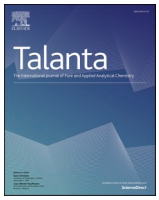
Talanta 289 (2025) 127749

Contents lists available at ScienceDirect

Talanta

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



A paper-based screen-printed electrochemical sensor combined with a 3D printed extracting cartridge for analysis of phosphorus in Antarctic lacustrine sediments

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ARTICLE INFO

Handling editor: Agata Michalska

Keywords:
Paper-based sensor
3D printing technology
Phosphorus
Sediments analysis
Antarctica

ABSTRACT

Here, we present a novel fully printed electrochemical sensing tool for determining phosphorus levels in sediment samples. The integrated electrochemical device is composed of an office paper-based sensor combined with a customized 3D printing cube-shaped holder used for the extraction of phosphorus from sediment samples. The extracted phosphorus was trapped on a filter pad placed over the sensor and preloaded with acidic ammonium molybdate, allowing for the formation of the phosphomolybdate complex, which is electroactive. The use of carbon black as a nanomodifier of office paper-based electrode together with square wave voltammetry enabled the detection of phosphorus with a detection limit of 0.011 ppm within a broad linear range of 0.039–20 ppm. Furthermore, this sensor demonstrated excellent selectivity towards phosphate ions among the several ions studied, namely NO_3^-, NO_2^-, F^-, SO_4^{2-}, CH_3COO^-, Cl^-, CO_2^{3-}, Mg^{2+}, K^+, Zn^{2+}, Ca^{2+}, Na^+, Cu^{2+}, and Ni^{2+}. The precision of the analytical platform was evaluated using eight distinct sensors, yielding a relative standard deviation below 5 %. The reliability of the paper-based integrated sensor was assessed by determining phosphorus levels in sediment samples obtained from various seasonal shallow coastal lakes situated in Northern Victoria Land, Antarctica, by comparing the data obtained with both the novel printed integrated device and the colorimetric reference method. The agreement of the data with a coefficient of correlation equal to 0.86 (r = 0.86) demonstrated the great potential of the developed sensing tool for use in real-world applications.

1. Introduction

Phosphorus (P) is one of three essential macronutrients (along with nitrogen (N) and potassium (K)) utilized by all organisms for growth and energy transport [1]. In contrast to nitrogen, P cannot be supplied through biochemical fixation and must be applied through alternative means, including commercial fertilisers, animal manures, and plant residues. Nevertheless, less than 15 % of the P applied as fertilizer is taken up by the crop during the year in which the fertilizer was added [2]. Moreover, more than 90 % of total P is present in insoluble and fixed forms, including primary phosphate minerals, insoluble phosphate of Ca, Fe, Al, and P fixed by hydrous oxides and silicate minerals [3]. Consequently, excessive amounts of P can enter waterways via surface and subsurface runoff, leading to the global problem of eutrophication [4].

In recent years, significant research has been conducted to develop effective methods for the optical and electrochemical monitoring of P concentrations in the environment. However, the majority of these studies have focused on the examination of surface water [5–14]. On the other hand, due to the poor solubility of P in water and the capacity of soil to act as a filter and retain nutrients, several studies using the colorimetric method were reported for assessing the availability/-scarcity of P in the soil, which is a naturally occurring material resulting from the weathering of the Earth's crust in situ [15–20]. The colorimetric method involves the reaction of P (in its orthophosphate form), ammonium molybdate, and potassium antimonyl tartrate to form

This article is part of a special issue entitled: Electroanalysis published in Talanta.

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https://doi.org/10.1016/j.talanta.2025.127749
Received 18 December 2024; Received in revised form 9 February 2025; Accepted 13 February 2025
Available online 16 February 2025

phosphomolybdic acid, which is subsequently reduced by ascorbic acid to produce the colored molybdenum blue [21]. While the mechanism appears straightforward, the potential for false positives due to the reaction between ammonium molybdate and ascorbic acid raises concerns about the reliability of the colorimetric method. The electrochemical detection is based on the exclusive interaction between P and ammonium molybdate followed by the electrochemical oxidation/reduction of the phosphomolybdate complex, thereby obviating the need for a reducing agent to form the electroactive complex. This approach has been demonstrated to be a promising alternative in analysing P extracted from soil samples. For instance, pencil graphite electrodes were electrochemically coated with molybdenum phosphate through the use of cyclic voltammetry [22]. The sensor demonstrated a limit of detection equal to 1.25×10^{-6} M using differential pulse voltammetry. Besides ammonium molybdate, Lu et al. have employed zirconium dioxide, zinc oxide, and multi-walled carbon nanotubes to modify screen-printed carbon electrodes [23]. Using cyclic voltammetry, the electrodes demonstrated the ability to detect phosphate anions at the nanomolar level. In addition, they exhibited high selectivity towards phosphate among four test anions, namely chloride, bicarbonate, nitrate, and sulfate. The applicability of both sensors was investigated through the analysis of P extracted from soil samples using in-lab procedures which require sonication, centrifugation, and filtration. Always with screen-printed carbon electrodes, Zeitoun et al. have adopted the Olsen method to extract P from soil samples and used both bare [24] and paper-polished [25] carbon screen-printed electrodes for P detection. By conducting cyclic voltammetry measurements to observe the oxidation of the phosphomolybdate complex, they achieved limits of detection of 0.18 and 0.10 ppm, using bare and paper-polished electrodes, respectively. The same group also used paper-polished carbon screen-printed electrodes for detecting P extracted from soil samples by incubating a filter paper preloaded with concentrated Mehlich-3 reagents (ammonium fluoride, nitric acid, ethylenediaminetetraacetic acid, ammonium nitrate, and acetic acid) together with soil sample and water in solution [26]. Using cyclic voltammetry measurements, the sensor exhibited a limit of detection equal to 0.11 ppm in phosphate standard solution.

Given the preceding studies, it is essential to consider environmental compounds beyond those of water and soil to gain a more profound understanding of nutrient dynamics within a specific ecosystem. Sediments are defined as a layer or collection of particulate matter that has been removed from the site of its initial weathering of the rock and subsequently deposited in a different location [27]. Coastal and continental sediments are regarded as the primary long-term sink of P through the burial of organic matter, adsorption to iron hydroxide minerals, and authigenic precipitation of carbonate fluorapatite [28]. Pis found in the Earth's crust, primarily in sedimentary rocks of marine origin. These sedimentary phosphorites were formed over geological time by the accumulation of organic marine debris and phosphate-rich sediments [29]. As these rocks undergo weathering and erosion, dissolved phosphates are released into the soil and subsequently transported via rivers to the ocean. In Antarctica, dissolved P can be transported by surface runoff to the surrounding water and subsequently deposited in the catchment situated close to penguin colonies. In such environments, P can be readily adsorbed by Fe/Al oxides under acidic conditions. Furthermore, sedimentary P can be released back into the overlying water as a result of the dissolution of ferric (hydr)oxides. This process increases the bioavailability of P, which in turn exacerbates the eutrophication of the water body [30]. Consequently, the quantification of total P levels in sediment samples may offer a first-hand assessment of environmental changes that have occurred in recent years to decades.

