearly the redox potential dynamics in these experimental systems would not have been observed by using discrete sampling designs (e.g., 1 sample/day or 1/week), nor would the data be appropriately handled using general linear statistical models. These observations bear directly on the design and sampling strategy of ecological microcosms, creation/remediation of wetland environments, and field studies for biogeochemical and pollutant fate evaluation.

The life cycles, ecological functioning, and productivity of species in many ecosystems are influenced by physicochemical cycles operating over a wide range of temporal scales (Ziser 1978; Odum 1983a; Odum 1983b; Sklar 1985; Lloyd and Stupfel 1991; Mann and Lazier 1991; Beyers and Odum 1993). Process "pulsing" at micro to global scales is thought to be central to ecosystem integration and homeostasis (Odum 1983b). Much work in microcosms and mesocosms (Beyers and Odum 1993) emphasizes the importance of periodic inputs (temperature, light, physical disturbance) as drivers of biological processes, with nonlinear or oscillating process outputs typically resulting (e.g., diurnal O_2/CO_2 fluxes). Periodic and other nonlinear disturbances are major determinants of biological community structure and diversity in natural systems (Odum 1983b; Reice 1994; Schmidt-Nielson 1994). Therefore, field and microcosm studies and environmental restoration attempts must address these physicochemical cycles within experimental designs and models, particularly if critical process rates or endpoints are directly influenced. Thus, endeavors including design of an effective microcosm or created ecosystem would require knowledge of, and the ability to provide, the appropriate forcing needed to influence process in ways characteristic of natural systems (Reddy 1993).

Acknowledgments

The author is indebted to Robert P. Gambrell, Ronald D. DeLaune, Gene Turner, Irving A. Mendelssohn, Pat Crawford, H. L. (Dharme) Dharmasena (data logger

development), Jimmy Johnston, and Jorje L. Aravena (wavelet transform and system design) for technical support, critique, and discussion of this and related work. Thanks also are extended to Karen L. McKee for advice and assistance in the area of *S. alterniflora* germination, growth, and maintenance indoors. Much of this work resulted from studies funded by the U.S. Environmental Protection Agency, National Biological Service, the U.S. Mineral Management Service, and private sponsors (Integrated Resources Inc., New Orleans, Louisiana; Bruno and Bruno Inc., New Orleans, Louisiana; and Martin Marietta Inc., Oak Ridge, Tennessee). There are no particulars that can summarize the importance of this support or my gratitude to these supporters.

References

Abraham, R.H., and C.D. Shaw. 1992. Dynamics: the geometry of behavior. Addison Wesley Publishers. 642 pp.

Anisfeld, S.C., and G. Benoit. 1997. Impacts of flow restrictions on salt marshes: an instance of acidification. Environmental Science and Technology 31(6):1650-1657.

Armstrong, W. 1975. Waterlogged soils. Pages 181-218 *in* J.R. Etherington, editor. Environmental and Plant Ecology. John Wiley & Sons, London.

Baas-Becking, L.G.M., I.R. Kaplan, and D. Moore. 1960. Limits of the natural environment in terms of pH and oxidation-reduction potentials. Journal of Geology 68(3):243-284.

Bailey, L.D., and E. Beauchamp. 1971. Nitrate reduction and redox potentials measured with permanently and temporarily placed platinum electrodes in saturated soils. Canadian Journal of Soil Science 51:51-58.

Benedetto, J., and M. Frazier. 1994. Wavelets: mathematics and applications. CRC Press, Boca Raton, Fla. 575 pp.

Beyers, R.J., and H.T. Odum. 1993. Ecological microcosms. Springer Advanced Texts in Life Sciences, Springer-Verlag, New York, N.Y. 572 pp.

Bohn, H.L. 1968. Electromotive force of inert electrodes in soil suspensions. Soil Science Society of America Journal 32:211-215.

Bohn, H.L. 1969. The emf of platinum electrodes in dilute solutions and its relation to soil pH. Soil Science Society of America Journal 33:639-640.

Bohn, H.L. 1971. Redox potentials. Soil Science 112(1):39-45.

