EFFECTS OF HYDROLOGIC CONDITIONS ON BIOGEOCHEMICAL PROCESSES AND ORGANIC POLLUTANT DEGRADATION IN SALT MARSH SEDIMENTS

W. James Catallo[1]

Abstract—This work addressed the influence of tidal vs. static hydrologic conditions on biogeochemical processes and the transformation of pollutant organic chemicals (eight representative N-, O-, and S-heterocycles (NOSHs) from coal chemicals, crude oils, and pyrogenic mixtures) in salt marsh sediments. The goals were to: (1) determine the effects of static (flooded, drained) vs. dynamic (tidal) hydrology on redox potential (Eh) dynamics, trace gas evolution, and pollutant transformation; (2) deploy hydrodynamic microcosms for this purpose that were reproducible, well controlled, and adequately monitored; and, (3) develop analytical approaches for target pollutant chemicals that allowed for detection of small but significant concentration differences between time points and treatments, i.e., isotopic dilution. NOSH-amended sediments were exposed to three hydrologic conditions: static drained (oxidized redox potentials), static flooded (reduced redox potentials), and diurnal-tidal (alternating redox potential). The rate of NOSH transformation and the number of NOSHs degraded decreased in the following order: drained = tidal flooded. This indicated that sediments and associated biota exposed to tidal pulsing removed more NOSH compounds faster and to lower levels than flooded, highly reducing sediments.

INTRODUCTION

The work summarized here examined the influence of hydrology on biogeochemical processes that govern transport and transformation of selected pollutant chemicals in wetland sediment-plant systems. “Biogeochemical” refers to a group of coupled biological, e.g., microbial, plant and physicochemical, e.g., flood-drain events from tides and floods, processes that to a large extent determine the productivity, habitat quality, and regional-global significance of wetland and other ecosystems (Catallo 1999, Catallo and others 1999). Previous microcosm studies have confirmed that degradation and transformation rates and pathways of aromatic hydrocarbons (AHs) and N-, O-, and S-heterocycles (NOSHs) differed significantly in marine sediments of different particle sizes and under oxidized vs. reduced conditions (Catallo 1996b, Catallo and Gambrell 1994). In the cited work, AH and NOSH transformation was evaluated in stirred, bubbled, controlled Eh/pH reactors containing sediment slurries maintained as “oxidized, aerobic,” “moderately reducing, anoxic,” and “highly reducing, methanogenic.” AH and NOSH degradation rates generally were: oxidized ≥ moderately reducing >> methanogenic. The reactors used were first-order feedback control systems whose output domains were predefined by desired Eh ranges for each treatment. As a result, Eh vs. time outputs were sinusoidal. Fourier spectral analysis of the Eh waveforms demonstrated that periodic sampling interventions and other system perturbations were detected by the electrodes and preserved in the time series for each system. This suggested that the Eh might change rapidly and reproducibly in response to other periodic forcing, such as diurnal tidal flushing, but this had not been well documented. Further, it was clear that the terms “oxidized, aerobic” applied to wetland sediments were something of an oxymoron. Nevertheless, this treatment type was evaluated because large quantities of wetland and aquatic sediments are disposed of in upland or otherwise well-drained situations, so evaluation of these sediments was deemed important, albeit not especially compelling from the perspective of “wetlands ecology.”

Apart from the differential NOSH and AH transformation rates observed in these experiments, results strongly suggested that measured redox potential (Eh) can be a dynamic nonlinear variable in wetland sediments that can respond quickly and significantly to changing conditions, and that this information can be preserved in a time series of Eh provided adequate sampling intervals are employed. As Eh is considered a biogeochemical “master variable” in many ecosystems, the behavior of this variable should be adequately and accurately represented by the data at all scales relevant to the experimental design (Catallo 1993, Catallo and others 1999, Lindsay 1991). It was clear that the interaction of tidal water level changes with sediments should be included as a treatment in studies of biogeochemical processing of contaminants. In order to do this, effort was expended in the design, monitoring, and evaluation of hydrodynamic sediment microcosms (20 gal) and, later, mesocosms (300 to 3000 gal) containing a biocenosis comprised of sediments, plants, microbes, meiofauna, and macrofauna (Catallo 1999).

The central aims of the current study were: (1) determine the effects of static vs. dynamic hydrology on biogeochemical

[1] Associate Professor of Environmental Toxicology, Laboratory for Ecological Chemistry, School of Veterinary Medicine, Louisiana State University, Baton Rouge, LA 70803.

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behavior of salt marsh sediments, particularly with respect to major output variables, e.g., Eh dynamics, trace gas signatures, and pollutant transformation; (2) design, build, and optimize microcosms for this purpose that are reproducible, well controlled, and adequately monitored in the laboratory or greenhouse; and, (3) develop extraction/analytical approaches for NOSH target chemicals that allow for detection of small but significant concentration differences between time points and treatments. This last item was important because most common methods used for identification of chemicals in sediments are semiquantitative, i.e., provide for order-of-magnitude differentiation in analyte concentrations, and it was expected that differences between NOSH transformation profiles in different treatments of this study would be below this threshold (Catallo 1996a).

