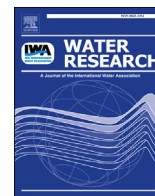




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A novel hybrid sensor for combined imaging of dissolved oxygen and labile phosphorus flux in sediment and water

Chao Han ^{a, **}, Jinghua Ren ^b, Zhaode Wang ^a, Hao Tang ^a, Di Xu ^{a, *}

^a State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China

^b Geological Survey of Jiangsu Province, Nanjing 210018, China

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ABSTRACT

A novel sensor assembled by a hybrid film was developed for 2D combined measurements of DO dynamic and labile P flux in sediment and water at sub-millimeter resolution based on PO and DGT techniques. The hybrid film is comprised of a transparent polyester membrane supporting two ultrathin sensing layers, i.e., a P binding layer (PBL) overlying a DO sensing layer (DSL). A robust, straightforward measuring strategy based on the referenced RGB and coloration-computer imaging densitometry (CID) methods was developed. Sensing properties for DO show a considerable homogeneity (RSD < 5%) and rapid response (<24 s) in fluorescent response. Calibration experiments reveal the sensitivity values for the DSL without/with PBL are 2.12/1.95, with an acceptable bias of less than 8%. The optimized PBL possesses a uniform distribution of zirconium-oxide microparticles at a relatively high DGT capacity (10.8 $\mu\text{g P cm}^{-2}$), in which the distribution of adsorbed-P can be imaged by the coloration-CID method. The performance of the sensor is compared to two conventional PO and DGT sensors. The hybrid sensor was successfully deployed in three types of benthic micro-interface and showed significant small-scale heterogeneity, providing new opportunities for advancing investigations into relevant biogeochemical processes.

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1. Introduction

The sediment-water interface (SWI) is often characterized by steep gradients of various physical and chemical parameters including dissolved oxygen (DO), pH and dissolved reactive phosphorus (DRP) over distances ranging from less than 0.5 mm to a few millimeters (Stockdale et al., 2009; Zhu et al., 2006). Extracting precise information on the gradients at fine-scale is essential for understanding the functions and regulations of the SWI's environmental biology and ecology processes. Since most

biogeochemical processes involve changes in two or more parameters, the information provided by a single-solute sensor cannot produce sufficient information for studying these processes. Simultaneous monitoring of two or more parameters at exactly the same position is highly desirable.

Phosphorus (P) and oxygen (O_2) are important parameters of biogeochemical processes, as these elements participate directly in a series of biogeochemical reactions. The biogeochemical cycling of P is of particular importance due to its role as the limiting nutrient of eutrophication and algal blooms in aquatic systems (Correll, 1998). P migration from sediment to water is critical for regulating a lake's trophic status, which is assumed to be mainly redox-sensitive and promoted by anoxic conditions (Ribeiro et al., 2014). O_2 is a central molecule for global element cycling and plays an important role in P cycling. It acts as an ultimate electron acceptor for the benthic degradation of organic materials; in this degradation process, O_2 is first consumed before other oxides follow. Consequently, this process induces changes in redox potential and the lability of P in sediment (Glud, 2008). It has long been recognized that the status of DO in hypolimnion affects the release of sediment-bound P (Hupfer and Lewandowski, 2008; Zhang et al.,

Abbreviations: 2D, two dimensional; P, phosphorus; O_2 , oxygen; DO, dissolved oxygen; DGT, diffusive gradient in the thin film; DET, diffusive equilibration in the thin film; PO, planar optode; PBL, P binding layer; DSL, DO sensing layer; RGB, Red-Green-Blue; CID, coloration-computer imaging densitometry methods; SWI, sediment-water interface; PtOEP, platinum (II) 2,3,7,8,12,13,17,18-octaethyl-21H, 23H-porphyrin; MFY-10GN, Macrolex[®] fluorescence yellow 10GN; Zr-oxide, zirconium oxide; HYD4, polyurethane hydrogel D4.

* Corresponding author.

** Corresponding author.

E-mail addresses: chan@niglas.ac.cn (C. Han), dxu@niglas.ac.cn (D. Xu).

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2015). However, details for the coupling between DO and labile P remain to be discovered since methodologies that can simultaneously capture both changes have until now not been available. The development of non-invasive technology for analyte measurement at millimeter-scale resolution or better is widely recognized as a research priority in aquatic systems. In particular, researchers are focusing on engineering planar imaging techniques, which enable high-resolution, 2D distributions of chemical parameters and, thus, reveal vertical and horizontal heterogeneity in sediment microstructure (Cesbron et al., 2014). The best option is the planar optode method (PO), which functions via a luminescent property (e.g., intensity, lifetime, polarization, etc.) that is differentially changed in the presence of such analytes as O₂, pH, CO₂, NH₄⁺ or H₂S (Borisov et al., 2006; Glud et al., 1996; Meier et al., 2014; Zhu and Aller, 2013). Another alternative method, including diffusive gradients/equilibrium in thin film technology (DGT/DET), are likewise promising for 2D measurement of the time-averaged flux or concentration of chemical species (e.g., P, arsenic and metals) with the use of high-resolution detection methods (Davison and Zhang, 1994; Pagès et al., 2011). All have been applied in parallel or integrated as a single-layer sensor for multi-parameter measurements (Santner et al., 2015). For example, a number of DGT/DET combinations have been developed for simultaneous measurements of multiple analytes, which have provided a great advantage in investigations of their relationships (Cesbron et al., 2014; Pagès et al., 2014; Gao et al., 2015). Moreover, several dual/multi analyte PO sensors were presented for simultaneously mapping the two or three parameters of oxygen, CO₂, temperature and pH (Meier et al., 2011; Stich et al., 2009). However, the development of a sensor that can be combined with DGT and PO and is capable of measuring multiple parameters is an ambitious task, thus, only few attempts have been made. Stahl et al. (2012) reported a sandwich micro-sensor consisting of oxygen-sensing PO and thin DGT layers capable of acquiring 2D co-distributions of O₂ and trace metal fluxes (Stahl et al., 2012). Such a method has recently been successfully applied to relevant biogeochemical processes associated with P/O₂ in heterogeneous substrates (Williams et al., 2014; Christel et al., 2016).

