



Determination of the Optimum Sampling Intervals in Sediment Pore Waters Using the Autocovariance Function

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Abstract. An approach to scaling that has found considerable utility in the field of physical oceanography is based on the auto-covariance function (ACF). It is demonstrated to also be useful in determining the characteristic length scale of the dominant variance of dissolved sulfide and ferrous iron in anoxic pore waters. The method begins with the analysis of a data series in which the measurement sampling interval is smaller than the expected length scales. A least squares polynomial fit to the data representing a background field is then removed from the data series making possible the analysis of the variability superimposed on the background field. The characteristic length scale is then defined as the distance in which the measurements become uncorrelated. This usually occurs at a significance-level or zero-crossing of the ACF. Characteristic lengths obtained for sediments from a variety of coastal environments are not distinguishable between second and third order polynomial fits with average values and standard deviations of, respectively, 7.0 ± 2.7 mm and 6.1 ± 2.3 mm. These values are close to the typical burrow diameter of 7.5 mm used by Aller (1978) in his bioirrigation model for sediment diagenesis. These results indicate that macrofauna dwelling in the sediment are probably responsible for the variability, although in the seagrass meadow rhizomes may also play a role.

Key words: scaling, sediment biogeochemistry, diagenesis, pore water, iron, hydrogen sulfide

1. Introduction

A fundamental problem, in studying benthic-pelagic coupling in the marine environment and early diagenesis in sediments, is determining optimum sampling intervals, both in space and time. If a system is under-sampled, critical information regarding processes of importance may be missed. If a system is over-sampled, a major waste of effort can occur. Therefore, it is necessary to develop quantitative approaches for determining what sampling intervals in time and space are needed to answer specific questions in a given environment. Such choices can significantly influence results in the marine environment (e.g., Fonseca, 1996; Whitlatch et al., 2001; Zajac, 2001) and are one of the most crucial decisions that researchers make (Dayton et al., 1992).

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Scale theory is a rapidly developing field in both the natural and social sciences which addresses these types of problems. It deals primarily with grain (or resolution, e.g. the number of pixels per given area) and extent in space and/or time (e.g., the size of a picture). Scaling deals with the translation or extrapolation of information between different scales. Wu and his associates (Wu, 1999; Wu and Qi, 2000; Wu et al., 2000) have written excellent reviews and discussions of scale theory, with applications to the conceptually similar field of landscape ecology. These papers, along the paper of Fonseca (1996) on the application of scaling methods to the study of seagrass systems, provide a good introduction to this field.

One-dimensional steady-state diagenetic models have been the most commonly used approach used for interpreting observations of sediment geochemistry, and understanding early diagenetic and biogeochemical processes in sediments for over a third of a century (e.g., Berner, 1964, 1974, 1980; Boudreau, 1997). However, there has been a growing body of evidence that in many instances this approach is not an accurate representation of what is occurring (e.g., Lavigne et al., 1997; Mannino and Montagna, 1997; Aller et al., 1998; Luther et al., 1998; Harper et al., 1999; Shuttleworth et al., 1999; Eldridge and Morse, 2000; Koenig et al., 2001, Bull and Taillfert, 2001). Spatial heterogeneities occur on scales that range from individual sediment grains to regional basins (Figure 1). Important non-steady-state processes can occur over time ranges from minutes to centuries. How best to design sampling patterns and diagenetic models for sediments from complex natural systems presents a major challenge that has generally not been well addressed by benthic biogeochemists. Our own experience in several research projects consisted of attempts to describe temporal changes which were all too often overwhelmed by lateral heterogeneity (e.g., Cooper and Morse, 1996; Eldridge and Morse, 2000; Hebert and Morse, 2003). A basic problem is how to establish an optimal sampling step size that will maximize the amount of useful information returned and minimize the number of samples needed to describe the dominant variability. A practical example of the application of this approach is, when designing a study, calculating what level of effort will be required to successfully test a set of hypotheses.

A potentially powerful approach to this problem, which has its origins in signal theory, has been developed and tested by physical oceanographers faced with generically similar problems associated with the dynamic processes that occur in the water column (Denman and Feeland, 1985; Poulain and Niiler, 1989). This approach, which is discussed in detail in the next section, uses correlation statistics and "scale theory" to determine, for a selected parameter or set of parameters, the optimal size of spatial or temporal steps which can describe the dominant variability of the parameter(s). In this paper, we describe and give examples of this scaling method's application to pore water chemistry. Data obtained using anodic stripping voltammetry for total dissolved sulfide ($\Sigma\text{H}_2\text{S}$) and ferrous iron (Fe^{2+}) at two seasonally hypoxic sites, one in Corpus Christi Bay, Texas, and the other on Louisiana shelf near the Mississippi river delta, and a seagrass meadow

