

Review Article

Nutrient Detection Sensors in Seawater Based on ISI Web of Science Database

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Marine ecosystem is increasingly deteriorating. In order to assess anthropogenic influence and instigate appropriate remedial actions, it is still of great significance to develop the technology of sensors applied for nutrient detection (e.g., nitrate, phosphate, and silicate) in seawater. This brief review shows an important direction for the development of nutrient detection sensors in seawater and also the limitations and challenges based on data from the ISI Web of Science database. Being different from previous review papers, in this short critical review paper (1) we unified the unit of limit of detection (LOD) for making the comparison within different researches possible; (2) only the literatures focusing on the technological development of sensors in seawater were used; and (3) not only the detection methods but also the detected analytes and publication years were discussed to supply more valuable information for the development of nutrient sensors applied in seawater. In total, 109 literatures were collected with regard to technological development. The quantity of literatures has increased most during 2011-2020. For analytes, literatures related to nitrate, phosphate, ammonium, and phosphate will continue to increase with more accurate data. For detection methods, spectrophotometry, colorimetry, fluorimetry, and electrochemistry are the most widely used sensors. LODs show thousands of orders. In general, there are lower LOD to nitrite and ammonium and fluorimetry method. Now, for analytes, nitrate (1.0983) > silicate (0.5495) > phosphate (0.4823) > ammonium (0.1324) > nitrite (0.0568). For detection methods, microfluidics (1.7617) > electrochemistry (1.2607) > colorimetry (0.4462) > spectrophotometry (0.2941) > fluorimetry (0.0558). This result indicated that the development level of detection methods is closer for nitrate, nitrite, phosphate, and silicate. For ammonium, spectrophotometry has significantly lower LOD than electrochemistry ($p < 0.05$), and fluorimetry also has significantly lower LOD than electrochemistry ($p < 0.05$). Our results imply that sensors with accurate LOD should be developed in the future. In addition, more detection methods should be considered by future sensors.

1. Introduction

Despite the fact that oceans cover more than 70% of our planet and have a profound impact on global climate, weather patterns, human health, agriculture, and commerce

[1, 2], human ability to make sustained measurements of ocean processes is limited and much of the oceans remain largely unexplored [3, 4]. Meanwhile, marine ecosystem is increasingly deteriorating due to continuous development and utilization of oceans by industrial pressures and growing

population [5, 6]. These ecosystems of coastal zones, estuaries, and gulfs have been gradually destroyed with different extents, such as dumping of waste, construction of harbours, dredging, and extraction processes [7, 8]. Furthermore, frequently occurred marine natural disasters (e.g., tsunamis and red tides) bring substantial social impacts and economic losses [9, 10]. Therefore, the work of ocean environmental monitoring is urgent and monitoring the concentration changes and spatiotemporal distribution of nutrients in ocean environments is significant. In order to assess the impacts of these activities and instigate appropriate remedial actions, it is of great significance to develop the technology of sensors applied for ocean environmental monitoring, including the detection of chemical elements (e.g., nitrate, nitrite, phosphate, ammonium, and silicate), physical elements (e.g., pH, DO, and heavy metals), and biology (e.g., phytoplankton, benthonic animal, and fish).

Determining the distributions and variations of chemical elements in oceans is key to fully understanding global geochemical cycles, evaluating seawater pollution, and forecasting the occurrence of harmful algal blooms (HABs) [11, 12]. Although a wide variety of elements are essential to life in oceans, only a relatively small number of essential elements (e.g., nitrate, phosphate, and silicate) are termed as nutrients [13]. These nutrients are essential for the survival of marine organisms, such as promoting the growth of biology and microorganisms. Besides, accurate quantification of these nutrients is also necessary for forecasting the occurrence of harmful red tides and comprehending the dynamics of marine ecosystems [14]. On the contrary, inadequate nutrients will restrict the growth of phytoplankton and excessive nutrients are prone to cause eutrophication and even further lead to harmful algal blooms, extreme depletion of DO, and even death of aquatic organism [12, 15].

Traditional nutrient monitoring is difficult to determine the distributions and variations of nutrients to support ocean environmental monitoring [16]. Because they are measured by manual processing of sampling: water is collected at known locations and times, preserved and transported to laboratory for analysis by standard detection methods such as spectrophotometry, colorimetry, or fluorescence [17]. Nevertheless, these traditional methods (1) cannot satisfy the long-term in situ monitoring demands of nutrient detection in seawater and (2) are rather costly and time-consuming with expensive and bulky high-tech instruments and professional operators. Moreover, these obtained data may be not accurate enough because these seawater samples may undergo unexpected reactions during the long-time operation [14].

Currently, sensors and sensing systems are applied for nutrient monitoring to obtain primary data, to assure time-series observations on remote permanent platforms [1]. Consequently, in situ nutrient sensors, the device placed on a mobile platform such as a submersible vehicle, have a unique and important role in ocean environmental monitoring [17]. Over the years, the development of low-cost portable devices that can be employed for onsite and continuous analysis of nutrients has been attracting scientific attention [18]. Now, various nutrient sensors, including electronic sensors, chemical sensors, and biosensors, have been widely

used for continuous observation in estuaries and seawater [19, 20]. And these nutrient sensors have been greatly improved during the past decades on accuracy, operability, sustainability, and other aspects [21–23]. Because of the unavoidable limitation of in situ seawater environment, the development of sensor technology has to be long duration of use, less wastewater output, low energy consumption, less reagent consumption, small volume, and strong ion selectivity. Some products with mature technology in market include Micro-Lab, EcoLAB2, and CYCL Phosphate sensors (Wetlabs, USA), SUNAV2 (Satlantic, Canada), and WIZ sensors (SYSTEAL, Italy) [24, 25]. However, the main bottlenecks that restrict the development of nutrient sensors are short duration, low precision, narrow range of detection concentration, and poor reproducibility [26, 27]. To be more specific, since sample pretreatment, such as enrichment and dilution, cannot be applied in the field detection of nutrients in seawater, an ideal chemical sensor needs to have a high precision and a wide measuring range. Taking precision of sensors (LOD, limit of detection) as another example, studies have shown that the nutrient concentrations in seawater before and after algal bloom in some oligotrophic zones are order of nmol/L, and the nutrient concentrations in the same sea area vary greatly in different sea areas and at different times, and the detected concentration ranges from nmol/L to $\mu\text{mol/L}$ (a difference of 5 orders of magnitude) [1, 28]. Hence, it is still necessary to utilize more appropriate methods to increase the precision of nutrient sensors in seawater, such as the limit of detection (LOD).

Previous valuable review papers have systemically reviewed either one analyte (or one group of analytes) or one category/type of sensors in seawater [1, 8, 9, 17, 29, 30]. With the increase of new literatures on nutrient sensors, how to utilize these resources to better service scientific development has been an important work. In this short critical review, after a brief introduction of necessity and need for higher precision of nutrient sensors in seawater, we collected related literatures focusing on the technological development of nutrient sensors in seawater and excluded those literatures focusing on application. We summarized the research status of nutrient sensors in seawater by quantity of literatures and then discussed the sensitivity of sensors (LOD) from two aspects of analytes and detection methods. Finally, a statistic analysis was performed to see if there existed any significant differences among five different detection methods (spectrophotometry, chromatography, colorimetry, electrochemistry, and fluorimetry) within one nutrient (nitrate, nitrite, phosphate, ammonia, and silicate). Being different from previous review papers, in this short critical review paper (1) we unified the unit of LOD to make the comparison within different researches possible; (2) only the literatures focusing on the technological development of sensors in seawater were used; and (3) not only the detection methods but also the detected analytes and publication years were discussed to supply more valuable information for the development of nutrient sensors applied in seawater. This brief review shows an important direction for the development of nutrient detection sensors in seawater and also the existing limitations and challenges.

