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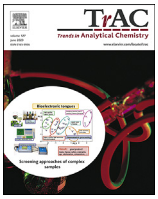

Recent advances in the determination of phosphate in environmental water samples: Insights from practical perspectives

Xiangyu Zhu, Jian Ma*

State Key Laboratory of Marine Environmental Science, Fujian Provincial Key Laboratory for Coastal Ecology and Environmental Studies, Dongshan Swire Marine Station, College of the Environment and Ecology, Xiamen University, Xiamen, 361102, People's Republic of China

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ABSTRACT

Phosphate plays a crucial role in driving biogeochemical cycles and directly affects environmental quality. Therefore, accurate, practical, and versatile methods for phosphate determination are important for both environmental researchers and analytical chemists. In this review, we address the recent trends in phosphate determination in environmental water samples, based on literature published from 2016 to the beginning of 2020. Developments in both methodologies (e.g., phosphomolybdenum blue spectrophotometry, fluorescence sensing, UV–Vis spectroscopy, chromatography and mass spectrometry) and analytical platforms (e.g., diffusive gradients in thin films, microfluidics, and flow analyzers) are critically reviewed. Issues of quality assurance and quality control are highlighted. The merits and limitations of different methods are evaluated according to their analytical performance and suitable application conditions, with a focus on their practical utility in environmental analysis. Recommendations for future research and development are also discussed.

1. Introduction

Phosphorus (P) is an essential element for all forms of lives, and the phosphorus cycle is one of the most important biogeochemical processes, affecting all ecosystems [1,2]. With rapid industrial development and rising global populations, humans have exerted a profound influence on the global P cycle, characterized by greatly enhanced P mobility [3,4]. Large amounts of P are released during anthropogenic processes such as phosphate rock mining, fertilizer application, livestock and food production, human consumption and the generation of excreta [4–8]. As global P consumption is projected to grow continuously in the 21st century [9], a recent study has estimated that the rate of P loss from cropland to freshwater (10.4 ± 5.7 Tg P yr^{-1}) outpaced loss from natural erosion (7.6 ± 3.3 Tg P yr^{-1}) [4]. Released P can accumulate in soils and sediments, causing P surplus and internal pollution issues, while excessive P can also remain in surface waters, resulting in eutrophication and the impairment of water quality [5]. In the marine environment, however, P is one of the limiting nutrients that drive biogeochemical processes [10]. P undergoes various interactions with nitrogen and carbon, as well as silicon and iron, influencing the production and distribution of phytoplankton and affecting primary production [11]. Dissolved inorganic P can be present at the nanomolar level in oligotrophic regions (<300 nM), presenting a challenge for accurate quantification [10]. An improved understanding of the P cycle and integrated P management is therefore critical for the effective development of anthropogenic activities and the sustainability of ecosystems [12]. This places a high demand on the effective environmental monitoring of P under various conditions.

Historically, P in its fully oxidized form, which is mainly phosphate in aqueous solution, has been a main research focus, with the role of phosphate in the biogeochemical cycle being the most comprehensively understood. Strictly speaking, phosphates are classified as being orthophosphates ($H_xPO_4^{(3-x)-}$), condensed phosphates (pyro-, meta- and other polyphosphates), and organic (or organically bound) phosphates [13]. They can occur in dissolved, particulate, and biological (within organisms) forms. In water quality analysis, however, phosphates are commonly referred to orthophosphates. Different categories of phosphates exhibit different levels of bioavailability, while no species or fraction is completely equal to bioavailable phosphorus [14]. It has been established that orthophosphate is the preferred substrate for most microorganisms in the marine environment, with other species

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* Corresponding author.
E-mail address: jma@xmu.edu.cn (J. Ma).

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also providing potential bioavailable pools [2]. From the perspective of P management, species in the form of condensed and organic phosphates are generally considered "non-reactive", although they comprise a substantial portion of total P. "Non-reactive" P have to be converted to the "reactive" form such as orthophosphates, so as to be removed to mitigate water pollution and recovered to recapture lost P [15,16]. For analysis, it is a common practice to transform other P fractions to orthophosphates prior to quantification [17]. Therefore, there is ongoing interest for both environmental researchers and analytical chemists to develop reliable, robust, and versatile phosphate determination methods, which are of crucial importance for environmental observation, quantification, modelling, and management [7].

A wide range of analytical methods has been used to determine phosphate in aquatic samples. Phosphomolybdenum blue (PMB)-based spectrophotometry is applied as the standard method worldwide [13,18], while fluorescent and electrochemical (bio) sensors are gaining attention due to their versatility. Major instrumental analysis techniques, including chromatography and mass spectrometry, have been recognized as powerful tools for the analysis of complex samples. However, from the perspective of environmental analysis, there are still numerous problems with the use of currently available methods, such as inaccuracy for trace determination, impaired analytical performance under harsh environmental conditions, and the instability of *in situ* analytical techniques with long-term application, resulting in an urgent need for the limitations of current methods to be overcome. During the past 50 years, many published reviews have addressed phosphate determination in water samples, as summarized in Table 1. These reviews have encompassed diverse aspects of the analytical chemistry of phosphate, including sampling, speciation and fractionation, covering specific categories of quantification techniques, which have greatly enhanced our understanding of phosphate analysis. In addition, there have been some useful reviews that incorporate phosphate determination in water as a sub-topic [19–22]. The full list of relevant reviews is provided in Table S1 in Supplementary Materials. Some valuable handbooks and book chapter references are also available [13,18,23]. In 2016, Worsfold et al. presented a historical and comprehensive overview of the development of phosphorus determination [17]. Recently, Chen et al. [24] discussed the detection of total phosphorus in water using photoelectric strategies, spectroscopy techniques, and modelling algorithms. Kalkhajeh et al. [25] published a review focusing on sampling techniques for different aquatic phosphorus sample matrices. Pal et al. [26] summarized synthetic receptors for the recognition, sensing, and extraction of phosphates. However, various new and exciting publications have emerged, contributing to the active research field of phosphate determination, which have not been covered in the previously published reviews. From 2000 to 2019, an annual average of 23 ± 7 articles regarding phosphate determination in water were published (Fig. S1 in Supplementary Materials), demonstrating the significance and popularity of this topic. Therefore, a timely synthesis of the latest knowledge and the identification of research trends are highly beneficial for future method development and practical application.

Herein, this review assesses advances in the determination of phosphate in environmental water samples that have been made from 2016 to the beginning of 2020. Targeted environmentally relevant phosphate concentrations span from nanomolar to several micromolar, although higher concentrations may be encountered in more polluted environments (such as wastewater). In the first section, the interfaces between the classical PMB method and various analytical platforms for extraction, automation, miniaturization and other functions, are addressed. The development of diffusive gradients in thin films (DGT) is then discussed, which has emerged as an important sampling technique in phosphate determination. Fluorescence (phosphorescence) sensing and other non-PMB spectroscopy-related methods, chromatography and mass spectrometry are also summarized and critically reviewed. The issues of quality assurance and quality control are highlighted, which are crucial for obtaining reliable and accurate data. Finally, future research directions are commented on. The present review deliberately excludes electrochemical methods, as these have recently been summarized and discussed by Forano et al. [27], as well as in several previous reviews [22,28–30]. In this review, methods are evaluated according to their working principles, analytical performance, practical utility, and suitable application conditions and scenarios in environmental water analysis. Ultimately, an improved understanding of phosphorus chemistry will be assisted by overcoming the limitations of current analytical methods.

2. Phosphomolybdenum blue-based methods

Spectrophotometry is undeniably the most widely used method for the determination of phosphate. Although in recent years nanomaterial-based colorimetric sensors [56–58] have attracted increasing research interest, PMB methods are still the most commonly applied. The chemical process first involves the reaction of orthophosphate with acidic molybdate, to produce 12-molybdophosphosphoric acid, which is subsequently reduced to PMB, as shown in Equations (1) and (2) [53]. For more information about the fundamental chemical aspects of this method, a recent comprehensive review of the PMB reaction is available [53].

$$\mathrm{PO_4^{3-}+12MoO_4^{2-}+27H^+\rightarrow H_3PO_4(MoO_3)_{12}+12H_2O} \tag{1}$$

$$\mathrm{H_3PO_4(MoO_3)_{12}+Reductant\rightarrow [H_4PMo(VI)_8Mo(V)_4O_{40}]^{3-}} \tag{2}$$

It is important to differentiate some of the specialist terms commonly used in the literature. Phosphorous fractions that readily react with acidic molybdate, without preliminary hydrolysis or digestion, are termed molybdate reactive phosphorus (MRP). For pre-filtered samples (typically passed through 0.45 μm filters), the fractions are operationally defined as dissolved reactive phosphorus (DRP) or soluble reactive phosphorus (SRP) [14,17]. It has been well established that DRP or SRP mainly include orthophosphates, although they also contain a small fraction of hydrolyzed condensed inorganic and labile organic P compounds, along with some colloidal fractions in the filtrate [14]. The term filterable reactive phosphorus (FRP) is also used, although the filter pore size should always be referenced. By comparison, dissolved inorganic phosphorous (DIP) is functionally defined as dissolved orthophosphates and condensed phosphates [14,17]. In this review, we use the term phosphate to represent DRP, SRP, FRP, and DIP, to eliminate the confusion.