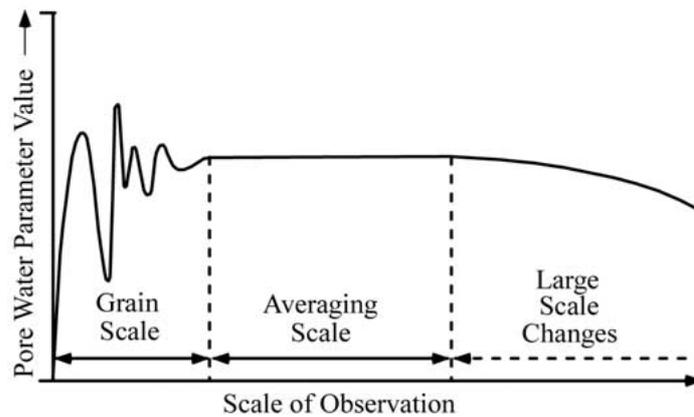


Figure 1. Schematic figure of different observational scales for a pore water parameter in a porous media ranging from the size of a grain to large-scale diagenetic changes. A meaningful continuous function for the parameter exists only on the averaging scale. (Based on Figure 3.2 in Boudreau, 1997).

with adjacent non-vegetated sediments in Yaquina Bay, Oregon, are used in these examples.

2. ACF Approach to Scaling Processes

The use of statistical methods to obtain characteristic length scales has a long and rich tradition in oceanography and meteorology. The most common use in meteorology is optimal interpolation, i.e., objective analysis, in which correlation scales are used to objectively map irregularly spaced observations to some type of regular grid. Gandin (1965) is perhaps the seminal work describing this application. In oceanography, Bretherton et al. (1976) described the use of correlation scales in the design of oceanographic experiments. Sciremammano et al. (1980) presented the spatial scales of temperature and flow in Drake Passage using cross-correlation from current measurements of different instruments along a series of mooring lines. Denman and Freeland (1985) applied the methodology to inhomogeneous, anisotropic, and non-stationary physical and biological data collected on the continental shelf. Poulain and Niiler (1989) present Lagrangian time and space scales of variability from correlation estimates based on drifter data in the California Current. These examples are but a small subset of the many applications of the methodology presented in this paper.

In physical oceanography, the operation of performing a scales analysis of collected data has essentially become a first-order analysis performed at the same time that basic statistics (record length mean and standard deviation) and power spectra are computed. Most physical oceanographic field programs deploy a scales array, i.e., an array consisting of closely spaced mooring elements, to verify that larger arrays are capturing the dominant modes of variability present during the meas-

urements. These analyses can reveal whether station spacing is too great thereby aliasing small scale processes into the observations without resolving them or too small thereby causing unnecessary redundancy and waste of resources.

Correlation scales can be defined for both temporal and spatial data; the methodology is functionally identical, requiring only a sequence of measurements. Conceptually, spatial correlation can be thought of as the minimum distance that two temporal sequences of simultaneous observations of the same parameter become uncorrelated. Temporal correlation can be thought of as the minimum time one must wait for spatial conditions to become uncorrelated with present conditions. We will explore a more rigorous explanation of criteria which constitute uncorrelated sequences later.

The method employs the basic statistical concept of covariance and the covariance function. Covariance is simply a measure of how two (or more) variables co-vary in sequence. This is usually written as:

$$C_{xy} = \frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x})(y_i - \bar{y}), \quad (1)$$

where x and y are sequences of two random variables, N is the number of points in each sequence, \bar{x} and \bar{y} are the mean values of the sequence, and C_{xy} is the covariance of the sequences x and y . When C_{xy} is divided by the variance of each sequence, the quantity is known as the correlation coefficient, r . The covariance, C_{xy} , is also known as the zero-lagged covariance. The covariance function is then defined by introducing an offset (or lag) between the two sequences and then recalculating the covariance. The covariance function then is dependent on the magnitude of the offset. The prefixes auto or cross are added to indicate if x and y are identical or different data series. The equation for the covariance function is:

$$C_{xy}(\tau_k) = \frac{1}{N-k} \sum_{i=1}^{N-k} (x_i - \bar{x})(y_{i+k} - \bar{y}), \quad K = 1, 2, 3 \dots M; M \ll N, \quad (2)$$

where the dependence on the lag, τ , is shown. The subscript k indicates the number of sampling increments, Δt , such that, $\tau_k = K \Delta t$. The covariance function is often normalized: $\rho_{xy} = C_{xy}/\sigma_x\sigma_y$, where σ_x and σ_y are the standard deviation of each sequence. This quantity is known as the normalized auto- (or cross-) covariance function and has maximum and minimum values of +1 and -1. Positive values of ρ indicate the sequences are correlated, while negative values indicate anti-correlation. Note that as k increases, the covariance estimate is based on fewer samples.

We can illustrate this concept by considering a simple sinusoidal sequence of constant magnitude and frequency. At zero lag, $k = 0$, the normalized auto-covariance function (NACF) will be the maximum value of +1. If τ is equal to

one-half of the period of the sinusoid, then the NACF becomes -1 , i.e., anti-correlation. At the lag equal to one-quarter of the period, the NACF is equal to zero, i.e., no correlation. At lags equal to the period of oscillation, the NACF returns to a value of $+1$. For a sinusoidal sequence, the NACF will simply oscillate from $+1$ to -1 with the same period as that found in the original sequence.

For realistic geophysical data, the NACF will often approach zero for very large lags. However, measurement costs rarely allow for record lengths to be sufficient for the NACF to approach zero. Therefore, low-frequency oscillations present in the data usually cause the NACF to oscillate around zero for large lags. We should note that as k approaches N , the NACF becomes statistically meaningless as fewer points are used in the estimation.

