



Redox Chemistry in the Root Zone of a Salt Marsh Sediment in the Tagus Estuary, Portugal

BJØRN SUNDBY^{1,2,*}, CARLOS VALE³, MIGUEL CAETANO³ and GEORGE W. LUTHER III

¹*Institut des Sciences de la Mer de Rimouski, Université du Québec à Rimouski, Rimouski, Québec G5L 3A1, Canada;* ²*Earth & Planetary Sciences, McGill University, Montreal, Québec H3A 2A7, Canada;* ³*IPIMAR, Avenida Brasília, 1400 Lisbon, Portugal;* ⁴*College of Marine Studies, University of Delaware, Lewes, DE 19958, USA*

(Received: 30 October 2002; accepted: 8 November 2003)

Abstract. Measurements of O₂, Fe(II), Mn(II) and HS⁻ in salt marsh sediments in the Tagus Estuary, Portugal, made with a voltammetric microelectrode, reveal strong seasonal differences in pore water composition within the 20 cm deep root zone. In spring, oxygen was below detection limit except close to the sediment surface. Fe(II) was present below 5 cm in concentrations ranging from detection limit to 1700 μM. In summer, oxygen was present in the pore water almost to the bottom of the root zone in concentrations ranging from detection limit to more than 100 μM. The spatial variability was intense: O₂ concentrations as high as 78 μM and as low as 25 μM existed within 2 mm of each other. Fe(II) was below detection limit except towards the bottom of the root zone. In late fall, oxygen was found to 8 cm depth, but in concentrations lower than in summer, and Fe(II) was present below 9 cm. Mn(II) was found at levels declining from typical values of 200 μM in spring to less than 20 μM in late fall. With one exception, sulfide was below the detection limit in all measurements. During periods when dissolved Fe(II) is available in the pore water at the same time as O₂ is delivered by roots, iron-rich concretions can form on roots. These conditions, which lead to precipitation of iron oxide in the sediment adjacent to roots, exist in spring, when new roots infiltrate anoxic Fe(II) containing sediment. They do not exist in summer, when dissolved Fe(II) is unavailable, or in winter, when oxygen is unavailable. The seasonal redox pattern revealed by the pore water chemistry is driven by the annual cycle of growth and decay of roots.

1. Introduction

Plants growing in waterlogged, anoxic environments such as salt marshes do not rely on the soil to provide their roots with the oxygen needed for respiration. These plants supply the oxygen themselves (Armstrong, 1978). This is accomplished via a continuous gas space within the plant tissue, the aerenchyma, in which oxygen diffuses from the aerial parts of the plants to the tips of the roots (Allaway et al., 2001; Anderson, 1974; Teal and Kanwisher, 1966). Diffusion in the gas phase, which is more than three orders of magnitude faster than in water, is an efficient mechanism for transporting oxygen within the hollow roots. When more oxygen

* Author for correspondence: E-mail: b.sundby@uquebec.ca

is available in the root than is needed for respiration, excess oxygen may diffuse across the root wall, leak into the surrounding soil, and react with reduced soil components. These reactions set up concentration gradients and drive mass fluxes in the rhizosphere.

Much of what is known about the effects of roots on soil chemistry has been inferred from the analysis of roots and soil, and pore water collected with dialysis samplers or extracted from bulk soil samples by centrifugation or squeezing. These techniques produce data that are integrated over relatively long temporal scales and large spatial scales. They do not take into consideration the spatial and temporal complexity of the distribution of roots within the soil. In a recent review, Clothier and Green (1997) pointed out that: “[The complexity] makes difficult any analytical description of root form that might be used as the framework against which to reference the processes of root functioning. (...) The spatial form changes temporally through seasonal cycles and as a result of local patterns of root growth and death. (...) Because roots are hidden below the surface, tightly enmeshed in the matrix of soil, it is difficult to observe root form. (...) There is a need to improve our abilities to observe the links between root form and function”.

Because roots interact with the soil matrix via water, the functional link between root and soil may be found in the composition of pore waters. Direct measurement of pore water constituents is now possible with various types of microelectrodes (Taillefert and Rozan, 2002). Among these, a recently developed voltammetric Au/Hg electrode (Brendel, 1995; Brendel and Luther, 1995) is of particular interest because it can measure, simultaneously, in real time, and with high spatial resolution, the concentration of the major redox species involved in soil chemistry (O_2 , Mn(II), Fe(II), and HS^-). We applied this tool to the study of porewater chemistry in the Rosario salt marsh in the Tagus Estuary, Portugal, in order to gain insight into redox processes occurring on small spatial scales and short temporal scales as a result of root-sediment interactions.

Ideally one would like to probe pore water properties in the immediate vicinity of a root and at known distances from the root surface. However, since roots are hidden, it is not possible to know *a priori* where a probe is positioned relative to a root. We were therefore obliged to use a hit-or-miss approach to measurements in the root environment. Although oxygen release may be limited to certain parts of an individual root (Conlin and Crowder, 1989) we make the simplifying assumptions that root biomass can be represented by the total combined length of roots in a volume of sediment, and that the individual root is a line source of oxygen. The strength of the oxygen source, which is a measure of the flux of oxygen into the soil, is then a function of root biomass. Since soil is reducing and consumes oxygen, the relative rates of oxygen supply (source strength) and oxygen consumption (reducing capacity of the soil) determine whether the porewater composition at a given time and place will be dominated by oxidizing or reducing species. Because the voltammetric probe has the capability to measure oxygen and Fe(II) simultaneously, we can tell whether the porewater is oxidizing (oxygen present)

or reducing (Fe(II) present). The actual concentrations of these species are not a simple function of distance from a root; they are a function of local rates of supply and consumption of oxidizing and reducing species. These vary over time.