The pollutant chemicals selected for this work included representative N-, O-, and S-heterocycles (NOSHs) that occur in coal chemicals, several crude oils, and pyrogenic (combustion-generated) mixtures (fig. 1) (Turov and others 1987). These and other NOSHs are found in large quantities in pollutant mixtures near certain industrial activity, hazardous waste sites, and major harbors. They enter coastal marine and wetland ecosystems through: (a) direct dumping/spillage; (b) fluvial transport of dissolved and sediment-associated chemicals from source outfalls, deposition of combustion-generated airborne particles, semivolatiles, e.g., from the so-called *in situ* burns of spilled oils, and polar residues; and, (c) assorted natural processes, including marine oil seeps and reactions between biogenic organic matter and sub- and supercritical water in various geochemical settings. They are of continuing interest because they can accumulate to bioavailable levels in aquatic sediments, and many NOSH compounds are acutely toxic, with some, e.g., the quinolines, carbazoles, and benzoquinolines and their oxidized metabolic and environmental transformation products, being mutagens or carcinogens or both (Catallo 1996b, Catallo and others 1994, Warshawsky 1992).

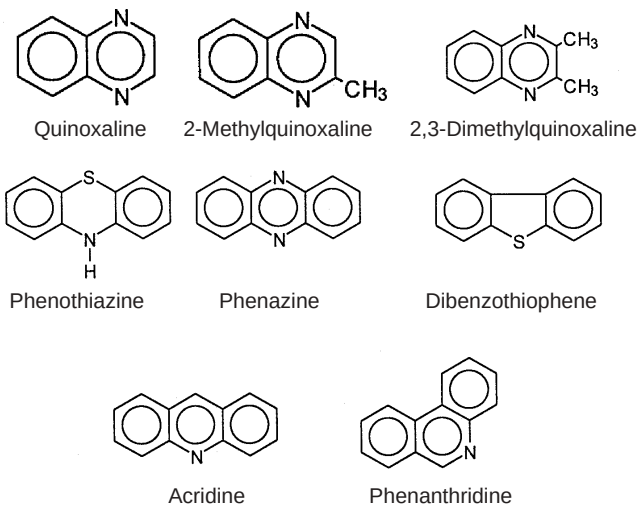


Figure 1—NOSH target analytes examined in this study.

MATERIALS AND METHODS

Hydrodynamic (Tidal) Wetland Microcosms

The microcosms for this work were comprised of 20 gal glass aquaria containing sediment columns as shown in figure 2. Sediment samples were collected from a streamside *S. alterniflora* salt marsh site in Terrebonne Parish, LA. The sediments were mixed with quartz sand and commercial seed starter (5 percent w/w) and then loaded into cylinders (26 cm i.d.) made first of wire, and ultimately of plastic mesh (0.5 cm) to a height of 38 cm. The wire mesh was discontinued after preliminary runs because it interfered with Eh measurements. The systems were covered with plexiglass containing throughputs for water lines, gas sampling, and electrode wire leads, and sealed with silicone plastic. A diurnal tide was simulated by pumping artificial seawater (15 g/L Instant Ocean) into and out of the aquarium once daily, i.e., one high and one low per 24 hour, using peristaltic pumps and controlled by battery-powered timers. The seawater reservoir was continuously aerated. At "high tide," the sediment columns were covered with ca. 8 cm of water. At "low tide" about 5 cm of water remained in the aquarium. Two Eh electrodes (below) were positioned in the top 1 cm of sediment (surface), and two additional electrodes were placed deep within the column in the continually flooded zone near the bottom. Trace gases were analyzed by direct sampling of headspace gases under vacuum to a 10-m cell connected to a Buck Scientific FTIR spectrometer with gold optics and 4 per cm resolution. Molecular sieve 5A and Ascarite A (Aldrich) traps were used to reduce water and CO_2 spectral interference and increase sensitivity. Compounds were identified using authentic gas standards (Scott Specialty Gases) and published spectral libraries from NIST. Digital background subtractions were performed using spectra of normal laboratory air sampled immediately prior to sampling the microcosms, and handled identically; i.e., reference air samples were passed through the sampling loop of the system and through the traps. Thus, CO_2 and water vapor signals in the experimental spectra represent excesses of these materials in the microcosm headspaces vs. the laboratory air.

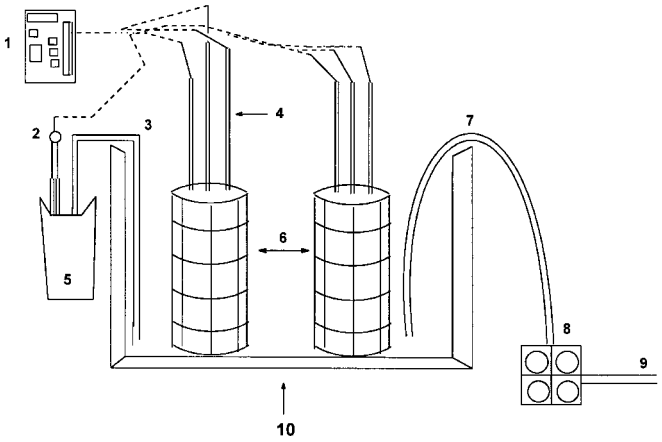
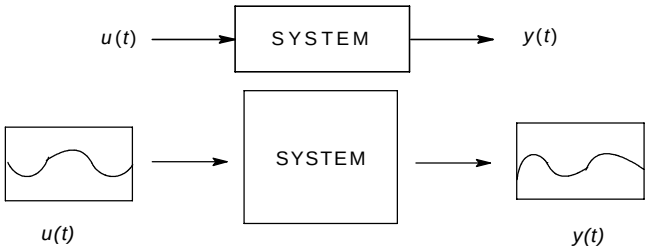


Figure 2—Schematic diagram of the tide simulation microcosm: (1) data logger, (2) calomel reference electrode, (3) salt bridge, (4) platinum electrodes, (5) concentrated KC1 solution, (6) soil column enclosures, (7) water inlet/outlet, (8) automatic peristaltic pumps, and (9) reservoir. Gas tight cover and FTIR feeds are not shown.