We define the scale length as the value of the lag in which the NACF goes from its maximum value of $+1$ (at zero lag) to zero, i.e., the first zero-crossing. The scale length is a temporal or spatial scale depending on the type of data sequence. This definition of scale length can be considered an upper bound of the true scale (Poulain and Niiler, 1989).

In practice a background sequence is often removed from the data sequence prior to estimating the NACF. This background or reference field generally represents large scale spatial patterns or trends in the data. Its removal allows for the analysis of the shorter (i.e., larger wavenumber) energetic spatial variability. Not removing the reference field will usually bias the scales to larger values. The reference field is usually estimated by fitting a polynomial to the original data. The order of polynomial is highly dependent upon the nature of the data set, the inherent characteristics of the system being measured, and the magnitude of the scales that are wished to be resolved. When investigating spatial scales of current dynamics on a continental shelf, Li et al. (1996) compared several different polynomial fits before selecting the quadratic fit to define the reference field. The partitioning of the data into a background and residual field can also be interpreted as separating the measurements into competing or independent mechanisms. The residual field in this sense is then thought to be caused by mechanisms with smaller scales than that responsible for the reference field.

The computer routines used to estimate the NACF have been optimized for speed and efficiency. To this end we will use the Wiener–Khinchine theorem (Hsu, 1984) to estimate the NACF using the Fast Fourier Transform (FFT). The theorem simply states that the NACF is the Fourier transform of the spectral energy density of that series. This technique is particularly efficient when the number of samples is large, i.e., on the order of 1000s.

Let us now consider the practical estimation of the scale length. We assume that the raw data have been examined for statistical outliers, calibration errors, and other problems and have passed quality control and assurance criteria, i.e., the data are suitable for scientific analysis. The raw data are first interpolated to a regular grid (e.g. concentration versus depth). This step is necessary when using the FFT to estimate the NACF. Usually the number of points in the new sequence is

a power of two to further maximize computational efficiency, but is not absolutely necessary. The interval length of the interpolated sequence should be at least as large as the interval length of the original sequence so that sampling resolution is not lost. Next, the reference field is determined. This step is the most subjective part of the analysis.

However, usually a plot of the data will indicate the type of reference field to use. The key is to identify the largest pattern of variability in the data. If the data are evenly distributed around a mean value, then the mean value is the reference field. However, if a more complex pattern is present a higher-order polynomial is required. A rule of thumb is that the ratio of variance in the residual field (raw field minus reference field) to variance in the raw field should exceed 0.10. For ratios less than this value, the scale estimates may be statistically meaningless.

After the reference field is identified and estimated it is then subtracted from the interpolated data to yield the residual field. The NACF of the residual field is then estimated using the FFT. Many mathematical software packages have easily-used built-in FFT subroutines (e.g., MATLAB, IDL, PV-WAVE, etc.). We note that the NACF is written as:

$$\rho_{xx} = \frac{1}{\sigma^2} \text{iFFT}[\text{FFT}[x]^2], \quad (3)$$

where σ is the standard deviation of the residual field x and FFT and iFFT indicate the operation of the FFT and inverse-FFT. Note that the iFFT operation is performed on the square of the absolute value of the FFT of the residual field.

Finally, the scale length is determined by identifying the lag of the first zero-crossing of the NACF (either objectively or visually from plots of the NACF versus lag). It is noteworthy that the first e-folding or significance-level crossing, in addition to the first zero-crossing, of the NACF can also be used to define scale length. However, as stated above, the first zero-crossing represents an upper bound of the true scale length. The e-folding scale is primarily used in meteorology and is the lag in which the NACF crosses e^{-1} , i.e., the natural decay rate. The significance level is the maximum value of the NACF which is indistinguishable from zero based on the effective degrees of freedom of the residual field (Emery and Thomson, 1997). The significance-level crossing, therefore, provides some estimate of the error associated with the zero-crossing scale.

The next step is to repeat the whole procedure outlined above for many independent sequences to create an ensemble of scale estimates. The scales should then be compared to other known parameters, and scales and processes known to exist in the system being measured.

3. Methods for Analytical Data

Voltammetric analysis of pore water components has been used in a wide variety of sediments to analytically quantify fine-scale (0.1 mm) spatio-temporal differences

in pore water geochemistry (Brendel and Luther, 1995; Bull and Taillefert, 2001; Theberge and Luther, 1997; Luther et al. 1998; Hebert and Morse, 2003). Solid-state, gold-mercury amalgam (100 μm sensing tip) microelectrodes were used to simultaneously measure concentrations of dissolved O_2 , Mn^{2+} , Fe^{2+} , and $\Sigma\text{H}_2\text{S}$ (Brendel and Luther, 1995). The microelectrodes were calibrated against O_2 and Mn^{2+} standards in seawater, and the pilot ion method was used for Fe^{2+} and $\Sigma\text{H}_2\text{S}$ (Brendel and Luther, 1995) whose detection limits were, respectively, 15 μM and $\sim 0.2 \mu\text{M}$. Precision was about 5%. Minimum detection limits for each analyte using a DLK-100A electrochemical analyzer from Analytical Instrument Systems Inc. (AIS) were as given in Brendel and Luther (1995). O_2 concentrations dropped below minimum detection limits in the first few millimeters of sediment and Mn^{2+} was generally below its detection limit. Consequently, only Fe^{2+} and $\Sigma\text{H}_2\text{S}$ concentrations are reported in this study. Core profiles were obtained at 2–5 mm depth intervals in replicate (for most cases) but may be collected at sub-millimeter depth resolution using a micromanipulator (Velmex).