The strategy we adopted consisted of making as many measurements with the micro electrode as could be completed on a given core within several hours of its collection, spacing the measurements along the depth axis of each core and/or at a fixed depth horizon. The expectation was that the proportion of oxidizing/reducing environments encountered by the probe in a given core would be proportional to the relative importance of these environments in the core at the time of measurement. Although each measurement can be related to a depth below the soil surface, the overall results should not be interpreted in the conventional sense of vertical profiles obtained on root free subaqueous sediments, i.e., they should not be interpreted as if oxygen were only supplied by diffusion in the porewater across the sediment-water interface.

2. Study Area

The Rosario salt marsh is located in the southern part of the Tagus Estuary, Portugal, in the vicinity of a large industrial complex. The marsh has a highly branched system of creeks and channels and is inundated daily by the tide. The dominant plant species are *Spartina maritima*, *Arthrocnemum fruticosum*, and *Haliomione portulacoides* (Caçador et al., 2000). Cylindrical concretions, whose diameter can reach 0.4 cm, are found on the roots of these plants (Sundby et al., 1998; Vale et al., 1990). These concretions are formed by precipitation of iron oxides in the interstices between sediment grains and contain as much as 12% Fe. The iron content of the sediment in which they are found is only 5%. The concretions are also enriched in Cd, Cu, Pb, Zn, As and P, whose concentrations are one order of magnitude higher in concretions than in the sediment in which they occur (Vale et al., 1990; Caetano and Vale, 2002).

The temperature in Tagus saltmarshes does not go below the freezing point, and the plants do not experience a true dormancy period but remain active to a varying extent throughout the year (Catarino and Caçador, 1981). Nevertheless, there is strong seasonality in root biomass, which varies between 3 and 8 kg m⁻² over the year (Caçador et al., 2000). The root biomass increases from March to September in response to increasing temperature and declines between September and March. The mass ratio of root to sediment varies between 1:12 in winter and 1:4 in summer. This variation is similar to what has been observed in other marshes (e.g., Schubauer and Hopkinson, 1984). The intense production and decay of root biomass also affects metals, which accumulate in the roots during the growth period and are released to the sediment during decomposition (Caçador et al., 2000). The thickness of the root zone is approximately 20 cm.

3. Methods

Sediment cores were collected from an area in the Rosario saltmarsh colonized by *H. portulacoides*. This plant grows along the banks of tidal creeks, where it forms pure stands. Samples were collected on July 18 and 24, November 25 and 27, December 5 and 11, 1996, and on May 26, 1998, using a 10-cm diameter stainless steel hand-held corer. Each core was collected at 8 a.m. and was immediately transported to the laboratory. The analysis began within 2-3 hours of collection and was completed 5-6 hours later.

Each core was analyzed at approximately 10 mm depth intervals. The core was laid out horizontally on a bench, cradled in a coring tube with part of the side cut away. In this way, the sediment could be accessed by inserting a microelectrode through the exposed side of the core. To exclude artifacts due to contamination with atmospheric oxygen, each measurement was made after inserting the microelectrode 20 mm below the exposed core surface. Measurements made on the anoxic sub root-zone portion of a core showed that oxygen from the atmosphere did not penetrate more than 1 mm below the exposed sediment surface during the time it took to complete the work on a core. Reference and counter electrodes were inserted into the side of the core within a few cm of the working electrode. To obtain an estimate of horizontal variability within the root zone, a series of measurements was made by moving the tip of the electrode 2 mm at a time through the interior of a core at a fixed depth relative to the core top. The choice of sampling spots was entirely arbitrary and, as pointed out above, was not intended to produce vertical profiles of pore water composition in the way normally done when horizontal variations can be assumed to be insignificant.

The voltammetric gold amalgam microelectrodes used in this study were made by sealing a 100 μm gold wire in a glass capillary and plating mercury onto the polished exposed gold surface (Brendel, 1995; Brendel and Luther, 1995). A fresh electrode was prepared for each core. This involved polishing the exposed gold surface with a series of diamond polishes, electroplating mercury on the gold surface, polarizing the electrode, and calibrating the electrode in seawater. A standard three electrode voltammetric cell, with the microelectrode as the working electrode, a 0.5 mm diameter platinum wire as counter electrode, and a saturated calomel electrode (SCE) as reference electrode, was used for all electrochemical measurements in conjunction with a DLK-100 electrochemical analyzer (Analytical Instrument Systems, Inc.). Each electrode was calibrated with standard additions of Mn(II) in seawater, and the electrode responses ($\mu\text{M/nA}$) for dissolved O_2 , Fe(II), Mn(II), and HS^- were calculated using the pilot ion method. This method is based on the constancy of the relative electrode sensitivities of individual species, which makes it possible to take data from a single calibration curve and apply it to other species (Meites, 1965; Brendel, 1995; Brendel and Luther, 1995). Oxygen was measured with linear sweep voltammetry (LSV), scanning at 200 mV sec^{-1} . Fe(II), Mn(II), and HS^- were determined with the more sensitive square wave voltam-

metry (SWV) using the following parameters: pulse height 15 mV, step increment 2 mV, frequency 100 Hz, scan rate 200 mV sec⁻¹. When H₂S was absent, the electrode was conditioned at a potential of -0.1 V for a period of 30 sec to restore the electrode surface before measuring Fe and Mn. This step removes any previously deposited Fe and Mn. Conditioning at -0.1 V is not necessary when measuring oxygen in sediment pore water in the absence of Mn and Fe. The fast scan rates do not deplete O₂ and other analytes to any significant extent. When H₂S was present, a conditioning potential of -0.8 V was used to remove any Fe, H₂S, and Mn deposited on the electrode; none of these species are electroactive at this potential. Detection limits at the 99% confidence limit for O₂, Fe(II), Mn(II), HS⁻ were 3, 5, 15, and <0.2 μM, respectively. Precision, based on replicates measurements at a given depth was typically 2–5% for each of the species measured.