Despite the popularity of the PMB method, it has been recognized that it suffers from relatively poor sensitivity and high levels of interference from species such as arsenate, silicate, and P-containing compounds. To overcome these limitations, great efforts have been made to improve and modify the PMB method, mainly from three aspects:

- **Addressing the problem of trace phosphate determination, particularly in seawater matrices.** Determination of nanomolar levels of nutrients in seawater has been reviewed [59,60]. This review focusses on recent advances in long pathlength absorbance spectrophotometry and extraction-based methods.
- **Delivering long-term *in situ* phosphate monitoring.** Field-deployable microfluidic devices show enormous potential in this regard, which will be discussed in detail.

Table 1
Chronological list of reviews pertinent to analysis of phosphate in water samples (1969-beginning of 2020).

Year	Title	No. of references	Notes	Ref.
1973	Problems in the analysis of phosphorus compounds	77	Early review that primarily summarized the critical problems faced in PMB method for analysis of natural waters, including P fractions, conditions of the chemical reaction, intercomparison of methods, automation, sampling and sample storage.	[31]
1988	Analytical determination of orthophosphate in water	88	Summary of analysis methods for orthophosphate in water mainly during 1970s–80s. PMB method, enzymatic methods, and other available techniques were reviewed.	[32]
1988	Particulate and dissolved phosphorus forms in freshwater: composition and analysis	162	Detailed review on fractionation, characterization, and analysis of particulate and dissolved phosphorus in freshwater.	[33]
1988	Bioavailability of different phosphorus forms in freshwater systems	77	Methods for analysis of particulate and dissolved bioavailable phosphorus in water were reviewed. Factors influencing phosphorus bioavailability were discussed.	[34]
1995	Techniques for the quantification and speciation of phosphorus in natural waters	102	Comprehensive review of determination methods of phosphorus in natural waters, with emphasis on PMB method. Preconcentration, *in situ* measurement, speciation techniques were included.	[35]
1998	The phosphate sensor	72	Review of ion selective electrodes and biosensors for direct determination of orthophosphate in both environmental and biological samples (1986 to mid-1997).	[36]
1998	Procedures for the storage and digestion of natural waters for the determination of filterable reactive phosphorus, total filterable phosphorus and total phosphorus	150	First systematic and comprehensive review of sample storage and digestion techniques of P in natural waters.	[37]
1999	Capillary electrophoresis of phosphorus oxo anions	104	Brief description of basic chemistry of phosphorus anions. Review of capillary electrophoresis (CE) for analysis of phosphates, phosphites, and their oligomers in various matrices including environmental waters.	[38]
1999	Separation of inorganic phosphorus-containing anions by capillary electrophoresis	69	Review of capillary isotachophoresis, capillary zone electrophoresis, and capillary gel electrophoresis for separation of inorganic phosphorus-containing anions in environmental waters and other matrices.	[39]
2002	Review of robust measurement of phosphorus in river water: sampling, storage, fractionation and sensitivity	96	P fractions and species, analytical methods (PMB), sampling and storage of river water samples were reviewed. Guidelines and protocols for different situations were recommended.	[14]
2005	Sampling, sample treatment and quality assurance issues for the determination of phosphorus species in natural waters and soils	172	Sampling, sample storage, digestion techniques in natural water and soil samples were reviewed, mainly from the perspective of PMB method. Quality assurance and quality control were highlighted.	[40]
2005	Flow analysis techniques for phosphorus: an overview	190	Brief description of P chemistry and flow analysis. Review of flow analysis techniques for P analysis in various matrices including environmental waters from the aspects of flow modes, detection methods, and analytical characteristics.	[41]
2005	Trace and ultratrace analysis methods for the determination of phosphorus by flow-injection techniques	86	Review of flow injection techniques for trace and ultratrace analysis of phosphorus in water samples, most of which were based on PMB reactions, fluorometry, and chemiluminescence.	[42]
2005	An overview on flow methods for the chemiluminescence determination of phosphorus	44	Brief description of chemiluminescence principles. Review of flow-based chemiluminescence methods for analysis of phosphate in water samples from the aspects of flow modes, reactions (chemical derivatization and enzymatic derivatization), and analytical characteristics.	[43]
2005	Mass spectrometry of natural organic phosphorus	36	Review of different ionization techniques and detectors for quantitative and qualitative mass spectrometry analysis of natural organic phosphorus. A study by the authors on organic phosphorus speciation in an oligotrophic wetland was also summarized.	[44]
2005	Characterizing phosphorus in environmental and agricultural samples by ^{31}P nuclear magnetic resonance spectroscopy	146	Requirements for successful phosphorus nuclear magnetic resonance spectroscopy (^{31}P NMR) were summarized. Studies on environmental samples by ^{31}P NMR were reviewed.	[45]
2005	Ion chromatographic separations of phosphorus species: a review	131	Advances of sample treatment, chromatographic systems, and applications of ion chromatography in separation of phosphorus species in water samples were reviewed (1997–2004).	[46]
2005	Determination of small phosphorus-containing compounds by capillary electrophoresis	89	Review of CE with different detection modes for analysis of phosphates and organophosphate in environmental samples including water.	[47]
2005	Phospholipids in marine environments: a review	165	Review of extraction, separation, and determination of phospholipids in marine environments. Environmental significance, presence, and dynamics of phospholipids in marine environments were discussed.	[48]
2005	Reduced inorganic phosphorus in the natural environment: significance, speciation and determination	102	Significance of reduced phosphorus in the natural environment, its speciation and determination methods were reviewed.	[49]
2005	Inductively coupled plasma mass spectrometry in separation techniques: Recent trends in phosphorus speciation	71	Inductively coupled plasma mass spectrometry (ICP-MS) coupled with high performance liquid chromatography, CE, and gel electrophoresis in speciation analysis briefly discussed. Applications (1999–2005) in phosphorus speciation in biological and environmental field were reviewed.	[50]

(*continued on next page*)

Table 1 (*continued*)

Year	Title	No. of references	Notes	Ref.
2009	Bioelectroanalytical determination of phosphate: A review	86	Brief introduction of potentiometric and voltammetric methods and highlight of biosensor methods (especially enzyme-based) for environmental analysis. Methods with potential features for environmental analysis were also included.	[28]
2012	Determination of inorganic phosphate by electroanalytical methods: A review	141	Review on electroanalytical methods of inorganic phosphate determination for both environmental and biological samples. Mechanisms, advantages, and disadvantages of potentiometric, voltammetric, amperometric, bioelectroanalytical, and other methods were discussed.	[29]
2013	Sensing and analysis of soluble phosphates in environmental samples: A review	78	Review of molecularly imprinted polymers, colorimetric and fluorescence synthetic receptors, and electrochemical sensors for analysis of environmental water samples.	[30]
2013	Progress and recent advances in phosphate sensors: A review	319	Review of phosphate biosensors, optical methods, and other electrochemical sensors for both environmental and biological samples (1970–2012).	[51]
2014	Recent advances in $H_2PO_4^-$ fluorescent sensors	78	Review of $H_2PO_4^-$ fluorescent sensors for life science purposes, based on synthetic organic molecules categorized by "turn-on", "turn-off", and ratiometric behavior.	[52]
2015	The molybdenum blue reaction for the determination of orthophosphate revisited: Opening the black box	205	Comprehensive review of the mechanisms and applications of the PMB reaction.	[53]
2015	A review on useful concepts for stable isotope of oxygen in phosphate ($\delta^{18}O_p$) extraction, purification and analysis of freshwater samples and other potential phosphate sources	33	Review on extraction of dissolved inorganic phosphate for stable isotope oxygen ($\delta^{18}O_p$) analysis in freshwater samples.	[54]
2015	Recent advances in phosphate biosensors	64	Summary and discussion of biosensors for estimation of phosphate in biological and environmental samples, categorized by the number of enzymes used in the biosensors.	[55]
2016	Determination of phosphorus in natural waters: A historical review	158	Comprehensive review of phosphorus determination in natural waters from a historical point of view.	[17]
2018	Recent trends in electrochemical detection of phosphate in actual waters	44	Publications on potentiometric and amperometric (bio)sensors for phosphate in water samples were reviewed (2015–2018), categorized by electrode materials.	[27]
2019	Methods for sample collection, storage, and analysis of freshwater phosphorus	171	Summary of sampling techniques for different aquatic samples. Sample treatment and storage, common methods used to determine phosphorus fractions were also briefly reviewed.	[25]
2019	Detection of phosphorus species in water: technology and strategies	128	Review of photoelectric strategies, spectroscopy techniques, and modelling algorithms for detection of total phosphorus in water.	[24]
2020	Recent advances in recognition, sensing and extraction of phosphates: 2015 onwards	201	Summary of synthetic receptors for the recognition, sensing, and extraction of phosphates with a focus on biological applications.	[26]

- **Using automated flow systems to support versatile features of operation and a wider range of applications.** Flow analysis techniques are generally combined with PMB-based methods. Some characteristic analytical systems are discussed, to demonstrate the broad range of features of these methods.