Data obtained using anodic stripping voltammetry for dissolved sulfide ($\Sigma\text{H}_2\text{S}$) and iron (Fe^{2+}) at two seasonally hypoxic sites and the seagrass meadow with adjacent non-vegetated sediments are used in these examples. One hypoxic site was located in Corpus Christi Bay, TX in 3–4 m of water with slightly sandy sediments and was sampled during July of 2002. The other hypoxic site was located on the Louisiana shelf near the Mississippi river delta in muddy sediments in ~ 50 m of water and was sampled in April of 2002. The seagrass meadow studied was at Idaho Point in Yaquina Bay, OR, and was sampled in October 2000. It was composed of *Zostera marina*, also commonly referred to as eelgrass (Hebert and Morse, 2003). Collection at all sites included use of 14 cm diameter polycarbonate push-cores to a depth of ~ 20 cm.

For the seagrass sites, cores of intact plants and adjacent (< 1 m) unvegetated cores were taken in the early morning (dark) at low tide and immediately brought to the laboratory where the initial concentration profiles were obtained. Microelectrode scans were replicated for reproducibility at each depth and used as backups. Three microelectrode profiles with three different working electrodes spaced 1.5 cm apart laterally were obtained using a multiplexer from AIS, Inc. and sequentially scanned with a 2 second lag time between scans. (See Hebert and Morse, 2003, for complete experimental design and results.) The Corpus Christi Bay hypoxic cores were collected in the same manner as the seagrass cores except by scuba divers. Three sites in the estuary were chosen for study based on prior hypoxic trends (Ritter and Montagna, 1999). A core was taken, at each site, for laboratory experiments for further anoxic observation, where single electrode profiles were made repetitively at different times. In this work, we have included four laboratory induced anoxic time periods for incubated cores from two of the three chosen sites, cores CCB3 and CCB5. The incubation time intervals for CCB3 (a–c; different sampling times) are 0, 41.5, 174.5, and 198 hours and CCB5 (a–c) are 0, 48.5, 88.5, and 144 hours. Additional “in-situ” cores were taken from the

beginning to the end of the study period as the local seasonal hypoxia intensified. Multiple simultaneous profiles were made with each collection. These cores were used to assess heterogeneity and used to compare the laboratory-to-natural setting. Core CCB1-M4 represents this collection, at 504 hours of monitoring, where one electrode profile is shown. For the purposes of this paper, at site CCB3 we analyzed the Fe^{2+} results, while at sites CCB1 and CCB5, we looked at the $\Sigma\text{H}_2\text{S}$ results.

The Louisiana shelf cores were sub-cored from a GOMEX boxcore aboard the R/V Gyre. This site was chosen based on previous hypoxic trends (Rowe et al., 2002). Laboratory cores were incubated in the same manner as the above Corpus Christi Bay cores where HP (a, b, c) represents Fe^{2+} at times 0, 168, 240, and 1754 hours.

4. Application of the ACF Method to Pore Water Data with Discussion

In this section we present examples of the application of the ACF approach to data sets for dissolved Fe^{2+} and $\Sigma\text{H}_2\text{S}$ obtained as described in the previous section. It is important to keep in mind that our purpose here is not to describe the processes that were under study, which are topics of other papers (e.g., Hebert and Morse, 2003; Sell and Morse, in preparation), but rather to illustrate major considerations and practical methodology when using the ACF approach to choose sampling intervals. As noted earlier, this involves both quantitative mathematics and some good common sense.

Before applying the ACF method to the data sets, it is useful to consider its utility in a broader context. The “golden rule” is don’t use it if you don’t need to. If only a few cores are to be studied or plenty of time and money is available, it is probably always best to obtain as much data as possible. In practice, this must always be initially done on a selected set of cores that are believed to be “representative” of the area to be studied. This in itself can be a difficult decision. Although concentrations and distributions may differ among them, if a similar scale length is obtained it will provide a solid guide for further work.