Redox potential (Eh) was logged using Pt wire–SCE electrode cells and a multichannel logger (Catallo 1999). The platinum electrodes were constructed by welding Cu wire to 0.5 cm-lengths of 12 gauge Pt wire. The junction and Cu lead were enclosed in glass tubes of varying lengths, and both ends were sealed using a blowtorch. Hence, a ca. 0.5-cm length of Pt was exposed to the sediments whereas junctions and leads were enclosed in sealed glass. The electrodes were polished with light emory paper, soaked in *aqua regia* and then distilled water. Each electrode was calibrated prior to use with a 1-percent quinhydrone solution. Samples were collected at rates between 1 Hz and 1 per hour, depending on the application (in general, the rates were 1 to 2 per hour).

Signal Acquisition and Analysis

A biogeochemical system can be viewed as a signal processor, with inputs, e.g., light and heat cycles, water fluctuations, inputs of organic matter and toxic chemicals, impinging on the system, influencing its behavior, e.g., aerobic vs. anaerobic microbial metabolism, and influencing the magnitude and time structure of numerous outputs (water chemistry, trace gas identities, and evolution time series). Shown schematically below is a generic system with single continuous input and output variable functions, *u(t)* and *y(t)*,



respectively. The inputs mentioned are impulses or excitation functions having importance to system processes, and all of these must be known (identified) and measured accurately with appropriate sampling frequencies. The former is important because confounding and collinear variables can invalidate normal statistical approaches and corrupt causal ascriptions (Asher 1983, Catallo and others 1999) and the latter because processes changing faster than the sampling rate applied to them can cause error (aliasing) when spectral analysis techniques are applied to the time series (Brockwell and Davis 1991, Mallat 1998). These functions, ($u(t)$), can be of many kinds, e.g., linear, spike, ramp, threshold, sinusoidal. Signals are outputs, $y(t)$ carrying information about system processes. Signals are structured in time, whereas noise is not, and increase relative to noise as the square root of the sampling repetitions; $(S/N)_n = n^{1/2}(S/N)_1$; where S is signal amplitude, N is noise amplitude, $(S/N)_1$ is signal:noise ratio after one data acquisition (scan), n is the number of sample scans, and $(S/N)_n$ is the signal:noise ratio after n scans. The states of the system can be defined by the stable and transient domains occupied by output signals *y(t)*.

It frequently is assumed that biogeochemical processes change slowly, i.e., weeks to months, and therefore adequate sampling of many outputs can be performed at rates on the order of 1 per day or longer (Catallo 1999, Picek and others 2000). Unfortunately, it must first be verified that there are no cyclic outputs from the system with frequencies greater than the sampling rate, and this is rarely done. As a result, the assumption that widely spaced data points from dynamic systems can be connected by linear interpolation to accurately reconstruct system temporal behavior becomes a matter of faith rather than demonstration. Further, attempts to analyze such a time series in order to determine its component waves can be highly inaccurate and misleading. The upshot of this is that complex system variables ($u(t)$) and signals ($y(t)$) cannot be interpreted accurately if data points are gathered at rates slower than the changes in the process. For virtually all ecological system processes, classical single resolution Fourier analysis of time series suffers from major analytical drawbacks, not the least of which being its inability to accommodate nonstationarity in the data; i.e., transients and other deviations from perfect statistical regularity in the signals. Single resolution analysis of nonstationary time series leads to aliasing of power spectra (Brockwell and Davis 1991, Mallat 1998) in ways that are not readily interpreted or identified. It was clear from Eh, pH, temperature, and other time series from the microcosms that nonstationarity was a major feature of the input and output variables of concern in this work. As a result, multiresolution "wavelet" analysis was applied to the time series of signals from the microcosms.

Wavelet analysis is a recent development in applied mathematics (Mallat 1998) that has stimulated an enormous interest in many disciplines including signal processing/ reconstruction, vision science, medical imaging, and physiology. The wavelet transform is a technique that allows for the acquisition of both localized time and frequency information about a signal. Its ability to dilate and shift time windows with respect to a signal allows for transient features to be accommodated, long- and short-term variations to be compensated, and periodic features to be isolated, identified, and, if needed, enhanced. In a sense, the wavelet approach has operational and conceptual affinities with the use of an oscilloscope to visualize waveforms in circuits: time sampling windows are varied by the analyst in an attempt to isolate component waveforms of complex signals as standing waves, with frequency data available as the inverse of the time window used to capture the particular wave of interest. Waveform components and their alterations by specific processors (distortion, clipping, chirping, and damping) are obtained by thoroughly permuting the available sampling windows.

The definition of the continuous time wavelet transform (CWT) entails an "analysis wavelet," $\psi(t)$, and the family of shifted and dilated versions

$$\psi_{a,b} = |a|^{-1/2} \psi(t-b)/a \qquad (1)$$

The transform of $x(t) \in L_2(R)$ is then

$$T^w[x](a, b) = |a|^{-1/2} \int x(t)\, P^*(t-b)/a\, dt \qquad (2)$$

The analysis wavelet, Ψ must satisfy the admissibility condition

$$C\,p = \int \left| \Psi(w) \right|^2 / w\, dw < \infty \qquad (3)$$

This condition guarantees the existence of the inverse transform

$$x = C\psi^{-1} \int \int T^w [x]\,(a,b)\ \psi\,^*(t-b)/a\ dadb; \quad \text{(intergrals evaluated } \pm\infty) \qquad (4)$$