4. Results and Discussion

4.1. SEASONAL VARIABILITY OF SEDIMENT PORE WATER COMPOSITION

The soil in the *H. portulacoides* stand in the Rosario salt marsh consists of a 20 cm thick surface layer infused with roots, which overlies a root-free fine-grained mud. The root layer is densely matted, and, unlike many marshes along the east coast of North America that are heavily bioturbated by fiddler crabs (Bertness, 1985; Kostka et al., 2002; Luther et al., 1991), there is no evidence of burrowing crabs disturbing the soil in this layer.

In the single core collected in *May* (Figure 1), oxygen was below detection limit except in two spots near the very top of the core. Below 5 cm depth, Fe(II) was present in concentrations as high as 1700 μM. Mn(II) was present in most of the measurements in concentrations reaching 200 μM. Sulfide was below detection limit except for one spot at 10 cm depth, where 2 μM HS⁻ was recorded.

In *July*, the situation was dramatically different. Oxygen was present to a depth of 20 cm, which corresponds to the depth of the root zone (Figure 2). This core is representative of other cores from July, including one that was collected during a spring tide while the marsh surface was completely inundated. Most of the oxygen measurements were in the 40–100 μM range, but included one spot with more than 100 μM oxygen as well as two spots where oxygen was below the detection limit of the electrode. No oxygen was detected in the grey mud below the root zone. Fe(II) was below detection limit except near the bottom of the root zone, and sulfide was not detected in any of the measurements. Mn(II) was present down to 15 cm, but in lower concentrations than in May.

In *November* and *December* measurable oxygen concentrations were found as deep as 8 cm, but oxygen (max. 55 μM) was considerably lower than in July and was below detection limit at three of the eight spots between 0 and 8 cm depth (Figure 3). Fe(II) was present below 9 cm, sulfide was below detection limit, and Mn(II) was present at several depths but in concentrations lower than in May and

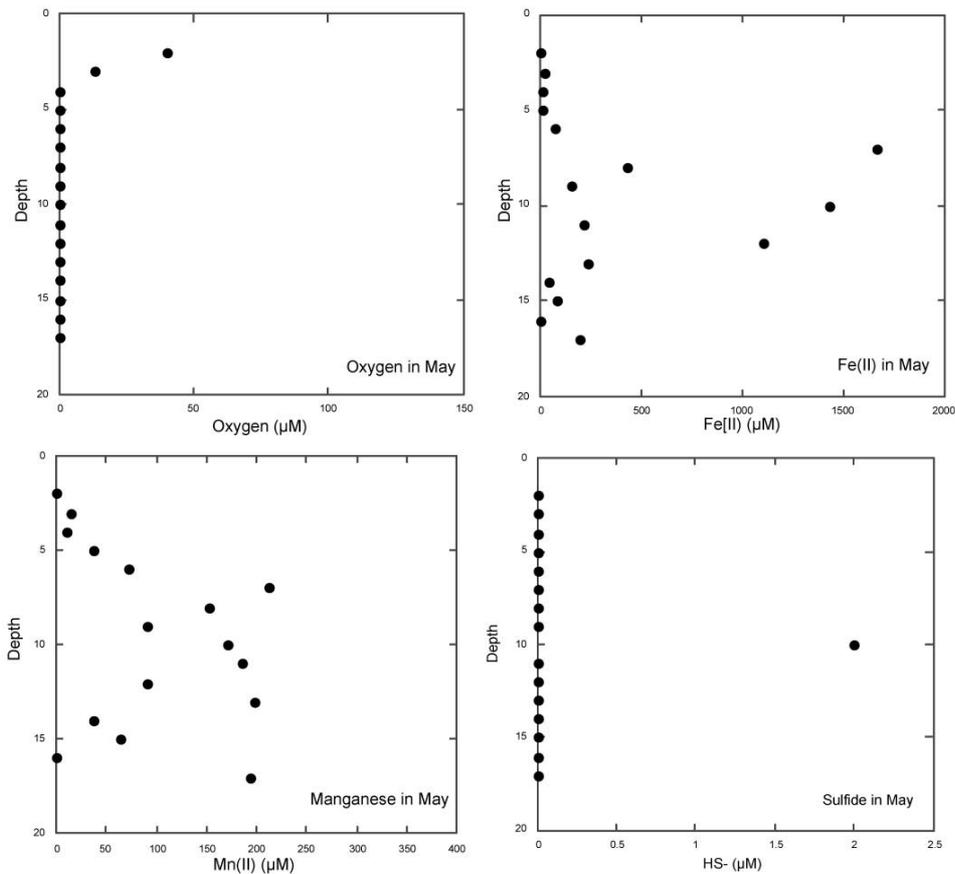


Figure 1. Distribution in May of O_2 , Fe(II), Mn(II) and HS^- in the porewater of Rosario saltmarsh. The depth scale is in cm. Data shown as zero values were measured but were below the respective detection limits.

July. The data shown in Figure 3 are representative of the other observations from this time of the year.

4.2. SMALL SCALE SPATIAL OXYGEN VARIABILITY

The variability of oxygen was not limited to the vertical dimension. Oxygen measurements made with 2 mm spatial resolution at a fixed depth show similar variability as the measurements made over the 20 cm deep root zone. Oxygen concentrations as high as $78 \mu M$ and as low as $25 \mu M$ were found to exist within 2 mm of each other (Figure 4).