As noted in the Introduction, spatial and temporal variability occur over a broad range of scales reflecting different physical and biogeochemical processes. A rather obvious “first rule” is that processes leading to variability on an incremental size smaller than that observable by the sampling method cannot be determined. For example, the traditional “slice and squeeze” method of obtaining pore waters that is still often about the only practical means of obtaining sufficient volumes of pore water for a variety of analyses (e.g., nutrients, dissolved organic carbon, dissolved inorganic carbon, sulfate, etc.) often requires sediment core intervals on the order of 1 to 4 cm. The changes that occur over several cm to tens of cm and the impact of some macrofaunal processes such as burrowing by shrimp and large bivalves are observable on this scale. Most of the major diagenetic models have consequently been built on fitting model results to data sets of this scale (e.g., Berner, 1974, 1980; van Cappellan and Wang, 1996; Boudreau, 1997, 2000; Eldridge and Morse,

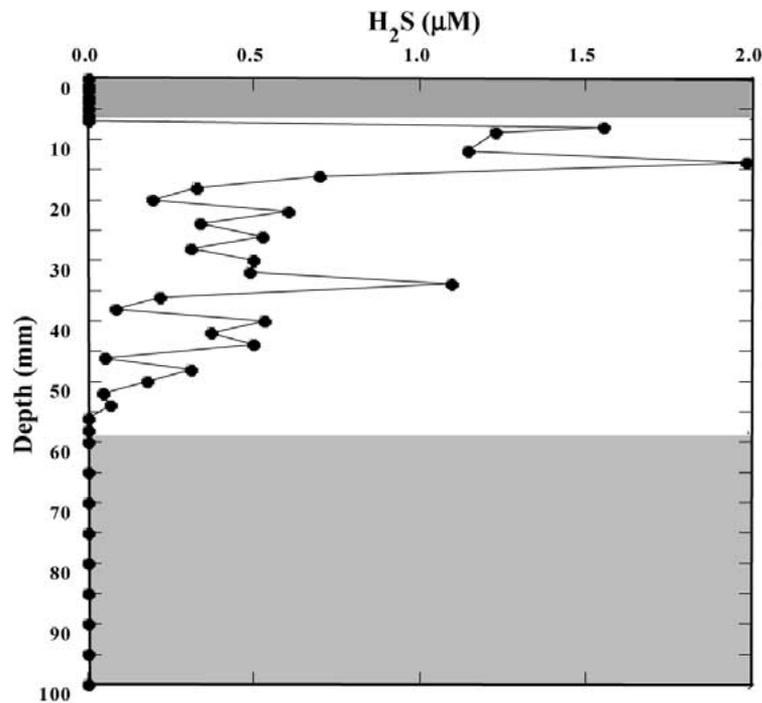


Figure 2. Total dissolved sulfide profile at Corpus Christi Bay Station 1. The shaded depth intervals would not be included in the fitting process to determine the scale length.

2000). However, while such models and the processes on which they are based have considerable utility, they cannot deal with smaller scale variability and essentially produce a description of an average composition of what is often a highly heterogeneous system at a smaller scale (e.g., Aller, 1980; Aller et al., 1998).

The microelectrode method, used in the data sets presented here improves the observable scale by about one to two orders of magnitude. As will be subsequently shown, this reveals an important scale length for the variability of dissolved reduced iron and sulfide on the order of a few mm that probably reflects the importance of macrofauna and, in vegetated sediments, small roots in controlling iron and sulfide distributions. Still beyond our analytical observation scale is the ability to determine the importance of the heterogeneous distribution of microorganisms such as iron oxide and sulfate reducing bacteria.

A “second rule” for applying the ACF method is that it should be used only over intervals where change is observable beyond the analytical precision or detection limit of the measuring technique. Including regions where no observable change is occurring leads to considerable fitting difficulties and can badly bias results where the objective is to determine the scale length of the dominant process leading to variability within the interval of change. An example of this is where no Fe^{2+} is observable until a few cm below the sediment-water interface, Fe^{2+} then goes

Table I. Values for different sites or cores using different polynomial least squares fits of varying order (Fit Order) of the zero crossing, normalized residuals (mean of the absolute value of the residual (mean AVR) normalized to the mean of the raw data) and the percent of the variance accounted for by the fit.

Site	Fit order	Zero crossing (mm)	Normalized Residuals	% of variance Accounted for	
CCB1-3 (SH2S)	1	21.1	0.21	45	
	2	3.9	0.11	83	
	3	4.4	0.09	89	
	4	4.5	0.10	90	
Yaquina Bay ($\Sigma\text{H}_2\text{S}$) Vegetated	2	9.9	0.17	75	
	3	6.1	0.10	90	
	Unvegetated	2	11.7	0.20	57
		3	11.8	0.19	61
CCB5 ($\Sigma\text{H}_2\text{S}$) Profile-1	2	5.4	0.09	42	
	3	4.6	0.07	64	
	Profile-2	2	3.6	0.12	55
		3	4.0	0.12	59
	Profile-3	2	8.3	0.08	46
		3	8.3	0.08	46
	Profile-4	2	4.6	0.08	68
		3	4.8	0.08	69
CCB3 (Fe^{2+}) Profile-1	2	8.7	0.41	50	
	3	6.7	0.18	90	
	Profile-2	2	4.4	0.12	73
		3	4.8	0.10	81
	Profile-3	2	8.3	0.17	10
		3	5.2	0.11	59
	Profile-4	2	7.7	0.17	63
		3	8.0	0.17	64
LA Shelf (Fe^{2+}) Profile-1	2	4.0	0.14	46	
	3	4.2	0.78	47	
	Profile-2	2	6.6	0.14	26
		3	3.1	0.11	46
	Profile-3	2	11.2	0.13	22
		3	8.5	0.08	69
	Profile-4	2	6.8	0.17	47
		3	6.6	0.16	49

