EI SEVIED

Contents lists available at ScienceDirect

# Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

# Electrochemical characterization of mangrove sediments: A proposal of new proxies for organic matter oxidation



Gerardo Cebrián-Torrejón<sup>a,b,1</sup>, Alexander Pérez<sup>c,d,1</sup>, Noemí Montoya<sup>b</sup>, Joan Piquero-Cilla<sup>b</sup>, Maritza S. Saldarriaga<sup>e</sup>, Dimitri Gutiérrez<sup>c,e</sup>, Christian J. Sanders<sup>f</sup>, Wilson Machado<sup>d,\*\*</sup>, Antonio Doménech-Carbó<sup>b,\*</sup>

<sup>a</sup> Université des Antilles, UFR Sciences Exactes et Naturelles, Département de Chimie, Campus de Fouillole, BP 250, 97157, Pointe-à-Pitre, Guadeloupe, France

<sup>b</sup> Departament de Química Analítica, Facultat de Química, Universitat de València, Dr. Moliner 50, 46100, Burjassot, Valencia, Spain

<sup>c</sup> Universidad Peruana Cayetano Heredia, Centro de Investigación para el Desarrollo Integral y Sostenible (CIDIS), Facultad de Ciencias y Filosofía, Laboratorios de

Investigación y Desarrollo (LID), Laboratorio de Biogeociencias, Av. Honorio Delgado 430, Urb Ingeniería, Lima 31, Peru

<sup>d</sup> Universidade Federal Fluminense, Departamento de Geoquímica, Rua Outeiro São João Baptista S/n, Niteroi, RJ, Brazil

e Universidad Peruana Cayetano Heredia, Facultad de Ciencias y Filosofía, Programa Maestría en Ciencias Del Mar, Av. Honorio Delgado 430, Lima 31, Peru

<sup>f</sup> National Marine Science Centre, School of Environment, Science and Engineering, Southern Cross University, Coffs Harbour, New South Wales, Australia

ARTICLE INFO

Editorial handling by Prof. M. Kersten Keywords: Mangrove sediments Electrochemistry Organic matter Redox state Oxidation proxies

#### ABSTRACT

The voltammetric response of microparticulate deposits resulting from solvent evaporation of ethanolic extracts of mangrove sediments in contact with aqueous acetate buffer is hereby described. Dated sediment cores sampled from the Peruvian mangrove system ("Manglares de Tumbes" National Sanctuary) presented voltammetric responses dominated by oxidative signals of organic components that exhibit significant variations depending on the depth. Voltammetric data allowed for the definition of electrochemical indexes representative of the electrochemically oxidable organic matter fraction. These electrochemical indexes were  $f_{EAOM}$  (for the total amount of organic matter being electrochemically active),  $f_{EROM}$  (for the fraction of organic matter electrochemically oxidizable in reversible form),  $f_{RDOX}$  (for the proportion between the fractions of electrochemically active organic matter which is in an oxidized state and in a reduced state) and  $f_{ROS}$  (capability for reaction with reactive oxygen species), while the spectroscopic index  $A_{1650}/A_{3400}$  (as a proxy analogous to  $f_{RDOX}$ ) was also applied. The mangrove forest presents a higher oxidized fraction of the electrochemically active organic matter, as confirmed by additional data obtained from infrared spectroscopy. These results indicate that the described electrochemical indexes may provide insights on organic matter degradation by oxidative processes in addition to chemical analyses of coastal vegetated systems that are currently used, such as mangrove wetlands.

#### 1. Introduction

The increasing importance of coastal vegetated systems (i.e., seagrasses, saltmarshes and mangroves) in carbon cycling has been increasingly acknowledged, playing an important role in accumulating organic matter within the colonized sediments across the land-ocean interfaces (Duarte et al., 2005; Alongi, 2014). This vegetation-driven carbon cycling also regulates many biogeochemical processes that are fueled by accumulated organic matter, such as the cycling of redoxsensitive elements within these systems and their exchanges with adjacent environments (Luther et al., 1998). Sedimentary organic matter has been shown to be an integral component in biogeochemical electron transfer reactions due to the capacity of its components to act as intermediates in microbial metabolic processes and facilitating the cycling of multi-oxidation state metals (Lovley et al., 1996). The redox chemistry of sedimentary organic matter plays an essential role in biogeochemical processes, where compounds containing aromatic, quinone/hydroquinone and N— and S-containing functional groups are involved (Scott et al., 1998; Gaberell et al., 2003; Meunier et al., 2005).

Electrochemical methods have traditionally been applied in two environmental sciences fields mainly: i) as techniques for monitoring the environmental risk of organic pollutants (Zhu et al., 2015), remediation (Li et al., 2016, 2017), and ii) as analytical tools typically aimed at the determination of pollutants or families of pollutants

https://doi.org/10.1016/j.apgeochem.2018.12.018

Received 26 September 2018; Received in revised form 11 December 2018; Accepted 13 December 2018 Available online 14 December 2018 0883-2927/ © 2018 Published by Elsevier Ltd.

 $<sup>^{\</sup>ast}$  Corresponding author.

<sup>\*\*</sup> Corresponding author.

E-mail addresses: wmachado@geoq.uff.br (W. Machado), antonio.domenech@uv.es (A. Doménech-Carbó).

<sup>&</sup>lt;sup>1</sup> Authors contributed equally to the present work.