The presence of oxygen in these sediments, and the spatial variability of dissolved oxygen, Fe(II) and Mn(II) can not be attributed to contamination with oxygen from the atmosphere: the measurements were made 20 mm or more below

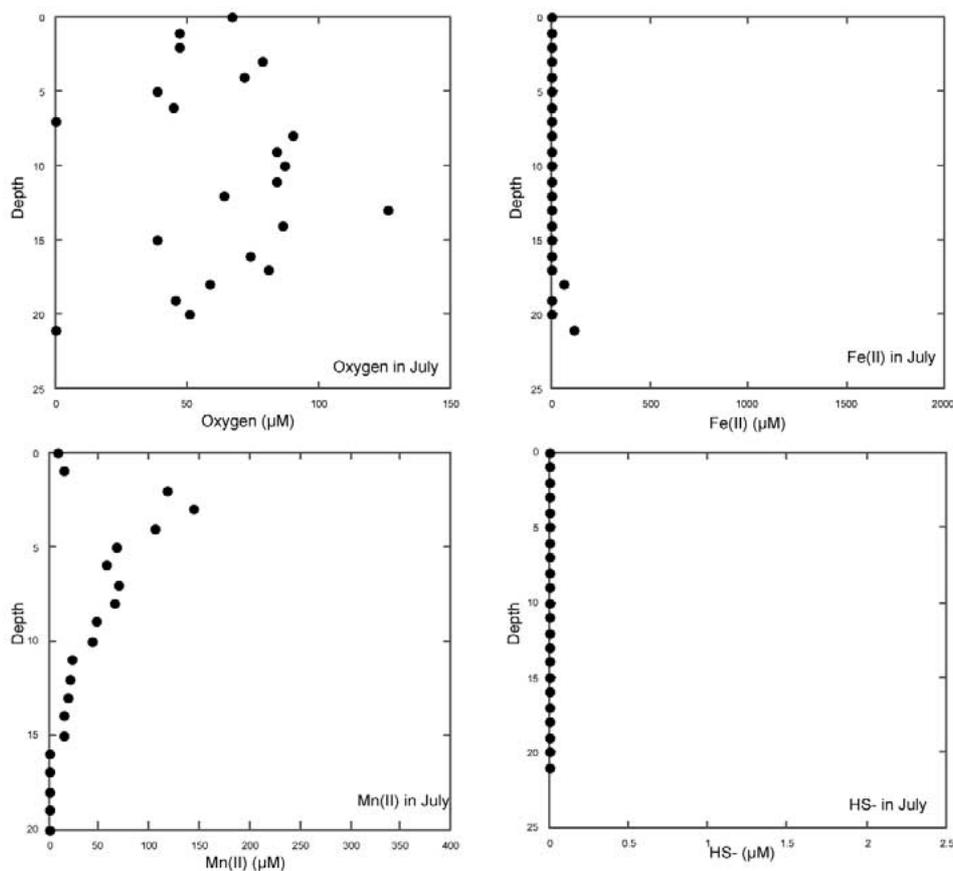


Figure 2. Distribution in July of O_2 , Fe(II), Mn(II) and HS^- in the porewater of Rosario saltmarsh. The depth scale is in cm. Data shown as zero values were measured but were below the respective detection limits.

the exposed core surface, and experiments with the lower anoxic part of a core showed that oxygen from the atmosphere did not penetrate more than 1 mm below the exposed sediment surface during the time it took to complete the analysis of the core. Nor can the presence of oxygen be attributed to burrowing macro-organisms: dissection and visual inspection of the core did not reveal burrows. In non-vegetated intertidal muds in the Tagus Estuary, oxygen penetration is limited to a few millimeters (Vale, unpublished data). The oxygen found at depth in these cores can therefore not be explained by diffusional transport across the sediment water interface. Caetano and Vale (2002), measuring the distribution of oxygen in sediment porewater as a function of distance from the surface of a single root, found detectable oxygen levels extending 4–8 mm beyond the root. Recently, Burdige and Zimmerman (2002) reported oxygen concentrations as high as $200 \mu M$ in the pore water of a seagrass stand, which was attributed to transport of photosynthet-