One way to realize the transform is using the filter bank interpretation and defining

$$h_a(t) = \psi(-t/a) \qquad (5)$$

It follows that

$$T^w [x]\,(a,b) = x(t)\, h_a(t) = \int x(t)\, h_a(b-t)dt \qquad (6)$$

So, for each scale, *a*, the CWT is comprised by the output of a filter with impulse-response $h_a(t)$. As the filters are dilated according to a scale parameter, their frequency response is modified accordingly, at the discretion of the analyst. Hence, the wavelet transform maps a function of one variable into a function of two independent variables (time, scale). There is, as a consequence, significant redundancy, and, if desired, the time/scale parameters can be rendered discrete, the signal preserved in the transform samples. A standard discretization approach employs a logarithmic step for the scale parameter and a scale-dependent discretization for the temporal parameter. Thus a discretized wavelet transform can be defined by

$$T^{w[m,n]} = T^w[x]\,(2^m, 2^m n) \qquad (7)$$

In effect, a family of wavelets of the form $\psi_{m,n} = 2^{-m/2}\psi(t / 2^m - n)$ is deployed.

Even in the discretized case, the representation can be optimized by requiring the wavelet family, $\psi_{m,n}$, to be an orthonormal as a set. In this case for each value of the integer *m*, the collection of vectors $\{\psi_{m,n};\ n \in Z\}$, defines a subspace, W_m. As the dilation parameter is held constant, all wavelets in that subspace have the same scale. The projection of a function, *x(t)*, on this subspace is interpreted as the details of the function at that particular scale. Since increasing the value of the integer, *m*, introduces larger dilations in the basic wavelet, its time resolution decreases. The sum of all details for all values $m \geq m_0$ is said to give a representation of *x(t)* up to resolution m_0. Mathematically, the representations exist in the subspace

$$V_m = \oplus_{k \geq m} W_k \qquad (8)$$

One of the bulwarks of multiresolution analysis is that a unique analysis function $\varphi(t)$ can be defined such that the collection $\{\varphi_{m,n} = 2^{-m/2}\psi(t / 2^m - n)\}$ spans the subspace, V_m, and these are easy to compute recursively. If, for example, the representation of a signal up to a fine resolution level, m_0, is in the form

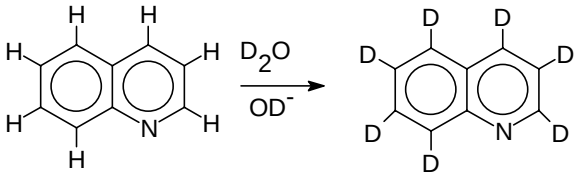
$$X^{mo} = \sum_n c^{mo}{}_n\, \varphi_{mo,n} \qquad (9)$$

one can define a digital filter, *H*, receiving as input the discrete signal, $\{c^{mo} = c^{mo}{}_n;\ n \in Z\}$, and producing as output the coefficients of the next lower resolution, c^{mo+1}. Similarly, the digital filter, *G*, can be defined as receiving the same input and producing as output the details at resolution level m_0.

The wavelet packet approach also applies to discrete time functions such as those obtained by sampling a continuous time signal. It can be considered as the discrete version of the multiresolution decomposition. Using suitable digital filter banks, a discrete time signal is decomposed into orthogonal components, which also have disjoint frequency changes. Then, by combining various orthogonal components one can develop representations of the signal at various resolution levels. For cases of nonstationary ecological signals, such as the Eh time series realized in the tidal microcosms of the current study, periodic features, transients, and long-term trends can be determined without unknown aliasing in resulting spectra. A further advantage is that the effects of low-resolution sampling can be examined, and the resulting effects of aliasing on the signal analysis evaluated. This also was applied to the Eh time series as an illustration of the perils of undersampling outputs dynamic systems and then applying spectral analytical or other analytical techniques to those data.

Synthetic Organic Chemistry

In order to quantify minor or subtle differences in transformation of target compounds between treatments, it is desirable to have stable isotope-labeled, e.g., deuterated, standards for each target compound of interest. These standards can be added to sediments before extraction and serve as internal “monitors” of extraction and analytical efficiencies for the target compounds. As these deuterated standards have properties virtually identical to the target compounds, their loss in the various steps of extraction and analysis is the same as the compounds under study. With appropriate controls and calibration, this allows for quantitative analyses (percent differences can be detected), rather than semiquantitative data (order-of-magnitude differences are detected) provided by many analytical approaches (Catallo 1996a). In addition to this advantage, isotopic dilution also allows for data streamlining: quantitation is simply a matter of integral ratios between the standard (known concentration and base peak integral) and the target analyte (concentration unknown, base peak integral known). Unfortunately, commercial availability of deuterated NOSHs is very limited. As a result, methods were developed in our laboratory to label the target compounds with deuterium either using *de novo* or postsynthetic approaches (reviewed in Junk and Catallo 1996, 1997), the latter typically using supercritical (T >374 ^{o}C/221 bar) deuterium oxide (D_2O), or “heavy water.” A basic example of this strategy is shown for the N-heterocycle, quinoline, below:



Supercritical water is extremely corrosive, and commercial stainless steel reactors leaked or exploded (destroying furnaces and part of a wall) after a few hours. As a result, a substantial amount of effort in the first year of this work was devoted to designing reactors that could withstand supercritical aqueous conditions and were large enough to permit multigram labeling of target compounds. With this accomplished, the target compounds were made in quantities sufficient for use in the transformation studies of NOSHs in the microcosms. Unfortunately, some NOSHs were unstable even in subcritical water, and novel synthetic protocols had to be devised for these compounds. Thus, quinoxaline-d6, 2-methylquinoxaline-d8, and 2,3-dimethylquinoxaline-d10 also were prepared by syntheses developed for this work (Junk and Catallo 1997, Junk and others 1997). Attempts to prepare phenazine-d8 and acridine-d9 by: (a) base-catalyzed supercritical isotope exchange at 400 °C for 6 hours following Junk and Catallo (1996); (b) acid catalyzed isotope exchange at 220 °C for 2 days; and (c) palladium-catalyzed exchange at 250 °C for 2 days, all resulted in extensive substrate decomposition. All compounds subsequently were prepared by base-catalyzed near-critical exchange at 300 °C for 4 hours. Exchange was carried out by heating 300 mg substrate, 15 mL D_2O, and 0.1 mL 40 percent NaOD (in D_2O) in a 30 mL Hastelloy C-22 autoclave. The crude products were extracted with dichloromethane (DCM), the solvent evaporated and deuterated quinoxaline, and 2,3-dimethylquinoxaline purified with a microdistillation apparatus. Phenazine and acridine were crystallized from methanol. Further purification was achieved by chromatography (200 mesh silica gel, hexane:DCM 10:1 v/v). Yields ranged from 45 to 55 percent. Dibenzothiophene-d8, phenothiazine-d8, phenanthridine-d9 were prepared using the published Supercritical Isotope Exchange technique (Catallo and Junk 1998, Junk and Catallo 1996). A 30-mL Hastelloy-C22 autoclave was charged with the 0.3 g of the respective substrates, 15 mL deuterium oxide, and 0.1-mL 40-percent deuterium deuteroxide solution. Exchange was achieved by heating to 400 °C for 6 hrs. Compounds were collected by filtration and purified by chromatography over 200-mesh silica gel using hexane as mobile phase for dibenzothiophene and phenanthridine, and DCM for phenothiazine. Yields for dibenzothiophene and phenanthridine were above 75 percent and have been reported along with a range of other AHs and NOSHs (Junk and Catallo 1996). The yield for phenothiazine was 86 percent. No attempts were made to preclude the facile back-exchange of the N-H proton of phenothiazine during work up under ambient (open-air) conditions because this analyte would be exposed to water during the sample extraction.

NOSH Transformation Studies

Three sediment columns prepared as described above were equilibrated under drained, flooded, and tidal conditions for 2 weeks. The sediments then were collected from the surface third of the enclosures from each hydrologic type. Protiated (hydrogenated) NOSH compounds in acetone were added to the sediments with mechanical mixing (2 hours) to provide uniform levels of the individual target contaminants between 200 and 400 parts per million (ppm) on a weight basis. Care was taken to maintain the electrochemical condition of the sediments (oxidized vs. reduced) during mixing by purging the system and flooding the headspace of the mixing enclosure with Ar (reduced, flooded) or air (oxidized, drained, and tidal). The sediments then were reintroduced to their respective microcosms in the appropriate column enclosure. The three hydrologic regimes were initiated and "time zero" samples were collected within 8 hours of placement using a clean glass corer. Subsequent samples were taken at intervals (1 to 4 weeks) depending on estimators of microbial activity, e.g., iodonitrotetrazolium reduction (Catallo and others 1990), and previous recovery of NOSH target analytes. After collection, the sediment-water samples (ca. 10 g) were weighed and amended with deuterated isotopic dilution standards for each NOSH target analyte at the levels near the sediment concentrations. The samples then were Soxhlet extracted with DCM for 48 hours, with the extract subsequently dried (Na_2SO_4) and concentrated under N_2. The residual sediments in the extraction thimbles were dried and weighed. The sample extracts then were subjected to GC-MS in the full-scan mode. NOSH target analyte concentrations in the extract were determined vs. the isotopic dilution standard by ratios of corresponding peak integrals. These extract concentrations were corrected for concentration factor and dry weight of sediment in the original sample.

RESULTS AND DISCUSSION

The biogeochemical behavior of the sediment columns in the microcosms was very similar to that observed in natural settings and in accord with prevailing theory (Catallo 1999, Jorgensen and Okholm-Hansen 1985, Odum 1981). With respect to the Eh, the continuously flooded and drained systems had reduced (mean = -428 mV) and oxidized (+ 73 mV) Eh values, respectively, with no evidence of daily or longer periodic variation. The routine (weekly) wetting/draining of the drained system, and water exchange in the flooded system, did not affect these trends; apparently the pre-equilibration of sediments prior to addition of the NOSH analytes afforded a degree of redox potential poising, i.e., "buffering," that was not affected by the brief maintenance interventions. The tidal systems, however, exhibited oscillating Eh values, with significant amplitudes (40 to 180 mV) (fig. 3). Analysis of these signals using the wavelet transform confirmed the presence of strong diurnal Eh variations, with a mean value period of 23.78 ± 2.10 hours. It has been shown that these diurnal signals were: (1) reproducible in the tide microcosms; (2) found in the corresponding tidal mesocosms, which also contained the plant *S. alterniflora*; and (3) observable in tidal field sites but not impounded areas isolated from diurnal tides (Catallo 1999). Thermal and light cycles in the laboratory had no discernable effect on the Eh time signature; variation of tide stage throughout the day and at different times of the year