(Ramnani et al., 2016). In this second field of application, electrochemical techniques have been concentrated on solution-phase electrochemistry; i.e., when the analyte/s is/are dissolved due to of a more or less complicated extraction procedure. To complement available analytical techniques for obtaining information on the chemical composition of sedimentary organic matter in sediments, the use of a solidstate electrochemical methodology is described. The voltammetry of immobilized particles (VIMP) may be employed for the direct estimate of organic content, inorganic pollutants and to evaluate their antioxidant capacity. This technique was developed recently (Scholz and Meyer, 1998: Doménech-Carbó et al., 2013: Scholz et al., 2014) and may provide analytical information on a variety of solid materials with no need for previous digestion/dissolution treatments using amounts of sample at a microgram-nanogram level. In the field of geosciences, it has been applied by Grygar et al. for determining Fe and Mn oxides in soils (Grygar and van Oorschot, 2002; Hradil et al., 2004; Grygar et al., 2006) and for screening soils contaminated by arsenic (Cepriá et al., 2005). In situ electrochemical measurements in sediment porewaters have been reported by Luther et al. (1998) using solution-phase electrochemistry methodologies.

Despite mangrove systems representing only  $\sim 1\%$  of the global coastal area, mangrove sediments may accumulate between 15 and 25% of the coastal organic carbon (Alongi, 2014; Breithaupt et al., 2012), derived mainly from autochthonous organic matter production (Sanders et al., 2014). However, we did not find previous application of voltammetric methods to elucidate the organic geochemistry in mangrove wetlands. Here, the VIMP methodology was applied to a series of sediment samples from a Peruvian mangrove system within the "Manglares de Tumbes" National Sanctuary. It is pertinent to note that, in so far as solid components are tested, the proposed methodology covers families of sparingly soluble electroactive substances such as lignins (Milczarek, 2009; Admassie et al., 2014; Cottyn et al., 2015), which are hard to be accounted for in solution-phase experiments, additionally avoiding the possibility of sample contamination or unexpected reactions accompanying dissolution processes required by other techniques of redox capacity evaluation. The study, however, was oriented to explore the capabilities of the technique so that no precautions were adopted for avoiding oxidative processes during the extraction and transport of the samples.

The proposed methodology explores the inherent capability of electrochemistry to detect oxidizable organic compounds, typically, polyphenolic compounds, complementing the aforementioned well-established techniques providing information on aspects such as electrochemical reversibility. The 'direct' electrochemistry of organic matter in sediment samples is complemented with an estimate of the antioxidant capability of the sediments based on the monitoring of the reaction of antioxidant compounds with reactive oxygen species (ROS) electrochemically generated in situ. This procedure, previously applied to vegetal matter (Doménech-Carbó et al., 2015, 2017), is based on the possibility of electrochemical generation of superoxide species via reduction of oxygen dissolved in aqueous electrolytes (Enache et al., 2009; Kapalka et al., 2009). The radical scavenging activity of plant extracts has also been studied electrochemically using chemical generation of ROS (Scholz et al., 2007; de Carvalho et al., 2010) while VIMP was used by Komorsky-Lovric and Novak for testing the antioxidant capacity of samples from fruits and vegetables (Komorsky-Lovrić and Novak, 2009, 2011). Electrochemical data were complemented with attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) to acquire some compositional information on the existing organic matter.

#### 2. Material and methods

# 2.1. Study area

The studied mangrove ecosystem is located in the Northern coast of



Figure 1. a) Map of the study area within the mangrove estuary; b) spatial location of the sediment cores within the sedimentary environments.

Peru, in Tumbes, associated to the "Manglares de Tumbes" (Fig. 1) National Sanctuary. This estuarine forest is influenced by the Zarumilla River and its secondary tributaries, providing freshwater to the estuarine system and facilitating the continuous transport of particulate organic matter (INRENA, 2011; Pérez et al., 2017). The mangrove forest presents high contents of silt and clay and is characterized by a  $\sim 1-5\%$ slope between the Pacific Ocean and the continent. The dominant mangrove species near the creeks are Rhizophora mangle, Rhizophora harrisonii and Avicennia germinans, where mangrove-derived organic matter is considered to be the main component of the sedimentary organic matter in estuarine mangrove forests (Kristensen et al., 2008; Sanders et al., 2014). This region is characterized by a semiarid climate, with temperatures ranging from 22 °C to 32 °C and two well defined seasons, namely the dry season (from June to December), characterized by a lack of heavy rainfalls and, the wet season (from January to May), characterized by an increase in heavy rains and, consequently, a growth of the Zarumilla's water flow that may significantly affect the textural composition within the mudflat area (Lavado and Espinoza, 2014; Sanders et al., 2014).

# 2.2. Sampling design

The fieldwork was carried out on October 15th, 2014 (dry season), during the low tide phase. Two sediment cores of 70-cm in length were sampled in the "Manglares de Tumbes" (Fig. 1A) National Sanctuary. The first core (Core MF) was collected in the mudflat zone, whereas the second core (core MG) was collected inside the mangrove covered area (Fig. 1B). The sediment cores were obtained using PVC tubes and sectioned on-site at 1-cm intervals from the top of the core to 10-cm, and then at 2-cm intervals to the base of the core. Sub-samples were bagged, placed on ice and returned to the lab to be kept frozen at -20 °C, where

they were thawed and lyophilized before analysis.