2.1. Long pathlength absorbance spectrophotometry

Long pathlength absorbance spectrophotometry based on the Beer–Lambert law, is considered an environmentally-friendly chemical method for trace analysis, due to the reduction in pretreatment procedure requirements, which commonly involve toxic organic solvents [61]. The liquid waveguide capillary cell (LWCC) has been recognized as a powerful tool to perform nanomolar phosphate determination in water samples, due to its high sensitivity (detection limits of ~1 nM) and ease of automation [62–64]. Connecting LWCC to flow systems also allows for the measurement of phosphate in other matrices, such as ice cores [65] and atmospheric particles [66]. However, the benefits of LWCC come with amplified blanks and interference, as well as an increased risk of contamination during reagent and sample handling. These issues should be given careful consideration, as they may introduce large uncertainty to the analytical results, particularly at nanomolar concentration levels. Troubles from bubbles and coating of PMB on the cell core also frequently arise, which requires careful maintenance of LWCC.

Ehama et al. [67] established the first LWCC-based method for the determination of particulate phosphorus fractions in oligotrophic seawater with a detection limit of 3 nM. Total particulate phosphorus (TPP) was measured after potassium persulfate oxidation, while the particulate inorganic phosphorus (PIP) fraction was determined via HCl extraction followed by neutralization with a NaOH solution. This method substantially lowered the water sample filtration volumes to a minimum of 15 mL and 52 mL for TPP and PIP, respectively, with determined concentrations in seawater samples from the eastern South Pacific being 8.4 nM and 1.3 nM, respectively [67]. The system was further modified by installing a long Teflon tube submerged in a water bath to measure arsenate, particulate arsenic, phosphate and particulate P in seawater [68]. However, the acid-extraction method may overestimate PIP, since labile organic P may also be hydrolyzed, while polyphosphate may be underestimated due to incomplete hydrolysis [69]. Therefore, it is recommended to explicitly describe the analytical protocols used to determine P fractions for accurate interpretation and comparison of data. Furthermore, for best practice in LWCC analysis, the authors carefully examined the procedural blanks and reagent blanks, and eliminated baseline shift by adding acetone and sodium dodecyl sulfate (SDS) solution to ascorbic acid [67].

2.2. Extraction-based methods

Extraction is the most straightforward and commonly used strategy to preconcentrate analytes or their derivatives. Many extraction methodologies have been applied to phosphate preconcentration [70,71], although a large proportion of them exhibit limited potential for routine analysis, mainly due to the requirements of lab-synthesized extraction media, time-consuming procedures, and unsatisfactory levels of recovery and reproducibility. To date, the most commonly practiced methods are magnesium-induced coprecipitation (MAGIC) [72] and solid phase extraction (SPE). The detection limit of MAGIC can reach a very low level of 0.15 nM [73]; however, the method is majorly limited by labor-intensive procedures and low throughput, with few improvements or modifications made to the method thus far. Although using a combination of Mg^{2+} and Al^{3+} instead of Mg^{2+} alone to coprecipitate phosphate in alkaline sample solutions has been reported to improve extraction efficiency [74], this modified method requires comprehensive evaluation under complex conditions.

SPE-based methods are robust, easily accessible, and can be fully automated. Colorimetric PMB reaction products can be loaded onto a hydrophilic-lipophilic balance (HLB) cartridge and then eluted using a NaOH solution. The color of PMB products can be recovered by adding a small amount of colorimetric solution and ascorbic acid solution, yielding a detection limit of 3.0 nM using a 50 mL sample [75]. The robustness of this manual method was demonstrated via the repeat analysis of 300 nM standard solutions over several days, by three different operators (two of which had only undergone a 30-min training session) with the same cartridge used for all repeat analysis (RSD = 2.6%, $n = 81$) [75]. The method was later applied to an automated on-line SPE flow system for a two-week on-board underway analysis of 2250 oligotrophic surface water samples from the South China Sea [76]. The method was verified as being free of salinity effects, operable at room temperature, with no baseline shift from PMB coating observed. The single HLB cartridge could be reused at least 100 times in field applications [76]. Recently, the method was further combined with an integrated syringe-pump-based environmental-water analyzer (*i*SEA), a fully-automated portable analytical system [77]. The *i*SEA is versatile and robust, and it has been reported that this is the first single instrument capable of measuring phosphate from nanomolar to micromolar levels (Fig. 1(A1)), achieving the linearity up to 12 μM and a low detection limit of 1.7 nM under different analysis modes. The *i*SEA was successfully applied to carry out fixed site on-line monitoring and real-time underway phosphate analysis in riverine-estuarine-coastal waters as a routine procedure (Fig. 1(A2-A3)).

2.3. *Microfluidics*

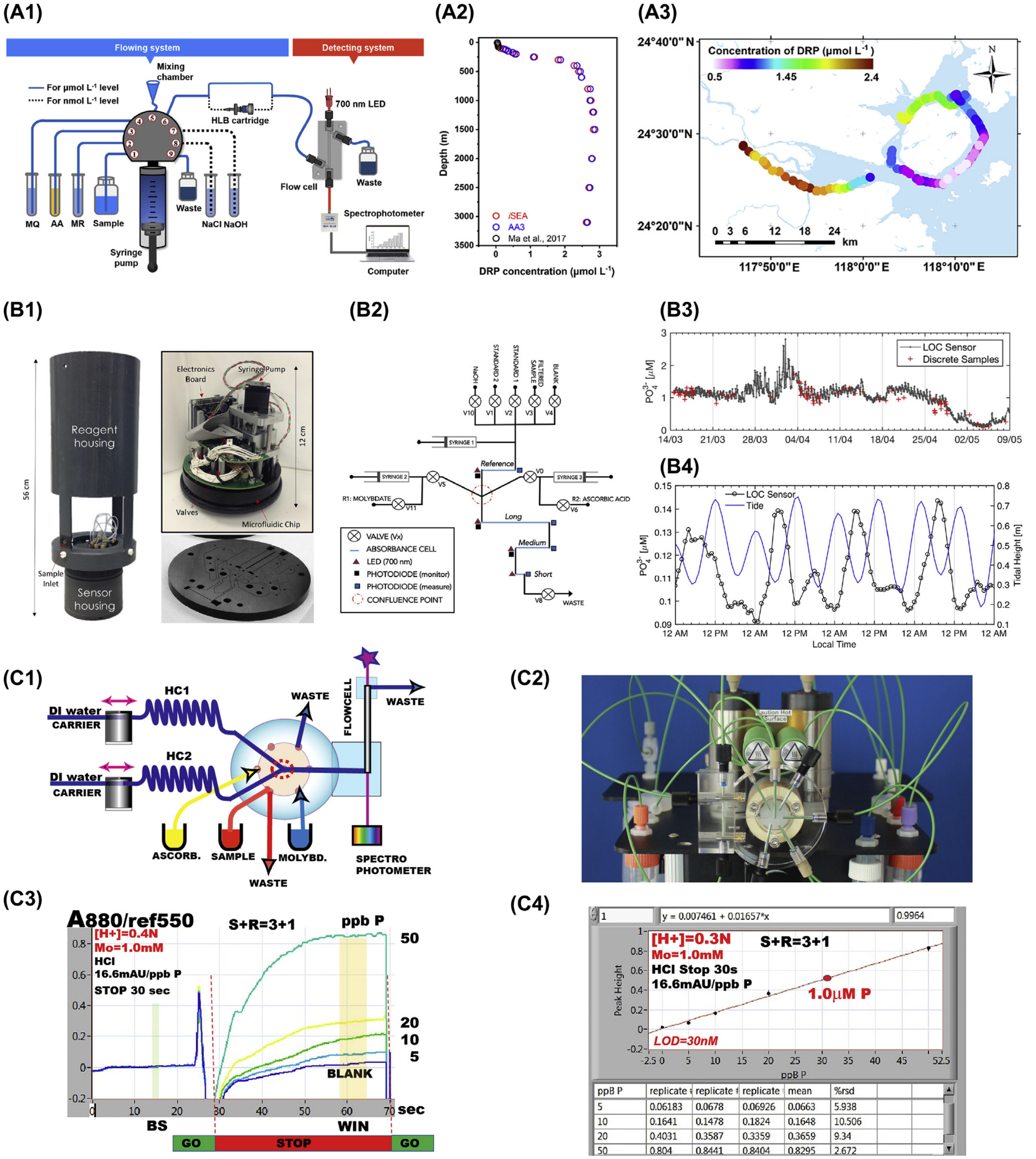
Microfluidics or lab-on-a-chip (LOC) systems, have the inherent advantages of being miniaturized, portable, and automated, showing much promise for on-site, *in situ*, and unmanned environmental monitoring [78–80]. Optical detection is the most commonly used microfluidics sensing strategy for phosphate measurement [78,81], although electrochemical methods are also frequently used in on-chip electrophoresis systems. To meet the requirements of field deployment, several critical issues need to be addressed which are challenging for the design and maintenance of microfluidic sensors, including the reduction of power and reagent consumption, integration of functional units, preservation of reagents, and calibration and correction for bias [82,83]. To date, microfluidic sensors have emerged as being reliable field-deployable systems [78,83–85].