Herein, we report a novel, fully printed paper-based electrochemical sensor for determining P levels in sediment samples. The integrated electrochemical device comprises two main components: (i) a three-electrode sensor that was printed using screen-printing technology on office paper, offering a range of compelling advantages (e.g., inexpensive, sustainable, incinerable) [31,32], and (ii) a filter pad preloaded with acidic ammonium molybdate, which enables the formation of the phosphomolybdate complex without requiring the addition of reagents by the end-users. Moreover, the extraction of phosphate ions from sediment samples was conducted within a lightweight, reusable, and portable cube-shaped holder, constructed using 3D printing technology. The extraction system is equipped with a lid on one side and a funnel-shaped outlet on the other side, enabling the secure containment of the sediment sample and the extraction solution (i.e., ammonium fluoride solution). Once extracted, phosphate ions are conveyed through the funnel-shaped outlet of the 3D design, ultimately reaching the surface of the filter pad. In turn, the phosphomolybdate complex is transported through the filter pad, reaching the surface of the sensor. At this point, the complex undergoes oxidation on the working electrode, which was modified with carbon black nanoparticles. The paper-based electrochemical sensor, when coupled with a ready-to-use filter pad, demonstrated excellent analytical performances in phosphate standard solutions. Furthermore, it was successfully used for the analysis of unbuffered extracts of sediment samples collected from multiple zones in the Antarctic.

2. Experimental section

2.1. Reagents and chemicals

Potassium phosphate monobasic (KH_2PO_4), ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$), potassium antimonyl tartrate ($C_8H_4O_{12}Sb_2K_2$), ascorbic acid ($C_6H_8O_6$), and ammonium fluoride (NH_4F) were purchased from Merck. Sodium nitrate ($NaNO_3$), sodium nitrite ($NaNO_2$), sodium fluoride (NaF), ammonium sulfate ($(NH_4)_2SO_4$), sodium acetate (CH_3COONa), sodium carbonate (Na_2CO_3), magnesium chloride ($MgCl_2$), potassium chloride (KCl), zinc chloride ($ZnCl_2$), calcium chloride ($CaCl_2$), sodium chloride (NaCl), copper sulfate ($CuSO_4$), and nickel chloride ($NiCl_2$) were purchased from Merck. Sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) were brought from Merck. Carbon black powder (CB) N220 was kindly gifted by Cabot (Ravenna, Italy).

Syringe filters (Φ = 0.2 μm) equipped with a hydrophobic polytetrafluoroethylene (PTFE) membrane were purchased from Cobetter filtration.

All commercial chemical reagents were of analytical grade and used without further purification. All solutions were prepared in ultrapure water obtained from a Millipore Milli-Q purification system (18.2 MΩ cm). Before use, all glassware was meticulously cleaned with nitric acid and ultrapure water.

2.2. Paper-based electrochemical sensor configuration

The integrated paper-based electrochemical sensor was devised by combining two distinct types of paper (i.e., filter and office papers) to create a reagent-free device that ensures the formation of the phosphomolybdate complex on one paper layer (i.e., the filter pad) and its subsequent oxidation on the second paper layer (i.e., the screen-printed office paper-based electrodes).

To prepare the filter pad, a hydrophobic pattern was designed using Adobe Illustrator software and then printed with wax on filter paper using a ColorQube 8580 Xerox printer (Xerox Corporation, USA). This resulted in the formation of hydrophobic zones surrounding the hydrophilic region, which is the site of the formation of the phosphomolybdate complex. Regarding the electrochemical sensor, it was printed on office paper (Copy 2, 80 g/m^2, Fabriano, Italy) using screen-printing technology. Ag/AgCl ink (Electrodag 477 SS) was used to print the pseudo-reference electrode, while the working (geometric surface area equal to 12.56 mm^2) and the counter electrodes were obtained by printing carbon ink (Electrodag 421). All the conductive inks were purchased from Acheson (Italy).

In each experimental setup, the final configuration of the integrated

paper-based electrochemical sensor comprised screen-printed office paper-based electrodes coupled with a filter pad, which was affixed to the surface of the sensor before collecting the analyte.

2.3. Electrochemical measurements

The electrochemical detection of phosphate ions was performed on homemade screen-printed office paper-based electrodes. The working electrode was modified with 3 x 2 μL drops of CB dispersion, made of 1 mg/mL of CB prepared in N,N-dimethylformamide: H_2O distilled at a 1:1 (v/v) ratio. The modified electrodes are reported as CB-SPEs in the present work. A portable potentiostat, EmStat3 Blue, (PalmSens, Netherlands) connected to a personal laptop and controlled by PSTrace 5.9 software was used to carry out square wave voltammetry (SWV) under the optimized settings. Potassium chloride at 0.1 M concentration was used as the supporting electrolyte. All the experimental data shown are the mean of at least three replicate measurements (mean ± SD, n = 3).

2.4. Spectrophotometric measurements

The colorimetric determination of P was performed following the procedure reported in the literature [33], with minor modifications. In summary, 5 mL of phosphate solution samples (either the standard solution or the sediment extract) in 0.1 M HCl were added to 0.8 mL of a molybdate preparation comprising 24.3 mM ammonium molybdate, 2 mM potassium antimonyl tartrate, and 2.8 M sulfuric acid. The three solutions were prepared separately in ultrapure water and subsequently combined in a volume ratio of 2:1:5, respectively. The mixture of phosphate samples and molybdate preparation was incubated for 20 min under shaking conditions. Subsequently, 0.2 mL of a 0.31 M ascorbic acid solution was added to the previous mixture and incubated for another 10 min under shaking conditions. The amount of P present in the samples was determined by measuring the intensity of the blue color developed, with the absorbance value at 831 nm being recorded using a double-beam UV–Vis spectrophotometer.

2.5. Sediment samples collection

The present study investigated seasonal shallow lakes in Terra Nova Bay (Northern Victoria Land, Antarctica). These lakes are frozen during the winter months but become ice-free for a few weeks during the austral summer. The only input of water is via runoff from snow and ice melt, carrying elements associated with the atmospheric aerosol and leached from the soil surrounding the lake.

Sediment samples were collected at Edmonson Point from two adjacent lakes, designated as Lake 15A (74.31 S–165.07 E) and Lake 14 (74.33 S–165.13 E). These lakes are situated close to the active volcano Mount Melbourne. It is important to note, however, that the dimensions of Lake 14 have undergone a significant reduction over the past decade [34]. Additional sediment samples were obtained from Lake 10b (74.88 S–163.72 E) on Inexpressible Island, which is a small rocky island in Terra Nova Bay.

The samples were collected from the surface of the sediments in those lakes and freeze-dried for three days. They were then sieved and homogenised using a Retsch RM 200 Mortar Grinder. The samples were stored in glass containers that had been thoroughly washed and decontaminated with *n*-hexane and dichloromethane.

2.6. Design and preparation of the 3D printed extracting device

The 3D printed device was designed using the Autodesk Fusion 360 computer-aided design (CAD) software. The CAD drawings were sliced for 3D printing using the UP-Studio slicer software. The extraction device was created using the fused deposition modelling (FDM) technique with a polylactic acid (PLA) filament. The Cetus 3D Printer MK2 printer was employed with the following parameters: printing temperature: 220 °C; plate temperature: 20 °C; extruder diameter: 0.4 mm; layer thickness: 0.2 mm.