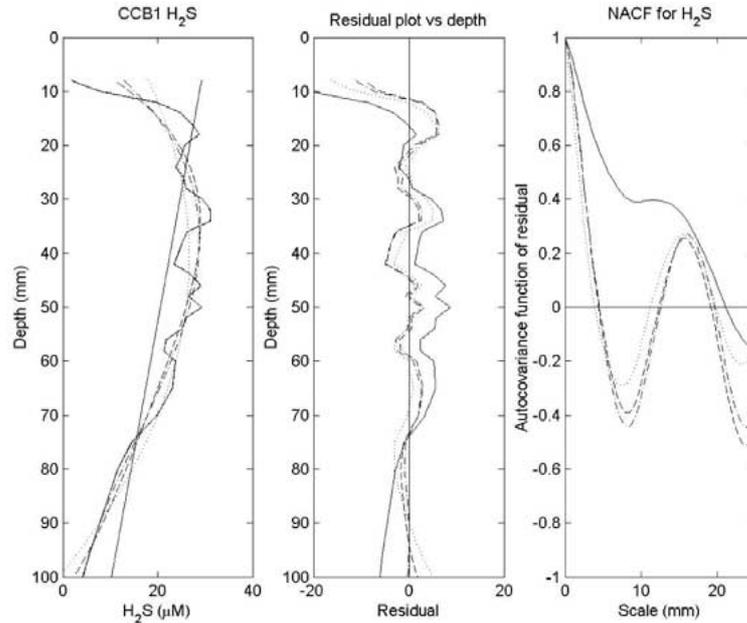


Figure 3. (Left panel) Dissolved $\Sigma\text{H}_2\text{S}$ concentration (solid jagged line) versus depth at Corpus Christi, Texas, station CCB1. Over-plotted are polynomial least-squares fits of order one (straight solid line), two (dotted line), three (dash-dot line) and four (dash-dash line). (Center panel) Residual of $\Sigma\text{H}_2\text{S}$ concentration minus polynomial fit versus depth. Line style denotes order of fit and is the same as that used in the left panel. (Right panel) Normalized ACF (NACF) versus distance for each residual curve plotted in center panel.

through a depth interval of several cm where it varies substantially and at greater depths is below detection limits (e.g., Figure 2). It should also be noted that such fitting will commonly be done over different depth intervals for different dissolved components. For example, detectable dissolved Fe^{2+} and $\Sigma\text{H}_2\text{S}$ usually do not extensively coexist over the same depth range.

Closely related to the “second rule” is the most mathematically arbitrary aspect of our approach to the ACF method. This is fitting the equation to the data to describe the large scale changes (background or reference data field). The resulting plot is similar to that which would be produced by the previously cited diagenetic models. Here we have used a least squares polynomial fit of varying degree. There is no theoretical basis for this and in specific cases other types of fitting equations (e.g., exponential) may be more appropriate. In Figure 3, we show results using first through fourth degree polynomial least squares fits to determine the characteristic length for A) dissolved $\Sigma\text{H}_2\text{S}$ versus depth with fits, B) the residual versus depth, and C) value of the normalized ACF versus scale length. In Table 1, for the different order fits, the value of the zero crossing, mean of the absolute value of the residual normalized to mean concentration and percent of the variance accounted for by the fit are given. In this case, the second through fourth order fits yield similar zero

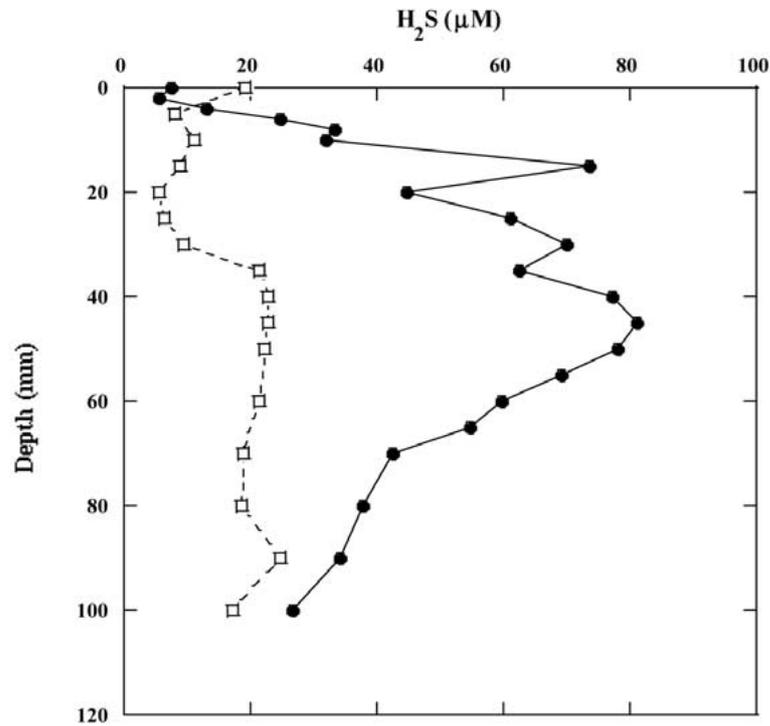


Figure 4. Total dissolved sulfide profiles for Yaquina Bay, Oregon, cores from a seagrass meadow (solid circles) and adjacent vegetated sediments (open squares) based on data from Hebert and Morse (2003).

crossing values of, respectively 3.9, 4.4, and 4.5 mm, indicating that a second order fit is probably adequate for estimating the characteristic length. It should be noted that if, upon visual inspection the more smoothly varying data below 60 cm depth is treated separately, its characteristic length is about 12 mm.