TABLE 1: Summary of sensors for the nutrient detection in seawater.

Analytes	Detection methods	LOD (μM)	Ref.	Year
Phosphate	Fluorimetry	0.4000	[31]	2020
Phosphate	Colorimetry	2.4211	[32]	2020
Nitrate	Chromatography	0.2200	[33]	2020
Nitrate	Microfiber	2.7419	[34]	2020
Nitrite	Colorimetry	0.1000	[35]	2019
Nitrate	Spectrophotometry	0.0200	[36]	2019
Phosphate	Colorimetry	1.8947	[37]	2019
Ammonium		1.5000		
Nitrate	Spectrophotometry	0.2000	[38]	2019
Ammonium	Spectrophotometry	0.1500	[39]	2019
Ammonium	Fluorimetry	0.0021	[40]	2018
Nitrate	Spectrophotometry	0.0074	[41]	2018
Nitrate	Spectrophotometry	0.1000	[42]	2018
Phosphate	Spectrophotometry	0.1000	[43]	2018
Silicate	Electrochemistry	0.5000	[23]	2018
Nitrate	Electrochemistry	0.0009	[44]	2018
Nitrate	Electrochemistry	0.9000	[14]	2018
Ammonium	Spectrophotometry	0.2000	[45]	2018
Ammonium	Spectrophotometry	0.0800	[46]	2018
Ammonium	Fluorimetry	0.0065	[47]	2018
Nitrite	Electrochemistry	0.2000	[48]	2018
Silicate	Spectrophotometry	1.6000	[49]	2018
Ammonium	Fluorimetry	0.1600	[50]	2018
Phosphate	Spectrophotometry	0.1000	[43]	2018
Ammonium	Fluorimetry	0.0010	[51]	2017
Nitrate	Spectrophotometry	0.3000	[52]	2017
Nitrite		0.1000		
Phosphate		0.1000		
Ammonium		0.3000		
Silicate		0.2000		
Phosphate	Colorimetry	0.0300	[53]	2017
Nitrate	Electrochemistry	0.3900	[54]	2017
Nitrate	Electrochemistry	0.8000	[55]	2017
Phosphate	Colorimetry	0.0526	[56]	2017
Phosphate	Colorimetry	0.0300	[53]	2017
Phosphate	Colorimetry	0.1000	[57]	2017
Silicate	Optofluidics	0.0451	[58]	2017
Ammonium	Electrochemistry	0.6400	[59]	2017
Ammonium	Colorimetry	0.0150	[60]	2017
Nitrate	Electrochemistry	0.8000	[61]	2016
Nitrite	Fluorimetry	0.1000	[62]	2016
Ammonium	Fluorimetry	0.0074	[63]	2016
Phosphate	Spectrophotometry	0.0014	[64]	2016
Phosphate	Electrochemistry	0.1000	[65]	2016
Phosphate	Electrochemistry	4.0000	[66]	2016
Silicate	Electrochemistry	0.5000	[67]	2015
Nitrate	Microfluidics	5.0000	[68]	2015
Nitrate	Electrochemistry	3.8000	[69]	2015
Ammonium	Spectrophotometry	0.0055	[70]	2015

TABLE 1: Continued.

Analytes	Detection methods	LOD (μM)	Ref.	Year
Ammonium	Fluorimetry	0.0058	[71]	2015
Nitrate	Microfluidics	0.0250	[72]	2015
Nitrite		0.0200		
Phosphate	Fluorimetry	0.0145	[73]	2014
Ammonium	Spectrophotometry	0.0036	[74]	2014
Nitrate	Spectrophotometry	0.0300	[75]	2014
Ammonium	Fluorimetry	0.0100	[76]	2013
Phosphate	Colorimetry	0.0520	[77]	2013
Ammonium	Fluorimetry	0.0007	[78]	2013
Nitrate	Colorimetry	0.5000	[79]	2013
Phosphate	Colorimetry	0.3000		
Silicate	Colorimetry	1.0000		
Ammonium	Fluorimetry	0.3000	[80]	2013
Phosphate	Electrochemistry	0.1900		
Nitrate	Spectrophotometry	0.2000	[81]	2013
Nitrate	Spectrophotometry	1.9355	[82]	2012
Silicate	Electrochemistry	0.1000	[83]	2012
Nitrate	Microfluidics	0.0250	[84]	2012
Nitrite		0.0200		
Ammonium	Carbon nanotube	0.0100	[85]	2012
Nitrite	Colorimetry	0.0150	[86]	2011
Nitrate	Spectrophotometry	1.7000	[87]	2011
Ammonium	Fluorimetry	0.0130	[88]	2011
Ammonium	Fluorimetry	0.0010	[89]	2011
Ammonium	Spectrophotometry	0.0035	[90]	2011
Ammonium	Fluorimetry	0.0050	[91]	2011
Phosphate	Electrochemistry	0.1200	[25]	2011
Ammonium	Colorimetry	0.0150	[92]	2011
Nitrate	Spectrophotometry	0.2000	[93]	2010
Nitrate	Spectrophotometry	0.3000	[94]	2010
Nitrate	Electrochemistry	10.0000	[95]	2010
Nitrite	Spectrophotometry	0.1000	[96]	2009
Nitrate	Electrochemistry	0.014	[97]	2009
Nitrate	Electrochemistry	0.0002	[98]	2008
Nitrate	Microfluidics	4.5000	[99]	2008
Silicate	Electrochemistry	0.3000	[100]	2008
Ammonium	Fluorimetry	0.0011	[101]	2008
Silicate	Electrochemistry	0.3000	[100]	2008
Nitrate	Colorimetry	0.0020	[102]	2008
Nitrite		0.0020		
Phosphate	Spectrophotometry	0.0015	[103]	
Nitrite		0.0001		
Nitrate	Electrochemistry	4.5000	[104]	2007
Silicate	Electrochemistry	1.0000	[105]	2007
Nitrate	Spectrophotometry	2.0000	[106]	2006
Ammonium	Spectrophotometry	0.0050	[107]	2005
Nitrate	Electrochemistry	1.0000	[108]	2005
Phosphate	Fluorimetry	0.0200	[109]	2003
	Spectrophotometry		[110]	2003

TABLE 1: Continued.

Analytes	Detection methods	LOD (μM)	Ref.	Year
Nitrate		0.1000		
Silicate		0.5000		
Phosphate		0.1000		
Nitrate	Spectrophotometry	0.2000	[111]	2002
Nitrate	Spectrophotometry	0.0452	[112]	2002
Nitrate	Spectrophotometry	0.0452	[112]	2002
Nitrite	Fluorimetry	0.0046	[113]	2000
Nitrate		0.0069		
Nitrate	Spectrophotometry	0.0226	[114]	1999
Nitrate	Spectrophotometry	0.1000	[115]	1998
Nitrate	Electrochemistry	0.1000	[116]	1994

2. Materials and Methods

2.1. Database Compilation. We build this database using the following topics searched in core database of Web of Science (1985-2020): “sensor” and “seawater or sea water or saline water or marine water or salt water or ocean” and “nutrient or nitrate or nitrite or phosphate or ammonia or silicate” in July 2020. Here, for supplying more valuable information for the development of nutrient sensors applied in seawater, we just collected literatures focusing on the technological development of sensors, excluded those focusing on application. In total, 42.21% of the screened literatures were published during the last five years (2016-2020). For each literature, we extracted the information: tested analytes, detection method of sensors, LOD, and publication year. All tested analytes were categorized into phosphate, nitrite, nitrate, ammonium, and silicate. As for the detection methods, we included spectrophotometry (ultraviolet spectrophotometry, visible light spectrophotometry), fluorimetry, colorimetry (visual colorimetry, photoelectric colorimetry), chromatography, microfiber, microfluidics, electrochemistry, optofluidics, and carbon nanotube. We unified all the units of LODs as μM ($\mu\text{mol/L}$).