As illustrated in Fig. 1A, the extraction device consists of two complementary cubic units. The extraction chamber serves as the chamber for introducing sediment samples and the requisite reagent for the extraction (ammonium fluoride solution). The filtration chamber is a cubic chamber that ends with a funnel outlet, on top of which a filtering paper was placed to separate the extract solution from the sediment particles.

2.7. Phosphorus extraction using the 3D printed design

The extraction process is initiated by the introduction of 250 mg of sediment sample into the cube. Subsequently, 2.5 mL of ammonium fluoride solution (0.03 M) prepared in 0.1 M HCl was added and gently stirred, allowing the sample to incubate for a few minutes. The extraction chamber is then inverted and placed into the filtration chamber to press the extract through the filter paper. The extract solution will finally flow through the funnel-shaped outlet and can be used to determine the amount of P present in sediments. Fig. 1 depicts the three-step process employed for the analysis of the sediment samples, focused on the extraction process.

On the other hand, the laboratory-setup extraction of P from sediment samples was carried out as follows: 1 g of air-dried and sieved sediment sample was added to a solution of 10 mL of 0.03 M ammonium fluoride prepared in 0.1 M HCl. Following a 10-min shaking period, the sample was subjected to centrifugation at 4000 rpm for a further 10 min. The resulting filtrate was collected using a 0.02 μm PTFE syringe filter and subsequently used in colorimetric experiments. In both extractions, the Bray II method [35] was employed, as it requires the use of a single chemical (ammonium fluoride), thus allowing for the selective extraction of P. This is because the fluoride ion facilitates the dissolution of the aluminum and iron-bound phosphate, thereby releasing P in solution [36].

2.8. Electrochemical analysis of phosphate ions using the paper-based sensor

The electrochemical determination of P levels in the Antarctic sediments was conducted using a three-step process. The first step involved the extraction of P using a homemade 3D printed system. The second step involved the interaction between the extracted P and an acidic molybdate solution preloaded on the filter pad described earlier. This resulted in the formation of an electroactive phosphomolybdate complex. The third step involved the oxidation of this electroactive complex on the office paper-based electrodes modified with CB.

To guarantee the most favourable acidic conditions for molybdate interaction, the filter pad was initially acidified with 10 μL of a 0.1 M HCl solution. Subsequently, 80 μL of a molybdate solution prepared in 0.1 M HCl was added to the reaction area and dried. At the analysis time, the modified filter pad was placed on the surface of the sensor, whereby the extracted P induced the formation of the phosphomolybdate complex on the filter pad, which then flowed towards the surface of the office paper-based electrodes modified with CB.

2.9. Selectivity study

To determine the potential applicability of the developed sensor for the detection of P among various elements that may be present in the same sediment, a deep selectivity study was conducted using different ions (NO_3^-, NO_2^-, F^-, SO_4^{2-}, CH_3COO^-, Cl^-, CO_2^{3-}, Mg^{2+}, K^+, Zn^{2+}, Ca^{2+}, Na^+, Cu^{2+}, Ni^{2+}). Each interfering element was added to a standard solution of P in a 1:1 M ratio, before being applied to the ammonium molybdate-filter pad. The recorded SWV signals were compared to the voltammogram corresponding to PO_4^{3-}.

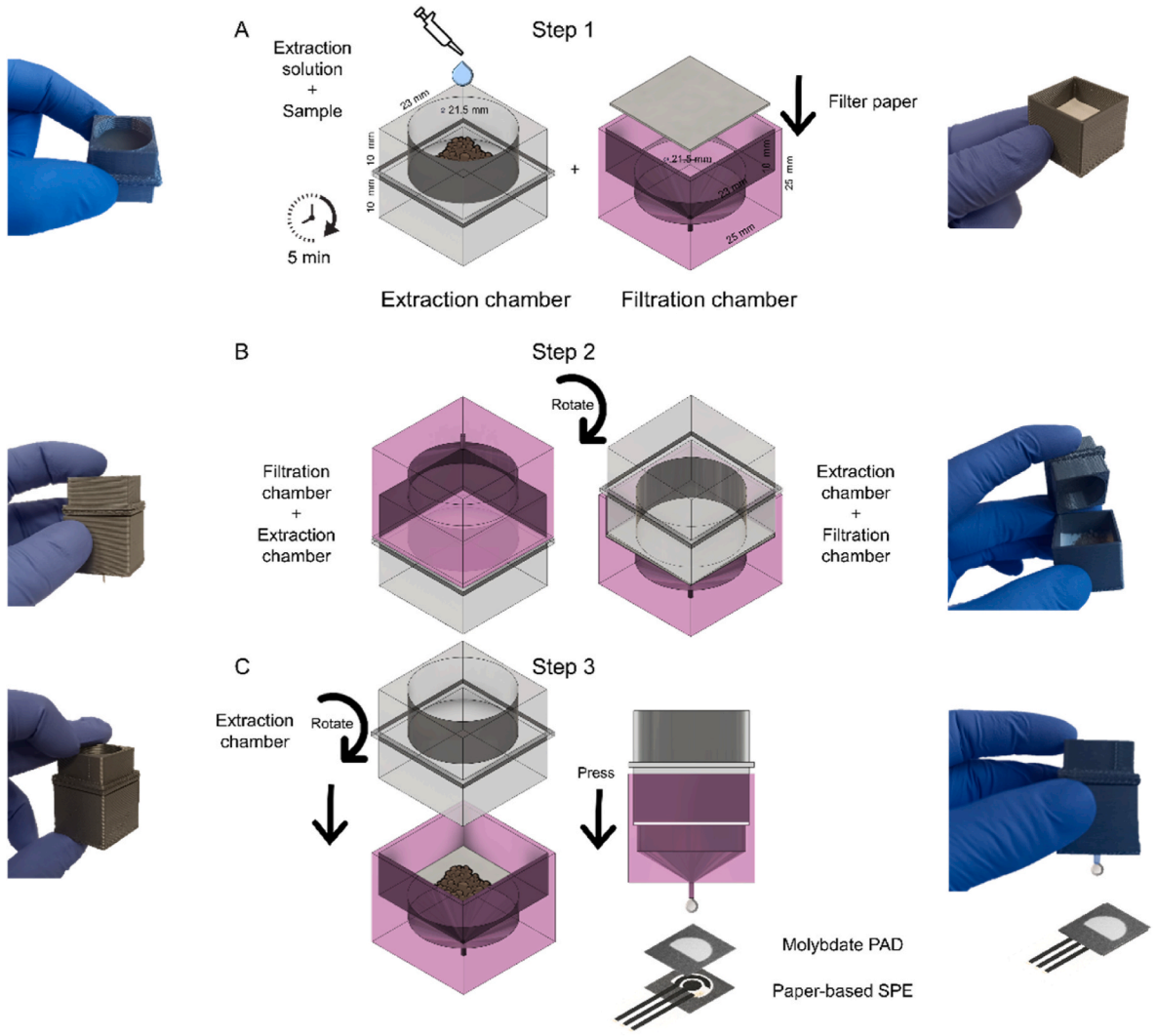

Fig. 1. A) The sample and extraction solution are introduced into the extraction chamber, where they are allowed to sit for 5 min to ensure optimal extraction. **B)** The sample is introduced into the filtration chamber and **C)** pressed, allowing the extracted solution to flow directly onto a filter paper pad that has been preloaded with ammonium molybdate. This pad is positioned on top of the office paper-based electrode for the electrochemical measurements.