Box, G.E.P., and G.M. Jenkins. 1976. Time series analysis: forecasting and control. Holden-Day Publishers, San Francisco, Calif.

Brockwell, P.J., and R.J. Davis. 1991. Time series: theory and methods. Springer Verlag, New York, N.Y.

Burdick, D.M., I.A. Mendelssohn, and K.L. McKee. 1989. Live standing crop and metabolism of *Spartina patens* as related to edaphic factors in a brackish, mixed marsh community in Louisiana. Estuaries 12:195-204.

Catallo, W.J. 1994. Ecotoxicology of wetland ecosystems. Current understanding and future research needs. Environmental Toxicology and Chemistry 12(12):2209-2224.

Catallo, W.J. 1996. Transformation of N-, O-, and S- heterocycles (NOSHs)in estuarine sediments: effects of redox potential and particle size. Chemosphere: 33(12):2543-2563.

Catallo, W.J., R.J. Gale, R.L. Wong, and M.E. Bender. 1990. The reducible dye 2-(p-iodophenyl)-3-(p-nitrophenyl)- 5-phenyl-2H-tetrazolium chloride (INT) for use in aquatic toxicology. Notes on chemical structure, electrochemistry, and toxicity. Pages 222-236 *in* W. G. Landis and W. H. van der Schalie, editors. Aquatic Toxicology and Risk Assessment. ASTM Special Technical Publication 1096. American Society for Testing and Materials, Philadelphia, Penn.

Catallo, W.J., and R.P. Gambrell. 1987. The effects of high levels of polycyclic aromatic hydrocarbons on sediment physicochemical properties and benthic organisms in a polluted stream. Chemosphere 16(5):1053-1063.

Catallo, W.J., and R.P. Gambrell. 1994. Fate and effects of N-, O-, and S- heterocycles (NOSHs) from petroleum and pyrogenic sources in marine sediments. U.S. Department of the Interior, Minerals Management Service, OCS Study MMS 94-0056. 72 pp.

Catallo, W.J., M. Schlenker, R.P. Gambrell, and B.S. Shane. 1995. Toxic chemicals and trace metals from urban and rural Louisiana lakes: recent historical profiles and toxicological significance. Environmental Science and Technology 29(6):1436-1445.

Chen, C.T. 1989. System and signal analysis. Saunders College Publishing, Orlando, Fla. 543 pp.

Cogger C.G., and P.E. Kennedy. 1992. Seasonally saturated soils in the Puget lowland. I, Saturation, reduction, and color patterns. Soil Science 153(6):421-433.

Cogger C.G., P.E. Kennedy, and D. Carlson. 1992. Seasonally saturated soils in the Puget lowland. II, Measuring and interpreting redox potentials. Soil Science 154(1):50-58.

Coleman, D.C., E.P. Odum, and D.A. Crossley, Jr. 1992. Soil biology, soil ecology, and global change. Biology and Fertility of Soils 14:104-111.

Cowles, H.C. 1899. The ecological relations of the vegetation on the sand dunes of Lake Michigan. Part I. Botanical Gazette; February 1889. Pages 28-58 *in* L.A. Real and J.H. Brown, editors. 1991. Foundations of Ecology, Classic Papers with Commentaries. University of Chicago Press, Ill.

DeLaune, R.D., W.H. Patrick, and J.M. Brannon. 1976. Nutrient transformations in Louisiana salt marsh soils. Louisiana Sea Grant Publication No. LSU-T-76-009, Louisiana State University, Baton Rouge, La.

DeLaune, R.D., W.H. Patrick, and M.E. Casselman. 1981. Effect of sediment pH and redox conditions on degradation of benzo(a)pyrene. Marine Pollution Bulletin 12(7):251-253.

DeLaune, R.D., and S.R. Pezeshki. 1991. Role of soil chemistry in vegetative ecology of wetlands. Trends in Soil Science 1:101-113.

DeLaune, R.D., C.J. Smith, and W.H. Patrick. 1983. Relationship of marsh elevation, redox potential, and sulfide to *Spartina alterniflora* productivity. Soil Science Society of America Journal 47:930-935.