2.2. Data Analysis. We performed one-way ANOVA to test the differences of LODs among different detection methods within one analyte. All data were checked for normality before conducting the ANOVA tests and were log-transformed to meet normality and homogeneity assumptions [19]. If significant effects are present in the ANOVA, then Tukey’s test was used for post hoc analysis of significant differences among detection methods. All statistical analyses were performed by SPSS statistics software (IBM, 20.0).

3. Results and Discussions

3.1. Research Status of Nutrient Sensors in Seawater. To a certain extent, quantity of literatures could reflect scientific research status in this area. After screening from 538 literatures searched in the core database of Web of Science, we finally collected 109 literatures focusing on the technological development of nutrient sensors applied in seawater. Table 1

shows the summary of sensors for the nutrient detection in seawater. Here, we classified analytes mainly by phosphate, nitrate, ammonium, and silicate related to different detection methods with LOD and publication date.

From Table 2, we can see that the quantity of literatures has increased with the development of decades. In particular, during 2011-2020 in both analytes and detection methods, there are more literatures focusing on the technological development of sensors. Furthermore, this trend also means that more literatures may appear during the next ten years to meet the needs from all walks of life and from many different areas. Actually, nitrate determination was firstly taken by electrochemical methods in 1834 [117]. It has been attracting more attention in the world today from different perspectives. A review published in 2021 summarizes the advances in knowledge in terms of the modes of action of devices and deployment strategies, identifying the current limitations and future challenges for the electrochemical detection of nutrients in marine environments [118]. The application of electrochemical sensors including potentiometric, voltammetric, and field-effect transistor sensors for nitrate, nitrite, ammonium, and phosphate determination in aqueous environments was reviewed [16]. The recent advances in ISE sensing platforms for environmental water analysis from on board to in situ approaches were also reviewed [119].

In terms of quantity, the above obvious result may mainly attribute to (1) emerging technologies. In 2003, Thouron developed a system with three analysers to measure phosphate, nitrate, and silicate together [110]. And Zhang et al. fabricated a self-supported electrode to detect ammonia based on electrodeposition of platinum-polypyrrole on Ni foam [120]. New technologies also promote the improvement of old ones. For example, scientists improved the sensitivity measurement of nitrate concentration based on new dispersion turning point (DTP) theory [34]. Meanwhile, the emergence of new technologies also brings more detection methods. For example, phosphate was detected by interfacial barrier effects of p-n junction on electrochemistry [121]. (2) Some problems previously hard to study are solved. It was well known that not extensively researches had studied voltammetric sensors for nitrate detection in seawater, because the LOD data from sensors was usually above $1 \mu\text{M}$, higher than the nitrate concentrations in seawater, particularly the concentration of nitrate at the ocean surface (at a nanomolar level) [122]. Nine years later, Legrand et al. developed an electrode by electrodeposition of silver nanoparticles on a gold disc electrode to test nitrate in synthetic seawater [54]. The sensor showed a limit of quantification of $0.39 \mu\text{M}$ and a linear range of $0.39\text{-}50 \mu\text{M}$. The peak current intensity remained at 95% of the initial value after regular detection of $25 \mu\text{M}$ nitrate for about 26 days. And (3) more and more emerging contaminants interference is still a technical challenge. For example, the challenges of nitrate biosensors based on reductases include oxygen interference [123], low electron transfer efficiency [124, 125], and high cost and low storage temperature, which promote relevant research and generate more literatures.

Although the quantity of relevant literatures has been increasing steadily, the research status within both analytes

TABLE 2: Literature number of nutrient sensors.

Category	In total	Years	2011-2020	2001-2010	1994-2000
Analytes					
Nitrate	39	1994-2020	21	14	4
Nitrite	12	2000-2019	8	3	1
Phosphate	21	2003-2020	18	3	0
Ammonium	26	2005-2019	24	2	0
Silicate	11	2003-2018	7	4	0
Detection methods					
Spectrophotometry	38	1998-2019	24	12	2
Colorimetry	18	2008-2020	15	3	0
Fluorimetry	19	2000-2020	15	2	2
Electrochemistry	24	1994-2018	15	8	1
Chromatography	1	2020	1	0	0
Microfiber	1	2020	1	0	0
Microfluidics	6	2008-2020	5	1	0
Optofluidics	1	2017	1	0	0
Carbon nanotube	1	2012	1	0	0

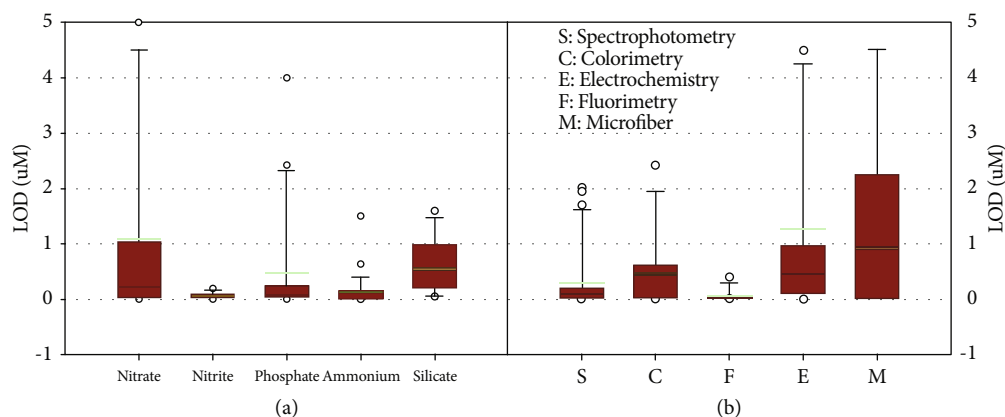


FIGURE 1: Average of LOD for (a) five nutrients and (b) five detection methods with more than five literatures. Green line: mean value.

and detection methods is very varied. For analytes, we can see that more research focused on nitrate, phosphate, and ammonium. This result should attribute to seriously increasing marine environmental and ecological problems, such as frequent red tide, green tide, and other ecological disasters [9, 10, 126]. Hence, for a period of time, literatures related to nitrate, phosphate, ammonium, and phosphate will continue to increase with more accurate data and new detection methods.

For the detection methods, we found a similar trend as one previous review paper that spectrophotometry, colorimetry, fluorimetry, and electrochemistry are the most commonly used sensors for the detection of nutrient detection in seawater [127]. These traditional and classic detection methods have been attracting a lot of attention for years, followed by emerging chromatography, microfiber, microfluidics, optofluidics, and carbon nanotube (Table 2). Then, other electrochemical sensors have been used for water analysis. As we know, we widely used electrochemical sensors as one of the most promising analytical tools for the rapid

detection of nitrate due to its high sensitivity, quick response, ease of operation and miniaturization, low sample and power consumption, low reagent consumption, and easy combination with automation devices [18, 128]. Nevertheless, some new methods also appeared with technical advantage. For example, a new method using a microfiber mode interferometric sensor to improve the sensitivity of nitrate concentration measurement in seawater based on dispersion turning point (DTP) theory is demonstrated [34]. Through interdisciplinary research within electronics, chemistry, materials science, etc., the application of microfluidic technology shows more advantages and gradually becomes a better way to further reduce energy consumption, reduce the amounts of reagents, and promote the miniaturization of sensors [129]. Therefore, more studies should focus on the development of new detection methods for clearer understanding of the nutrient in seawaters.