3. Results and discussion

3.1. Sensing principle of the integrated paper-based electrochemical sensor

In the present study, a paper-based electrochemical sensor was developed for the analysis of P in Antarctic sediment samples. As illustrated in Fig. 2, the three-electrode system was printed on office paper, using screen-printing technology, and coupled with a filter pad used as a reservoir to store the acidic molybdate solution. The filter pad was mounted on the surface of the sensor at the time of analysis to ensure the uptake of phosphate ions extracted from the sediment samples, thus enabling the formation of the phosphomolybdate complex, also known as the Keggin anion, according to equations (1) and (2) [7,23]. The formation of the electroactive complex and its subsequent oxidation at the surface of the sensor occurred within a few seconds.

$$7H_3PO_4 + 12Mo_7O_{24}^{6-} + 51\ H^+ \rightarrow 7\ PMo_{12}O_{40}^{3-} + 36\ H_2O \quad (1)$$

$$PMo_{12}O_{40}^{3-} + nH^+ + ne^- \rightarrow [H_nPMo_{12}O_{40}]^{3-} \quad (2)$$

As illustrated in Fig. 2, the phosphate necessary for the formation of the Keggin anion was extracted within a 3D printed structure designed to house both the sediment sample and the ammonium fluoride solution.

The operation steps involved in the extraction and the analysis of sediment samples can be summarized as follows.

3.1.1. Sample preparation

1. Collect sediment samples from designated zones.
2. Place the sediment sample into the extraction chamber.

3.1.2. Extraction process

1. Add ammonium fluoride solution to the extraction chamber to initiate phosphate ion extraction.
2. Allow sufficient time for the extraction process to occur (5 min).
3. Once extraction is complete, pour the solution from the cube-shaped extraction chamber to the funnel-shaped outlet to allow the extraction solution containing phosphate ions to flow onto the paper-based detection platform.

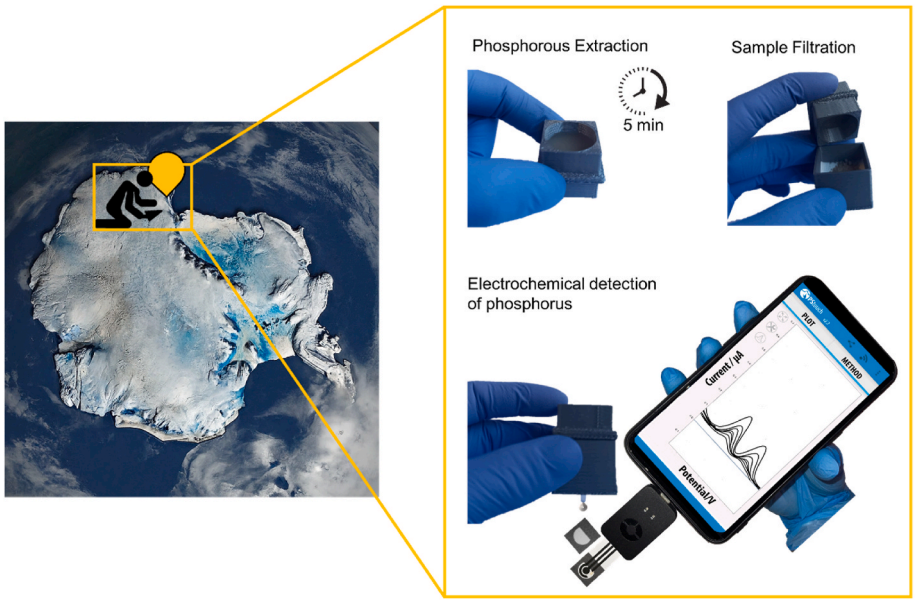

Fig. 2. Illustration of different steps used for the electrochemical detection of phosphorus extracted from Antarctic lacustrine sediments.

3.1.3. *Electrochemical measurement*

1. Ensure that the filter paper pad remains in contact with the sensor surface during this process.
2. Connect the modified paper-based electrode to the potentiostat.
3. Initiate the measurement protocol as per the device specifications.
4. Monitor for oxidation of the phosphomolybdate complex on the working electrode, which indicates phosphate presence.

3.1.4. *Data analysis*

Record electrochemical responses and analyze data against standard phosphate solutions to determine concentration levels in sediment samples. Compare results with established colorimetric methods for

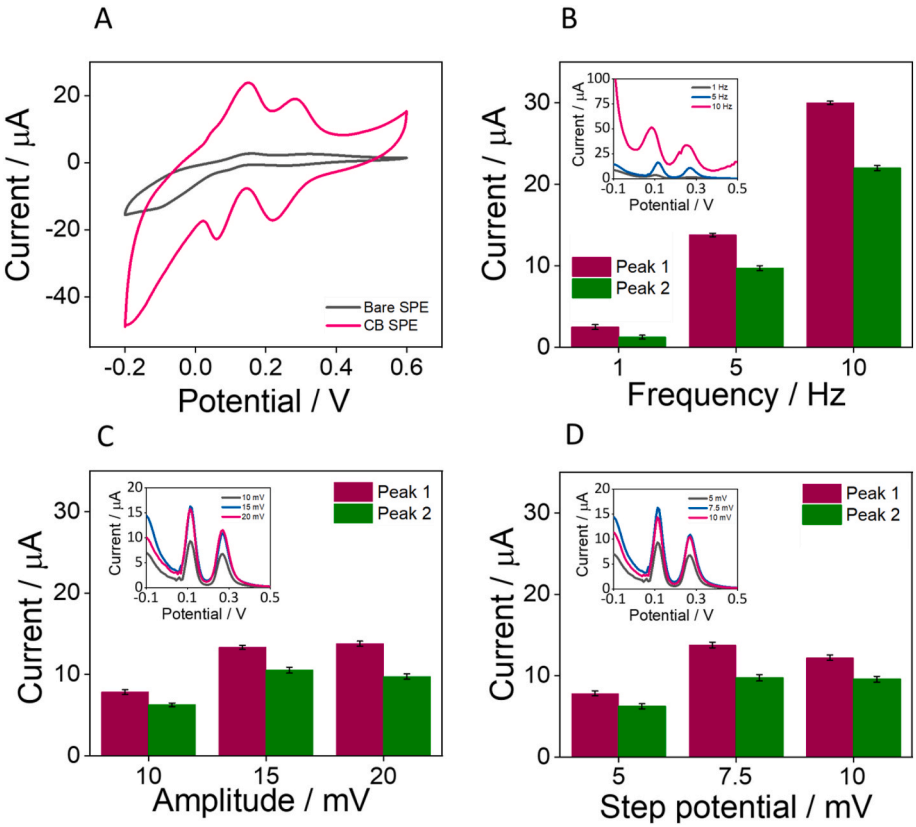

Fig. 3. A) Cyclic voltammograms corresponding to the detection of the phosphomolybdate complex using bare (black) and CB-modified (pink) office paper-based electrodes. Histograms and related voltammograms (insets) regarding the studies of square wave voltammetry parameters, **B)** frequency, **C)** potential amplitude, and **D)** potential step. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

validation.