Clinton-Bailey et al. [84] and Grand et al. [85] presented a highly integrated and automated *in situ* LOC analyzer, which was successfully deployed in river and costal environments for continuous phosphate measurements (Fig. 1(B1)). In the analyzer, syringe pumps injected samples and colorimetric reagents into the absorbance cells on the microfluidic chip via a confluence point situated upstream of the cells, followed by stopped-flow reaction and LED-photodiode detection (Fig. 1(B2)). It was found that the addition of 0.01% (w/v) polyvinylpyrrolidone to the ascorbic acid solution could reduce PMB coating and mitigate the effects of temperature on the PMB reaction, by lowering the activation energies (E_a), allowing the analyzer to be more robust in temperature-fluctuating environments [84]. During a nine-week deployment in the River Avon, the LOC analyzer was powered by a solar panel, achieving hourly measurements with 1.8 W power consumption per analytical cycle. The inlet filter and 500 mL reagent bags were replaced every 4.5 weeks. Determined phosphate concentrations varied from 1 to 2.5 μM with an in-field accuracy of 4.0 ± 4.5% ($n = 5$) as compared to grab sample results [84]. The LOC analyzer was further deployed in more challenging estuarine and coastal environments [85]. To eliminate optical interference from salinity and colored samples, the inherent absorbance of samples prior to the addition of colorimetric reagents was first recorded and then subtracted from the absorbance level after the reaction. This method was applied in a macrotidal and hypernutrified estuary, where 1267 unattended measurements were obtained at hourly intervals over 56 days, with phosphate concentrations ranging from 0.09 to 2.80 μM (Fig. 1(B3)). In addition, 741 hourly measurements were taken over 31 days in a relatively oligotrophic semi-enclosed tropical embayment, with recorded values ranging from 0.07 to 0.23 μM, showing an accuracy of 16 ± 12% compared to the results of discrete samples in the concentration range of 0.1–0.2 μM [85]. The deployment of unmanned, *in situ* LOC analyzers allows for the capture of transient and episodic events such as rainfall and flooding, which may have great significance in ecosystem dynamics. Combining high-resolution LOC data with other related parameter records (salinity, temperature, dissolved oxygen, discharge, rainfall, etc.), both short-term dynamics and long-term variation in phosphate can be interpreted, including source apportionment, diurnal cycling, and biogeochemical processes (Fig. 1(B4)).

Although many reported microfluidic devices are not capable of *in situ* deployment due to incomplete integration and automation, they exhibit valuable and distinct features in different aspects, including sample and reagent introduction [86–88], on-chip fluid control [89,90], modification of the detection unit [91,92], and on-chip digestion [92,93]. These features increase the portability and versatility of LOC devices, rendering them more suitable for rapid analysis under certain situations.

Khongpet et al. [86–88] combined programmable hydrodynamic sequential injection (HSI) with a microfluidic platform. The operation of HSI was similar to that of sequential injection analysis, but the system was less expensive due to the replacement of syringe pumps and selection valves with solenoid pumps and a peristaltic pump. This miniaturized system was successfully applied to the determination of phosphate, providing a detection limit of 3.2 μM and a throughput of 30 h^{-1} [86]. It is of note that recently, they developed the system for sequential determination of phosphate and ammonium [87], and sequential measurement of phosphate, nitrite, and nitrate [88]. Multifunctional analyzers that are capable of simultaneous determination of multi-parameters are highly desirable.

An automated microfluidic flow loop analyzer (10 cm × 11 cm × 15 cm in size) has been proposed [89]. Fluids on the chip were driven and mixed using seven microvalves actuated by linear micromotors, and a peristaltic micropump located above the loop channel. The micropump continually extruded the channel with the presence of three steel balls rolling over it. The average power consumption of the analyzer in measuring mode was low as 343 mW, with only 2 μL of ascorbic acid and 4 μL of ammonium molybdate consumed per sample, providing a detection limit of 1.8 μM [89]. However, the accuracy and precision of the analyzer were not sufficient, which may be partly due to the ultralow fluid



1

y = 0.007461 + 0.01657*x

0.9964

ppB P	replicate	replicate	replicate	mean	%rsd
5	0.06183	0.0678	0.06926	0.0663	5.938
10	0.1641	0.1478	0.1824	0.1648	10.506
20	0.4031	0.3587	0.3359	0.3659	9.34
50	0.804	0.8441	0.8404	0.8295	2.672

Fig. 1. Representative analytical systems for phosphate determination based on PMB methods. (A) Integrated syringe-pump-based environmental-water analyzer (*i*SEA). (A1) Schematic diagram; (A2) Vertical profiles of phosphate concentrations obtained by different methods at a station in the Pacific Ocean; (A3) Underway phosphate analysis in the Jiulong River Estuary and Xiamen Bay (China). Reprinted with permission from Ref. [77]. Copyright (2020) American Chemical Society. (B) Lab-on-Chip phosphate analyzer. (B1) A fully assembled analyzer (left), an analyzer without housing (top-right), a microfluidic PMMA layer of the microfluidic chip (bottom); (B2) Schematic diagram of the analyzer; (B3) Hourly unattended *in situ* measurement data ($n = 1267$) over 56 days; (B4) Diurnal phosphate variations and tide data in Kaneohe Bay (USA) over four days, with phosphate data smoothed using a 6-h moving average. Copyright © 2017 Grand, Clinton-Bailey, Beaton, Schaap, Johengen, Tamburri, Connelly, Mowlem and Achterberg. Front. Mar. Sci. 4 (2017) 255. (C) Programmable Flow Injection (pFI) in lab-on-valve format. (C1) Schematic diagram; Reprinted from Ref. [101] with permission from Elsevier; (C2) MiniSIA-2 analyzer; with permission from Global FIA (https://www.globalfia.com/); (C3) Stopped-flow response curves established by analyzing 0–50 μg P L^{-1} standards under optimized conditions; (C4) Calibration curve obtained from data collected in (C3). Reprinted from Ref. [102] with permission from Elsevier.

volumes in this system. Another integrated and miniaturized setup was recently reported by the same group, which comprised a custom-built colorimeter, a microcontroller, and a wireless communication module consisted of a ZigBee and a Global System for Mobile Communications module [94]. This setup may offer advantages for measurements in remote wireless situations in the future.

Centrifugal microfluidics can integrate sample processing, reagent mixing, and chemical detection onto the same disc. Duffy et al. [90] fabricated a 3D-printed microfluidic disc containing three mixing reservoirs in the center of the disc and three corresponding optical channels. Samples and colorimetric reagents were manually added into the reservoirs and the disc was then rotated using a motor, after which the fluids were mixed and propelled into the optical channels by centrifugal force, allowing three simultaneous analyses with a detection limit of 0.16 μM. This setup requires no pump and operated with a maximum power consumption of 2 W [90]. However, only two discrete water samples were analyzed, and further on-site analysis is expected to be carried out to confirm the efficacy of this system.

To overcome the possible sensitivity limitations of LOC due to its short optical pathlength, Zhu et al. [91] designed a Fabry—Pérot resonator which consisted of two parallel optical fibers with gold films covering the inner facets of the fibers. This design resulted in the optical pathlength being increased 3-fold, due to the multiple reflections of light between the two reflectors. Likewise, Jung et al. [92] increased the optical pathway by etching the substrate channel into a 45°-trapezoid shape, which was deposited with an aluminum reflective layer, so that the light beam not only perpendicularly passed through the fluids but was also reflected along the direction of the channel. In the future, the integration of novel optical approaches with microfluidics will undoubtedly allow improved analytical performance.

2.4. *Other flow-based and automated methods*

The crucial role of flow analysis in phosphate determination has been well described [41,95]. Traditional continuous flow analysis [96] and flow injection analysis [97—99] are still being practiced, yet programmed flow analysis is increasingly recognized for its ease of use, versatility, and robust manipulation capability [100—102]. As demonstrated by the “programmable Flow Injection (pFI)” in lab-on-valve format (Fig. 1(C1—C2)), the advantages of flow injection and sequential injection can be combined with the aid of computer programs. The flow rates, volumes and numbers of samples and reagents, as well as their time, ratio, and sequence of mixing can be changed easily without physical reconfiguration. Furthermore, flow-batch or stopped-flow analysis can be achieved using software protocols [100—102]. These features make pFI highly suitable for optimizing reagent-based manual assays on a flow manifold, as well as for investigating the mechanisms of the “black box” PMB reaction [53]. The reaction conditions can be controlled and information on kinetics and spectra during chemical reactions can be captured (Fig. 1(C3—C4)).