Advance in sensor development is driven by the development of 2D detecting strategies for analyte quantification. For high resolution analysis, 2D imaging of DGT gels through laser-ablation coupled with plasma mass spectrometry (LA-ICP-MS) is often performed (Guan et al., 2015; Stahl et al., 2012). The method offers excellent sensitivity and spatial resolution of ~100 μm but requires much more sophisticated, expensive measurement devices; hence, it is not available to many laboratories. Ding et al. (2011) developed a slicing-eluting-colorations procedure for gel analysis; however, this procedure is time and reagent consuming and is not suitable for sample batch analysis. Teasdale et al. (1999) developed a computer imaging densitometry (CID) technique in combination with DGT for the high-resolution, 2D determination of sulfide, which was easily operated at high efficiency and was considered as an alternative choice for high-resolution, 2D chemical imaging. Thereafter, CID as a robust quantitative method coupled with colorimetric DET and DGT techniques were successively developed to image 2D distributions of phosphate (Pagès et al., 2011; Ding et al., 2013) and ferrous iron (Robertson et al., 2008; Bennett et al., 2012) at a sub-millimeter spatial resolution. As for PO imaging approaches, fluorescence imaging methods based on intensity and lifetime have been widely used in optical chemical sensing systems (Glud et al., 1996; Stahl et al., 2006; Vieweg et al., 2013). The intensity-based imaging method always suffers from various interfering factors, and thus, only a few studies have used this method to date (Santner et al., 2015). Lifetime-based methods provide better accuracy and signal stability compared to both intensity-based and ratiometric methods (Schroder et al., 2007); however, these methods always

require a more sophisticated and expensive, fast gateable CCD camera, making them economically unviable (Santner et al., 2015). The ratiometric referencing method is one alternative approach to fluorescent imaging, where an analyte-insensitive excitation or a luminescence band of the luminophores is ratioed with the analyte-dependent band. It can, in principle, alleviate the inherent disadvantages associated with single intensity-based imaging methods (Larsen et al., 2011) and be operated using simple, commercially available digital single-lens reflex or other color cameras that are inexpensive compared to those required by lifetime-based methods (Santner et al., 2015).

Herein we present a novel sensor assembled by a hybrid film containing a P DGT binding layer and a planar O₂ optode sensing layer. A robust, facile detecting strategy was developed by accommodating two independent layers for DO and labile P imaging using the modified ratiometric referencing and coloration-CID techniques, respectively. The performances and applicability of the hybrid sensor for combined imaging DO and labile P in sediment and water were evaluated.

2. Materials and methods

2.1. Basic construction of the hybrid sensor

Fig. 1 presents a schematic illustration of a cross section of the hybrid film. It consists of two sensing layers, DSL and PBL, which overlay each other on a transparent polyester membrane (120 μm, PET). The hybrid film is combined with two measuring schemes—the modified referenced RGB method (Larsen et al., 2011) and a modified coloration-CID method (Ding et al., 2013), which are used for measuring DO and labile P flux, respectively.

2.2. Preparation of DSL

For the DSL fabrication, we used a highly photo-stable oxygen-sensitive dye, platinum (II) 2,3,7,8,12,13,17,18-octaethyl-21H, 23H-porphyrin (PtOEP) (Porphyrin Systems GbR, Lübeck, Germany). The coumarin dye MACROLEX[®] fluorescence yellow 10GN (MFY-10GN), purchased from Bayer China (Beijing), was used as the reference dye and antenna dye (Larsen et al., 2011; Mayr et al., 2009). Polystyrene (Sigma-Aldrich), which possesses excellent permeation selectivity that excludes other potential quenchers (Meier et al., 2011), was used as an optode matrix for achieving optimal sensitivity. DSL was prepared following a reported method (Larsen et al., 2011). PtOEP (10 mg), MFY-10GN (10 mg) and polystyrene (500 mg) were dissolved in 10 mL toluene (Sinopharm Ltd.) and vortexed for ~5 min. Immediately after mixing, 200 μL of the stock solution was knife-coated onto a transparent PET substrate of 120 μm thickness. The final thickness of the DSL was <2 μm after being dried

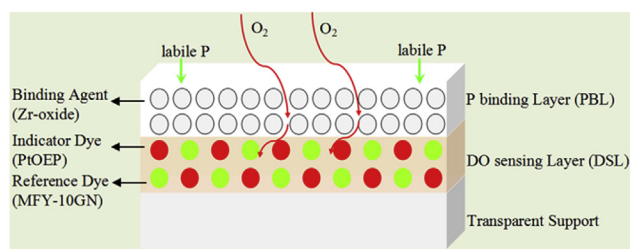


Fig. 1. A schematic illustration of a cross section of the hybrid sensor. The upper layer consists of Zr-microparticles embedded in polyurethane hydrogel used for imaging labile P, while the middle layer consists of two fluorescent dyes embedded in gas-permeable polystyrene for imaging DO. The bottom layer acts as an inert mechanical support for the two sensing layers.

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