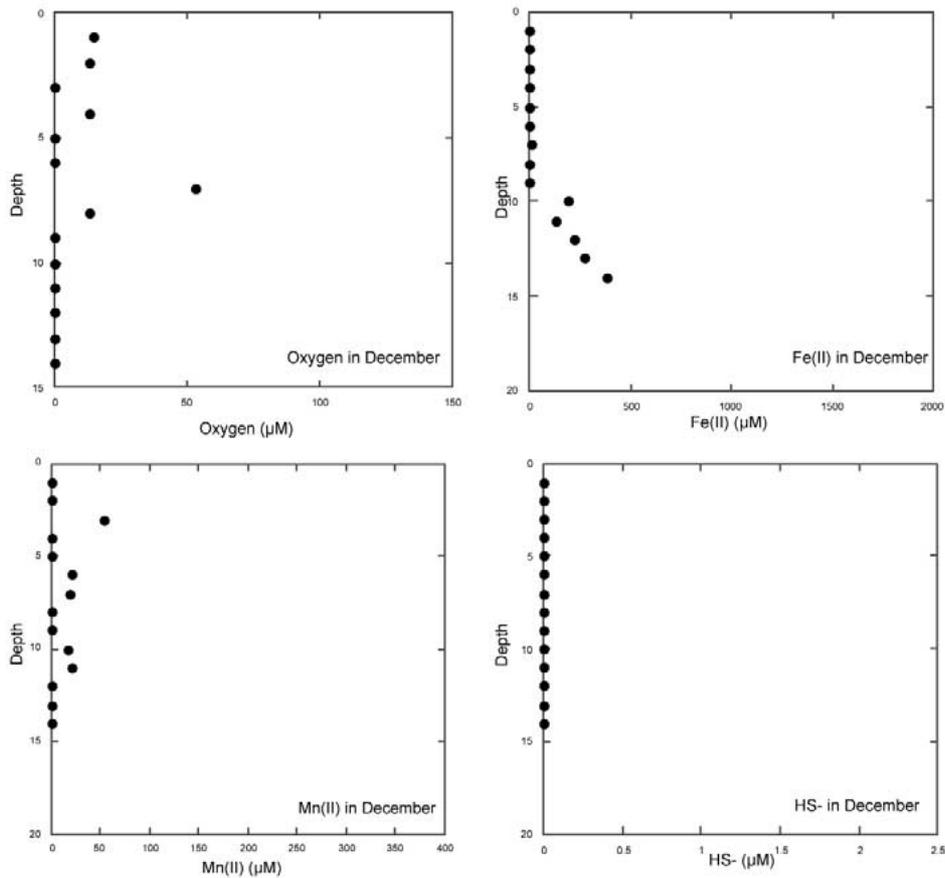


Figure 3. Distribution in December of O_2 , $Fe(II)$, $Mn(II)$ and HS^- in the porewater of Rosario saltmarsh. The depth scale is in cm. Data shown as zero values were measured but were below the respective detection limits.

ically produced oxygen into the sediment via roots and rhizomes. We conclude that the oxygen we observe in the pore water of Rosario salt marsh sediments was supplied via roots, and that spatial variability is due to heterogeneous distribution of roots and reactive sediment components, including organic matter undergoing decomposition.

4.3. ROOT DENSITY AND OXYGEN SUPPLY

The presence of oxygen in the root zone in July and December implies that the flux of oxygen from the roots had overcome the local demand for oxygen by reduced sediment components, of which plant produced organic matter is quantitatively the most important. Considering that diffusion is only efficient over short distances, the critical factor that governs the balance between oxygen supply and consumption is

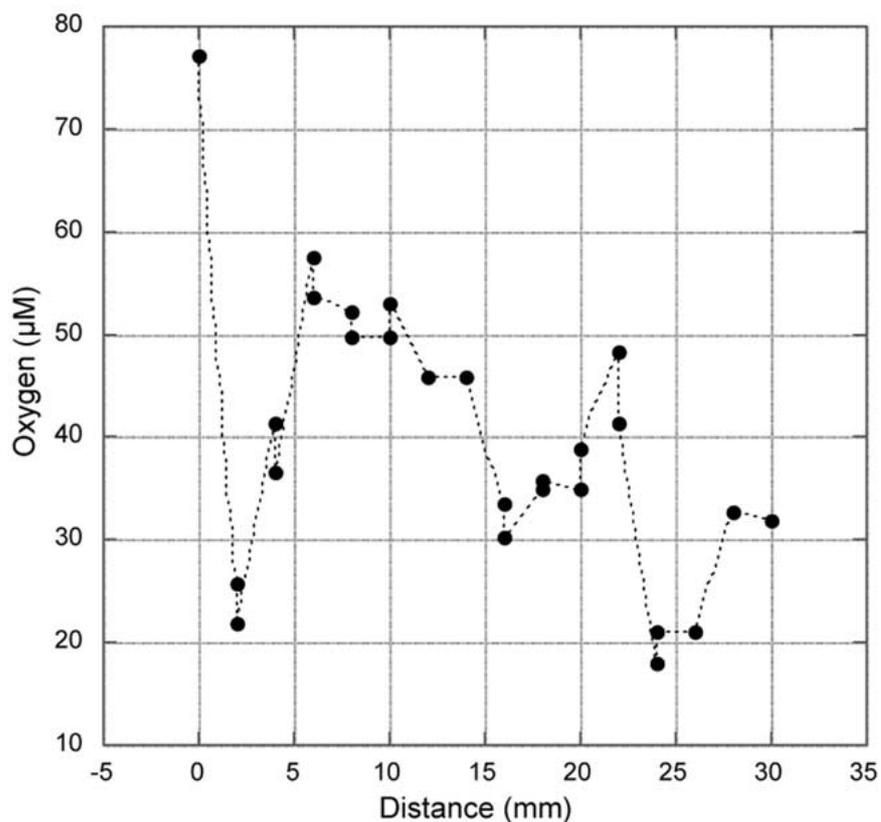


Figure 4. Distribution of O_2 across a horizontal section at 8 cm depth in a collected in the Rosario saltmarsh in July. Measurements were made in duplicate. Where duplicates differ, they are connected by a vertical line.

the average distance between two adjacent roots. If root density is high, such that the distance between roots is short, oxygen supply by diffusion may overcome the oxygen consumption by the reducing sediment between the roots. In the following order-of-magnitude calculation, we will assume that oxygen is supplied to the sediment by molecular diffusion from individual roots. This assumption ignores evapotranspiration, which drives advective water fluxes against which oxygen has to diffuse, but we have no information on the importance of this process for oxygen fluxes. Second, since we did not detect oxygen in the porewater at the same time as $Fe(II)$ or HS^- (see below), we will assume that more reactive sediment components such as ammonia, sulfide, and reduced metals had been oxidized by the time oxygen reached measurable concentration levels, leaving organic matter as the principal reactant consuming oxygen. Third, we will assume that the consumption

of oxygen by organic matter can be described by first order reaction kinetics. In this case the governing equation can be written as

$$d[\text{O}_2]dt = D(\partial^2[\text{O}_2]/\partial z^2) - kC$$

where $[\text{O}_2]$ is the concentration of oxygen in the pore water, t = time, D = diffusion coefficient for oxygen in the sediment, z = depth, k = first order rate constant for organic carbon oxidation, and C = concentration of organic carbon. The relative rates of supply and consumption of oxygen are then described by a dimensionless Damkohler number (Da) of the form $Da = kL^2/C$, where L is the characteristic length scale of diffusion (e.g., Boudreau, 1999). In order for supply of oxygen to exceed demand, Da must be < 1 , or $L^2 < D/k$. Adopting a length scale L on the order of 1 cm, a diffusion coefficient on the order of $10^2 \text{ cm}^2 \text{ y}^{-1}$ for oxygen in water, it would take a value of $k \geq 10^2 \text{ y}^{-1}$ for consumption to overcome the supply of oxygen. Values of k for fresh algal material at 20 °C (Westrich and Berner, 1984) and for organic matter decomposing in estuarine sediment (Bianchi and Findlay, 1991; Burdige, 1991; D'Andrea et al., 2002) are one order of magnitude lower than this, which may explain why free oxygen can sometime be present in the root zone. If the length scale L were smaller than 1 cm, k would have to be correspondingly higher. This may be the case in summer in the Rosario salt marsh. Visual inspection of the root system in this marsh in summer indicated that the typical root spacing can be less than one cm. Adopting a cylindrical representation of the environment surrounding the individual root, the length scale L is less than one cm.