#### 2.3. Electrochemical methods

Electrochemical experiments were performed at 298 ± 1 K in a conventional three-electrode cell. Sample-modified working electrodes were combined to a platinum wire auxiliary electrode and an Ag/AgCl (3M NaCl) reference electrode. Measurements were carried out with CH 660I equipment using 0.25 M acetic acid/sodium acetate aqueous buffer at pH 4.75 as a supporting electrolyte. Commercial graphite leads (Staedtler HB type, 68 %wt graphite) were used as a working electrode. Before sampling, the electrode surface was polished with alumina, rinsed with water and dried by pressing over paper. For sample-modified electrode preparation, an amount of ca. 1-2 mg of the solid sample was extended on the plane face of an agate mortar, forming a spot of finely distributed material. Then, the lower end of the graphite electrode was gently rubbed over that spot of sample; as a result, an amount below a microgram of soil sample was adhered to the graphite surface. This was rinsed with water to remove ill-adhered particles and then the electrode was dipped into the electrochemical cell so that only the lower end of the electrode containing the adhered sample was in contact with the electrolyte solution. To mimic the natural environment and electrochemically generate ROS, no degasification of the electrolyte was performed. Semi-derivative deconvolution was optionally applied to voltammetric data to enhance signal resolution.

# 2.4. Spectroscopical methods

ATR-FTIR spectroscopy was carried out using a VERTEX 70 (Bruker Optics) Fourier transform infrared spectrometer using a MKII Golden Gate Attenuated Total Reflectance (ATR) accessory and a fast recovery deuterated triglycine sulphate (FRDTGS) temperature-stabilized coated detector. 16 scans were collected at a resolution of  $4 \text{ cm}^{-1}$ .

# 2.5. Total organic carbon analysis

Total organic carbon (TOC) contents were determined after inorganic carbon removal by acidification using a Thermo Finnigan elemental analyzer set to an analytical precision of 0.1%.

#### 2.6. Statistical analyses

Pearson correlation tests were performed to evaluate the relationship between geochemical proxies and TOC, whereas the spatial variability between sedimentary environments (mudflat and mangrove forest) was evaluated by using an analysis of variance (ANOVA), with previous data normalization and testing by Shapiro–Wilk Test of data normality. A significance level of 0.05 was accepted for all tests.

# 3. Results and discussion

# 3.1. Voltammetric patterns

Fig. 2 shows the cyclic voltammogram, after semi-derivative convolution, of a glassy carbon electrode modified with an exemplified sample immersed into aqueous acetate buffer at pH 4.75. In the anodic region, the voltammetry of sample-modified electrodes produced one or more oxidation peaks at potentials between +0.2 and +0.8 V vs. Ag/AgCl (A<sub>org1</sub>) preceding a prominent but ill-defined wave at ca. +1.0 V (A<sub>org2</sub>) overlapped with the oxygen evolution process appearing as a rising current at potentials above +1.1 V. In the cathodic region, there are no cathodic counterparts (C<sub>org2</sub>) for the above oxidation processes, instead a signal reduction of around +0.60 V (C<sub>org1</sub>) appears, often accompanied by a series of weak overlapping cathodic signals between -0.2 and -0.6 V (C<sub>org3</sub>). These signals precede a prominent cathodic



**Fig. 2.** Cyclic voltammogram, after semi-derivative convolution, of a glassy carbon (conditioning protocol ii) electrode modified with a sample immersed into 0.25 M HAc/NaAc aqueous buffer at pH 4.75. Potential scan initiated at 0.0 V in the negative direction; potential scan rate  $50 \text{ mV s}^{-1}$ .

wave presumably resulting from the superposition of the reduction of dissolved oxygen to any reduction of organic matter ( $C_{\rm ox} + C_{\rm org4}$ ) at ca. -0.75 V, in turn preceding the rising cathodic current for the hydrogen evolution reaction at ca. -0.75 V ( $C_{\rm HER}$ ).

Although they may be attributed to the electrochemical oxidation or reduction of organic substances, the observed processes may result from the superposition of the signals for a relatively high number of compounds, so that no identification of concrete components is allowed from voltammetric data exclusively. In spite of this, comparisons with VIMP data for lignins (Milczarek, 2009; Admassie et al., 2014; Cottyn et al., 2015) and different organic compounds (Komorsky-Lovrić and Novak, 2009, 2011; Doménech-Carbó et al., 2015, 2017) suggest that the Aorg1 process may be attributed to the oxidation of o-catechol groups to the corresponding o-quinones, whereas the oxidation of single phenol groups and/or methoxi phenols would occur at more positive potentials (Aorg2 process). The Corg1 process would be the cathodic counterpart of the fraction of Aorg1 oxidations, having electrochemical reversibility. In turn, the  $C_{\rm org3}$  and  $C_{\rm org4}$  processes might mainly be attributed to the reduction of organic compounds having quinone functionalities. In the second anodic scan, the A<sub>org1</sub> and A<sub>org2</sub> peaks lowered, whereas a series of additional oxidation signals (Aoxorg) between -0.2 and +0.2 V appeared, thus suggesting (vide infra) that new electrochemically oxidizable organic components have been generated during electrochemical turnovers (Doménech-Carbó et al., 2015, 2017).