3.2. Optimization of the electrochemical parameters for the detection of phosphate

In light of the distinctive characteristics and operational capabilities of paper-based sensors, as compared to the conventional screen-printed electrodes manufactured from polyester, a study related to the electrochemical behavior of the office paper-based sensor was carried out. The electrochemical behavior of phosphomolybdate complex was investigated by cyclic voltammetry using unmodified and CB-modified paper-based electrodes in the presence of 10 ppm phosphate solution. As illustrated in Fig. 3A, the introduction of molybdate and phosphate solution to the surface of an unmodified electrode (black voltammogram) resulted in the observation of two insignificant oxidation and reduction peaks associated with the phosphomolybdate complex, characterised by a current intensity below 1.5 μA. However, the modification of the working electrode with 6 μL of CB (pink voltammogram) resulted in the appearance of two well-defined oxidation peaks of phosphomolybdate at 0.14 V and 0.29 V, as well as two reduction peaks at 0.06 V and 0.22 V, emphasizing the importance of the modification of the surface of the sensor with CB. The incredible enhanced sensitivity (>10 fold) observed in the case of the CB-modified electrode, along with the low cost of this nanomaterial, in addition to the availability and affordability of office paper, make this combination a promising avenue for the manufacture of a performant and inexpensive paper-based electrochemical sensor for the analysis of soils and sediments.

To minimise the measurement of background current, which is typically obtained with cyclic voltammetry, and to facilitate rapid analysis, SWV was selected as the method of detection for phosphate anions. Therefore, the SWV parameters were optimized to achieve the highest anodic peak current of the phosphomolybdate complex. The main parameters investigated that directly influence the current intensity are square-wave frequency, square-wave amplitude, and potential step (E_{step}). Fig. 3B shows that an increase in the frequency value from 1 to 10 Hz results in a significant enhancement in the current values of the two anodic peaks observed for the phosphomolybdate complex. However, the voltammogram corresponding to a high frequency (i.e.,10 Hz) exhibits an elevated background current due to insufficient time for the electrical double layer to fully discharge between voltage pulses, thus the frequency of 5 Hz was selected for the rest of the work. Fig. 3C depicts the relationship between the current intensity and the pulse amplitude. The results indicate that the current response increases with increasing square-wave amplitude from 10 mV to 15 mV, reaching its maximum with 20 mV, which was the value selected. Fig. 3D shows the study of the influence of the E_{step} on the oxidation of the phosphomolybdate complex. It is observed that as the E_{step} increases from 5 mV to 7.5 mV, the Ip also increases before starting to decrease with E_{step} beyond 7.5 mV, thus this value was selected. Consequently, the optimized values of the SWV parameters that lead to the enhanced electrochemical response using paper-based electrode modified with CB were the following ones: frequency = 5 Hz, amplitude = 20 mV, and E_{step} = 7.5 mV.

3.3. Optimization of the working solution for the detection of phosphate

The concentration of molybdate is of paramount importance in forming the phosphomolybdate complex. Accordingly, the concentration of the molybdate solution was investigated across a wide range of phosphate concentrations (0.1–100 ppm). Increasing concentrations of phosphate solutions were mixed with varying concentrations of molybdate solutions (0.5, 1, 2 mM), and subsequently added to the surface of the sensor made of office paper. By analysing the current intensities displayed in voltammograms of Fig. 4A, B, and 4C, it appears that concentrations of molybdate solution equal to 0.5, 1- and 2-mM result in the formation of the phosphomolybdate complex across a

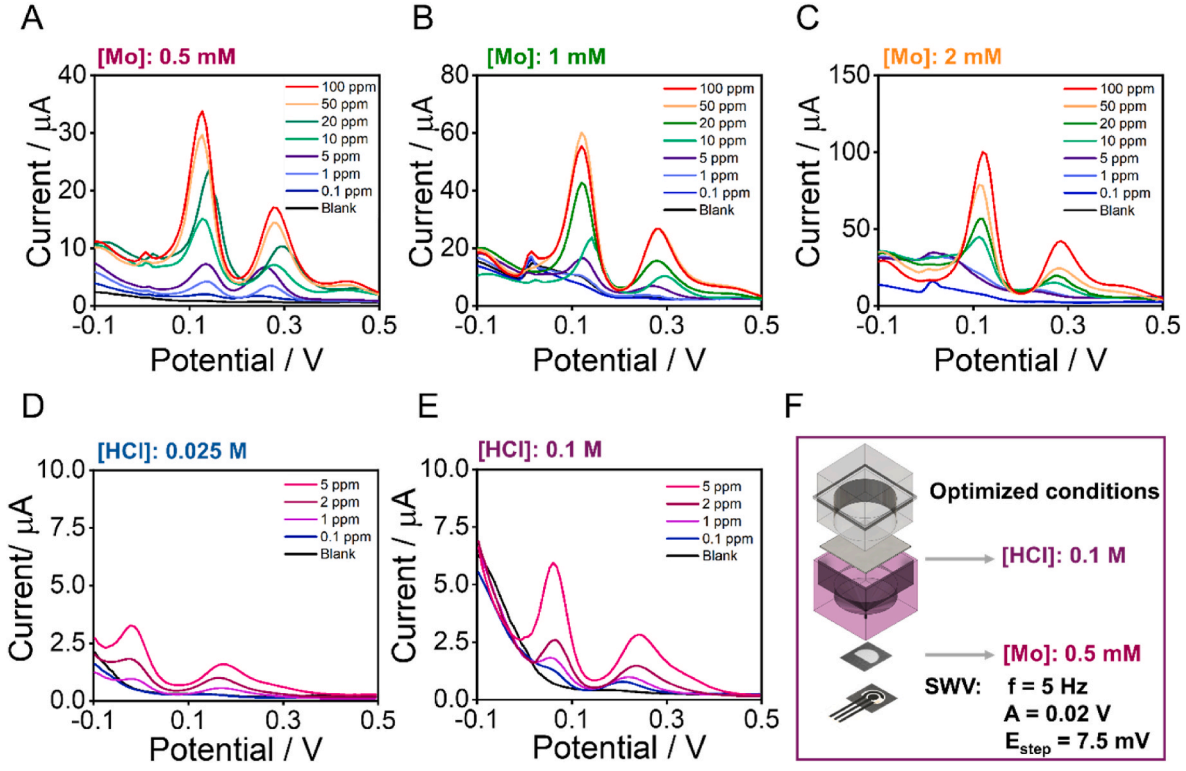

Fig. 4. Voltammograms obtained for the detection of phosphate in the range of 0.1–100 ppm, using molybdate concentrations of 0.5 mM (**A**), 1 mM (**B**), and 2 mM (**C**). Voltammograms obtained for the detection of phosphate in the range of 0.1–5 ppm, using HCl concentrations of 0.025 M (**D**) and 0.1 M (**E**). **F**) Schematic set-up highlighting the optimized working conditions to use for the integrated printed device.

broad range of phosphate concentrations. In addition, a 0.5 mM molybdate solution yielded two well-defined oxidation peaks associated with the phosphomolybdate complex. These peaks exhibited increased intensity with rising analyte concentration from 0.1 ppm, as shown in Fig. 4A. However, the formation of the phosphomolybdate complex was not observed when 1 mM of molybdate solution was used with P concentrations below 1 ppm, as reported in Fig. 4B. Also, the oxidation peaks of the phosphomolybdate complex became larger with low concentrations of phosphate anions (1 ppm), and the current intensity decreased beyond 50 ppm of the analyte. The 2 mM molybdate solution exhibited a more pronounced broadening of the oxidation peaks in the presence of low concentrations of phosphate (≤5 ppm). Conversely, well-defined oxidation peaks were only obtained when a phosphate concentration of at least 10 ppm was used, as shown in Fig. 4C. Accordingly, 0.5 mM was selected as the molybdate solution concentration to conduct the rest of the experiments. This concentration falls within the previously reported concentration range of ammonium molybdate [5–7,23–25], typically between 0.5 and 1.5 mM.