Ehleringer, J.R., and C.B. Field, editors. 1993. Scaling physiological processes: leaf to globe. Academic Press, San Diego, Calif. 388 pp.

Faulkner S.P., W.H. Patrick, and R.P. Gambrell. 1989. Field techniques for measuring wetland soil parameters. Soil Science Society of America Journal 53:883-890.

Fenchel, T.M. 1978. The ecology of micro and meio benthos. Annual Review of Ecology and Systematics 9:99-121.

Fessel, K.E. 1994. An examination of the reproducibility and reliability of oxidation-reduction potentials in soils across a forested wetland to upland transect. M.S. thesis, Louisiana State University, Baton Rouge. 145 pp.

Gambrell, R.P. 1994. Trace and toxic metals in wetlands—A review. Journal of Environmental Quality 23:883-891.

Giblin, A.E., and R.W. Howarth. 1984. Porewater evidence for a dynamic sedimentary iron cycle in salt marshes. Limnology and Oceanography 29(1):47-63.

Gleason, M.L., and J.C. Zieman. 1981. Influence of tidal innundation on internal oxygen supply of *Spartina alterniflora* and *Spartina patens*. Estuarine Coastal Shelf Science 13:47-57.

Grenthe I., W. Stumm, M. Laaksuharju, A.C. Nilsson, and P. Wikberg. 1992. Redox potentials and redox reactions in deep groundwater systems. Chemical Geology 98:131-150.

Hambrick, G.A., R.D. DeLaune, and W.H. Patrick. 1980. Effect of estuarine sediment pH and oxidation-reduction potential on microbial hydrocarbon degradation. Applied and Environmental Microbiology 40(2):365-369.

Haraguchi, A. 1995. Seasonal changes in oxygen consumption rate and redox properties of floating peat in a pond in central Japan. Wetlands 15(3):242-46.

Howarth, R.W., and J.M. Teal. 1980. Energy flow in a salt marsh ecosystem: the role of reduced inorganic sulfur compounds. American Naturalist 116:862-872.

Howes, B.L., R.W. Howarth, J.M. Teal, and I. Valiela. 1981. Oxidation reduction potentials in a salt marsh: spatial patterns and interactions with primary production. Limnology and Oceanography 26:350-360.

Hudnall, W.H., A.E. Tiarks, W.C. Waddell, and W.B. Patterson. 1995. Soil water relationships within the long-term forest management plots, USFS, Louisiana. Pages 85-89 *in* H.M. Selim and W.H. Brown, editors. Proceedings of a Conference on Environmental Issues LSU Agricultural Center, 7/24-7/25 1995.

Khalid, R.A. 1980. Chemical mobility of cadmium in sediment-water systems. Pages 258-304 *in* J.O. Nriagu, editor. Cadmium in the Environment. John Wiley & Sons, New York, N.Y.

King, G.M., M.J. Klug, R.G. Wiegert, and A.G. Chalmers. 1982. Relation of soil water movement and sulfide concentration to *Spartina alterniflora* production in a Georgia salt marsh. Science 218:61-63.

Koepfler, E.T., and H.I. Kator. 1986. Ecotoxicological effects of creosote contamination on benthic microbial populations in an estuarine environment. Toxicity Assessment 1:465-485.

Lindsay, W.L. 1991. Iron oxide solubilization by organic matter and its effect on iron availability. Pages 29-36 *in* Y. Chen and Y. Hadar, editors. Iron Nutrition and Interactions in Plants. Kluwer Academic Publishers, The Netherlands.

Lloyd, D., and M. Stupfel. 1991. The occurrence and functions of ultradian rhythms. Biological Reviews of the Cambridge Philosophical Society 66:275-299.

Mann, K.H., and J.R.N. Lazier. 1991. Dynamics of marine ecosystems. Blackwell Scientific Publications, Oxford, U.K.

Masscheleyn, P.H., R.D. Delaune, and W.P. Patrick, Jr. 1990. Transformations of selenium as affected by sediment oxidation-reduction potential and pH. Environmental Science and Technology 24(1):91-96.