3.2. *Sensitivity of Nutrient Sensors in Seawater.* LODs in Table 1 show thousands of orders for different analytes and

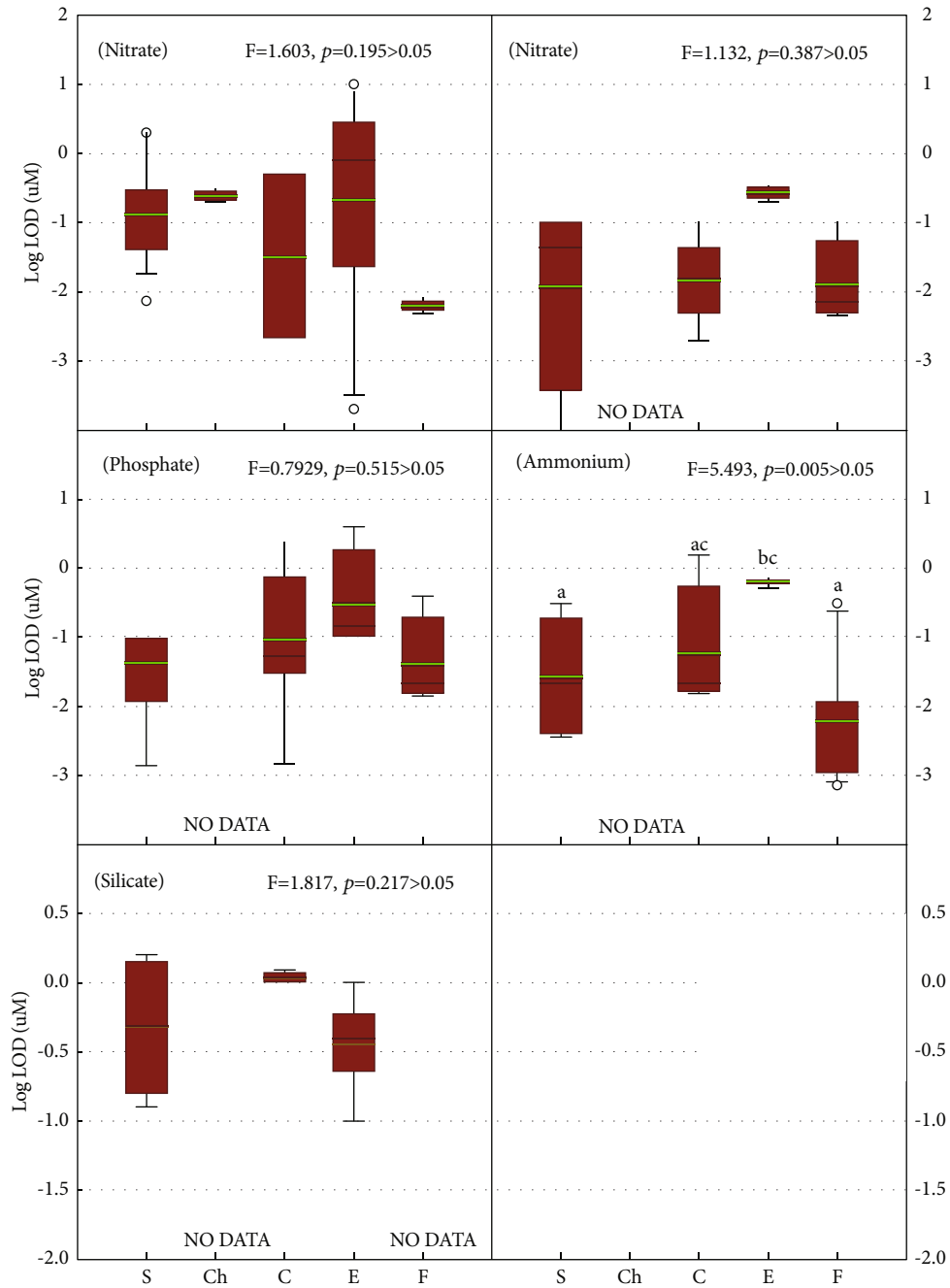


FIGURE 2: Analysis of one-way ANOVA for different detection methods. Green line: mean value. $p < 0.05$.

detection methods. Here, the average LOD of nutrient sensors included was μM . Among all the sensors checked, the most sensitive sensor was developed by Chen and Chumbimuni-Torres in which the indirect detection of nitrate through spectrophotometry and electrochemistry method was used [98, 103]. Above sensor could achieve an ultrasensitive LOD, as low as 0.1 nM [103]. By contrast, some other sensors are relatively “insensitive” with the LODs at the level of 2-10 μM , distributed from 2006 to 2016 [66, 68, 95, 104].

Figure 1(a) shows the average LOD of five nutrients at the level almost below $1\ \mu\text{M}$ with descending sequence: nitrate (1.0983) > silicate (0.5495) > phosphate (0.4823) >

ammonium (0.1324) > nitrite (0.0568). Figure 1(b) only shows the average LOD of five detection methods with more than five literatures at the level almost below $1\ \mu\text{M}$ (except for microfluidics at the level of $2\ \mu\text{M}$) with descending sequence: microfluidics (1.7617) > electrochemistry (1.2607) > colorimetry (0.4462) > spectrophotometry (0.2941) > fluorimetry (0.0558). For the rest four detection methods, chromatography, microfiber, optofluidics, and carbon nanotube have a LOD of 0.2200, 2.7419, 0.0451, and 0.01, respectively.

In general, both detection of nitrite and ammonium and fluorimetry method seem to have lower LODs (Figure 1).

Nevertheless, we cannot just draw a simple conclusion that these related research develop best. This result could mainly attribute to the following: (1) some new literatures based on special detection technique usually increase the mean value with their own high LODs. For example, Yang et al. used a new technique to improve the sensitivity of sodium nitrate concentration measurement in seawater based on dispersion turning point [34]. Although the sensor shows advantages of easy to construct, low cost, high precision, and high sensitivity, which provides a new optical detection method for in situ detection of marine environment or low concentration substances sensing in other liquids, its LOD is $2.7419 \mu\text{M}$. The same situation applies to Khongpet et al. who used a compact hydrodynamic sequential injection system for consecutive online determination of phosphate and ammonium, with a LOD $1.8947 \mu\text{M}$ [37]. On a long view, these technologies are constantly developing with lower LOD. And more literatures related to these technologies will finally lower the average LOD. Before we get too excited about that, we may have to face the situation that the emergence of other new technologies (in embryonic stage) may increase the mean value with their own high LODs, again. (2) Different detection methods have their own special value. For example, a variety of approaches have been used for the determination of phosphate in seawater, including colorimetric detection, fluorescent detection, and electrochemical detection. For all are reagent-based methods, phosphate cannot be detected directly. Therefore, autonomous systems tend to employ the colorimetric method rather than fluorescent or electrochemical methods [130]. Previous study has shown that when algal blooms erupt, the nutrient concentration in seawater is on the order of 10^{-9} mol/L [131]. So it is very necessary to utilize more appropriate methods to increase the accuracy of the sensor. In addition to accuracy, the nutrient concentration in the same sea area varies significantly at different times or in different sea areas and the ranges from 10^{-9} to 10^{-6} mol/L, with a difference of 5 orders of magnitude [131]. Hence, an ideal sensor should better have wide measurement range.

3.3. Comparison of Detection Methods. Figure 2 shows the result of analysis of one-way ANOVA for different detection methods ($p < 0.05$). In general, at the present stage, we could see that not all methods (NO DATA) can be used for detection within one nutrient in seawaters such as chromatography to nitrite, phosphate, ammonium, and silicate (Figure 2). Clearly, future studies should focus on the development of chromatography sensors applied in seawater.

Furthermore, except ammonium ($p < 0.05$), there were no significant differences among different detection methods applied in any nutrient sensor. This result indicated that, for nitrate, nitrite, phosphate, and silicate, their development level of detection methods is closer to each other. For ammonium, spectrophotometry has a significantly lower LOD than electrochemistry ($p < 0.05$), and fluorimetry also has a significantly lower LOD than electrochemistry ($p < 0.05$). This result is in accordance with the consensus that electrochemical sensors have been widely used as one of the most promising analytical tools for the rapid detection

of nitrate in environmental matrices due to low sample and power consumption, high sensitivity, quick response, and ease of operation and miniaturization [18, 128].