As reported in the previous equations, acidic media is primordial for the formation of the phosphomolybdate complex. Thus, the concentration of HCl, used as the working media, was optimized. Herein, the use of HCl guarantees the acidic conditions necessary for the molybdate to react with phosphate anions, and it's used together with ammonium fluoride to extract P from sediment samples following the Bray I and II methods [35]. It is therefore essential to find a compromise between the concentration of HCl required to ensure the formation of the phosphomolybdate complex as well as the efficient extraction of P from sediment samples. Fig. 4 (D, E) illustrates the current intensities obtained when mixing a molybdate solution with increasing concentrations of phosphate (from 0 to 5 ppm) under two distinct working conditions: 0.025 M HCl and 0.1 M HCl. The former serves as the working electrolyte for the Bray I method, while the latter is used for the Bray II method, both of which are employed for the extraction of phosphate from soil samples.

As indicated in Fig. 4D, the formation of the phosphomolybdate complex was not observed with phosphate concentrations below 1 ppm when 0.025 M HCl was used as the working electrolyte. Moreover, the two oxidation peaks of the phosphomolybdate complex exhibited poor peak definition. Regarding the voltammograms of Fig. 4E, recorded in the case of 0.1 M HCl, the formation of the phosphomolybdate complex was achievable from 0.1 ppm of phosphate. Moreover, the oxidation peaks exhibited a better definition than those obtained with 0.025 M HCl, and the current values were more intense. To guarantee the optimal sensitivity of the sensor, 0.1 M HCl was selected as the optimum working electrolyte, resulting in the formation of a detectable phosphomolybdate complex. Furthermore, the Bray II method was considered the most appropriate, in our study, for the extraction of P from the sediment samples.

3.4. Analytical characterization of the filter pad-integrated paper-based sensor for phosphate detection

This study aims to deliver a reagents-free sensor equipped with chemicals needed for the electrochemical analysis of P in sediments. As depicted in Fig. 4F, the filter pad was preloaded with the optimized concentration of molybdate solution and incorporated into the developed electrochemical sensor. In this configuration, the filter pad fulfills three functions: firstly, it traps the acidic molybdate solution; secondly,

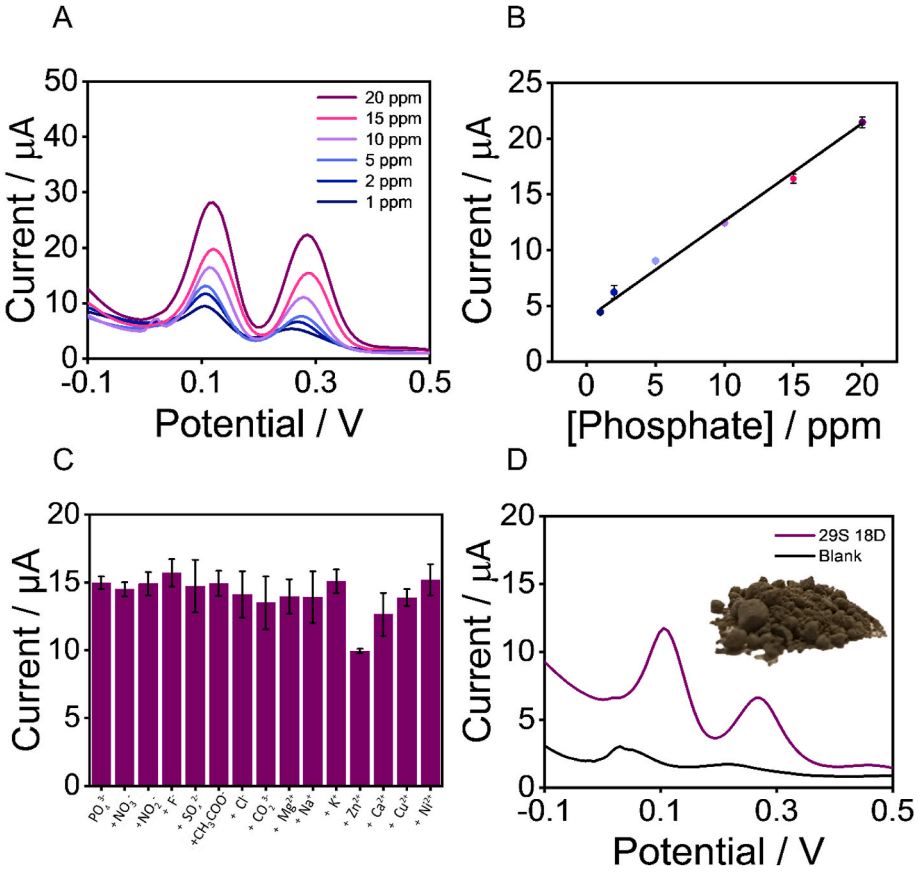

Fig. 5. A) Voltammograms and **B)** the corresponding calibration curve obtained using the paper-based sensor coupled with the filter pad preloaded with acidic molybdate solution; **C)** Histograms obtained for interference measurements carried out using phosphate anions and interfering ions at equimolar concentration; **D)** Voltammograms obtained from the analysis of the sediment sample 29S 18D (purple) compared to the extraction solution (black). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

it is the site for the formation of the phosphomolybdate complex; and thirdly, it ensures the diffusion of the formed electroactive complex towards the paper-based electrode modified with CB. By operating under the optimized working conditions, increasing concentrations of phosphate solution were added to the filter pad preloaded with molybdate solution, and subsequently analysed using SWV. Fig. 5A represents well-defined voltammetric peaks, which exhibit an increase in intensity with rising phosphate concentrations from 0 to 20 ppm. Accordingly, a linear regression between the concentration of phosphate ions and the current intensity was observed, as reported in Fig. 5B. The following equation describes the calibration curve obtained under the optimized conditions: $I/\mu A = (0.881 \pm 0.026)$ ([P/ppm]) + (3.812 ± 0.011), $R^2 = 0.995$. Therefore, the integrated paper-based sensor is capable of detecting phosphate anions in standard solutions with a sensitivity of 0.881 μA ppm, as represented by the slope of the calibration curve. Besides, the limits of detection (LOD) and quantification (LOQ) are equal to 0.011 ppm and 0.033 ppm, respectively. These values were calculated as 3 times, for the LOD, and 10 times, for the LOQ, the standard deviation of the blank divided by the slope of the calibration curve. Hence, the developed paper-based sensor exhibits a wide linear range from 0.039 to 20 ppm.