Mendelssohn, I.A., B.A. Kleiss, and J.S. Wakeley. 1995. Factors controlling the formation of oxidized root channels: a review. Wetlands 15(1):37-46.

Mendelssohn, I.A., K.L. McKee, and W.H. Patrick. 1981. Oxygen deficiency in *Spartina alterniflora* roots: Metabolic adaptation to anoxia. Science 214:439-441.

Meyers, P.A., and R. Ishiwatari. 1993. Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. Organic Geochemistry 20(7):867-900.

Norman, J.M. 1993. Scaling processes between leaf and canopy levels. Pages 41-76 *in* J.R Ehleringer and C.B. Field, editors. Scaling Physiological Processes: Leaf to Globe. Academic Press, San Diego, Calif.

Nyman, J.A., and R.D. DeLaune. 1991. CO_2 emission and soil Eh responses to different hydrological conditions in fresh, brackish, and saline marsh soils. Limnology and Oceanography 36(7):1406-1414.

Odum, E.P. 1983a. Basic ecology. Sanders College Publishing, Philadelphia, Penn.

Odum, E.P. 1985. Trends expected in stressed ecosystems. BioScience 35(7):419-422.

Odum, H.T. 1983b. Ecological and general systems. University Press of Colorado, Boulder. 644 pp.

Pardue, J.H., R.D. DeLaune, W.H. Patrick, and J.H. Whitcomb. 1989. Effect of redox potential on fixation of ^{137}Cs in lake sediment. Health Physics 57(5):781-789.

Patrick, W.H. 1966. Apparatus for controlling the oxidation-reduction potential of waterlogged soils. Nature 212(5067):1278-1279.

Patrick, W.H., B.G. Williams, and J.T. Moraghan. 1973. A simple system for controlling redox potential and pH in soil suspensions. Soil Science Society of America Proceedings 37:331-32.

Patrick, W.H., and R. Wyatt. 1964. Soil nitrogen loss as a result of alternate submergence and drying. Soil Science Society of America Proceedings 28(5):647-653.

Ponnamperuma. F.N. 1972. The chemistry of submerged soils. Advances in Agronomy 24:29-96.

Reddy, K.R., and W.H. Patrick. 1976. Effect of frequent changes in aerobic and anaerobic conditions on redox potential and nitrogen loss in a flooded soil. Soil Biology and Biochemistry 8:491-95.

Reddy, K.R., and W.H. Patrick. 1993. Wetland soils—opportunities and challenges. Soil Science Society of America Journal 57:1145-47.

Reddy, K.R., W.H. Patrick, and R.E. Philips. 1978. The role of nitrate diffusion in determining the order and rate of denitrification in flooded soil: I. Experimental results. Soil Science Society of America Journal 42(2):268-272.

Reice, S.R. 1994. Nonequilibrium determinants of biological community structure. American Scientist 82:424-435.

Schmidt-Nielsen, K. 1994. How are control systems controlled? American Scientist 82:38-44.

Sklar, F.H. 1985. Seasonality and community structure of the backswamp invertebrates in a Louisiana cypress-tupelo wetland. Wetlands 5:69-86.

Smith, C.J., and W.H. Patrick. 1983. Nitrous oxide emission as affected by alternate anaerobic and aerobic conditions from soil suspensions enriched with ammonium sulfate. Soil Biology and Biochemistry 15(6):693-697.

Sorensen, L.H. 1974. Rate of decomposition of organic matter in soil as influenced by repeated air drying-rewetting and repeated additions of organic material. Soil Biology and Biochemistry 6:287-292.

Tate, R.L. 1979. Effect of flooding on microbial activities in organic soils: carbon metabolism. Soil Science 128(5):267-273.

Turner, R.E. 1977. Intertidal vegetation and commercial yields of penaeid shrimp. Transactions of the American Fisheries Society 106(5):411-416.

Whisler, F.D., C. Lance, and R.S. Linebarger. 1974. Redox potentials in soil columns intermittently flooded with sewage water. Journal of Environmental Quality 3(1):68-74.