4. Conclusions

From 109 literatures, the general status of nutrient detection sensors in seawater including the research status, sensitivity, detection methods, and future challenges was reviewed, with most published during 2011-2020. For analytes, literatures related to nitrate, phosphate, ammonium, and phosphate will continue to increase with more accurate data. For detection methods, spectrophotometry, colorimetry, fluorimetry, and electrochemistry are the most widely used sensors. LODs show thousands of orders. In general, there are lower LOD to nitrite and ammonium and fluorimetry method. Now, for analytes, nitrate (1.0983) > silicate (0.5495) > phosphate (0.4823) > ammonium (0.1324) > nitrite (0.0568). For detection methods, microfluidics (1.7617) > electrochemistry (1.2607) > colorimetry (0.4462) > spectrophotometry (0.2941) > fluorimetry (0.0558). This result indicated that the development level of detection methods is closer for nitrate, nitrite, phosphate, and silicate. For ammonium, spectrophotometry has significantly lower LOD than electrochemistry ($p < 0.05$), and fluorimetry also has significantly lower LOD than electrochemistry ($p < 0.05$). Our results are expected to indicate that higher sensitivity sensors should be developed in the future. In addition, more detection methods should be considered by future sensors. We can see that although the stability, sensitivity, and detection limit of sensors have greatly improved, there are still some certain technical issues that restrict the large-scale use of this technology, including low reproducibility, low accuracy, narrow detection concentration ranges, and short continuous measurement time. Besides, good stability is important to an ideal sensor achieved by improving sensor antifouling ability, which is a hot topic partially in biocompatibility and blood compatibility [132]. So, it is a feasible solution to further explore new antifouling materials and approaches for maintaining long-term sensor durability and stability. In short, this brief review shows an important direction for the development of nutrient detection sensors in seawater and many limitations and challenges still existed. Clearly, much work still needs to be done in many areas of sensor development and for a variety of seawater environments.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Authors' Contributions

Lina Cao and Hongyong Xiang have equal contributions.

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References

- [1] C. Whitt, J. Pearlman, B. Polagye et al., “Future vision for autonomous ocean observations,” *Science*, vol. 7, 2020.
- [2] X. Hongyong, K. Li, L. Cao, Z. Zhang, and H. Yang, “Impacts of pollution, sex, and tide on the time allocations to behaviours of *Uca arcuata* in mangroves,” *Science of the Total Environment*, vol. 742, article 140609, 2020.
- [3] M. G. Mostofa Khan, C.-Q. Liu, W. Zhai et al., “Reviews and syntheses: ocean acidification and its potential impacts on marine ecosystems,” *Biogeosciences*, vol. 13, no. 6, pp. 1767–1786, 2016.
- [4] N. L. Williams, L. W. Juranek, K. S. Johnson et al., “Empirical algorithms to estimate water column pH in the Southern Ocean,” *Geophysical Research Letters*, vol. 43, no. 7, pp. 3415–3422, 2016.
- [5] S. D. Thomson, R. C. Quinn, A. J. Ricco, and J. E. Koehne, “Electrochemistry for life detection on ocean worlds,” *Chem-electrochem*, vol. 7, no. 3, pp. 614–623, 2020.
- [6] L. D. Talley, I. Rosso, I. Kamenkovich et al., “Southern Ocean biogeochemical float deployment strategy, with example from the Greenwich meridian line (GO-SHIP A12),” *Journal of Geophysical Research-Oceans*, vol. 124, no. 1, pp. 403–431, 2019.
- [7] I. L. Justino Celine, A. C. Freitas, A. C. Duarte, A. P. Teresa, and R. Santos, “Sensors and biosensors for monitoring marine contaminants,” *Analytical Chemistry*, vol. 6-7, pp. 21–30, 2015.
- [8] M. Graham and G. Fones, “A review of in situ methods and sensors for monitoring the marine environment,” *Sensor Review*, vol. 32, no. 1, pp. 17–28, 2012.
- [9] D. L. Li, X. B. Xu, Z. Li, T. Wang, and C. Wang, “Detection methods of ammonia nitrogen in water: a review,” *Analytical Chemistry*, vol. 127, article 115890, 2020.
- [10] T. Toste, S. Pouliquen, J. Hausman et al., “Ocean FAIR data services,” *Frontiers in Marine Science*, vol. 6, 2019.
- [11] A. J. Birchill, G. Clinton-Bailey, R. Hanz et al., “Realistic measurement uncertainties for marine macronutrient measurements conducted using gas segmented flow and lab-on-chip techniques,” *Talanta*, vol. 200, pp. 228–235, 2019.
- [12] F. Wang, J. M. Zhu, L. F. Chen, Y. F. Zuo, X. J. Hu, and Y. Yang, “Autonomous and in situ ocean environmental monitoring on optofluidic platform,” *Micromachines*, vol. 11, no. 1, p. 69, 2020.
- [13] M. Li, K. Xu, M. Watanabe, and Z. Chen, “Long-term variations in dissolved silicate, nitrogen, and phosphorus flux from the Yangtze River into the East China Sea and impacts on estuarine ecosystem,” *Estuarine, Coastal and Shelf Science*, vol. 71, no. 1-2, pp. 3–12, 2007.
- [14] C. Maria, G. Crespo, T. Cherubini et al., “In situ detection of macronutrients and chloride in seawater by submersible electrochemical sensors,” *Analytical Chemistry*, vol. 90, no. 7, pp. 4702–4710, 2018.
- [15] J. C. Robidart, J. D. Magasin, I. N. Shilova et al., “Effects of nutrient enrichment on surface microbial community gene expression in the oligotrophic North Pacific Subtropical Gyre,” *The ISME Journal*, vol. 13, no. 2, pp. 374–387, 2019.
- [16] C. Xiaoyan, G. Zhou, S. Mao, and J. Chen, “Rapid detection of nutrients with electronic sensors: a review,” *Environmental Science-Nano*, vol. 5, no. 4, pp. 837–862, 2018.
- [17] A. M. Nightingale, A. D. Beaton, and M. C. Mowlem, “Trends in microfluidic systems for in situ chemical analysis of natural waters,” *Sensors and Actuators B-Chemical*, vol. 221, pp. 1398–1405, 2015.
- [18] J. Chunbo, Y. He, and Y. Liu, “Recent advances in sensors for electrochemical analysis of nitrate in food and environmental matrices,” *Analyst*, vol. 145, no. 16, pp. 5400–5413, 2020.
- [19] X. Hongyong, Q. Cai, Y. Li et al., “Sensors applied for the detection of pesticides and heavy metals in freshwaters,” *Journal of Sensors*, vol. 2020, 22 pages, 2020.
- [20] A. G. Vincent, R. W. Pascal, A. D. Beaton et al., “Nitrate drawdown during a shelf sea spring bloom revealed using a novel microfluidic in situ chemical sensor deployed within an autonomous underwater glider,” *Marine Chemistry*, vol. 205, pp. 29–36, 2018.
- [21] C. Frank, D. Meier, D. Voß, and O. Zielinski, “Computation of nitrate concentrations in coastal waters using an in situ ultraviolet spectrophotometer: behavior of different computation methods in a case study a steep salinity gradient in the southern North Sea,” *Methods in Oceanography*, vol. 9, pp. 34–43, 2014.
- [22] J. R. Etheridge, F. Birgand, J. A. Osborne, C. L. Osburn, M. R. Burchell II, and J. Irving, “Using in situ ultraviolet-visual spectroscopy to measure nitrogen, carbon, phosphorus, and suspended solids concentrations at a high frequency in a brackish tidal marsh,” *Limnology and Oceanography: Methods*, vol. 12, no. 1, p. 10, 2014.
- [23] C. Barus, D. C. Legrand, N. Striebig et al., “First deployment and validation of in situ silicate electrochemical sensor in seawater,” *Frontiers in Marine Science*, vol. 5, 2018.
- [24] D. Aguilar, C. Barus, W. Giraud et al., “Silicon-based electrochemical microdevices for silicate detection in seawater,” *Sensors and Actuators, B: Chemical*, vol. 211, pp. 116–124, 2015.
- [25] J. Jońca, V. León Fernández, D. Thouron, A. Paulmier, M. Graco, and V. Garçon, “Phosphate determination in seawater: toward an autonomous electrochemical method,” *Talanta*, vol. 87, no. 1, pp. 161–167, 2011.
- [26] K. S. Johnson, J. A. Needoba, S. C. Riser, and W. J. Showers, “Chemical sensor networks for the aquatic environment,” *Chemical Reviews*, vol. 107, no. 2, pp. 623–640, 2007.
- [27] Z. Ye, J. Yang, N. Zhong, X. Tu, J. Jia, and J. Wang, “Tackling environmental challenges in pollution controls using artificial intelligence: a review,” *Science of the Total Environment*, vol. 699, p. 134279, 2020.
- [28] L. R. Adornato, E. A. Kaltenbacher, D. R. Greenhow, and R. H. Byrne, “High-resolution in situ analysis of nitrate and phosphate in the oligotrophic ocean,” *Environmental Science and Technology*, vol. 41, no. 11, pp. 4045–4052, 2007.