Hatta et al. [101] used pFI to reveal the effects of surfactants on the PMB reaction by stopping the reaction mixture in the flow cell to obtain the kinetics and spectra. It was found that Brij 35 slowed the reaction both in deionized water and seawater, but changed the spectrum to show a single peak at 760 nm in the first 5 min, the absorbance of which was much higher compared to the absorbance at 880 nm without the addition of a surfactant. In the presence of SDS, the reaction curve in both deionized water and seawater reached a plateau and no salinity effects were observed, making SDS more suitable for the determination of phosphate in seawater [101]. Ruzicka et al. [102] further investigated the complicated issues of the molar absorptivity of PMB products and the optimization of reagents. By varying the concentrations of the acid and molybdate, it was directly confirmed that sensitivity was affected by both acidity and the molybdate concentration, as well as their combination, resulting in no definite range of pH or $[H^+]$:[Mo(VI)] being suitable. Knochen et al. [103] investigated the effect of the order of addition of reagents on sensitivity. The highest calibration curve slope was obtained by mixing separate molybdate, antimony, and phosphate, followed by acidification and reduction, rather than using the commonly adopted pre-mixed reagents. The enhancement in sensitivity may occur due to unidentified differences in formation mechanisms of the PMB products [103]. It is interesting that after almost 200 years since the discovery of the PMB reaction, the comprehensive details have still not been established [53]. It has been recommended that analysis of the kinetics and spectra should always be carried out when optimizing or modifying the PMB method [101]. It is expected that such programmed flow analysis, combined with mass spectrometry analysis, may help provide a deeper insight into the underlying chemical mechanisms of the PMB reaction.

There is increasing interest in the reduction or even elimination of use of pumps and valves in automated analytical systems since they are costly and require maintenance during long-term measurement. This requires the development of novel patterns of sampling, sample and reagent delivery, and system configuration. Bakker's group proposed an elegant flow system modification to deliver protons and molybdates via ion-exchange membranes for seawater phosphate measurement [104]. High concentrations of Na^+ and Cl^- in seawater induced protons and molybdates from the two reagent reservoirs to separately and passively counter diffuse across the membranes and into the flow lines. The membrane-based reagent delivery method offers a new opportunity for developing *in situ* marine sensors [104,105]. More recently, a submersible automated analyzer to collect samples and deliver reagents without the use of valves and pumps was reported [106]. The innovative “Fish-Bite” reservoirs made of acrylonitrile butadiene styrene plastics were pushed by a motor through a sloped rail and opened, allowing water samples to enter before closing, mimicking the “swallowing” process. Reagent capsules made of polydimethylsiloxane were located on the reservoir and were pressed by the motor when the reservoir reached the detection position, releasing reagents into the reservoir, allowing the reaction to occur and colorimetric measurements to be taken. Because no filters were used during sampling, the PMB formation reaction rate rather than the final absorbance was used for calibration, to reduce the influence of turbidity and chromophoric dissolved organic matter. The analyzer was successfully deployed in an irrigation canal and the accuracy compared to batch sampling was 20.2% and 11.7% for phosphate and nitrite, respectively [106]. New types of 3D-printed self-sampling cells were recently designed, which were controlled by rubber bands and dissolvable threads for *in situ* self-sampling. Equipped with a portable document scanner, the submersible analyzer allows for simultaneous determination of phosphate, iron, silicate, and nitrite [107].

3. Diffusive gradients in thin films

Diffusive gradients in thin films (DGT) is an *in situ* passive sampling technique, which can provide representative time-weighted average concentrations of analytes with less cost, lower labor intensity, and reduced risk of contamination compared with traditional grab sampling [108]. Some commercially available DGT samplers, such as Metsorb (titanium oxide) -DGT [109,110] and Zr-oxide DGT [111—114], have been used to measure phosphate in water [109,111], sediments [112], and soils [113] (Fig. 2A).

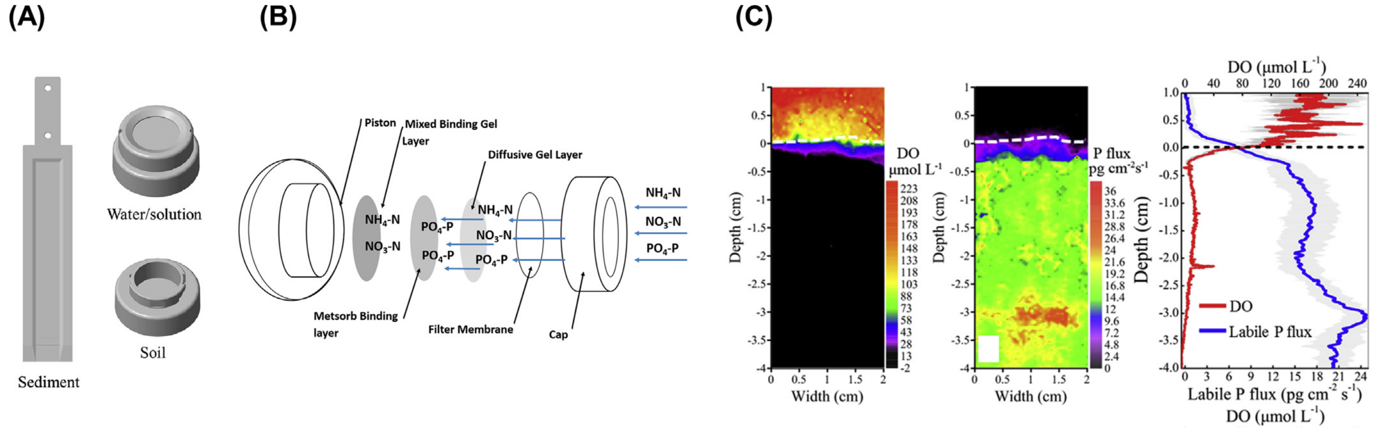


Fig. 2. DGT samplers for phosphate determination. (A) Common types of DGT samplers. Reprinted from Ref. [121] with permission from Elsevier. (B) A hybrid DGT sampler for simultaneous measurement of ammonium, nitrate, and phosphate in freshwaters. Reprinted from Ref. [110] with permission from Elsevier. (C) Two-dimensional distributions of DO concentration and labile P flux across the SWI (dotted lines) imaged using a hybrid DO-phosphate sensor in aerobic microcosms and extraction of one-dimensional profiles. Reprinted from Ref. [122] with permission from Elsevier.

In pursuit of higher binding capacity and selectivity, greater physical and chemical stability, and enhanced compatibility for multiple purposes, various novel binding agents have been proposed. Recently reported DGT samplers for phosphate analysis in water, together with their analytical parameters (detection limit, etc.) and field applications, are summarized in Table S2. Materials successfully developed as adsorbents for the removal of phosphate, such as UiO-66 (Zr-based metal organic frameworks, MOFs) [115], Fe_3O_4 nanoparticles [116], phosphate ion-imprinted polymers [117], basic magnesium carbonate [118], and ceria oxide nanoparticles [119], can be considered as potential binding agents. However, binding capacity is not always the most important factor. Before applying DGT to real water matrices, especially seawater and eutrophic waters, the effects of varying ionic strength, pH, interference, and biofouling should be investigated. Varying environmental conditions may affect the diffusion coefficient (D), diffusion boundary layer (DBL), and other factors that can affect the accuracy of measurements. It is important to investigate these issues in synthetic water matrices or water samples from targeted deployment water bodies, rather than just in an ultrapure water matrix. For example, Qin et al. [115] found that the D of phosphate in the dialysis membrane increased with ionic strength and can be calibrated using exponential regression. Based on the corrected D, measurements were found to be independent of solution pH (6.5–8.5) and ionic strength (0.01–100 mM). Deployment of the samplers in eight sites of Lake Chaohu yielded results consistent with those of grab sampling [115]. Feng et al. [117] observed a linear increase in the thickness of nitrocellulose filter membranes due to biofouling and a linear decrease in the D of phosphate with field deployment time. The effective D value can then be quantitively corrected based on the thickness of the DBL, the thickness of the biofilm, and the linear coefficient of D decrease identified under specific environmental conditions.

