



# Visual assessment of redoxcline compared to electron potential in coastal marine sediments



Michelle Simone\*, Jon Grant

Department of Oceanography, Dalhousie University, Halifax, Nova Scotia B3H 4R2, Canada

## ARTICLE INFO

### Article history:

Received 25 May 2016

Received in revised form

16 February 2017

Accepted 16 February 2017

Available online 21 February 2017

### Keywords:

Apparent redox potential discontinuity

Redox potential

Sediment profile imaging

Coastal marine sediments

## ABSTRACT

A geochemical proxy often utilized in marine benthic health assessment is the depth of the apparent redox potential discontinuity (aRPD), a visual signature representing the transition from lighter oxidized to darker reduced sediments. Traditionally this boundary is defined by the redox potential discontinuity (RPD), a 0 mV isovolt measured by platinum electrodes. In order to verify the use of visual transitions as a proxy for electrochemical RPD, these measurements were compared in subtidal sandy muds (13.5 m depth) in coastal Nova Scotia, Canada. The apparent RPD was measured from sediment profile imagery (SPI) images and diver-retrieved cores. Pre-drilled cores with vertical holes allowed for the coupling of electrochemical and visual boundary measurements in the same sample. The mean discrepancy of the RPD is  $0.6 \pm 2.6$  cm (mean  $\pm$  maximum variation) above the aRPD depth. The Eh range at the aRPD,  $-14.94 \pm 52.21$  mV, encompassed the 0 mV isovolt, suggesting the aRPD can be applied as a sound proxy for the transition between redox states.

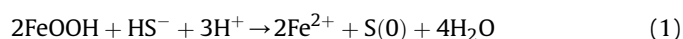
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## 1. Introduction

Organic matter deposited in marine sediments from conditions such as eutrophication can result in undesirable phase shifts from aerobic to anaerobic dominated systems. This transition from oxic to hypoxic or anoxic states can be collectively described by the oxidation-reduction or redox reactions. Oxic conditions are achieved when the supply of oxygen exceeds the metabolic demands of the sediments. The balance of oxidation and reduction reactions generates an electrical potential that can be measured with a platinum electrode corrected to a normal hydrogen reference electrode ( $E_{\text{HNE}}$ ). When sediments are oxidized, positive potentials are measured because the pore-water has a strong tendency to accept protons from the reaction ( $E_{\text{HNE}} \geq 0$ ). In contrast, negative potentials are measured when oxygen is in short supply and metabolic demand and organic matter breakdown is facilitated by other less thermodynamically favourable oxidants (Bernier, 1980, 1981b; Claypool and Kaplan, 1974; Curtis et al., 1977). These anaerobic processes result in an incomplete reduction of organic compounds and benthic redox state is considered reducing ( $E_{\text{HNE}} \leq 0$ ). The transition, between positive and negative redox

potentials ( $E_{\text{HNE}} = 0$ ), defines the redoxcline or the redox potential discontinuity (RPD) (Fenchel, 1969; Fenchel and Riedl, 1970).

In benthic marine environments, the availability of sulfate ( $\text{SO}_4^{2-}$ ) exceeds other major oxidants (nitrate, iron and manganese), making it the most important electron acceptor in the upper anaerobic zone (Thamdrup et al., 2000; Finke et al., 2007; Jørgensen, 1977). Sulfate-reducing bacteria oxidize organic compounds by reducing sulfate into unstable sulfur species ( $\text{H}_2\text{S}$  and  $\text{HS}^-$ ). These reduced products are collectively referred to as dissolved sulfide ( $\text{S}^{2-}$ ), and are highly toxic to aerobic fauna (Grieshaber and Volkel, 1998; Bagarinao and Lantin-Olaguer, 1998; Gray et al., 2002). In a region where both oxygen and sulfide are present in low concentrations ( $\leq 1 \mu\text{M}$ ) Eh becomes negative (Bernier, 1981a; Froelich et al., 1979; Fenchel and Riedl, 1970) and ferric oxidation becomes the dominant chemical oxidation pathway to detoxify sulfide:



Oxidized iron minerals present in the sediment react with dissolved sulfide to produce reduced iron ions and elemental sulfur. The reduced iron can then further sequester sulfide by precipitating amorphous iron sulfides or monosulfides (Jørgensen, 1977; Bernier, 1980, 1984; Howarth, 1979):

\* Corresponding author.

E-mail addresses: [m.simone@dal.ca](mailto:m.simone@dal.ca), [mnhsimone@gmail.com](mailto:mnhsimone@gmail.com) (M. Simone).



The monosulfides produced are no longer toxic to fauna (Brooks and Mahnken, 2003), but they are still thermodynamically unstable under oxidizing conditions and contribute to the acid volatile sulfide (AVS) biogeochemical system (Jørgensen, 1977; Otero et al., 2006; Rickard and Morse, 2005). The precipitates are dark grey-black in colour, contrasting the lighter oxidized sediments. This forms a visual signature, representative of the transition from dominantly aerobic to dominantly anaerobic conditions (Rosenberg et al., 2001; Jørgensen and Fenchel, 1974; Rhoads, 1974; Pearson and Rosenberg, 1978; Lyle, 1983). The visual colour boundary, known as the apparent RPD (aRPD), has long been considered and indirect measure of the electrochemical RPD (Froelich et al., 1979; Lyle, 1983; Rosenberg et al., 2001). Moreover, despite the transition from aerobic to anaerobic conditions inherent to the RPD, the redox potential is not a measure of the dissolved oxygen concentration, but more an indication of dominance of anaerobic processes (Fenchel, 1969; Fenchel and Riedl, 1970).