- [29] C. D. M. Campos and J. A. F. da Silva, "Applications of autonomous microfluidic systems in environmental monitoring," *Advances*, vol. 3, no. 40, pp. 18216–18227, 2013.
- [30] R. D. Prien, "The future of chemical in situ sensors," *Marine Chemistry*, vol. 107, no. 3, pp. 422–432, 2007.
- [31] J. M. Zhu, G. W. Han, X. J. Hu et al., "A portable and accurate phosphate sensor using a gradient Fabry–Pérot array," *Acs Sensors*, vol. 5, no. 5, pp. 1381–1388, 2020.
- [32] J. M. Racicot, T. L. Mako, A. Olivelli, and M. Levine, "A paper-based device for ultrasensitive, colorimetric phosphate detection in seawater," *Sensors*, vol. 20, no. 10, p. 2766, 2020.
- [33] T. L. Mako, A. M. Levenson, and M. Levine, "Ultrasensitive detection of nitrite through implementation of N-(1-naphthyl)ethylenediamine-grafted cellulose into a paper-based device," *Acs Sensors*, vol. 5, no. 4, pp. 1207–1215, 2020.
- [34] L. Yang, J. Wang, S. S. Wang, Y. P. Liao, and Y. Li, "A new method to improve the sensitivity of nitrate concentration measurement in seawater based on dispersion turning point," *Optik*, vol. 205, p. 164202, 2020.
- [35] S. C. Morgan, A. D. Hendricks, M. L. Seto, and V. J. Sieben, "A magnetically tunable check valve applied to a lab-on-chip nitrite sensor," *Sensors*, vol. 19, no. 21, p. 4619, 2019.
- [36] F. Tengyue, P. Li, K. Lin et al., "Simultaneous underway analysis of nitrate and nitrite in estuarine and coastal waters using an automated integrated syringe-pump-based environmental-water analyzer," *Analytica Chimica Acta*, vol. 1076, pp. 100–109, 2019.
- [37] W. Khongpet, S. Pencharee, C. Puangpila, S. K. Hartwell, S. Lapanantnoppakhun, and J. Jakmunee, "A compact hydrodynamic sequential injection system for consecutive on-line determination of phosphate and ammonium," *Microchemical Journal*, vol. 147, pp. 403–410, 2019.
- [38] K. S. Johnson, S. C. Riser, and M. Ravichandran, "Oxygen variability controls denitrification in the Bay of Bengal oxygen minimum zone," *Geophysical Research Letters*, vol. 46, no. 2, pp. 804–811, 2019.
- [39] L. Peicong, Y. Deng, H. Shu et al., "High-frequency underway analysis of ammonium in coastal waters using an integrated syringe-pump-based environmental-water analyzer (i SEA)," *Talanta*, vol. 195, pp. 638–646, 2019.
- [40] Z. Yong, J. Chen, X. Shi et al., "Development and application of a portable fluorescence detector for shipboard analysis of ammonium in estuarine and coastal waters," *Analytical Methods*, vol. 10, no. 15, pp. 1781–1787, 2018.
- [41] M. Eichhorn, C. Ament, M. Jacobi et al., "Modular AUV system with integrated real-time water quality analysis," *Sensors*, vol. 18, no. 6, p. 1837, 2018.
- [42] D. Meyer, R. D. Prien, L. Rautmann, M. Pallentin, J. J. Waniek, and D. E. Schulz-Bull, "In situ determination of nitrate and hydrogen sulfide in the Baltic Sea using an ultraviolet spectrophotometer," *Frontiers in Marine Science*, vol. 5, 2018.
- [43] S. Sateanchok, N. Pankratova, M. Cuartero, T. Cherubini, K. Grudpan, and E. Bakker, "In-line seawater phosphate detection with ion-exchange membrane reagent delivery," *Acs Sensors*, vol. 3, no. 11, pp. 2455–2462, 2018.
- [44] L. Emilie, P. Fau, M. Comtat et al., "In situ metalorganic deposition of silver nanoparticles on gold substrate and square wave voltammetry: a highly efficient combination for nanomolar detection of nitrate ions in sea water," *Chem*, vol. 6, no. 4, p. 50, 2018.
- [45] M. Jian, P. Li, K. Lin et al., "Optimization of a salinity-interference-free indophenol method for the determination of ammonium in natural waters using o-phenylphenol," *Talanta*, vol. 179, pp. 608–614, 2018.
- [46] L. Kunning, P. Li, W. Qiaoling, S. Feng, J. Ma, and D. Yuan, "Automated determination of ammonium in natural waters with reverse flow injection analysis based on the indophenol blue method with o-phenylphenol," *Microchemical Journal*, vol. 138, pp. 519–525, 2018.
- [47] Z. Min, T. Zhang, Y. Liang, and Y. Pan, "Toward sensitive determination of ammonium in field: a novel fluorescent probe, 4,5-dimethoxyphthalaldehyde along with a hand-held portable laser diode fluorometer," *Sensors and Actuators B-Chemical*, vol. 276, pp. 356–361, 2018.
- [48] Y. Zhang, J. T. Nie, H. Y. Wei et al., "Electrochemical detection of nitrite ions using Ag/Cu/MWNT nanoclusters electrodeposited on a glassy carbon electrode," *Sensors and Actuators B-Chemical*, vol. 258, pp. 1107–1116, 2018.
- [49] X. Cao, S. W. Zhang, D. Z. Chu, N. Wu, H. K. Ma, and R. Ma, "Development of lab-on-chip spectrophotometric silicate sensor in situ analysis of seawater," *Spectroscopy and Spectral Analysis*, vol. 38, no. 3, pp. 895–900, 2018.
- [50] C. Wang, Z. Li, Z. L. Pan, and D. L. Li, "Development and characterization of a highly sensitive fluorometric transducer for ultra low aqueous ammonia nitrogen measurements in aquaculture," *Computers and Electronics in Agriculture*, vol. 150, pp. 364–373, 2018.
- [51] G. Georgia, E. Trikas, M. Petala, T. Karapantsios, G. Zachariadis, and A. Anthemidis, "An integrated sequential injection analysis system for ammonium determination in recycled hygiene and potable water samples for future use in manned space missions," *Microchemical Journal*, vol. 133, pp. 490–495, 2017.
- [52] H. L. Wang, S. W. Zhang, C. L. Guo, and D. Z. Chu, "Development of an in-situ analyzer for nutrient monitoring in seawater," in *In Proceedings of the 2017 6th International Conference on Energy, Environment and Sustainable Development*, pp. 550–553, Zhuhai, China, 2017.
- [53] M. M. Grand, G. S. Clinton-Bailey, A. D. Beaton et al., "A lab-on-chip phosphate analyzer for long-term in situ monitoring at fixed observatories: optimization and performance evaluation in estuarine and oligotrophic coastal waters," *Frontiers in Marine Science*, vol. 4, p. 4, 2017.
- [54] L. D. Chen, C. Barus, and V. Garcon, "Square wave voltammetry measurements of low concentrations of nitrate using Au/AgNPs electrode in chloride solutions," *Electroanalysis*, vol. 29, no. 12, pp. 2882–2887, 2017.
- [55] N. Pankratova, M. Cuartero, T. Cherubini, G. A. Crespo, and E. Bakker, "In-line acidification for potentiometric sensing of nitrite in natural waters," *Analytical Chemistry*, vol. 89, no. 1, pp. 571–575, 2017.
- [56] D. Gillian, I. Maguire, B. Heery, C. Nwankire, J. Ducree, and F. Regan, "PhosphaSense: a fully integrated, portable lab-on-a-disc device for phosphate determination in water," *Sensors and Actuators B-Chemical*, vol. 246, pp. 1085–1091, 2017.
- [57] J. M. Zhu, Y. Shi, X. Q. Zhu et al., "Optofluidic marine phosphate detection with enhanced absorption using a Fabry–Pérot resonator," *Lab on a Chip*, vol. 17, no. 23, pp. 4025–4030, 2017.
- [58] X. Cao, S. W. Zhang, D. Z. Chu, N. Wu, H. K. Ma, and Y. Liu, "A design of spectrophotometric microfluidic chip sensor for analyzing silicate in seawater," in *In 3rd International*