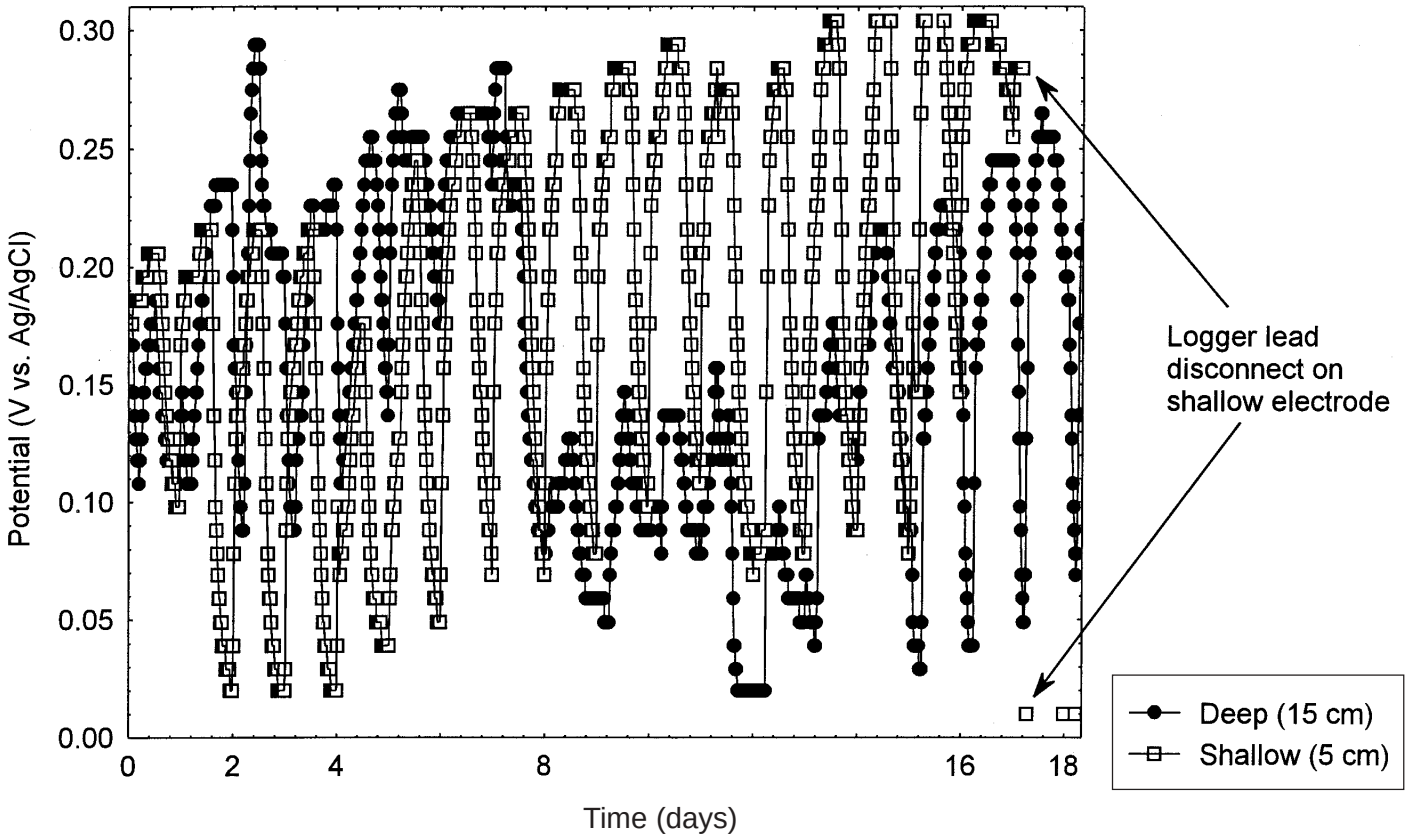


Figure 3—Time series of Eh from shallow and deep electrodes placed in tide simulation microcosms.

(the experiments were conducted in an annex not equipped with climate control) did not affect the tide-derived Eh signal period.

The Eh traces shown in figure 3 are characteristic of the tidal systems in three main respects: (1) the sinusoidal Eh oscillations continued for as long as the tides were applied, but ceased immediately when static conditions ensued; (2) the waveforms are asymmetric, exhibiting hysteresis with respect to oxidation and reduction; and (3) electrodes at the different depths were out of phase (as expected), with deeper electrodes showing smaller amplitudes (probably reflecting the effects of compaction). These features were consistent throughout the experimental runs and in subsequent work with large hydrodynamic mesocosms containing plants and invertebrates (Catallo 1999). The hysteresis of measured redox potentials (item 2, preceding) suggests that the Pt electrode-SCE cell is quasi-reversible with respect to oxidation and reduction in sediments; i.e., it is patently non-Nernstian. This almost certainly reflects compositional as well as bulk phase chemical variables *in situ*. Unpacking these factors and adequately describing the physics involved is far beyond the scope of this communication and might well be impossible given the current level of theory on heterogeneous electrochemical systems (Southampton Electrochemistry Group 1985). In spite of this, the electrodes in the tidal systems remained functional throughout the duration of the experiments and rarely had to be replaced. The electrodes in the oxidized and reduced static microcosms, however, were replaced frequently because of passivation with oxides and sulfides (respectively) and consequent loss of calibration. It would seem that dynamic Eh conditions in the tidal systems reduced the level of passivation on the working electrodes and provided for conditions most favorable for obtaining accurate potential values vs. the more static, well-poised conditions in the other treatments. “Reconditioning” of solid electrode surfaces by alternating oxidation-reduction cycles, i.e., cyclic removal of surface metal oxides and sulfides by alternating redox processes, apparently has not been reported elsewhere and represents an area of interest for further research.

Biogeochemical gas mixtures leaving the sediments also reflected the hydrological status of the treatments: the major gases observed were CO_2 from microbial respiration (drained and tidal) vs. large amounts of sulfide and methane (flooded conditions) (fig. 4). The gas profiles in each treatment were checked weekly and were consistent throughout the experiment.