Whitfield, M. 1972. The electrochemical characteristics of natural redox cells. Limnology and Oceanography 176:383-393.

Wilson, C.A., and L.H. Stevenson. 1980. The dynamics of the bacterial population associated with a salt marsh. Journal of Experimental Marine Biology and Ecology 48:123-138.

Zhi-Guang, L., and Y. Tian-Ren. 1984. Depolarization of a platinum electrode in soils and its utilization for measurement of redox potential. Journal of Soil Science 35:469-479.

Ziser, S.W. 1978. Seasonal variations in water chemistry and diversity of phytophilic macroinvertebrates of three swamp communities in southeastern Louisiana. The Southeastern Naturalist 23:545-562.

REPORT DOCUMENTATION PAGE

Form approved
OMB No. 0704-0188

Public reporting burden for this collection is estimated to average 1 hour per response, including time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188) Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)

2. REPORT DATE
April 1999

3. REPORT TYPE AND DATES COVERED
Biological Science Report

4. TITLE AND SUBTITLE
Hourly and Daily Variation of Sediment Redox Potential in Tidal Wetland Sediments

5. FUNDING NUMBERS

6. AUTHOR(S)
W. James Catallo

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESSES
U.S. Department of the Interior
U.S. Geological Survey
Biological Resources Division

8. PERFORMING ORGANIZATION REPORT NUMBER
USGS/BRD/BSR--1999-0001

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESSES
U.S. Department of the Interior
U.S. Geological Survey

10. SPONSORING, MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Release unlimited. Available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161 (1-800-553-6847 or 703-487-4650). Available to registered users from the Defense Technical Information Center, Attn: Help Desk, 8722 Kingman Road, Suite 0944, Fort Belvoir, VA 22060-6218 (1-800-225-3842 or 703-767-9050).

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Variation of electrochemical oxidation-reduction (redox) potential was examined in surface salt marsh sediments under conditions of flooding and tidal simulation in mesocosms and field sites. Time series were generated of redox potential measured in sediment profiles at 2-10 cm depth using combination Pt-Ag/AgCl (ORP) electrodes. Redox potential data were acquired at rapid rates (1-55 samples/h) over extended periods (3-104 days) along with similar times series of temperature (water, air, soil) and pH. It was found that redox potential varied as a result of water level changes and was unrelated to diurnal changes in temperature or pH, the latter of which changed by <0.5 units over the tide cycles. In closed, hydrostatic microcosms isolated from atmospheric oxygen, development of negative redox potentials proceeded rapidly (>370 mV redox potential decrease in under 48 h). Attenuation of microbial activity by ã-radiation and toxic chemicals eliminated this response. In tidal salt marsh mesocosms where the sediment-plant assemblages were exposed to a simulated diurnal tide, redox potential oscillations of 40-300 mV amplitude were recorded that had the same periodicity as the flood-drain cycle. Periodic redox potential time series were observed repeatedly in sediments receiving tidal pulsing but not in those sediments exposed to static hydrological conditions. Data collected over 12 days from a coastal marsh site experiencing diurnal tides showed similar fluctuations in redox potential. Data from these experiments indicated that (a) redox potential can be a dynamic, nonlinear variable in coastal and estuarine wetland sediments over hourly and daily scales, and the designs of biogeochemical experiments should reflect this, (b) redox potential can change rapidly and significantly in coastal wetland sediments in response to flooding and draining, (c) microbial community processes are primary determinants of the time course of redox potential in wetland sediments, and elimination or inhibition of microbial activity (e.g., by pollutants) can significantly alter that behavior, and (d) fast redox potential dynamics appear to be characteristic of sediments that experience changes in hydrology. The rapid redox potential changes observed in these systems indicated dynamic metabolic and biogeochemical conditions in the field, and confirmed that hourly and daily redox potential variations should be resolved in studies of sediment functioning.

14. SUBJECT TERMS (Keywords)
redox potential, coastal sediments, time series, ecological function

15. NUMBER OF PAGES
iv + 10 pp.

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
Unlimited