On the other hand, the precision of the analytical platform was assessed using eight distinct paper-based sensors combined with the filter pad loaded with acidic molybdate solution. Repeated measurements with a 15-ppm phosphate solution yielded a relative standard deviation (RSD) of less than 5 % (4.85 %), thereby demonstrating the high reproducibility of the developed paper-based sensor.

In our previous work, we developed a reagent-free paper-based sensor for the analysis of phosphate ions in water, by printing the electrochemical sensor on a filter paper preloaded with ammonium molybdate solution [8]. By conducting cyclic voltammetry measurement, the sensor demonstrated a detection limit of 4 μM within the linear range up to 300 μM. Its performance was evaluated by analyzing untreated river water samples spiked with 150 μM phosphate, achieving a recovery of 96 ± 10 % across three replicates with no matrix effect. On the other hand, the current study provides further confirmation of the potential of paper substrates, including both filter and office paper, as a platform for developing effective and sustainable electroanalytical platforms for the analysis of phosphate. However, by loading the ammonium molybdate solution onto a filter pad, separately from the sensor, we were able to improve the limit of detection by a factor of about 50 in the present study. This improvement may be attributed to the exclusive interaction of phosphate ions with ammonium molybdate to form the phosphomolybdate complex before reaching the working electrode, which was printed on another layer of paper (i.e., office paper) and then modified with CB nanomaterial.

3.5. Interference studies

The primary issue in determining phosphate using ammonium molybdate is the interference of silicate, which can form the silicomolybdate complex. As reported in the literature [6], the ratio of protons over molybdates close to 70 at pH 1 allows for the rapid reaction rate of the formation of a stable phosphomolybdate complex $[PMo_{12}O_{40}]^{3-}$ compared to the silicomolybdate complex $[SiMo_{12}O_{40}]^{4-}$. In our previous work [7], we used 0.1 M H_2SO_4 and 1 mM molybdate as working conditions, without observing any significative silicate interference during silicate addition. Considering the same ratio used $[H^+]/[Mo]$ in this work, the selected working conditions avoid silicate interference, harnessing the different rates of formation of phosphomolybdate complex and silicomolybdate complex in the selected working condition. The selectivity of the integrated sensor towards phosphate ions was then investigated through the analysis of a wide range of anions (NO_3^-, NO_2^-, F^-, SO_4^{2-}, CH_3COO^-, Cl^-, CO_2^{3-}) and cations (Mg^{2+}, Na^+, K^+, Zn^{2+}, Ca^{2+}, Cu^{2+}, Ni^{2+}) that may co-exist in the same sediment. The ions under examination were mixed with phosphate ions in an equimolar ratio of 15 ppm and subsequently added to the filter pad preloaded with molybdate solution. As illustrated in Fig. 5C, the sensor's response to phosphate anions (PO_4^{3-}) was not affected by the addition of different ions, except zinc cations (Zn^{2+}), which exhibited a slight reduction in current intensity. Nevertheless, it is unlikely that Zn^{2+} cations will interfere with the analysis of P in sediments since the concentration of this micronutrient is significantly lower than that of P. Indeed, in previous studies conducted to determine the total metal concentrations in lacustrine sediments from Terra Nova Bay, it was found that the concentration of Zn^{2+} is comprised between 8.75 and 110 mg/kg, while the concentration of P in the same sediments ranged from 976 to 2022 mg/kg [37].

3.6. Analysis of sediment samples

The applicability of the developed sensor was demonstrated in the determination of P levels in sediment samples through comparison with the established colorimetric method.

The electrochemical analysis of sediment samples (for example, 29S 18D collected from Inexpressible Island n. 10b, and reported in Fig. 5D) yielded a defined voltammogram whose intensity was employed to quantify the concentration of P in the same sample. By employing the equation of the calibration curve plotted in Fig. 5B, the concentration of P (in mg/L) was calculated for each sample. This concentration was then converted to mg/kg of sediment, taking into account the quantity of sediment and the volume of ammonium fluoride solution used during the extraction. The corresponding results are expressed as the mean value ± standard deviation and reported in Table 1 together with those obtained with the colorimetric method. Each sediment sample is identified by a code, accompanied by details of the sampling conditions.

The comparison of the results obtained from both methods reveals that, in some samples, the concentrations of P calculated using the standard method exceed those of the developed sensor. This difference is attributed to the longer extraction time required by the colorimetric method (20 min) as opposed to the electrochemical sensor's (5 min), which resulted in the extraction of more phosphate ions. Interestingly, a very strong positive correlation between the two approaches was identified, characterised by a coefficient of correlation equal to 0.86 ($r = 0.86$), indicating that the developed paper-based electrochemical sensor modified with CB combined with the 3D printed extracting system holds significant potential for use in the detection of P in sediment samples from Antarctica.

A detailed examination of the data presented in Table 1 reveals a notable increase in P concentrations within the sediment samples collected at Lake 15A (Edmondson Point) between 1993 and 2012, except for sample 6S 8B, collected in 1990. The increase in P concentration was found to be more pronounced in the case of the sediment sample 29S 8C1 collected from Lake 14. This increasing trend is corroborated by both the electrochemical and the colorimetric methods. The observed increase in P concentrations at Edmondson Point can be attributed to the high level of terrestrial vegetation diversity, including moss and epilithic lichen communities, as well as a diverse range of freshwater habitats that support microalgae, cyanobacteria proliferation [38].

Furthermore, Lake 14 exhibits distinctive geographical characteristics when compared to Lake 15A. These include a higher altitude (22 m above sea level), in contrast to 3 m above sea level for Lake 15A [39], which contributes to its richness in nutrients of avian origin, namely guano, which is a nitrogen and phosphate-rich mass of seabird excrement. This may explain the variation in P concentrations between the two lakes at Edmondson Point.

On the other hand, sample 29S 8C1 collected from Lake 14 at Edmondson Point (22 m above sea level), and sample 29S 18D collected from Lake 10b at Inexpressible Island (32 m above sea level [39]), showed important differences in P concentrations even if they were collected on the same period of the year (January 2014). This

Table 1
Determination of phosphorus in sediment samples using colorimetry and the developed paper-based electrochemical sensor.

Sediment sample	Sampling date	Sampling Lake	[P]/mg. Kg^{-1} of sediment (Spectrophotometric analysis)	[P]/mg. Kg^{-1} of sediment (Electrochemical analysis)
6S 8B	25-12-1990	Edmonson Point n.15A	75.15 ± 13.84	88.80 ± 8.21
9S 8B1	24-12-1993	Edmonson Point n.15A	48.28 ± 1.68	26.98 ± 10.75
11S 8B1	19-01-1996	Edmonson Point n.15A	56.29 ± 1.09	49.99 ± 5.47
25S 8B	14-12-2009	Edmonson Point n.15A	61.74 ± 8.47	75.34 ± 5.59
8B A2A	07-01-2012	Edmonson Point n.15A	106.69 ± 13.99	90.94 ± 12.92
8B A3U3	14-01-2012	Edmonson Point n.15A	123.60 ± 4.14	105.58 ± 10.48
29S 8C1	11-01-2014	Edmonson Point n.14	174.03 ± 13.75	116.96 ± 11.19
21S 18D	22-01-2006	Inexpressible Island n. 10b	103.88 ± 4.70	111.07 ± 12.07
29S 18D	05-01-2014	Inexpressible Island n. 10b	42.51 ± 1.94	30.36 ± 8.44

phenomenon can be explained by the geomorphological conditions of each lake. These include the total surface area, distance from the sea, and the mineralogical characteristics of the soils surrounding the lake. Furthermore, Inexpressible Island is subjected to greater exposure to katabatic winds than Edmondson Point, which renders it less favourable for the survival of life forms.