Further examples are presented by giving depth profiles for Dissolved $\Sigma\text{H}_2\text{S}$ in mud-dominated estuarine sediments that are from a seagrass meadow and nearby unvegetated area in Yaquina Bay, Oregon (Figure 4), and multiple depth profiles in mixed sand and mud sediments from Corpus Christi Bay, Texas (Figure 5). Multiple dissolved Fe^{2+} depth profiles are provided from a nearby site in Corpus Christi Bay (Figure 6). Also included in the examples are results from multiple $\Sigma\text{H}_2\text{S}$ profiles in rapidly accumulating fine-grained sediments on the Louisiana shelf west of the Mississippi River delta in the region where seasonal hypoxia occurs (Figure 7). The parameters previously described for Table I are given for second and third order polynomial least squares fits for these profiles. These multiple examples provide profiles and results of our approach for quite differing profile shapes and variability, and from different coastal environments containing both dissolved iron and sulfide dominated pore waters.

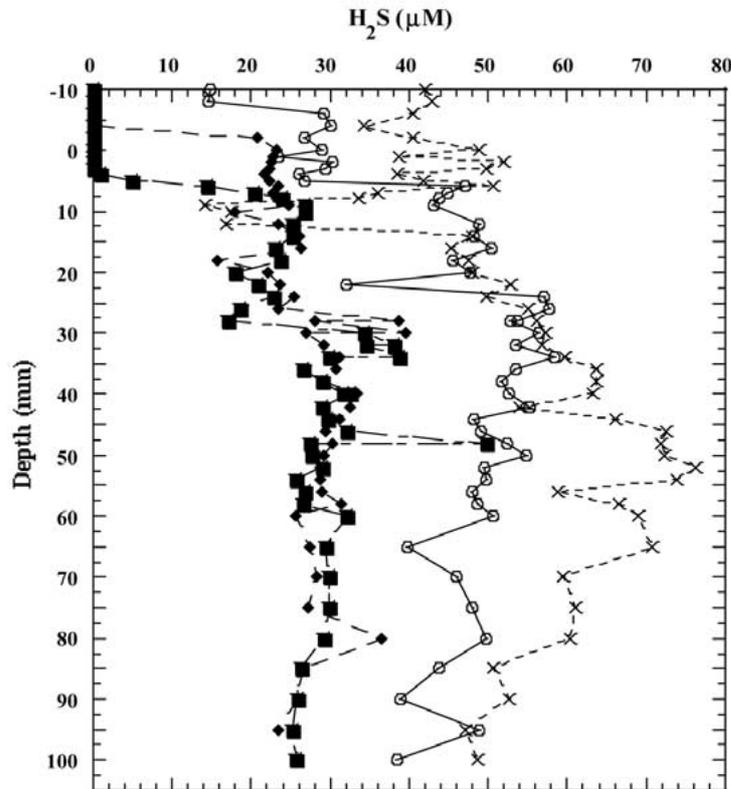


Figure 5. Total dissolved sulfide profiles in a core from Site 5 in Corpus Christi Bay, Texas, in which the overlying water's oxygen concentration was varied with time. Time in hours: 0 (solid square), 48.5 (open circle), 88.5 (solid diamond), and 144 (\times). Data from Sell and Morse (in preparation).

Results of the ACF approach for these 14 cores yield a considerable range of normalized residuals (0.08 to 0.78) and percent of variance accounted for (26% to 90%) reflecting the major differences in the complexity of the profile shape and "noisiness" of the data. However, the results for the scale length are more consistent. The range is only from 3.1 to 11.8 mm. Results from the second and third order polynomial fits are statistically not distinguishable with average values and standard deviations of, respectively, 7.0 ± 2.7 mm and 6.1 ± 2.3 mm. One way of expressing this result is that although the amplitude of signal is quite variable, the frequency falls in a narrow range.

As noted in the Introduction, scale length can often be associated with some physical process or characteristic of the system. In sediments, the scale length is often likely to reflect a biogeochemical process. The scale length that we have observed is similar in size to the diameter of common macrofaunal organisms such as polychaete worms (e.g., Aller and Yingst, 1978). It is in excellent agreement