Transformation of the NOSH analytes was significantly different in each of the hydrologic regimes, with the rate of transformation and the number of NOSHs degraded decreasing in the following order: drained > tidal > flooded. This can be discerned in figures 5 through 7 with respect to the number of NOSHs transformed so as to afford a recovery of under 50 ppm at 16 weeks. Except for one sample showing a spike at week 18, the drained system showed the most complete degradation of quinoxaline, 2-

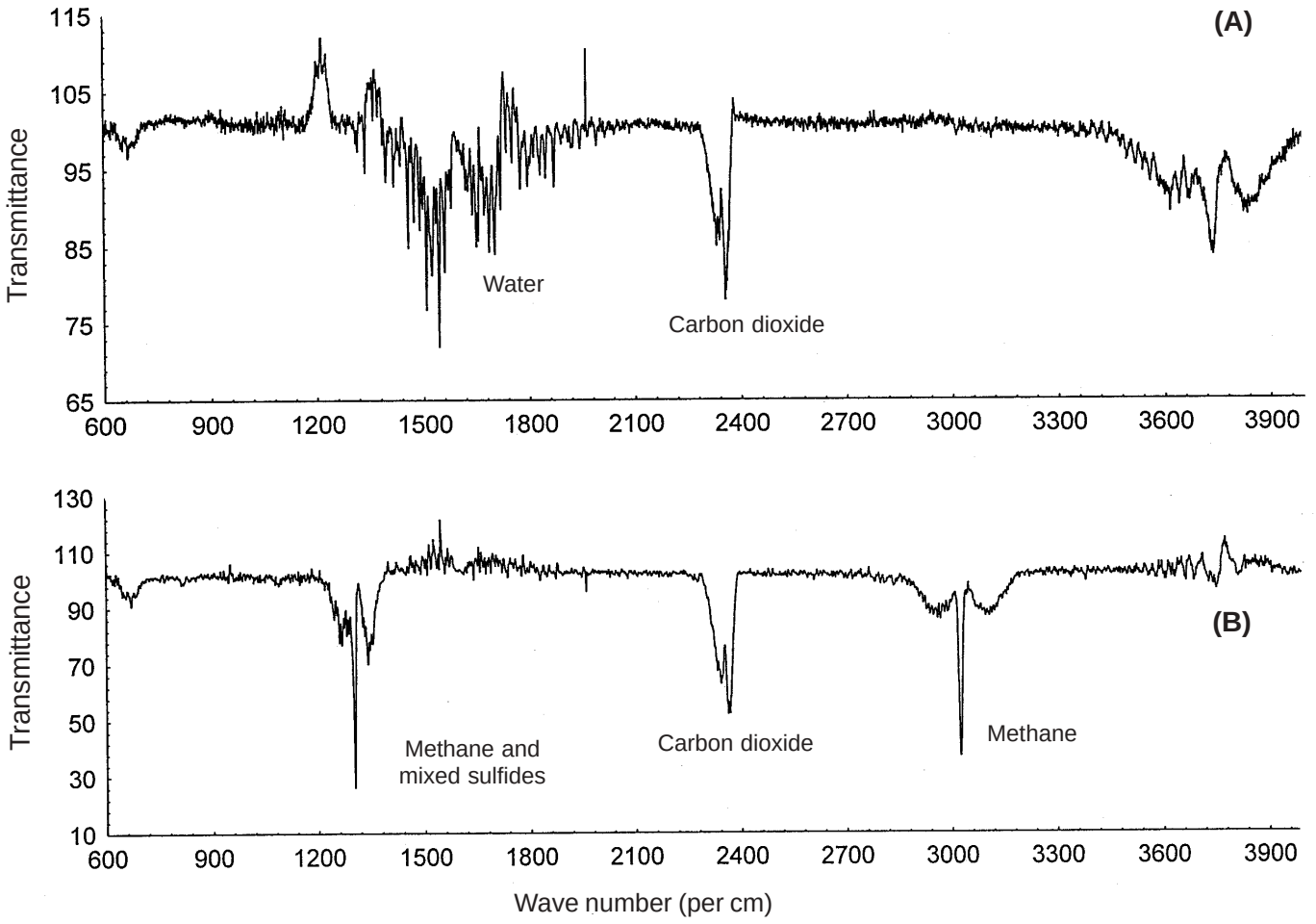


Figure 4—Headspace gases from the tidal (A) and flooded (B) microcosms by FTIR. (Gases from the drained system were similar to A.)

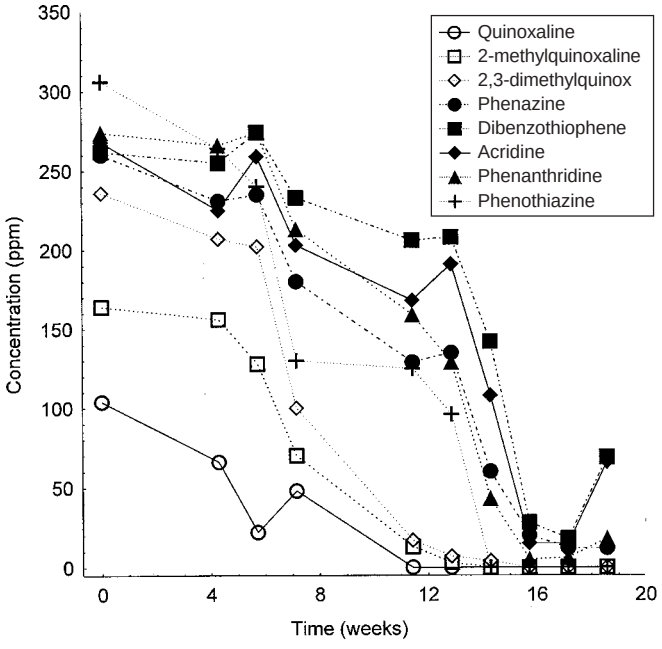


Figure 5—NOSH transformation profiles from the drained/ oxidized microcosm.