Conference on Water Resource and Environment, Qingdao, China, 2017.

- [59] L. Ding, J. W. Ding, B. J. Ding, and W. Qin, "Solid-contact potentiometric sensor for the determination of total ammonia nitrogen in seawater," *International Journal of Electrochemical Science*, vol. 12, no. 4, pp. 3296–3308, 2017.
- [60] L. O. Šraj, M. I. Almeida, M. K. ID, and S. D. Kolev, "Determination of trace levels of ammonia in marine waters using a simple environmentally-friendly ammonia (SEA) analyser," *Marine Chemistry*, vol. 194, pp. 133–145, 2017.
- [61] P. Nadezda, M. G. Afshar, D. Yuan, G. A. Crespo, and E. Bakker, "Local acidification of membrane surfaces for potentiometric sensing of anions in environmental samples," *Acs Sensors*, vol. 1, no. 1, pp. 48–54, 2016.
- [62] C. Chen, Z. Q. Yuan, H. T. Chang, F. N. Lu, Z. H. Li, and C. Lu, "Silver nanoclusters as fluorescent nanosensors for selective and sensitive nitrite detection," *Analytical Methods*, vol. 8, no. 12, pp. 2628–2633, 2016.
- [63] Z. Yong, D. Yuan, H. Lin, and T. Zhou, "Determination of ammonium in seawater by purge-and-trap and flow injection with fluorescence detection," *Analytical Letters*, vol. 49, no. 5, pp. 665–675, 2016.
- [64] S. X. Li, W. J. Liang, F. Y. Zheng, H. F. Zhou, X. F. Lin, and J. B. Cai, "Lysine surface modified $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ microspheres-based preconcentration and photocatalysis for in situ selective determination of nanomolar dissolved organic and inorganic phosphorus in seawater," *Actuators B-Chemical*, vol. 224, pp. 48–54, 2016.
- [65] C. Barus, I. Romanytsia, N. Striebig, and V. Garcon, "Toward an *in situ* phosphate sensor in seawater using square wave voltammetry," *Talanta*, vol. 160, pp. 417–424, 2016.
- [66] S. Cinti, D. Talarico, G. Palleschi, D. Moscone, and F. Arduini, "Novel reagentless paper-based screen-printed electrochemical sensor to detect phosphate," *Analytica Chimica Acta*, vol. 919, pp. 78–84, 2016.
- [67] D. Aguilar, C. Barus, W. Giraud et al., "Silicon-based electrochemical microdevices for silicate detection in seawater [J]," *Sensors and Actuators B-Chemical*, vol. 211, pp. 116–124, 2015.
- [68] C. Deirdre, C. Fay, D. Boyle et al., "Development of a low cost microfluidic sensor for the direct determination of nitrate using chromotropic acid in natural waters," *Analytical Methods*, vol. 7, no. 13, pp. 5396–5405, 2015.
- [69] C. Maria, G. A. Crespo, and E. Bakker, "Tandem electrochemical desalination-potentiometric nitrate sensing for seawater analysis," *Analytical Chemistry*, vol. 87, no. 16, pp. 8084–8089, 2015.
- [70] K. Taketoshi, T. Ichikawa, K. Hidaka, and K. Furuya, "A highly sensitive and large concentration range colorimetric continuous flow analysis for ammonium concentration," *Journal of Oceanography*, vol. 71, no. 1, pp. 65–75, 2015.
- [71] L. Ying, Y. Pan, Q. Guo, H. Hongzhi, W. Chancui, and Q. Zhang, "A novel analytical method for trace ammonium in freshwater and seawater using 4-methoxyphthalaldehyde as fluorescent reagent," *Journal of Analytical Methods in Chemistry*, vol. 2015, 7 pages, 2015.
- [72] M. Yucel, A. D. Beaton, M. Dengler, M. C. Mowlem, F. Sohl, and S. Sommer, "Nitrate and nitrite variability at the seafloor of an oxygen minimum zone revealed by a novel microfluidic in-situ chemical sensor," *PLoS One*, vol. 10, no. 7, article e0132785, 2015.
- [73] L. Krockel, H. Lehmann, T. Wieduwilt, and M. A. Schmidt, "Fluorescence detection for phosphate monitoring using reverse injection analysis," *Talanta*, vol. 125, pp. 107–113, 2014.
- [74] Z. Yong, D. Yuan, Y. Huang, J. Ma, S. Feng, and K. Lin, "A modified method for on-line determination of trace ammonium in seawater with a long-path liquid waveguide capillary cell and spectrophotometric detection," *Marine Chemistry*, vol. 162, pp. 114–121, 2014.
- [75] K. Wild-Allen and M. Rayner, "Continuous nutrient observations capture fine-scale estuarine variability simulated by a 3D biogeochemical model," *Marine Chemistry*, vol. 167, pp. 135–149, 2014.
- [76] A. Natchanon, J.-Z. Zhang, P. B. Ortner, J. Stamates, M. Shoemaker, and M. W. Kindel, "A portable analyser for the measurement of ammonium in marine waters," *Environmental Science-Processes & Impacts*, vol. 15, no. 3, pp. 579–584, 2013.
- [77] L. Francois-Eric, V. J. Sieben, E. Malcolm et al., "A high performance microfluidic analyser for phosphate measurements in marine waters using the vanadomolybdate method," *Talanta*, vol. 116, pp. 382–387, 2013.
- [78] Z. Yong, D. Yuan, Y. Huang, J. Ma, and S. Feng, "A sensitive flow-batch system for on board determination of ultra-trace ammonium in seawater: method development and shipboard application," *Analytica Chimica Acta*, vol. 794, pp. 47–54, 2013.
- [79] M. Gilbert, J. Needoba, C. Koch, A. Barnard, and A. Baptista, "Nutrient loading and transformations in the Columbia River estuary determined by high-resolution in situ sensors," *Estuaries and Coasts*, vol. 36, no. 4, pp. 708–727, 2013.
- [80] J. Jonca, W. Giraud, C. Barus et al., "Reagentless and silicate interference free electrochemical phosphate determination in seawater," *Electrochimica Acta*, vol. 88, pp. 165–169, 2013.
- [81] K. S. Johnson, L. J. Coletti, H. W. Jannasch, C. M. Sakamoto, D. D. Swift, and S. C. Riser, "Long-term nitrate measurements in the ocean using the in situ ultraviolet spectrophotometer: sensor integration into the APEX profiling float," *Journal of Atmospheric and Oceanic Technology*, vol. 30, no. 8, pp. 1854–1866, 2013.
- [82] L. Bulgariu and D. Bulgariu, "Direct determination of nitrate in small volumes of natural surface waters using a simple spectrophotometric method," *Reviews in Analytical Chemistry*, vol. 31, no. 3–4, pp. 201–207, 2012.
- [83] W. Giraud, L. Lesven, J. Jonca et al., "Reagentless and calibrationless silicate measurement in oceanic waters," *Talanta*, vol. 97, pp. 157–162, 2012.
- [84] A. D. Beaton and L. Christopher, "Lab-on-chip measurement of nitrate and nitrite for in situ analysis of natural waters," *Environmental Science & Technology*, vol. 46, no. 17, pp. 9548–9556, 2012.
- [85] C. W. Jang, Y. T. Byun, and Y. M. Jhon, "Detection of 10 nM ammonium ions in 35‰ NaCl solution by carbon nanotube based sensors," *Journal of Nanoscience and Nanotechnology*, vol. 12, no. 3, pp. 1765–1769, 2012.
- [86] A. D. Beaton and J. Vincent, "An automated microfluidic colourimetric sensor applied *in situ* to determine nitrite concentration," *Sensors and Actuators B-Chemical*, vol. 156, no. 2, pp. 1009–1014, 2011.
- [87] O. Zielinski, D. Voss, B. Saworski, B. Fiedler, and A. Kortzinger, "Computation of nitrate concentrations in