This voltammetry may be rationalized by considering that the sediment samples contain a variety of organic components. Much of some components (i.e., hydrocarbons and humic acids) are in principle electrochemically silent, but they would be accompanied by compounds able to experience electrochemical oxidations and/or reductions (i.e., indolic, polyphemolic and quinonic compounds). In particular, lignins, cross-linked phenolic polymers could experience electrochemical oxidations and reductions, being coupled to substitution, addition, coupling and bond cleavage reactions (Milczarek, 2009; Admassie et al., 2014; Cottyn et al., 2015). In this context, the Aorg1 and Aorg2 electrochemical signals may be attributed to the oxidation of organic compounds existing in the sample. The first signal (Aorg1), coupled to the Corg1 cathodic wave, may be assigned to processes with high electrochemical reversibility, typically, oxidation of o-catechol units in flavonoids and related polyphenolic compounds (Komorsky-Lovrić and Novak, 2009, 2011; Doménech-Carbó et al., 2015, 2017). The second



**Fig. 3.** Cyclic voltammograms, after semi-derivative convolution, of glassy carbon (conditioning protocol ii) electrodes modified with samples increasing in depth from a to b, immersed into 0.25 M HAc/NaAc aqueous buffer at pH 4.75. Potential scan initiated at 0.0 V in the negative direction; potential scan rate  $50 \text{ mV s}^{-1}$ . Dotted lines represent the base lines used for measuring peak currents.

oxidation process ( $A_{org2}$ ) may be attributed to irreversible oxidations, typically involving phenol and methoxy units, whereas the  $C_{org2}$  cathodic signal, which is frequently absent, would correspond to the reduction of quinonic compounds in the sediment (Doménech-Carbó et al., 2015, 2017).

#### 3.2. Electrochemical indexes

The recorded voltammetric pattern changed significantly from one sediment sample to another, as may be seen in Fig. 3. The cyclic voltammograms were recorded at glassy carbon electrode modified with four examples of sediments, as depicted.

The significant variability observed in the relative height of the different voltammetric signals suggests that the chemical composition of the organic fractions have experienced significant changes. Taking into account the interpretation of voltammetric signals, several innovative electrochemical indexes may be operationally defined:

a) The sum of the intensities of voltammetric signals  $A_{org1}$ ,  $A_{org2}$ ,  $C_{org3}$  and  $C_{org4}$  (the latter after subtracting the current for process  $C_{ox}$ ) would be representative of the total amount of organic matter *being electrochemically active* (in the following, electrochemically active organic matter, EAOM). As far as the amount of sample transferred onto the graphite electrode cannot be accurately fixed, one may operationally define a EAOM index,  $f_{EAOM}$  as the ratio of the sum of the above peak currents and the peak current for the reduction of dissolved oxygen:

$$f_{\text{EAOM}} = [i_{p}(A_{\text{org1}}) + i_{p}(A_{\text{org2}}) + i_{p}(C_{\text{org3}}) + i_{p}(C_{\text{org4}})] / i_{p}(C_{\text{ox}})$$
(1)

b) The ratio between the peak currents of the  $C_{org1}$  and  $A_{org1}$  coupled signals would be representative of the fraction of organic matter electrochemically oxidizable which displayed a reversible behavior. This will be termed in the following as the fraction of organic matter electrochemically oxidizable in reversible form (electrochemically reversible organic matter, EROM) and the corresponding index represented by  $f_{EROM}$ .

$$f_{\text{EROM}} = i_{\text{p}}(C_{\text{org1}}) / i_{\text{p}}(A_{\text{org1}})$$
<sup>(2)</sup>

c) The ratio between the  $C_{org3}$  plus  $C_{org4}$  signals and the  $A_{org1}$  plus  $A_{org2}$  signals would be representative of the proportion between the fractions of electrochemically active organic matter which is in an oxidized state



Fig. 4. ATR-FTIR spectrum of sample. Inset: detail of the spectrum in the region between 3800 and  $1200 \text{ cm}^{-1}$ . Continuous arrows mark the absorption bands associated to organic matter and dotted arrows those resulting of the superposition of organic and inorganic components in the OH stretching region.



--- Mudflat •- Mangrove

**Fig. 5.** Electrochemical and spectroscopical indexes obtained for the mudflat ("MF") and mangrove ("MG") cores. Fraction of electrochemically active organic matter ( $f_{EAOM}$ ); electrochemical ( $f_{RDOX}$ ) and FTIR ( $A_{1650}/A_{3440}$ ) indexes for the relative proportion between organic matter in oxidized redox state and in reduced state are given against sediment depths and ages (derived from <sup>210</sup>Pb-dating).

and in reduced state, represented by the  $f_{RDOX}$  index.

$$f_{\rm RDOX} = [i_{\rm p}(C_{\rm org3}) + i_{\rm p}(C_{\rm org4})] / [i_{\rm p}(A_{\rm org1}) + i_{\rm p}(A_{\rm org2})]$$
(3)

d) Since, as previously noted, the  $A_{org1}$  and  $A_{org2}$  signals appearing in the first anodic potential scan behave differently in the second and successive anodic scans when the potential is switched at potentials under -1.0 V and are accompanied by additional  $A_{oxorg}$  signals resulting from the reaction of parent organic compounds with electrochemically generated ROS, an index quantifying the capability for reaction with such reactive species,  $f_{ROS}$  may be defined as:

$$f_{\rm ROS} = [i_{\rm p}(A_{\rm oxorg})]/[i_{\rm p}(A_{\rm org1}) + i_{\rm p}(A_{\rm org2})]$$

$$\tag{4}$$

The variation of the  $f_{\text{EROM}}$  (Fig. 5) and  $f_{\text{RDOX}}$  (Fig. 5) indexes exhibit significant variations that are more pronounced for mudflat samples. In both cases, however, there is a common smooth tendency to increase the value of  $f_{\text{EROM}}$  above 20 cm depth. In contrast (Fig. 5) the  $f_{\text{ROS}}$  including depth follows a similar, irregular pattern for both mangrove forest and mudflat samples. This behavior can reflect a close similarity in the reactivity with ROS.