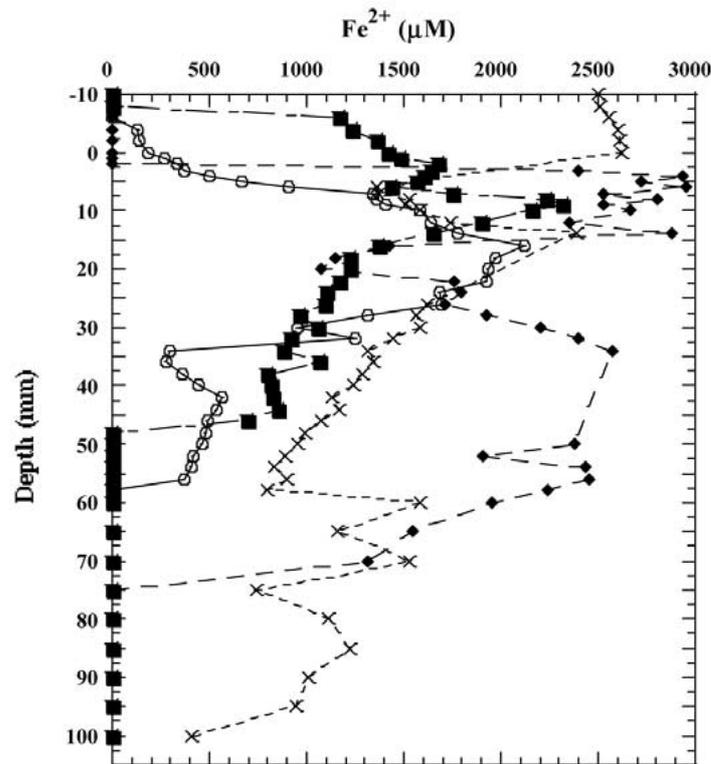


Figure 6. Dissolved Fe^{2+} profiles in a core from Site 3 in Corpus Christi Bay, Texas, in which the overlying water's oxygen concentration was varied with time. Time in hours: 0 (solid square), 41.5 (open circle), 174.5 (solid diamond), and 198 (\times). Data from Sell and Morse (in preparation).

with the burrow diameter value of 7.5 mm used by Aller (1978) in his model for the importance of bioirrigation in controlling sediment chemistry near the sediment-water interface. Although, physically there may be wide variation in the density of infaunal organisms leading to variations in the normalized residuals (something worthy of further investigation), the size range of the dominant organisms (or their burrows) appears to be limited and reasonably predicted by the ACF method for a wide variety of coastal sediments. It should also be noted that the seagrass rhizomes are also in this approximate size range and probably exert an influence in the sediments from the seagrass meadow. These results add to the growing appreciation of the importance of small scale coupled diagenetic biogeochemical processes and point to the need for more sophisticated diagenetic models that can properly incorporate small-scale variability.

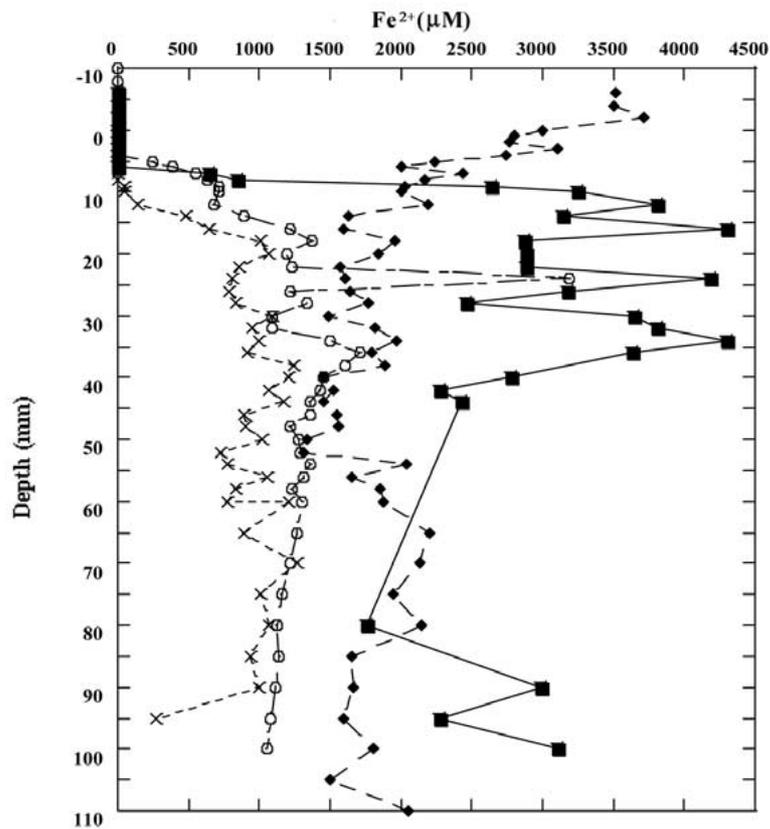


Figure 7. Dissolved Fe^{2+} profiles in a core from Site 5 in Corpus Christi Bay, Texas, in which the overlying water's oxygen concentration was varied with time. Time in hours: 0 (solid square), 168 (open circle), 240 (solid diamond), and 1754 (\times). Data from Sell and Morse (in preparation).

5. Summary

In studies of sedimentary biogeochemistry where large numbers of samples must be analyzed, such as those directed at spatial or temporal change, the ACF method provides a relatively easily applied scaling approach to choosing sample spacing. Results can be used to optimize the sampling interval in time and/or space necessary to minimize the number of samples without losing the dominant source of variability beyond the general large scale process that cause change. The scale length that is obtained usually reflects the size of the physical or biological process that produces it. This relationship can be used both as a guide for searching for important factors leading to variability or in helping to confirm, as in our examples, expected sources of variability.

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