Implied in the second of our assumptions is that the seasonal oxygen supply via roots is sufficient to oxidize completely the pool of reduced sediment components such as ammonia, sulfides, and reduced metals, which are more reactive towards oxygen. This may not always happen in marshes where plants are active for a shorter time than in the Tagus marshes. If the growing season is short, the time available for decomposition is correspondingly longer. This leaves more time to build up the pool of reduced material, particularly sulfides, and leaves less time to reoxidize it. Under these circumstances oxygen in the pore water may never reach detectable levels because all the oxygen supplied by roots is consumed rapidly in the reoxidation of the pool of reduced compounds.

4.4. OXIDATION-REDUCTION DYNAMICS OF IRON IN THE ROOT ZONE

As shown by Giblin and Howarth (1984), Luther and Church (1988) and Kostka and Luther (1995), iron in salt marshes cycles between iron sulfides, including pyrite, in winter and iron oxides in summer. Madureira et al. (1997), examining the seasonal abundance of acid volatile sulfide (FeS), showed that this cycling also occurs in Tagus estuary salt marshes. Iron oxide reduction and sulfide production can be attributed to the intense seasonality in production and decomposition of

root biomass (Caçador et al., 2000). The following discussion will focus on the interaction between seasonal root dynamics and iron geochemistry.

At the end of winter dormancy, when marsh plants initiate a new growth cycle and begin to produce new roots, the sediment in the root zone is anoxic and the pore water contains high concentrations of Fe(II) (Figure 1). The new roots infiltrate the anoxic sediment and provide a conduit for oxygen, which then can begin to leak into the pore water. As long as Fe(II) is present, oxygen will be consumed in the oxidation of soluble Fe(II) to insoluble Fe(III). The rate of this reaction is very fast (Sung and Morgan, 1980), which explains why we did not observe measurable levels of oxygen when Fe(II) was present. In view of the high reaction rate, the oxidation of Fe(II) can initially be expected to take place predominantly in the immediate vicinity of the root surface. This would create a sharp concentration gradient and drive a flux of dissolved Fe(II) towards the root. Iron (hydr)oxides would then accumulate on the root surface and in the sediment adjacent to the root. Depending on the life expectancy of the individual root and the availability of dissolved Fe, this can lead to the formation of iron rich cylindrical concretion of various diameters (Sundby et al., 1998).

The process of moving dissolved iron towards a root must come to a stop when all available Fe(II) in the sediment surrounding the root has been oxidized to insoluble Fe(III). If the rate of oxygen consumption by other reduced sediment constituents is lower than in the reaction with Fe(II), then oxygen can build up in the pore water and ultimately reach detectable concentration levels, as discussed above. This was apparently the case in the Rosario saltmarsh in July, when oxygen was present throughout the entire 20 cm deep root zone and Fe(II) was undetectable (Figure 3). We note that Mn(II) was present in the root zone even in the presence of oxygen, but the concentration levels were for the most part significantly lower than in May. This may reflect the reaction kinetics of Mn(II) oxidation by oxygen, which is slower than for Fe(II) oxidation (Stumm and Morgan, 1996).

Following the period of intense plant activity in summer, root biomass begins to decline (Caçador et al., 2000). Since the flux of oxygen into the soil is a function of root density, the oxygen flux can then be expected to diminish. Unlike environments where the seasonal influence is very clear, the seasonal pattern of plant activity in Tagus marshes can be more nuanced. In 1996, when our summer and fall measurements were made, the weather remained warm until late in the fall, and the plants apparently remained active quite late in the season. As late as November-December, in the Rosario salt marsh, we were still detecting oxygen in the root zone. However, unlike in July, detectable levels of oxygen were confined to the upper 8 cm of the sediment, which could indicate that the roots that reach deepest into the sediment are the first to die out. As during other times of the year, Fe(II) was not detected when oxygen was present. However, below 8 cm depth, where the oxygen concentration was below detection limit, Fe(II) was present.

4.5. RHIZOCONCRETIONS

Characteristic of Tagus estuary saltmarshes is the presence of cylindrical iron-rich concretions on roots. The concretions are formed by the oxidation and precipitation of dissolved iron, diffusing towards the root from the surrounding sediment (Sundby et al., 1998). There are comparably few concretions in the upper 3 cm of the sediment column, which coincides with low abundance of roots. However, concretions are abundant within the root zone (3–20 cm) and in the anoxic sediment below the root zone, and they comprise on the average 4% (d.w.) of the total sediment mass. The concentration of the major rock forming elements Al, Si, Ca, and Mg in the concretions is similar to that in the sediment within which they occur. In contrast, the iron content of the concretions ($11.7 \pm 1.6\%$ d. w.) is much higher than in the surrounding sediment, which only contains $4.9 \pm 0.3\%$ iron. The iron is present mostly as iron oxides and hydroxides (Caçador, 1994; Vale et al., 1990) in agreement with previous studies of the mineralogy of iron plaque (Chen et al., 1980). Concretions are also enriched in Mn, but the low abundance of Mn in these sediments makes this element less important than iron for concretion formation. The precipitated iron oxide partly fills the original pore space and cements the sediment particles together. However, mass balance considerations indicate that only 1/6 of the originally available pore space is filled by the Fe precipitated in the concretions, which thus retain much of the porosity of the original sediment (Sundby et al., 1998).