Table 1 summarizes statistical tests comparing these datasets, showing that core MG had significantly higher  $f_{\text{RDOX}}$ , while no significant difference was found for  $f_{\text{EAOM}}$ . These findings revealed that the different environmental conditions resulted in contrasting redox states of organic matter.

# 3.3. ATR-FTIR spectra

Fig. 4 depicts the ATR-FTIR spectrum of a sample representative of

#### Table 1

Analysis of variance (ANOVA) results for the geochemical proxies and TOC contents within sedimentary zones in the "Manglares de Tumbes" National Sanctuary. M: Mudflat core; MG: Mangrove forest core. \*p < 0.05; NS, not significant.

Variables	Average values	Statistical significance
f rdox	F: $1.68 \pm 0.60$	* MF $<$ MG
f <sub>eaom</sub>	M: $0.69 \pm 0.30$ F: 0.47 $\pm 0.24$	NS
A1650/3400	M: $0.63 \pm 0.26$ F: $1.02 \pm 0.25$	* MF < MG
	$M: 0.74 \pm 0.08$	
TOC (µmol g <sup>-1</sup> )	F: 2223.87 ± 768.26 M: 895.43 ± 159.80	* MF $<$ MG

typical sediment spectra. Such spectra are dominated by intense absorption bands around 1000 cm<sup>-1</sup> which may be attributed to silicate bands representative of clays forming the majority of absorbing species in the samples. Obviously, silicate bands obscure a significant part of the spectra due to organic matter, which is unambiguously represented by weak bands at ca. 1650 and 1400  $\text{cm}^{-1}$ . The former may be assigned to the highly characteristic carbonyl band, whereas the latter would be mainly representative of C-H vibrations. A detail of such bands may be seen in the inset in Fig. 4, corresponding to the spectral region between 3800 and  $1200 \text{ cm}^{-1}$ . The absorption band around  $1650 \text{ cm}^{-1}$  is characteristic of carbonyl groups, whereas the band at  $1400 \text{ cm}^{-1}$  may be assigned to C-H vibrations of alkanes and also to C=C bonds of aromatic compounds, (as for example phenolic compounds). In the region between 3800 and 3000 cm<sup>-1</sup>, a weak broad band was also recorded, accompanied by the narrow bands at ca. 3600 and 3650 cm<sup>-1</sup>. The latter can be attributed to crystalline silicates containing OH units, while the broad bands can result from both organic substances containing OH groups and minerals containing water of hydration.

Based on the preceding electrochemistry, one may consider, on first approximation, that the intensity of the C=O band,  $A_{1650}$ , would be representative of the amount of organic substances in an oxidized state that could be electrochemically reducible (assuming the previously indicated reduction of quinones to catechols) whereas the intensity of the broad OH band,  $A_{3400}$ , would be roughly representative of the fraction of organic matter having OH units (potentially oxidizable to carbonyls) (Doménech-Carbó et al., 2015, 2017). The  $A_{1650}/A_{3400}$  ratio may tentatively be treated as equivalent to the ratio between the organic matter in oxidized state and the organic matter in reduced state, previously represented by the electrochemical index  $f_{RDOX}$ . Pertinent comparison will be further described (*vide infra*).

## 3.4. Comparisons of proxies and correlations with TOC

Fig. 5 compares electrochemical and spectroscopical indexes for samples in this study. It may be observed that there is a coherence between the depth variation of the  $f_{\text{RDOX}}$ ) and spectrochemical ( $A_{1650}/A_{3400}$ ) indexes. Table 1 summarizes the data for the statistical correlation between the different series of data for mudflat and mangrove forest samples. The data suggest that it is possible to attribute a geochemical ( $A_{1650}/A_{3400}$ ) indexes. Firstly, the values of such parameters evidenced that the organic matter within the mangrove forest is in a more oxidized state in comparison with the organic matter within the

mudflat area, suggesting that the mangrove vegetation favors a higher organic matter accumulation (Kristensen et al., 2008; Sanders et al., 2014).

The non-significant differences in the  $f_{\rm EAOM}$  index values between both sedimentary environments (Table 1) suggest that the sedimentary organic matter suffered degradation by hydrolysis or bacterial respiration processes being representative of the global organic electroactive matter by EAOM (Lovley et al., 1996). Furthermore, the  $f_{\rm EAOM}$ values increased with depth, suggesting that the organic matter located below 20-cm depth (Fig. 5) represents the organic matter that has been exposed to an oxidative degradation for a longer period of time in comparison with the more recent and fresh organic matter present in superficial sediments (Kaushal and Binford, 1999; Kristensen et al., 2008).

The  $f_{\text{RDOX}}$  index was significantly higher within the mangrove forest in comparison with the mudflat area (Fig. 5), suggesting that the EAOM within the mangrove forest is in a more oxidized state as compared with the EAOM within the mudflat area. The mangrove forest tends to accumulate more organic matter for longer periods of time (Duarte et al., 2005; Sanders et al., 2014), whereas a fraction of the organic matter that reaches the mudflat area tends to be transported by the tidal regime (Kristensen et al., 2008; Kathiresan and Bingham, 2001). In this context, the accumulated organic matter within the mangrove forest is more influenced by the environmental oxidizing conditions, turning this sedimentary environment into a more refractory area (because it is already oxidized) in comparison with the mudflat area which would present more phytoplanktonic-derived organic matter and lower mangrove contribution than the mangrove forest (Fig. 5).