To simultaneously sample multiple elements of interest, mixed binding agents have been developed. Feng et al. [120] applied a biochar-zeolite-zirconium oxide mixed binding phase for simultaneous measurement of phosphate and ammonium in freshwaters (Lake Nanhu). Wang et al. [121] reported a ZrO-Chelex mixed binding phase for simultaneous measurement of eight cations and eight oxyanions, including phosphate. This DGT sampler was tested in the laboratory for collected freshwater, seawater, and sediment, but not in real environmental scenarios. An alternative approach for multi-elemental assay is to use multiple binding layers. Simultaneous measurement of dissolved inorganic nitrogen and phosphorus in freshwater was achieved using a Metsorb binding layer for phosphate overlying a mixed binding layer for ammonium and nitrate (Fig. 2B) [110]. It was found that ammonium uptake was affected by competing ions so that the conductivity of targeted water matrices should not exceed 400 $\mu S\ cm^{-1}$ and the deployment time no longer than 24 h to ensure the performance of the sampler for all three analytes [110]. Another novel hybrid sensor assembled by a planar O_2 optode and a Zr-oxide P binding layer was reported for combined two-dimensional imaging of dissolved oxygen (DO) distribution and labile phosphorus flux across the sediment-water interface (SWI) in laboratory mesocosm experiments [122] (Fig. 2C). In another study, Han et al. [123] used a precipitated zirconia-based DGT followed by two-dimensional ion chromatography for phosphite separation and detection. The adsorbed gels or eluents can be refrigerated in darkness for 3 days with no species transformation observed. Using this method, an *in situ* vertical profile of phosphite and phosphate concentrations across the SWI was captured. These examples demonstrate the ability of DGT to help interpret complex environmental processes which commonly involve the interaction of different elements [108]. However, it is recommended that these multi-functional setups should be performed in comparison with single-analyte DGT to identify possible differences in performance, such as reduced binding capacity for specific analytes or increased interference [110].

Undoubtedly, DGT samplers overcome some of the major shortcomings of traditional grab (spot) sampling. Grab sampling can only provide a snapshot of the targeted analytes within a constrained time and space, although it is able to capture short-term variability [109], which often has significant environmental implications. In contrast, DGT sampling provides time-weighted average concentrations, which may better describe the real state of analytes during a specific period. Therefore, the two methods can be considered complementary [109]. However, in the calculation of DGT concentration, D is the most important parameter, which is determined experimentally and influenced by environmental conditions, which may introduce bias into results as shown by previously stated examples [115,117]. In this regard, automated active sampling is less limited and may provide a more promising method [124]. In the future design of novel DGT binding agents and diffusive phases, the capacity, selectivity, and antifouling features should be considered under complex real-world conditions.

4. Fluorescence and phosphorescence sensing

In recent years, various types of fluorescent and phosphorescent sensors have continually emerged (Table S3), based on organic fluorophores [125,126], metal complexes [127–130], quantum dots [131–136], and coordination polymers [137–139]. These sensors commonly feature high selectivity and rapid detection. As this review is focused on environmental monitoring demands, sensors with no demonstrated practical application in real or synthetic water samples are excluded from discussions here. More general information on phosphate recognition and sensing is available in previous literature [26,52].

Purkait et al. [125] designed a turn-on fluorescent sensor containing a simple hydrazine-based thiocarbamide fluorophore. The detection limit for PO_4^{3-} was 34 nM, while AsO_3^{3-} also showed a significant response (detection limit of 15 nM) with the same mechanism of hydrogen bond formation to enhance structural rigidity and fluorescence intensity. Sarwar et al. [126] loaded a commercially available complex of *E. coli* phosphate-binding protein and thiol-reactive coumarin fluorophore onto a wax-printed paper strip, which was then inserted into a 3D-printed handheld device. The fluorescence signal induced after depositing the sample was captured using a smartphone fixed outside the chamber, providing the potential for field measurement [126].

The introduction of some metal ions, especially transition metals, can be very useful in designing phosphate sensors due to the high affinity between the metal ions and the oxygen-donor atoms of phosphate. For example, Eu^{3+}, Al^{3+}, Dy^{3+}, and Ce^{3+} were found to induce the aggregation of quantum dots (QDs), due to their bridging among the surfaces of QDs by electrostatic interaction and coordination, resulting in fluorescence (or phosphorescence) either being quenched [131,132,135] or enhanced [134]. Upon the addition of phosphate, however, the strong interaction between phosphate and metal ions led to disaggregation, restoring the luminescence (turn-on) [131,132,135] or reducing the enhancement of luminescence (turn-off) [134], allowing quantitative relationships to be obtained. Based on these phenomena, a single-layered graphene quantum dots-Dy^{3+} sensor was developed, with turn-on fluorescence emission at 500 nm when excited at 417 nm and a detection limit of 0.1 μM [135]. The interference from twelve anions, six cations, and two amino acids was investigated and found to be negligible, with successful analysis of spiked artificial wetland water samples [135]. Likewise, a phosphorescent Mn doped ZnS QDs-Ce^{3+} sensor was applied to the detection of phosphate in river and lake water. However, the samples required preconcentration by 30-fold before analysis due to insufficient sensitivity (detection limit of 2.71 μM) [132]. Another emerging class of sensor material is luminescent lanthanide coordination polymer (Ln-CP). In Ln-CP sensors, such as Eu-based MOFs, organic ligands can enhance the luminescence of lanthanide ions via an energy transfer process (antenna effect). The subsequent addition of phosphate interrupts the energy transfer process due to phosphate binding with metal ions or causes the collapse of the sensor structure, resulting in turn-off luminescent sensing [137,139].

If fluorescent sensors were to be used in trace determination, higher sensitivity would be desired (for example, detection limit <0.1 μM). Applying a ratiometric detection strategy may provide a feasible solution. Ratiometric detection allows for self-calibration of instrumental and environmental fluctuations with fluorescence emissions at two wavelengths used for quantification [140]. Cheng et al. [138] designed a Eu–H_3L (*p*-terphenyl-3,4″,5-tricarboxylic acid) Ln-CP sensor with a detection limit of 52 nM. The introduction of phosphate reduced the antenna effect, causing a decrease in the characteristic fluorescent emission of Eu at 614 nm, whereas the ligand-based emission intensity at 368 nm was enhanced due to hydrogen bond formation causing a reduction in vibrational movements. The intensity ratio I_{614}/I_{368} showed good linearity with phosphate concentrations in the range of 0.1–15 μM [138]. Another approach to improve sensitivity is the surfactant-enhanced antenna effect recently proposed [128] (Fig. 3A). The addition of a small amount of sodium dodecylbenzenesulfonate (SDBS) was found to greatly induce the fluorescence resonance energy transfer (FRET) from ciprofloxacin (CIP) to Eu^{3+} in the CIP-Eu^{3+} sensor complex. This resulted in complete quenching of the native fluorescence of CIP at 415 nm and the increase in the emission of Eu^{3+} at 615 nm. The subsequent addition of phosphate quantitatively recovered the fluorescence intensity at 415 nm with an impressive detection limit of 4.3 nM. Interference by 18 cations, 12 anions, and fulvic acid was investigated, among which Cr^{3+} and $P_2O_7^{4-}$ had non-negligible effects. Total phosphorous in digested natural water samples, wastewater samples, total suspended particulates, and $PM_{2.5}$ was measured [128]. In a recent study to develop sensitive fluorescent sensors, Ramírez-García et al. [141] synthesized a core@shell nanocomplex by coating Yb, Er doped ZrO_2 upconversion nanoparticles with a layer of undoped ZrO_2 (Fig. 3B). This design can provide more high affinity Zr^{4+} sites for phosphate binding and enhance the upconversion emission intensity of the nanoparticles excited by near infrared at 975 nm. Fast Green (FG) dye was attached to the surface of the nanocomplex to quench the upconversion emission via FRET. The addition of phosphate replaced the dye via strong competition for Zr^{4+} and recovered the upconversion emission, resulting in a detection limit of 20 nM and linearity up to 1 μM.

Although many functional materials have been developed for use in novel fluorescent sensors, efforts still need to be devoted to the rational design of sensors that can selectively, sensitively, accurately, and practically determine phosphate concentrations in real water samples. Selectivity is one of the most critical criteria for fluorescent sensing, especially in real-world applications. Common anions and cations in natural waters, as well as dissolved organic matter, should be tested to evaluate the performance of these new sensing materials. In addition, the sensing mechanisms should also be thoroughly investigated. Cost-effective sensors that can be facilely prepared and conveniently used (e.g., allow for visual detection) have an added advantage, which should be a key focus and future research direction.

5. Other spectroscopy-related methods

UV–Vis spectroscopy (referring to the direct measurement of water sample spectra by spectrophotometers followed by algorithm deconvolution) has been well described for high-frequency measurements of nitrate, dissolved organic carbon (DOC), and total suspended solids (TSS). UV–Vis spectroscopy can contribute greatly to routine water monitoring, providing data of higher spatial and temporal resolution than wet chemistry analyzers. Phosphorus species generally do not absorb light in the UV–Vis spectrum. However, recent studies have shown that it is still possible to predict concentrations of phosphorus fractions based on the UV–Vis spectra [142,143]. This is achieved by using algorithm models such as partial least squares regression, to establish the covariance and correlation between properties of the absorbance spectra and phosphorus fraction concentrations. Vaughan et al. [143] reported the concurrent prediction of TP, TDP, and SRP in riverine phosphorus fractions, although the accuracy at low concentrations was limited. It is of note that calibrations or models may be highly site-specific due to differences in water matrices, which affect covariance relationships. In the future, the use of machine learning is likely to facilitate the design of more robust algorithms.