Additionally, the difference in P concentration observed between the samples 21S 18D and 29S 18D, both collected from Lake 10b at Inexpressible Island, is likely attributable to disparate sampling dates. This is because the sedimentation process occurring over eight years (from January 2006 to January 2014) has the potential to alter the composition of the sediments significantly. It can therefore be surmised that the observed decline in P concentration is attributable to the heterogeneity among the samples. Furthermore, the sediments of Lake 10b at Inexpressible Island, also referred to as Penguin Lagoon, are significantly influenced by penguin guano input, which in turn is influenced by the continued global warming [40].

In summary, the observed variability within the sediment samples is primarily a consequence of geographical and meteorological factors characterising each lake, such as distance from the sea and altitude. Additionally, P levels are primarily regulated by biological processes, which may vary from year to year as a function of temperature and subsequent vegetation growth. Nevertheless, further research is required to gain a comprehensive understanding of the sediments and to ascertain the extent to which environmental factors influence the concentration of P.

It is worth noting that the good correlation with the colorimetric laboratory setup method demonstrates that our printed sensing device displayed considerable promise for use in the analysis of sediment samples. Furthermore, the selection of different parts of the sensor made of paper allows for a sustainable, reagent-less, low-cost, and portable analytical device. Indeed, the sensor, comprising working, counter, and reference electrodes, was produced using a printing process on office paper, which is readily available, affordable, and flexible. The sensor was supplied with a further filter pad containing an acidic molybdate solution. The functions fulfilled by this additional pad were dual-fold: firstly, the formation of the electroactive phosphomolybdate complex, and secondly, its diffusion towards the surface of the paper-based electrode modified with CB, where it undergoes oxidation.

Additionally, the extraction of P from sediment samples was conducted using a miniaturised and portable 3D printed cartridge. It was used as a reservoir to incubate a few milligrams of sediment samples with a Bray-II solution, which consisted of ammonium fluoride and hydrochloric acid. As summarized in Table 2, the developed printed sensing tool demonstrated remarkable analytical capabilities in analysing phosphate ions in sediment samples. The use of CB as a nano-modifier boosted the sensitivity of the office paper-based printed electrode. Furthermore, the Bray-II method reduced the extraction time to approximately 5 min while requiring fewer reagents than other extraction methods, offering a significant practical advantage to the

Table 2
A comparative analysis of reported electrochemical sensors developed for the determination of phosphorus in soil and sediment samples.

Sensor type	Sensor modification/pre-treatment	LOD	Analytical method	Interfering ions studied	P extraction system	Extracting reagents	Extraction time	Sensor application	Ref
Pencil graphite electrode	MoP	1.25×10^{-6} M (0.17 mg L^{-1})	DPV	–	Sonication Filtration	0.001 M H_2SO_4	>30 min	Soil samples	[22]
Carbon-SPE	ZrO_2/ZnO/MWCNTs	2×10^{-8} M (2.72×10^{-3} mg L^{-1})	CV	NO_3^-, SO_4^{2-}, HCO_3^-, Cl^-	Centrifuga-tion Filtration	0.5 M CH_3COOH, 0.025 KHP	>1h	Farmlands soil samples	[23]
Carbon-SPE	–	0.18 mg L^{-1}	CV	NO_3^-, SO_4^{2-}, CO_3^{2-}, Cl^-	Olsen method	0.5 M $NaHCO_3$	30 min	Agricu-ltural soil samples	[24]
Carbon-SPE	Polished with office paper	0.10 mg L^{-1}	CV	–	Olsen method	0.5 M $NaHCO_3$	30 min	Soil samples	[25]
Carbon-SPE	Polished with office paper	0.11 mg L^{-1}	CV	SiO_4^{4-}	Mehlich-3 reagents were loaded on a filter pad that was incubated, in a solution, with soil and water	0.015 M NH_4F, 0.013 M HNO_3, 0.001 M EDTA, 0.25 M NH_4NO_3 0.3 M CH_3COOH	2 min	Soil samples	[26]
Office paper-SPE	CB	0.011 mg L^{-1}	SWV	NO_3^-, NO_2^-, F^-, SO_4^{2-}, CH_3COO^-, Cl^-, CO_3^{2-}, Mg^{2+}, Na^+, K^+, Zn^{2+}, Ca^{2+}, Cu^{2+}, Ni^{2+}	Bray-II method inside a homemade 3D printed design	0.03 M NH_4F, 0.1 M HCl	~5 min	Sediment samples	Our work

SPE: screen-printed electrode; ZrO_2: zirconium dioxide; ZnO: zinc oxide; MWCNTs: multi-walled carbon nanotubes; DPV: differential pulse voltammetry; CV: cyclic voltammetry; SWV: square wave voltammetry; MoP: molybdenum phosphate; CB: carbon black.

operator. The aforementioned characteristics provide a rationale for utilising the sensor in real-life applications to determine P levels in sedimentary samples collected from diverse geographical locations within the Antarctic region.

4. Conclusion

This work presents the development of a paper-based integrated electrochemical sensor combined with a 3D printed scaffold to analyze phosphorus in sediment samples. This innovative sensing platform is entirely composed of paper, specifically office paper for the printing of the electrochemical sensor and filter paper for the preparation of the molybdate pad. The filter pad was placed on the surface of the sensor at the analysis stage, offering an all-in-one configuration.

When operated under the optimized settings, the integrated sensor demonstrated excellent analytical performance in terms of sensitivity and reproducibility. Furthermore, an impressively selective response towards phosphate anions was observed among the fourteen interfering ions tested.

Moreover, the manufacture of a miniaturised 3D printed holder for the extraction of phosphorus from sediment samples has resulted in a more convenient and time-efficient process, necessitating only a minimal quantity of sediment (in the range of a few mg) and a reduced volume of extracting solution.

By determining the phosphorus levels in Antarctic sediments, we have further emphasised the extensive applicability of paper-based electrochemical sensors in the environmental field, extending beyond the conventional applications of water and soil analysis. Furthermore, the analysis of this macronutrient in Antarctic sedimentary deposits can provide invaluable insights into phosphorus biogeochemical cycling without much anthropogenic disturbance.

CRediT authorship contribution statement

Narjiss Seddaoui: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Chiara Di Gregorio:** Formal analysis. **Ludovica Gullo:** Writing – review & editing, Methodology. **Elena Argiriadis:** Writing – review & editing. **Fabiana Arduini:** Writing – review & editing, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the project “BioCyCLeS” (PNRA18_00184) funded by the Italian National Antarctic Research Program (PNRA 2018) and National Operational Program on Research and Innovation 2014-2020 (PON). The authors have obtained permission for the use of Antarctic Lake sediment samples for research purposes from the Italian National Antarctic Museum (MNA) and from the Bank of Antarctic Environmental Samples (BCAA) of Genoa.

Data availability

The data that has been used is confidential.

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