



Research article

Characterization and evaluation of phosphate microsensors to monitor internal phosphorus loading in Lake Erie sediments



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ABSTRACT

Monitoring phosphate concentration is very important to prevent and control eutrophication in natural waters. In this study, cobalt-based microsensors were modified, characterized, and tested to monitor internal soluble phosphorous (SRP) loading in lakes with improved detection limits. The effectiveness of surface modification on the performance of a cobalt-based microelectrode was fully examined by determining detection limit, response time, selectivity, interference with ions (sulfate, nitrate, and nitrite) and dissolved oxygen (DO). To assess their performance, phosphate sensors were applied to sediment samples collected from Lake Erie. SRP loading from sediments was determined under different DO conditions. After increasing the phosphate sensing area and modifying the surface, phosphate microsensors showed an increased detection limit of up to 10^{-8} M concentration of phosphate ion. The phosphate microsensor also showed its ability to measure sediment SRP profiling without disturbing sediment structure, and diffusion coefficients of phosphate in sediment could be determined under both oxic and anoxic conditions. Modified phosphate sensors showed improved sensitivity and could be applied to both water and sediment samples with high spatial resolution; however, signal interferences (especially with oxygen) required consideration during sample analysis. Overall, obtained results showed that phosphate microsensors can be an effective tool for measurement of phosphate in lake water and sediment samples for SRP monitoring.

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1. Introduction

As a result of anthropogenic impacts, including sewage effluent and agricultural fertilizer release into the water or soil, phosphorus is considered a universal concern for environmental managers, as it contributes to the eutrophication of water bodies (Ritter et al., 2002; Sharpley et al., 1994). In a water system, phosphorus loading is comprised of two major parts: external and internal loading. External phosphorus loading refers to the phosphorus load deposited into the water column, while internal phosphorus loading refers to the accumulation of phosphorus in the sediment (Ekholm et al., 1997). Studies show that phosphorus becomes accumulated in sediment when external phosphorus loading is high (Granéli, 1999; Søndergaard et al., 2003). Furthermore, the required recovery periods in lakes after the reduction of the

external phosphorus loading are lengthened due to release of the internal phosphorus load (Molen and Boers, 1994; Søndergaard et al., 1999; Steinman et al., 2004; Xiang and Zhou, 2011). As a major influence on the duration of recovery, reports indicate that phosphorus content in sediment can be approximately 1000 times higher than that found in the water column (Rivas et al., 2000). Thus, even small phosphorus release from sediment may significantly affect lake water phosphorous concentration (Pettersson, 1998).

Total phosphorus (TP) has been accepted as a good indicator of a lake's nutrient status to prevent eutrophication, as it remains more stable than soluble reactive phosphorous (SRP) in lakes. However, SRP has received more attention than total phosphorus (TP) recently as an approach for managing eutrophication. SRP is largely comprised of the inorganic orthophosphate (PO_4), and this labile phosphorus variant is a great concern as it is directly ingested by algae and accelerates eutrophication (Hilton et al., 2006). To monitor SRP release to water bodies from different sources, various analytical methods have been used. The common analysis of phosphorus in sediment involves two general procedures. First,

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digestion of phosphorus is performed by oxidizing various forms of phosphorus to dissolved phosphate in a strong acidic media (Colina et al., 1996). After digestion, the digested phosphate is determined using various detection techniques such as spectrometry and ion-chromatography (Chen et al., 1998; Colina et al., 1996). Although these techniques provide very accurate results, such analytical methods require complex and time-consuming sample pretreatment procedures. In addition, the instruments are prohibitively expensive and inappropriate for field sample analysis (Kim et al., 2007).

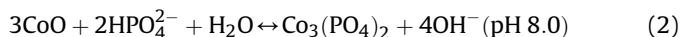
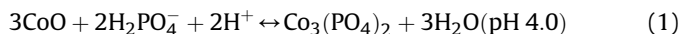
Microsensors, also called microelectrodes, are useful tools that have been applied for measurements of various analytes in micro-environments, such as soil pores, biofilm, and activated sludge floc (Dalsgaard and Revsbech, 1992; Li and Bishop, 2004; Xue et al., 2014; Zhang and Pang, 1999). This technology, which has drawn increased attention in recent studies, offers several advantages over standard phosphate detection methods, including low cost, simple fabrication procedures, portability, and ability to be applied in both direct and indirect detection of phosphorus (Korostynska et al., 2013). However, to date, few microelectrodes are used for direct determination of phosphate since they are not commercially available (Carey and Riggan, 1994; Chen et al., 1998). In a previous study, a cobalt wire based phosphate sensor with small tip diameter (5–10 μm) was successfully fabricated and tested to directly monitor phosphate ion concentration changes in activated sludge floc during the anaerobic phase of an enhanced biological phosphorus removal (EBPR) process (Lee et al., 2009). In comparison with other colorimetric techniques, such as wet-chemical oxidation and microfluidic technology, this cobalt wire based microelectrode showed a much quicker response time and a wide detection range (Al-Dasoqi et al., 2011). However, the sensor showed limited field application capability beyond samples from wastewater with high phosphate concentration, due to its detection limit. In addition, phosphate detection interferences from co-existing ions, common to fresh water systems (lake water and sediment), have not yet been evaluated. Because of deficiencies in sensing devices for directly monitoring SRP in sediments, internal SRP loading from lake sediment is not well understood.