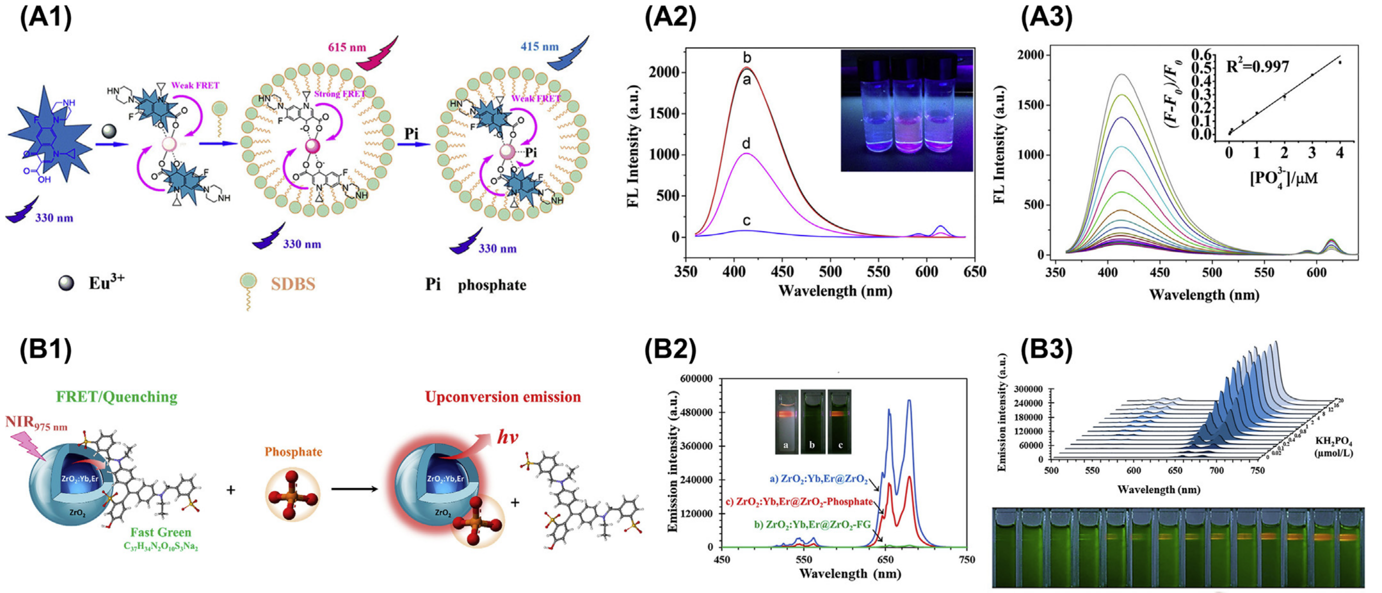


Fig. 3. Representative fluorescent sensors for sensitive phosphate determination. (A) CIP-Eu^{3+} sensor. (A1) Schematic illustration of phosphate sensing based on surfactant-enhanced FRET from CIP to Eu^{3+}; (A2) Emission spectra of (a) CIP, (b) CIP + PO_4^{3-}, (c) CIP + Eu^{3+}+SDBS, and (d) CIP + Eu^{3+}+SDBS + PO_4^{3-}. Inset shows the color change of the solution corresponding to (a, c, d) under UV lamp excitation at 365 nm; (A3) Quantitative relationship between fluorescence intensity at 415 nm and phosphate concentrations. Reprinted with permission from Ref. [128]. Copyright (2018) American Chemical Society. (B) ZrO_2:Yb,Er@ZrO_2-FG sensor. (B1) Schematic illustration of phosphate sensing based on FRET from the upconversion nanoparticles to the FG acceptor; (B2) Emission spectra of different sensor complexes. Inset shows the color change of the upconversion emission of the corresponding nanocomplexes excited at 975 nm; (B3) Upconversion emission spectra and images of sensor suspensions under various concentrations of KH_2PO_4. Reprinted with permission from Ref. [141]. Copyright (2019) American Chemical Society.

Although phosphate does not contribute to UV–Vis absorbance, the infrared and Raman spectroscopic features of phosphate can be utilized for quantification. However, low sensitivity due to weak signal strength (detection limit usually at the millimolar level) precludes these features from use in the routine analysis of natural water samples. Attenuated total reflectance-Fourier transform infrared spectroscopy is known to be suitable for *in situ* and real-time measurement, with reports showing the successful quantification of bicarbonate, carbonate, dihydrogen phosphate, and hydrogen phosphate ions in microalgal cultures using the partial least squares model [144]. Persichetti et al. [145] used a capillary nozzle to produce a liquid jet which acted as an optical waveguide in the air, inside which Raman spectroscopic detection of phosphate occurred. This design eliminated the need for a liquid container or flow cell, effectively reducing background noise.

6. Chromatography and mass spectrometry

Conventional ion chromatography methods have been well established for the separation and determination of anions including phosphate, but suffer from insufficient sensitivity and matrix inference issues [35]. Sorbent packed chromatography columns for the on-line extraction of phosphate derivatives have been reported to exhibit a detection limit down to the nanomolar level [71], while the functionalization of sorbents and column packing may be time-consuming. ICP-MS can provide rapid and sensitive measurements, although severe polyatomic interference to ^{31}P must be overcome. Recently, Ma et al. [146] reported the use of inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) for trace determination of phosphate, with a detection limit of 0.26 nM and the avoidance of polyatomic interference.

Chromatography and mass spectrometry are also powerful tools to study speciation and fractionation of P, which have a strong influence on the bioavailability, removal, recovery, and management of P [5]. The relationship between operationally defined fractions and bioavailable P remains unclear [14]. The traditional methods for functional P fractionation, such as enzymatic hydrolysis, fail to answer critical questions including the difference between SRP and orthophosphates [147], and the identification of non-reactive P species [16]. Recently, size exclusion chromatography was coupled to ICP-MS to obtain the molecular weight distribution of dissolved P in water samples [148]. In another study, two-dimensional ion chromatography coupled with electrospray ionization high-resolution mass spectrometry was used to quantify phosphate along with 11 phosphate-containing metabolites and two inorganic condensed phosphates in surface water samples [149]. In the future, the combination of multiple technologies including chemical and enzymatic extraction, chromatography, mass spectrometry, and ^{31}P NMR, will greatly enhance our understanding of complex phosphorus fraction pools.

7. Quality assurance and quality control (QA/QC)

Strict and robust QA/QC procedures lead to best quality and comparable data. A complete QA/QC framework covers the whole process of sample collection and storage, sample analysis, and data analysis. Requirements and specific procedures may vary for different measurement purposes and monitoring programs. One can refer to related standards, manuals, or protocols (e.g., for routine water and wastewater analysis [13], for using an Auto-Analyzer in seawater [150], for *in situ* nutrient analysis in marine environments [151]), and establish their own standard operational procedures according to practical conditions. While it is not possible to discuss all the procedures here, some key issues which influence the quality of data are highlighted.

Sample storage is one of the very first things that should be considered in terms of QA/QC. The adsorption of phosphate onto the walls of containers appears to be inevitable, no matter whether plastic or glass bottles are used. However, the amount of adsorption is affected by phosphate concentrations, pH, ionic strength, surface properties, and the specific surface area of containers [14,149]. A recent isotopic study showed that about 30% phosphate loss occurred with initial sample concentrations of 0.71 μM, over 24 h of storage in polypropylene, high density polyethylene (HDPE), and borosilicate glass containers [149]. It has been proposed that only on-site immediate analysis of samples can provide fully accurate phosphate results [149]. Unfortunately, on-site, *in situ* analysis, or field isotope spiking is not always possible, and various contradictions exist in the recommended sample storage protocols in different documents. The use of HDPE bottles rinsed with HCl and ultrapure water may be prevalent now for oceanic phosphate measurement [150], while acid-rinsed glass bottles are recommended in Ref. [13] (Table 1060: I), especially for low concentration samples. Opinions on sample preservation strategies are also divided. Recently reported methods include freezing [68], acidification and freezing [84], and NaOH induced precipitation of $Mg(OH)_2$ (MAGIC) [152]. More comprehensive discussions on sampling and sample storage are available in previous reviews [14,17,31,37,40]. At present, there is no universal sample storage protocol that can be applied for different aqueous samples (e.g., seawater, surface water, groundwater). Protocols should be tailored for different monitoring programs to be purpose-oriented and site-specific, taking account of the characteristics of the targeted water matrix, available resources, and acceptable levels of uncertainty. Furthermore, explicit descriptions of the protocols applied and the scientific reasoning behind the selected protocols (whether based on literature or field tests), should always be provided. In the same manner, the stability of phosphate standard solutions, which may also be susceptible to adsorption, warrants a regular check, with some suggesting newly preparing primary standards at a minimum of three months for seawater analysis [150].