As described above, concretion formation requires Fe(II) and oxygen simultaneously in order to induce a flux of Fe(II) towards the root and precipitate the iron oxide that accumulates between the sediment grains and cements them into a cohesive agglomerate. We can therefore be certain that, in July, when Fe(II) was no longer available in the pore water, concretion formation had stopped. During fall and winter, when the diminished root biomass reduces the supply of oxygen into the sediment pore water, anaerobic processes, including sulfate reduction, may gradually take over. As a result, the iron oxide in concretions will become exposed to a reducing, likely sulfidic environment. Fe(III) is reduced to Fe(II) and precipitated as FeS and possibly as pyrite (Madureira et al., 1997). Conversion of iron oxides to sulfides should not in itself destroy a concretion by dispersing the iron it contains. This is because the accumulated iron, even if present in reduced soluble form, can not be transported away from a concretion unless there is a concentration gradient that can drive the flux. As our data indicate, Fe(II) gradients only develop when oxygen is supplied; hence there should be little or no transport of Fe(II) when the sediment is anaerobic. It seems therefore that concretions, in the sense of Fe-rich agglomerates, may be preserved in oxygen depleted reduced sediment.

The process of developing concentration gradients and moving Fe(II) towards roots can begin again in spring, when new roots once again allow oxygen to reach the interior of the sediment. Fe(II) can then be supplied not only by the bulk reduced sediment but also by concretions. Because concretions are highly enriched

in Fe (12% in the Rosario marsh) they would be a strong source of Fe for new concretions. The net result is a gradual disappearance of old concretions in favour of new concretions. Concretions thus participate in a cycle whereby previous years' concretions supply iron for new concretions. This dynamic cycle is intimately connected with the annual cycle of growth and decay of roots.

5. Conclusions

Clothier and Green (1997) pointed out that the spatial form of the root system and the seasonal changes it undergoes as a result of local patterns of growth and death of roots are the keys to understanding soil processes. In the salt marshes of the Tagus Estuary, where root biomass, expressed as percent of total dry weight sediment, can vary between 8% in winter and 24% in summer, the annual cycle of root growth and decay is the dominant control of the redox chemistry of the sediment. The state of the sediment fluctuates between completely oxidized in summer to completely reduced in winter because roots provide conduits through which oxygen can be injected into the interior of the sediment column. The network of roots, distributed heterogeneously throughout the sediment, creates a correspondingly heterogeneous pattern of sediment redox properties. This is reflected in strong local and temporal variations in the concentrations of oxidizing and reducing sediment components, including but not limited to oxygen and metals. The spatial heterogeneity is in turn reflected in local accumulations and depletions of redox sensitive elements.

Acknowledgements

This study was made possible by a grant from the Portuguese Foundation for Science and Technology, which funded the senior author's travels and stays in Portugal for the extensive periods required to learn and apply the principles of electrochemistry to the study of salt marsh geochemistry. Financial support from the Natural Sciences and Engineering Research Council of Canada to BS and from the National Oceanic and Atmospheric Administration to GWL (NA16RG0162-03) is likewise gratefully acknowledged. Comments by Dr. Tim Shaw and two anonymous reviewers helped improve the manuscript.

References

- Allaway, W. G., Curran, M., Hollington, L. M., Ricketts, M. C., and Skelton, N. J. (2001) Gas space and oxygen exchange in roots of *Avicennia marina* (Forssk.) Vierh. var. *australasica* (Walp.) ex N.C. Duke, the Grey Mangrove, *Wetlands Ecology and Management* **9**, 211–2001.
- Anderson, C. E. (1974) A review of structure in several North Carolina salt marsh plants, In: *Ecology of Halophytes* (eds. R. J. Reimold and W. H. Queen), Academic Press, pp. 307–344.
- Anschutz, P., Zhong, S., Sundby, B., Mucci, A., and Gobeil, C. (1998) Burial efficiency of phosphorus and the geochemistry of iron in continental margin sediments, *Limnology & Oceanography* **43**(1), 53–64.