Finally, the  $A_{1650}/A_{3400}$  index (Fig. 5) exhibited significantly higher values within the mangrove forest in comparison with the mudflat area (Table 1), suggesting that the organic matter contents within the mangrove forest presents higher carbonyl groups, which is expected to be found in more degraded sedimentary organic matter (Canfield, 1993; Li and Lee, 1998), whereas the organic matter contents within the mudflat area would present higher contents of hydroxyl groups, suggesting the presence of organic matter displaying lower oxidation states (Meyers, 2003). Nevertheless, the sediment profiles exhibited the highest values towards the base of the sediment core for both sedimentary environments (Fig. 5), suggesting that the organic matter in subsurface intervals is in a more oxidized state (Kathiresan and Bingham, 2001; Kristensen et al., 2008) being consistent with the other electrochemical indexes.

Fig. 6 shows a large contrast in the variability of TOC concentrations in the studied sediments, with low variable values along the core "MF"



and much higher values within the upper 50 cm depth of core "MG". Therefore, TOC contents were significantly higher within the mangrove forest (Table 1). Indeed, studies have shown that estuarine areas that are directly exposed to the tidal forces are frequently washed out (Gibbs, 1985; Furukawa et al., 1997; Pérez et al., 2018a), whereas sedimentary areas with less energy diffusion retain greater amounts of organic matter in sediments (Derrau, 1978; Badarudeen et al., 1996; Pérez et al., 2017). Our results are consistent with the dynamic described above, exhibiting the higher contents of TOC within a mangrove forest (Fig. 6) that is less exposed to the wash out process, which in turn may positively influence carbon accumulation in this sedimentary environment (Canfield, 1993; Breithaupt et al., 2012; Pérez et al., 2017). Additionally, mangrove forest sediments contain dense root systems that provides stability in muddy waterlogged sediments (Kathiresan and Bingham, 2001; Black and Shimmield, 2003), and protection against the hydrological forces (Alongi, 2014; Pérez et al., 2018b), which probably influenced the greater TOC contents observed above 50 cm depth (Fig. 5). It is important to note that these findings were consistent even considering that the results showed in Table 1 present relatively important uncertainties, associated to a temporal variability exceeding one century in the organic matter input to the sediments studied (Fig. 6).

These higher TOC contents of core "MG" presented statistically significant correlations with the electrochemical index  $f_{\text{RDOX}}$  and the spectroscopic index  $A_{1650}/A_{3400}$ , while the results from core "MF" did not display any significant correlation trend (Fig. 7). These significant correlations observed for the mangrove forest sediments were negative, indicating that the larger organic matter accumulation along with sediment depth is associated with a less oxidized state. This finding supports the interpretation that the mangrove organic matter accumulated during the last century tends to be less oxidized than in adjacent bare sediments where the contributions from non-mangrove organic matter (i.e., algal organic matter) tend to be higher. Since the conditions of the study site are almost pristine, further studies should be conducted in order to evaluate how the electrochemical and spectroscopic indexes would respond to eutrophicated conditions, since the anthropogenic fertilization in the coastal zone may affect the nature of organic matter accumulated within the mangrove ecosystems, resulting in larger algal material deposition in mangrove fringes than under natural conditions (Sanders et al., 2014).

#### 4. Conclusions

Application of the voltammetry of immobilized particles methodology for analyzing mangrove sediments yields well-defined electrochemical responses using microparticulate deposits from ethanolic extracts of samples from the "Manglares de Tumbes" National Sanctuary (Perú). Voltammetric features corresponding to the oxidation of organic matter in contact with aqueous acetate buffer presented significant variations in regard to the reversibility and relative intensity of the signals depending on the depth and origin of the sediments. Different electrochemical indexes may be defined as being representative of the fraction of electrochemically oxidable organic matter, the reversibility of such oxidation and the reactivity with electrochemically generated reactive oxygen species. Voltammetric indexes may be correlated with data from infrared spectroscopy as well as conventional analytical data (i.e., total organic content and isotopic signatures), suggesting that there exists a possibility of incorporating this solid-state electrochemical methodology to the pool of analytical techniques implemented in chemoecology.

#### Acknowledgements

AP is supported by the "Fondo Nacional de Desarrollo Científico, Tecnológico y de Innovación Tecnológica" (Fondecyt - Peru), through the MAGNET research program. The collection of sampling was carried



Fig. 7. Scatterplots of studied indexes against TOC contents. Correlation coefficients and trend lines are given when a statistically significant result is obtained (p < 0.05).

out within the framework of the "Impacto de la Variabilidad y Cambio Climático en el Ecosistema de Manglares de Tumbes" project. Supported by the International Development Research Centre of Canada under management of the Instituto Geofísico del Perú (IGP). WM is supported by research grants from the Brazilian Research Council (CNPq). CJS is supported by the Australian Research Council (DE160100443, DP150103286 and LE140100083), in cooperation with Universidade Federal Fluminense. Project CTQ2011-28079-CO3-02 which is also supported with ERDF. We would like to thank Kelly Ronchi for the language revision.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2018.12.018.