To obtain accurate results using PMB methods, special attention should be paid to the control of blanks [67], preservation of PMB colorimetric reagents [153], and the elimination of baseline shift due to the coating of products in flow systems [66,67,84]. These issues are relatively easy to handle in land-based or field-based laboratories but can present a major challenge when using *in situ* wet chemistry analyzers [83]. Recalibration by measuring a blank and a standard at regular intervals is now commonly adopted [84,85]. It may be feasible that in the future, automated QA/QC procedures will be implemented to reduce the workload, such as data screening and baseline correction.

It is of concern, that not all studies reviewed here have considered the potential interference from co-existing species in the sample matrix. For PMB methods, it is well known that arsenate and silicate could affect results as they also react with molybdate [53]. Arsenate has received relatively less attention, which may be due to the fact that arsenate is normally present at trace concentrations and the kinetics of arsenate reacting with molybdate is much slower [154]. However, arsenate interference was found to increase linearly with phosphate concentrations at the nanomolar level [154], and this synergistic effect or "catalysis" by phosphate should be considered [53,154]. The effects of silicate are generally mitigated by controlling acidity and heating [53]. In some cases, however, the measurement of trace phosphate may still be affected by the presence of silicate at micromolar levels in natural waters. On the other hand, the reaction of arsenate and silicate with molybdate can be leveraged to simultaneously determine phosphate and arsenate [68], or phosphate and silicate [155,156]. Fluoride, iron, sulphide and other species can also interfere with the PMB reaction [53], and their influence should be studied if significant amounts of these species exist in the assessed water environment. Effects of hydrolysis of condensed and organic phosphorus during analysis should also be examined, using a series of model compounds. Both the water matrix and the analytical procedures applied influence the extent of hydrolysis, which requires assessment on a case-by-case basis. For example, the contribution of hydrolysis in an automated method was reported to

Table 2
Comparison of state-of-the-art analytical methodologies and platforms for phosphate measurement in waters.

	Advantages	Limitations	Preferable (potential) applications
Methodologies			
Spectrophotometry (mainly PMB-based)	• Well-developed and reliable • Easy accessibility and operation • Easy automation	• Sensitivity and interferences • Cannot measure orthophosphate alone	• Serve as standard method • Routine analysis and monitoring program • On-board, on-site, *in situ* analysis
Fluorescence sensing	• High selectivity and sensitivity • Potential for miniaturization	• Interferences from matrix • Tedious fabrication	• Rapid, portable sensing
Electrochemical sensing	• Sensitive and rapid measurement • Miniaturized and portable • Possibility of mass production and deployment	• Physical and chemical stability • Tedious fabrication	• *In situ* sensors
Chromatography-Mass spectrometry	• High selectivity and sensitivity • Multi-species identification and quantification	• Costly and bulky instruments • Interferences from matrix or instrument • Time-consuming procedures	• Trace determination in complex samples • Speciation and fractionation of phosphorus
UV−Vis spectroscopy	• Provide high spatial and temporal resolution data • Reagentless	• Limited accuracy • Require sophisticated and site-specific algorithm model	• *In situ*, semi-quantitative screening
Platforms			
DGT	• Reduced need of tedious grab sampling and analysis • Provide representative time-weighted average concentration of analytes	• Bias from the interferences of environmental conditions • Account for only part of the environmental behavior of analytes	• Indicate the lability and bioavailability of analytes • Help elucidate biogeochemical processes
Flow analysis	• Automated, high-throughput, good reproducibility • Compatible with various detection strategies	• Require regular calibration and system check	• Real-time, automated, and continuous monitoring • Field-deployable systems, *in situ* sensors
Microfluidics	• Miniaturized and integrated • Greatly reduced consumption of reagents, samples, and power	• Relatively high cost and technical barriers • Maintenance inconvenience • Difficulty in calibration and interference elimination	• Real-time, automated, and continuous monitoring • Field-deployable systems, *in situ* sensors

Please note that the advantages, limitations, and preferable (potential) applications of these methodologies and platforms apply to general scenarios. Differences or exceptions may exist within the same category of methods, due to the use of different chemical derivatization reactions, functionalized materials, etc.

be less significant than in the corresponding manual method, due to reduced reaction duration [75,76]. Therefore, it is recommended that interference should always be evaluated at environmentally relevant concentrations when new analytical systems or measurement protocols are developed [60,154].

The accuracy and precision of a method determine the comparability of data. Great efforts have been made in the intercomparison of methods [157]. Effler et al. [158] reported systematic differences in phosphate concentrations of lake water samples, as determined by two versions of the standard PMB method. Although there may be influences from sampling and storage, the finding of this report again highlights the need for improved validation of the accuracy and precision of methods. The use of certified reference materials (CRM) is highly recommended [40,60]. It has recently been proposed that combining routine analysis of CRM and statistical techniques is an effective and simple method to determine the combined uncertainty of methods for marine nutrient determination, so that better compatibility of measurement results can be achieved [159].

The unit for expression of data is a minor yet non-negligible issue. While mass concentrations expressed in terms of weight/volume (e.g., μg L^{-1}) are replaced by molar concentrations (e.g., μmol L^{-1}) in the oceanographic community [151], inexplicit expression of mass concentrations is still common in literature and water monitoring databases [160]. There is an almost threefold difference in concentrations expressed by "μg L^{-1} as P" or "μg L^{-1} as PO_4". Some have suggested the use of "μg L^{-1} as PO_4" based on "safety-first" and "elimination of ambiguity" principles [160], to avoid misunderstandings and misinterpretation.

8. Conclusions and perspectives

Phosphate measurement is an old question, but also a new challenge. This review summarized contemporary methods for the determination of phosphate in environmental water samples, based on published reports from 2016 to the beginning of 2020. Each category of techniques is characterized by its own merits and suitable scenarios, as well as obstacles that limit its practical application (Table 2). No single method can meet all analytical requirements or be appropriate for every application.

PMB-based methods will continue to hold a dominant position due to their feasibility and versatility. Coupling these methods with new sampling and automation techniques breathes new life into the classic PMB reaction. The development of other methods should be strongly encouraged to provide an alternative to spectrophotometry, which can offer choices for method comparison and be important for the production of CRM. The rise of nanotechnology provides exciting opportunities for the design of novel fluorescent and electrochemical sensors, which are promising for achieving highly sensitive and selective measurements. Advanced chromatography and mass spectrometry will help to decipher the nature of phosphorus reactions and the complexity of phosphorus fraction pools.

Despite various methods being available, several intractable problems remain unsolved. Methods for environmental analysis put a high priority on practical functionality under real-world conditions, whereas biological assays may focus more on miniaturization, point-of-care, and molecular-level analysis. It is recommended that the future design of methods should be application-driven to overcome current limitations, and the choice of methods should be purpose-driven to maximize practical utility.

Methods that are applicable in highly variable environments are still lacking. Variations in salinity, hydrologic conditions, and large gradients in nutrients in riverine-estuarine-coastal continuum pose significant challenges to analysts. In contrast, in the ocean where trace concentrations are often encountered, sensitive and delicate methods are required. Multifunctional methods for multi-analyte measurements are also required. The trend of moving laboratories to the field calls for the development of automated techniques to deliver on-site or on-board analysis [161], as well as sampling methods like DGT. *In situ* sensors are recognized as critical tools to improve the spatial and temporal resolution of nutrient profiles for deeper and finer insights into natural processes, which require better physical robustness and chemical stability. Compared to nitrate, the development of *in situ* phosphate sensors is less advanced, with only wet chemistry analyzers commonly practiced at present. UV–Vis spectroscopy is in its early stages and may be more suitable for semi-quantitative screening. Electrochemical sensors hold great promise to fulfil the requirements of *in situ* analysis [27,162], although they still require special attention in terms of their reliability (e.g., issues of calibration, biofouling, physical and chemical stability), especially in saline and harsh environment. The importance of QA/QC during the whole analytical process can never be overemphasized, which also has implications for the determination of other nutrients and metals. International programs and partnerships such as Alliance for Coastal Technologies [163] and Global Ocean Ship-Based Hydrographic Investigations (GO-SHIP) [150], will support the harmonization of establishing analytical protocols and developing analytical devices.

More versatile methods can be expected to be developed in the future. Modern analytical chemistry is becoming more connected with Internet of Things (IoT) [164]. New modalities of analytical setups, such as smartphone-based devices [165], paper-based microfluidic analytical devices [166], and miniaturized sensors with wireless communication [167], can provide smart measurement of phosphate with point-of-use detection and network monitoring. Together with a more comprehensive knowledge of the analytical chemistry of phosphorus in waters, soils, and organisms, a better understanding of the interactions among different phosphorus pools, and ultimately, improved environmental quality and ecosystem sustainability can be envisaged.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.trac.2020.115908.

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