Due to the value of this visual transition as an indicator of redox state, especially in response to organic loading, various observational techniques have been employed. For instance, in intertidal mudflats the depth of the RPD colour change has been measured by trenching (Gerwing et al., 2013). In subtidal environments, sediment profile imagery (SPI) is a technique in which a closed wedge-shaped core is inserted vertically into the sediment. An internal mirror system allows an image of the sediment column to be obtained with an on-board camera. Image analysis is then used to extract various features from the sediments, including the depth of the aRPD and other physical-chemical properties and biological parameters (Rhoads and Germano, 1982). Although this method was pioneered to investigate organism-sediment relations in the 1970s (Rhoads and Cande, 1971), it has since been used as a tool applied to monitoring benthic biogeochemical cycling on various temporal and spatial scales both quantitatively and qualitatively (Rhoads and Germano, 1982, 1986; Van Hoey et al., 2014; Karakassis et al., 2002; Grizzle and Penniman, 1991; Valente et al., 1992; Mulrow et al., 2006; Carlsson et al., 2012; Nilsson and Rosenberg, 1997, 2000). Variables measured from image analysis have also been combined into indices as a qualitative measure of benthic community health (Nilsson and Rosenberg, 1997; Rhoads and Germano, 1982; Simone, 2014).

Redox potential has been used extensively in environmental monitoring to infer the desired oxic state of sediments (Wildish et al., 1999, 2001; Hargrave et al., 2008; Hansen et al., 2001). For example, eutrophication of coastal waters is a significant concern globally (Selman et al., 2008), and regulatory agencies are interested in efficient and effective techniques for evaluating benthic health. The ability to resolve sedimentary biogeochemical variables, with the benefit of an undisturbed *in situ* view is a powerful approach for benthic assessments. For this reason, use of the depth of the RPD colour change quantitatively by relating it to electrochemical measures of redox is an important step in the application of *in situ* methods such as SPI to environmental assessment.

Comparisons between the visual indicators and the chemical redox state in pore-water, measured with electrodes have been made previously in both intertidal and subtidal sediments (Rosenberg et al., 2001; Gerwing et al., 2013). However, due to varying conclusions in the literature and the development of new sampling techniques, a key objective of this study was to examine the accuracy of the aRPD as a proxy for the electrochemically measured RPD in soft-bottom, subtidal environments. In this study, the aRPD was measured with an *in situ* SPI instrument and in transparent acrylic cores; cores were also used for redox potential

measurements. By coupling these measurements, we reduced physical separation with the objective of developing an electrochemical range for the visual signature.

## 2. Materials and methods

Samples were collected in Shelburne Harbour, Nova Scotia (Fig. 1). The head of the bay is the mouth of Roseway River and narrows approximately 9 km south at Sandy Point where it is joined by Birchtown Bay. Further south the system widens to the larger bay and open ocean. The small town of Shelburne at the head of the harbour includes a fishing port and other commercial activity. Fish farming has been conducted in Shelburne Harbour for many years, although, at the time of sampling, most sites had been fallowed. Four locations were sampled in Shelburne Bay and a single location in Birchtown Bay on July 24, 2014, all in muddy sand. Redox measurements are not possible in SPI deployments, so cores obtained by divers were used for these measurements with the additional benefit of resolving spatial variation. Sampling was conducted in 80 m<sup>2</sup> areas with similar depths (13.5 ± 1.13 m) and bottom water temperatures (7.4 ± 0.3 °C). Station locations were selected so both cores and SPI images would have a visually oxic sediment surface (>2 cm) followed by > 2 cm of visually reduced sediments.

Three inactive salmon leases are visible in the map (Fig. 1); two north of S1 (fallowed since Sept. 2008 and July 2009, respectively; Spector and Spector, 2010) and one south of S6 (fallowed from Aug 2008–July 2009 and then retired all operation in 2011; Milewski, 2013). Only one active steelhead farm lease operates in the upper harbour approximately 100 m north of S1 (not shown).

### 2.1. Sediment profile imaging

At each 80 m<sup>2</sup> (approximately 9 × 9 m) station, the SPI-camera was deployed three times and four acrylic cores were retrieved by divers. The SPI-camera was centred on a Canon EOS Rebel T3i digital camera with 18.0 megapixel resolution, powered with internal batteries and a hot shoe flash. It was linked to the vessel via an ethernet extended USB cable allowing for remote viewing and shutter control with the Canon LiveView software on a tablet computer.

The aluminum camera housing had been lined with black felt to minimize flash bounce and the profile window, composed of bulletproof glass (15.5 × 22.5 cm), was located at the base of the pressurized housing. This was all suspended in a minimal aluminum frame (approximately 50 × 50 × 50 cm) with weighted feet to aid in stability and to increase vertical penetration.

### 2.2. Core sampling

Four transparent acrylic sediment cores (64 mm internal diameter; 320 mm long) were obtained at each station by divers to assess the mean aRPD and provide an estimate of natural spatial variability of the local redox conditions (Fig. 2). The use of divers allowed for disturbance to the core samples to be minimized during collection. Cores were returned to the surface with clear overlying water. Cores were then used to visually measure the aRPD, from the sediment surface (tan) to the colour change (dark-grey or black) (Fig. 3A). A station mean aRPD was calculated from all the cores with standard deviation used to represent the spatial variability of the local redox state (Wildish et al., 1999).

### 2.3. Redox measurement

Two of the cores were also used to measure redox potentials

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