The main goal of this study was to assess performance of the phosphate microsensor and its applicability for *in-situ* SRP monitoring. To achieve this goal, cobalt-based microsensors were modified, characterized and tested to improve detection limits for phosphate ($<10^{-5}$ M). The effectiveness of surface modification of a cobalt-based microelectrode was examined by determining detection limit, response time, selectivity, reproducibility, lifetime, interference with ions (sulfate, nitrate, and nitrite), and dissolved oxygen (DO). Then, the microsensor was further characterized and tested on sediment samples collected from Lake Erie to assess its applicability to detect internal SRP loading under different redox conditions.

2. Materials and methods

2.1. Microsensor fabrication

The basic detection mechanism of the cobalt based phosphate sensor involves measurement of the voltage output response to phosphate concentrations. When the cobalt first makes contact with water, a cobalt oxide film is formed on the surface. This oxide layer subsequently interacts with phosphate ions in solution and creates a unique cobalt phosphate complex layer on the surface, depending on the pH level of the solution (Engblom, 1999) [Equations (1)–(3)].



In order to construct the phosphate sensor, two fabrication methods were considered. First, glass pipette barrels were used and tested for phosphate sensor fabrication. Then, a new type of phosphate sensor was fabricated using polymer based sealants (see Supporting information Fig. S1). For glass pipette based sensor fabrication, glass pipette barrels (O.D.: 1.2 mm, I.D.: 0.69 mm, 15 cm length, Sutter instrument Co.) were purchased, heated, and pulled over the flame. After pulling the barrels, a section of cobalt wire (0.1 mm diameter, 99.995% pure, Aldrich Chemical Company) was inserted into the pulled glass micropipette. Without the use of an etching process, the cobalt wire maintained its initial tip size. The micropipette was then melted in the middle section using a trough heating filament (Sutter instrument Co.) to completely seal the cobalt wire in the stretched glass pipette barrel. The tip of the sensor was then beveled using a diamond abrasive plate (BV10-1684, Sutter instrument Co.) to hone the sensor tip to a 45° angle and expose the cobalt surface. Then, the microelectrode was connected to copper wire by melting a small section of bismuth alloy (44.7% bismuth, 22.6% lead, 19.1% indium, 8.3% tin and 5.3% cadmium) (Lee et al., 2009). To fabricate a new type of phosphate sensor, cobalt wires were dipped in a polymer solution, and the polymer layer was solidified and beveled to expose the cobalt surface. To measure electrical sensor response during calibration and sensor performance experiments, the potential between the working microelectrode and reference electrode was monitored using a millivolt (mV) meter (Model 250, Denver instruments). An Ag/AgCl reference mini-electrode (MI-401, Microelectrodes Inc.) was used as the reference electrode. The pH/mV meter was connected to a computer and data was acquired with a spread data logger (Balance Talk SL TM, Labtronics Inc.) to record responses at five second intervals.

After fabricating the microsensors, the sensors were pretreated prior to calibration. In detail, sensors were first immersed into DI water to form a cobalt oxide (CoO) layer on the surface of sensor tips. Upon reaching a stable potential, the sensors were removed from DI water and immersed into potassium phosphate (KH_2PO_4 , 10^{-4} M) solution at pH 7 until a new steady-state potential was obtained. Following the pretreatment process, phosphate sensors were calibrated. Several phosphate standard solutions were prepared using KH_2PO_4 at a range of 10^{-1} M to 10^{-8} M, where the solution pH was maintained at 7. Sensor calibration and experiments were conducted under condition of ambient oxygen levels and room temperature (20 °C). To monitor sensor performances, tested sensors were calibrated again after being applied to samples.

2.2. Ion and DO (dissolved oxygen) interference tests

Considering the co-presence of other ions in the natural environment and their potential interference with sensor performance, sulfate, nitrite, and nitrate ions were used to investigate potential ion interferences on the phosphate sensor response. For each ion interference experiment, interfering ions were kept constant while phosphate ion concentrations were varied from 10^{-3} M to 10^{-6} M. Ion interference tests were also conducted by keeping the phosphate ion concentration constant while the other ion concentrations were varied. Table S1 shows the tested ions and the ranges of tested ion concentration. The concentrations of three interfering

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