- Armstrong, W. (1978) Root aeration in the wetland condition, In: *Plant Life in Anaerobic Environments* (eds. D. D. Hook and C. R. M. M. Crawforth), Ann Arbor Science Publishers, pp. 269–298.
- Bertness, M. D. (1985) Fiddler crab regulation of *Spartina alterniflora* production on a New England saltmarsh, *Ecology* **66**, 1042–1055.
- Bianchi, T. S. and Findlay, S. (1991) Decomposition of Hudson River macrophytes: Photosynthetic pigment transformations and decay constants, *Estuaries* **14**, 65–73.
- Boudreau B. P. (1996) *Diagenetic Models and Their Implementation*, Springer-Verlag.
- Brendel, P. J. (1995) Development of a mercury thin film voltammetric microelectrode for the determination of biogeochemically important redox species in porewaters of marine and freshwater sediments, Ph.D., University of Delaware.
- Brendel, P. J. and Luther, G. W., III. (1995) Development of a gold amalgam voltammetric microelectrode for the determination of dissolved Fe, Mn, O₂, and S(-II) in porewaters of marine and freshwater sediments, *Environmental Science & Technology* **29**, 751–761.
- Burdige, D. J. (1991) The kinetics of organic matter mineralization in anoxic marine sediments, *Journal of Marine Research* **49**, 727–761.
- Burdige, D. J. and Zimmerman, R. C. (2002) Impact of sea grass density on carbonate dissolution in Bahamian sediments, *Limnology and Oceanography* **47**(6), 1751–1763.
- Caçador, I., Vale, C., and Catarino, F. (2000) Seasonal variation of Zn, Pb, Cu and Cd concentrations in the root-sediment system of *Spartina maritima* and *Halimione portulacoides* from Tagus estuary salt marshes. *Marine Environmental Research* **49**, 279–290.
- Caetano, M. and Vale, C. (2002) Retention of arsenic and phosphorus in iron-rich concretions of Tagus salt marshes, *Marine Chemistry* **79**, 261–271.
- Catarino, F. and Caçador, I. (1981) Produção de biomassa e estratégia de desenvolvimento em *Spartina maritima* e outros elementos da vegetação dos sapais do estuário do Tejo, *Boletim da Sociedade Broteriana* **2**, 384–403.
- Christensen, K. K., Jensen, H. S., Andersen, F. Ø., Wigand, C., and Holmer, M. (1998) Interferences between root plaque formation and phosphorus availability for isoetids in sediments of oligotrophic lakes, *Biogeochemistry* **43**, 107–128.
- Clothier, B. R. and Green, S. R. (1997) Roots: The big movers of water and chemicals in soil. *Soil Science* **162**(8), 534–543.
- Conlin, T. S. S. and Crowder, A. A. (1989) Location of radial oxygen loss and zones of potential iron uptake in a grass and two nongrass emergent species, *Can. J. Bot.* **67**, 717–722.
- D'Andrea, A. F., Aller, R. C., and Lopez, G. R. (2002) Organic matter flux and reactivity on a South Carolina sandflat: The impacts of porewater advection and microbiological structures, *Limnology & Oceanography* **47**(2), 1056–1070.
- Giblin, A. E. and Howarth, R. W. (1984) Porewater evidence for a dynamic sedimentary iron cycle in salt marshes, *Limnology & Oceanography* **29**, 47–63.
- Kostka, J. E., Gribsholt, B., Petrie, E., Dalton, D., Skelton, H., and Kristensen, E. (2002) The rates and pathways of carbon oxidation in bioturbated saltmarsh sediments, *Limnology & Oceanography* **47**(1), 230–240.
- Kostka, J. E. and Luther, G. W., III (1995) Seasonal cycling of Fe in saltmarsh sediments, *Biogeochemistry* **29**, 159–181.
- Krom, M. D. and Berner, R. A. (1980) Adsorption of phosphate in anoxic marine sediments, *Limnology & Oceanography* **25**, 797–806.
- Krom, M. D. and Berner, R. D. (1981) The diagenesis of phosphorus in a nearshore marine sediment, *Geochimica et Cosmochimica Acta* **45**, 207–216.
- Luther G. W., III and Church T. M. (1988) Seasonal cycling of sulfur and iron in porewaters of a Delaware saltmarsh, *Marine Chemistry* **23**, 295–309.

- Luther, G. W., III, Ferdelman, T. G., Kostka, J. E., Tsamakis, E. J., and Church, T. M. (1991) Temporal and spatial variability of reduced sulfur species (FeS_2 , $\text{S}_2\text{O}_3^{2-}$) and porewater parameters in salt marsh sediments, *Biogeochemistry* **14**, 57–88.
- Madureira, M. J., Vale C., and Gonçalves, M. L. (1997) Effect of plants on sulphur geochemistry in the Tagus salt-marshes sediments, *Marine Chemistry* **58**, 27–37.
- Meites, L. (1965) *Polarographic Techniques*, 2nd edn, Wiley, New York.
- Rozan, T. F., Taillefert, M., Trouwborst, R. E., Glazer, B. T., Ma, S., Herszage, J. L., Valdes, M. K., Price, S., and Luther, I. G. W. (2002) Iron, sulfur and phosphorus cycling in the sediments of a shallow coastal bay: Implications for sediment nutrient release and benthic macroalgal blooms, *Limnology & Oceanography* **47**, 1346–1354.
- Schubauer, J. P. and Hopkinson, C. S. (1984) Above- and belowground emergent macrophyte production and turnover in a coastal marsh ecosystem, Georgia, *Limnology & Oceanography* **29**(5), 1052–1065.
- Stumm, W. and Morgan, J. J. (1996) *Aquatic Chemistry*, Wiley.
- Sundby, B., Gobeil, C., Silverberg, N., and Mucci, N. (1992) The phosphorus cycle in coastal marine sediments, *Limnology & Oceanography* **37**(6), 1129–1145.
- Sundby, B., Vale, C., Caçador, I., Catarino, F., Madureira, M.-J., and Caetano, M. (1998) Metal-rich concretions on the roots of salt-marsh plants: Mechanism and rate of formation, *Limnology & Oceanography* **43**, 19–26.
- Sung, W. and Morgan, J. J. (1980) Kinetics and product of ferrous iron oxygenation in aqueous systems, *Environmental Science and Technology* **14**, 561.
- Taillefert, M. and Rozan, T. F. (2002) Electrochemical methods for the environmental analysis of trace elements biogeochemistry. In: *Environmental Electrochemistry* (eds. M. Taillefert and T. F. Rozan), American Chemical Society, pp. 2–13.
- Teal, J. M. and Kanwisher, J. W. (1966) Gas transport in the marsh grass, *Spartina alterniflora*, *J. Exp. Bot.* **17**, 355–361.
- Vale, C., Catarino, F., Cortesão, C., and Caçador, I. (1990) Presence of metal-rich rhizoconcretions on the roots of *Spartina maritima* from the salt marshes of the Tagus estuary, Portugal, *Science of the Total Environment* **97/98**, 617–626.
- Westrich, J. T. and Berner, R. A. (1984) The role of sedimentary organic matter in bacterial sulfate reduction: The G model tested, *Limnology & Oceanography* **29**, 236–249.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.