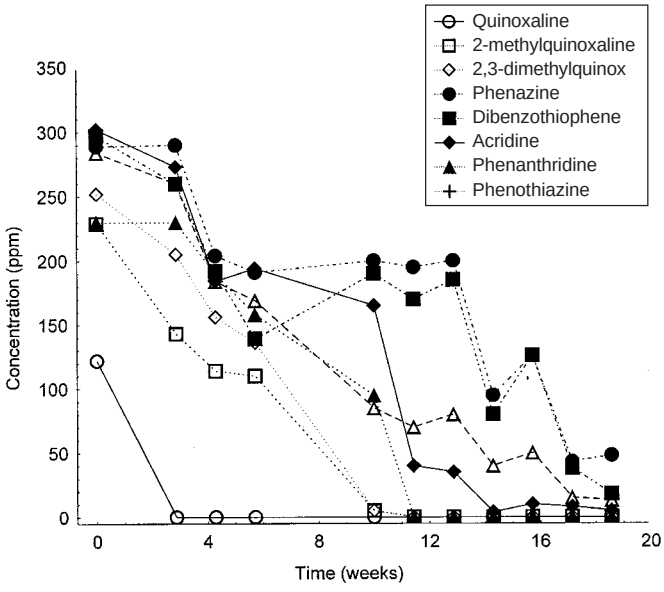


Figure 6—NOSH transformation profiles from the diurnal tidal microcosm.

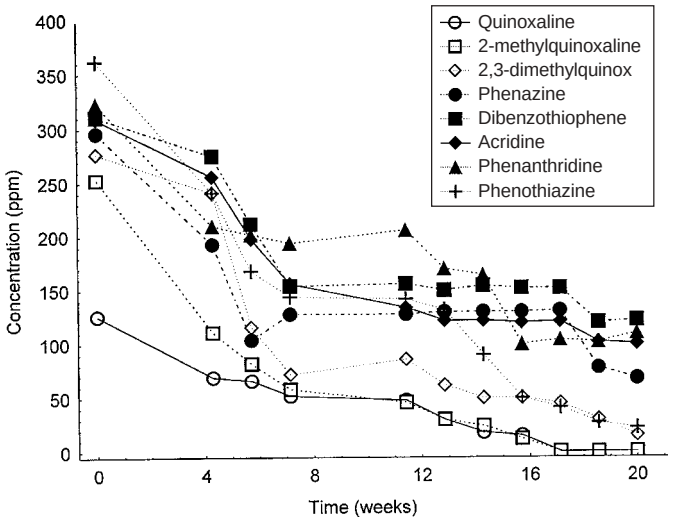


Figure 7—NOSH transformation profiles from the flooded/reduced microcosm.

methylquinoxaline, 2,3-dimenthylquinoxaline, and phenanthridine by week 16, with the recovered concentrations of the other NOSHs also diminished to or below 25 ppm, i.e., a tenfold concentration reduction. Under tidal conditions, quinoxaline, 2-methylquinoxaline, and phenothiazine were eliminated more rapidly than in any other treatment, with phenazine and phenanthridine reduced below 25 ppm by week 16. By 17.5 weeks, all NOSH analytes were transformed so that recoveries were less than 25 ppm. Under flooded conditions, only quinoxaline and dimethylquinoxaline were degraded to recovery levels below 50 ppm within 16 weeks, and these were completely eliminated by week 17. Other than these, only phenothiazine and 2,3-dimethylquinoxaline were transformed to below 50 ppm recovery by week 20. The sediment concentrations of the other NOSHs remained static, with recovery levels remaining relatively constant between 100 and 170 ppm for acridine, phenanthridine, and phenazine between weeks 7 and 20. It would seem then, that except for quinoxaline, 2-methylquinoxaline, and perhaps phenothiazine, there was a pronounced Eh effect on transformation rates for the NOSH compounds studied here.

These transformation studies, while preliminary, clearly indicated that tidal pulsing optimized the transformation of some NOSH compounds relative to flooded conditions, and that *in situ* or "passive" remediation of coal- and petro-chemical pollution in coastal wetlands should include design features that accommodate prevailing hydroperiods, including tides and seasonal events. For most settings where NOSH and AH contamination is a problem, the statically well-drained/oxidized approach is not an option unless excavation or draining/impounding of the system is envisaged. In these cases, changes in sediment physicochemical properties, e.g., acidification, resulting from such approaches are not easily reversible and would attenuate the usability of these sediments in post-treatment applications, e.g., marsh restoration. On the other hand, in many cases so called passive remediation approaches could be adopted that exploit natural hydroperiodicities and the biogeochemical processes that are coupled to them, rather than artificially manipulating them, i.e., by impounding or dredging, and further compromising the functioning of the ecosystem.

In an abstract sense, the use of hydroperiodicity for enhanced chemical remediation and ecological recovery of polluted systems seems promising in light of this and related work (Catallo 1996b). It would involve, at the least, attempts to optimize the tidal volume of the wetland without compromising its integrity and function. Obviously, this kind of undertaking in a real wetland would involve a set of engineering interventions and monitoring strategies that encompass hydrologic, sedimentologic, and biogeochemical variables in a progressive sense. The same is true of the use of marginally contaminated dredge materials and other wastes, e.g., phosphogypsum, bauxite red mud, for coastal habitat restoration projects. The author is aware of no actual cases in which the goals and approaches of chemical remediation and wetland creation/restoration have been successfully coupled. Much further ecological study is called for in microcosms and other controlled settings where variables and causal relationships can be identified and ranked with respect to holistic endpoints including, but not limited to, pollutant transformation.

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