#### References

- Admassie, S., Nilsson, T.Y., Inganäs, O., 2014. Charge storage properties of biopolymer electrodes with (sub)tropical lignins. Phys. Chem. Chem. Phys. 16, 24681–24684. Alongi, D.M., 2014. Carbon cycling and storage in mangrove forests. Annu. Rev. Mar. Sci.
- 6, 195–219. Badarudeen, A., Damodaran, K.T., Sajan, K., Padmalal, D., 1996. Texture and geochem-
- istry of the sediments of a tropical mangrove ecosystem, southwest coast of India. Environ. Geol. 27, 164–169.
- Black, K.D., Shimmield, G.B., 2003. Biogeochemistry of Marine Systems. Blackwell Publishing Ltd, Oxford UK.
- Breithaupt, J.L., Smoak, J.M., Smith, T.J., Sanders, C.J., Hoare, A., 2012. Organic carbon burial rates in mangrove sediments: strengthening the global budget. Global Biogeochem. Cycles 26, GB3011. https://doi.org/10.1029/2012GB004375.
- Breithaupt, J.L., Smoak, J.M., Smith, T.J., Sanders, C.J., Hoare, A., 2012. Organic carbon burial rates in mangrove sediments: strengthening the global budget. Global Biogeochem. Cycles 26, GB3011.
- Canfield, D.E., 1993. Organic matter oxidation in marine sediments. In: Wollast, R., Mackenzie, F.T., Chou, L. (Eds.), Interactions of C,N,P and S Biogeochemical Cycles

and Global Change. vol. 14. Springer, Berlin, pp. 333–363 NATO ASI Series.

- Cepriá, G., Alexa, N., Cordos, E., Castillo, J.R., 2005. Electrochemical screening procedure for arsenic contaminated soils. Talanta 66, 875–881.
- Cottyn, B., Rivard, M., Majira, A., Beauhaire, J., Allais, F., Martens, T., Baumberger, S., Ducrot, P.-H., 2015. Comparative electrochemical study on monolignols and dimers relevant for the comprehension of the lignification process. Phytochem. Lett. 13, 280–285.
- de Carvalho, L.M., Hilgemann, M., Scholz, F., Kahlert, N., da Rosa, M.B., Wuster, M., Lindequist, U., do Nascimento, P.C., Bohrer, D., 2010. Electrochemical assay to quantify the hydroxyl radical scavenging activity of medicinal plant extracts. Electroanalysis 22, 406–412.
- Derrau, M., 1978. Geomorfología. Prólogo de Luis sole sabaris. pp. 325 Editorial Ariel. Doménech-Carbó, A., Cebrián-Torrejón, G., Montya, N., Ueberschaar, N., Scotti, M.T.,
- Benfodda, Z., Hetweck, C., 2017. Electrochemical monitoring of ROS generation by anticancer agents: the case of chartreusin. RSC Adv. 7, 45200–45210.
- Doménech-Carbó, A., Gavara, R., Hernandez, P., Domínguez, I., 2015. Contact probe voltammetry for *in situ* monitoring of the reactivity of phenolic tomato (*Solanum lycopersicum* L.) compounds with ROS. Talanta 144, 1207–1215.
- Doménech-Carbó, A., Labuda, J., Scholz, F., 2013. Electroanalytical chemistry for the analysis of solids: characterization and classification (IUPAC Technical Report). Pure Appl. Chem. 85, 609–632.
- Duarte, C.M., Middelburg, J.J., Caraco, N., 2005. Major role of marine vegetation on the oceanic carbon cycle. Biogeosciences 2, 0 1–8.
- Enache, T.A., Chiorcea-Paquim, A.M., Fatibello-Filho, O., 2009. Hydroxyl radicals electrochemically generated in situ on a boron-doped diamond electrode. Electrochemistry Comm. 11, 1342–1345.
- Furukawa, K., Wolanski, E., Mueller, H., 1997. Currents and sediment transport in mangrove forests. Estuar. Coast Shelf Sci. 44, 301–310.
- Gaberell, M., Chin, Y.P., Hug, S.J., Sulzberger, B., 2003. Role of dissolved organic matter composition on the photoreduction of Cr(VI) to Cr(III) in the presence of iron. Environ. Sci. Technol. 37, 4403–4409.
- Gibbs, R.J., 1985. Estuarine flocs: their size, settling velocity and density. J. Geophys. Res. 90, 3249–3251.
- Grygar, T., Kadlec, J., Pruner, P., Swann, G., Bezdicka, P., Hradil, D., Lang, K., Kovotna, K., Hoberhänsli, H., 2006. Paleoenvironmental record in Lake Baikal sediments: environmental changes in the last 160 ky. Paleogeogr. Paleoclimat. Paleoecol. 237, 240–254.
- Grygar, T., van Oorschot, I.H.M., 2002. Voltammetric identification of pedogenic iron oxides in paleosol and loess. Electroanalysis 14, 339–344.
- Hradil, D., Grygar, T., Hrušková, M., Bezdička, P., Lang, K., Schneeweiss, O., Chvátal, M., 2004. Green earth pigment from Kadan region, Czech Republic: use of rare Fe-rich

smectite. Clay Clay Miner. 52, 767-778.

- INRENA, 2011. Plan Maestro del Santuario Nacional Los Manglares de Tumbes 2007-2011.
- Kapałka, A., Fóti, G., Comninellis, C., 2009. The importance of electrode material in environmental electrochemistry formation and reactivity of free hydroxyl radicals on boron-doped diamond electrodes. Electrochimica Acta 54, 2018–2023.
- Kathiresan, K., Bingham, B.L., 2001. Biology of mangrove and mangrove ecosystems. Adv. Mar. Biol. 40, 81–251.
- Kaushal, S., Binford, M.W., 1999. Relationship between C:N ratios of lake sediments, organic matter sources, and historical deforestation of Lake Pleasant, Massachusetts, USA. J. Paleolimnol. 22, 439–442.
- Komorsky-Lovrić, Š., Novak, I., 2009. Estimation of antioxidative properties of tea leaves by abrasive stripping electrochemistry using paraffin-impregnated graphite electrode. Collect. Czech Chem. Commun. 74, 1467–1475.
- Komorsky-Lovrić, Š., Novak, I., 2011. Abrasive stripping square-wave voltammetry of blackberry, raspberry, strawberry, pomegranate, and sweet and blue potatoes. J. Food Sci. 76, C916 – C920.
- Kristensen, E., Bouillon, S., Dittmar, T., Marchand, C., 2008. Organic carbon dynamics in mangrove ecosystems: a review. Aquat. Bot. 89, 201–219.
- Lavado, W., Espinoza, J.C., 2014. Impactos de El Niño y La Niña en las lluvias del Perú (1965-2007). Revista Brasileira de meteorología. 29, 171–182.
- Li, D., Sun, D., Hu, S., Hu, J., Yuan, X., 2016. Conceptual design and experiments of electrochemistry-flushing technology for the remediation of historically Cr(VI)-contaminated soil. Chemosphere 144, 1823–1830.
- Li, J., Lin, H., Zhu, K., Zhang, H., 2017. Degradation of Acid Orange 7 using peroxymonosulfate catalyzed by granulated activated carbon and enhanced by electrolysis. Chemosphere 188, 139–147.
- Li, M.S., Lee, S.Y., 1998. The particulate organic matter dynamics of Deep Bay, eastern Pearl River estuary, China I. Implications for waterfowl conservation. Mar. Ecol. Prog. Ser. 172, 73–87.
- Lovley, D.R., Coates, J.D., Blunt-Harris, E.L., Phillips, E.J.P., Woodward, J.C., 1996. Humic substances as electron acceptors for microbial respiration. Nature 382, 445–448.
- Luther III, G.W., Brendel, P.J., Lewis, B.L., 1998. Simultaneous measurement of O<sub>2</sub>, Mn, Fe, I<sup>\*</sup>, and S(-II) in marine pore waters with a solid-state voltammetric microelectrode. Limnol. Oceanogr. 43, 325–333.

- Meunier, L., Laubscher, H., Hug, S.J., Sulzberger, B., 2005. Effects of size and origin of natural dissolved organic matter compounds on the redox cycling of iron in sunlit surface waters. Aquat. Sci. 67, 292–307.
- Meyers, P.A., 2003. Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. Org. Geochem. 34, 261–289.
- Milczarek, G., 2009. Preparation, characterization and electrocatalytic properties of an iodine|lignin-modified gold electrode. Electrochim. Acta 54, 3199–3205.
- Pérez, A., Gutiérrez, D., Saldarriaga, M., Sanders, J.C., 2017. Hydrological controls on the biogeochemical dynamics of a Peruvian mangrove system. Hydrobiol. (Sofia) 803, 69–86.
- Pérez, A., Gutiérrez, D., Saldarriaga, M.S., Sanders, C.J., 2018a. Tidally driven sulfidic conditions in Peruvian mangrove sediments. Geo Mar. Lett. 38, 457–465.
- Perez, A., Libardoni, B.G., Sanders, C.J., 2018b. Factors influencing organic carbon accumulation in mangrove ecosystems. Biol. Lett. 14, 20180237.
- Ramnani, P., Saucedo, N.M., Mulchandani, A., 2016. Carbon nanomaterial-based electrochemical biosensors for label-free sensing of environmental pollutants. Chemosphere 143, 85–98.
- Sanders, C.J., Smoak, J.M., Sanders, L.M., Santos, I.R., Maher, D.T., Breithaupt, J.L., 2014. Elevated rates of organic carbon, nitrogen, and phosphorus accumulation in a highly impacted mangrove wetland. Geophys. Res. Lett. 41, 2475–2480.
- Scholz, F., González, G.L.L., de Carvalho, L.M., Hilgemann, M., Brainina, KhZ., Kahlert, H., Jack, R.S., Minh, D.T., 2007. An electrochemical system to detect free radicals and radical scavengers in solution. Angew. Chem. Int. Ed. 46, 8079–8082.
- Scholz, F., Meyer, B., 1998. Voltammetry of solid microparticles immobilized on electrode surfaces. In: In: Bard, A.J., Rubinstein, I. (Eds.), Electroanalytical Chemistry, a Series of Advances, vol. 20. Marcel Dekker, New York, pp. 1–87.
- Scholz, F., Schröder, U., Gulabowski, R., Doménech-Carbó, A., 2014. Electrochemistry of Immobilized Particles and Droplets, second ed. Springer, Berlin-Heidelberg.
- Scott, D.T., McKnight, D.M., Blunt-Harris, E.L., Kolesar, S.E., Lovley, D.R., 1998. Quinone moieties act as electron acceptors in the reduction of humic substances by humicsreducing microorganisms. Environ. Sci. Technol. 32, 2984–2989.
- Zhu, L., Santiago-Schübel, B., Xiao, H., Thiele, B., Zhu, Z., Qiu, Y., Hollert, H., Küppers, S., 2015. An efficient laboratory workflow for environmental risk assessment of organic chemicals. Chemosphere 131, 34–40.