- turbid coastal waters using an in situ ultraviolet spectrophotometer,” *Journal of Sea Research*, vol. 65, no. 4, pp. 456–460, 2011.
- [88] H. Burkhard, C. M. Duarte, and V. Cerda, “A miniature and field-applicable multipumping flow analyzer for ammonium monitoring in seawater with fluorescence detection,” *Talanta*, vol. 85, no. 1, pp. 380–385, 2011.
- [89] A. Natchanon, J.-Z. Zhang, and P. B. Ortner, “An autonomous batch analyzer for the determination of trace ammonium in natural waters using fluorometric detection,” *Analytical Methods*, vol. 3, no. 7, pp. 1501–1506, 2011.
- [90] C. Guohe, M. Zhang, Z. Zhang, Y. Huang, and D. Yuan, “Online solid phase extraction and spectrophotometric detection with flow technique for the determination of nanomolar level ammonium in seawater samples,” *Analytical Letters*, vol. 44, no. 1-3, pp. 310–326, 2011.
- [91] S. K. Bey, A. Kaed, D. P. Connelly, F.-E. Legiret, A. J. K. Harris, and M. C. Mowlem, “A high-resolution analyser for the measurement of ammonium in oligotrophic seawater,” *Ocean Dynamics*, vol. 61, no. 10, pp. 1555–1565, 2011.
- [92] S. R. Alves, R. B. R. Mesquita, M. T. S. O. B. Ferreira, C. F. C. P. Teixeira, A. A. Bordalo, and A. O. S. S. Rangel, “Development of a sequential injection gas diffusion system for the determination of ammonium in transitional and coastal waters,” *Analytical Methods*, vol. 3, no. 9, pp. 2049–2055, 2011.
- [93] R. Pidcock, M. Srokosz, J. Allen et al., “A novel integration of an ultraviolet nitrate sensor on board a towed vehicle for mapping open-ocean submesoscale nitrate variability,” *Journal of Atmospheric and Oceanic Technology*, vol. 27, no. 8, pp. 1410–1416, 2010.
- [94] K. S. Johnson, S. C. Riser, and D. M. Karl, “Nitrate supply from deep to near-surface waters of the North Pacific subtropical gyre,” *Nature*, vol. 465, no. 7301, pp. 1062–1065, 2010.
- [95] F. Katia, V. Ynam, B. Chaudret, V. Garcon, D. Thouron, and M. Comtat, “An original nitrate sensor based on silver nanoparticles electrodeposited on a gold electrode,” *Electrochemistry Communications*, vol. 12, no. 10, pp. 1439–1441, 2010.
- [96] W. D. Gong, M. Mowlem, M. Kraft, and H. Morgan, “A simple, low-cost double beam spectrophotometer for colorimetric detection of nitrite in seawater,” *IEEE Sensors Journal*, vol. 9, no. 7, pp. 862–869, 2009.
- [97] J. N. Plant, K. S. Johnson, J. A. Needoba, and L. J. Coletti, “NH₄-Digiscan: an in situ and laboratory ammonium analyzer for estuarine, coastal, and shelf waters,” *Limnology and Oceanography: Methods*, vol. 7, no. 2, pp. 144–156, 2009.
- [98] K. Y. Chumbimuni-Torres, P. Calvo-Marzal, J. Wang, and E. Bakker, “Electrochemical sample matrix elimination for trace-level potentiometric detection with polymeric membrane ion-selective electrodes,” *Analytical Chemistry*, vol. 80, no. 15, pp. 6114–6118, 2008.
- [99] S. Aravamudhan and S. Bhansali, “Development of microfluidic nitrate-selective sensor based on doped- polypyrrole nanowires,” *Sensors and Actuators B-Chemical*, vol. 132, no. 2, pp. 623–630, 2008.
- [100] M. Lacombe, V. Garcon, D. Thouron, N. Le Bris, and M. Comtat, “Silicate electrochemical measurements in seawater: chemical and analytical aspects towards a reagentless sensor,” *Talanta*, vol. 77, no. 2, pp. 744–750, 2008.
- [101] A. Natchanon and J.-Z. Zhang, “Shipboard fluorometric flow analyzer for high-resolution underway measurement of ammonium in seawater,” *Analytical Chemistry*, vol. 80, no. 4, pp. 1019–1026, 2008.
- [102] A. Abbassi, A. Mihi, and R. Benbouda, “Monitoring of hydrogen generated by corrosion reactions of steel,” *Materials and Corrosion*, vol. 59, no. 12, pp. 942–947, 2008.
- [103] G. H. Chen, D. X. Yuan, Y. M. Huang, M. Zhang, and M. Bergman, “In-field determination of nanomolar nitrite in seawater using a sequential injection technique combined with solid phase enrichment and colorimetric detection,” *Analytica Chimica Acta*, vol. 620, no. 1-2, pp. 82–88, 2008.
- [104] S. Aravamudhan, S. Ketkar, and S. Bhansali, “Development of nitrate-selective electrochemical sensor with integrated micro-fluidics,” in *In 2007 Ieee Sensors*, Atlanta, GA, USA, 2007.
- [105] M. Lacombe, V. Garcon, M. Comtat et al., “Silicate determination in sea water: toward a reagentless electrochemical method,” *Marine Chemistry*, vol. 106, no. 3-4, pp. 489–497, 2007.
- [106] K. S. Johnson, L. J. Coletti, and F. P. Chavez, “Diel nitrate cycles observed with in situ sensors predict monthly and annual new production,” *Deep Sea Research Part I: Oceanographic Research Papers*, vol. 53, no. 3, pp. 561–573, 2006.
- [107] Q. P. Li, J. Z. Zhang, F. J. Millero, and D. A. Hansell, “Continuous colorimetric determination of trace ammonium in seawater with a long-path liquid waveguide capillary cell,” *Marine Chemistry*, vol. 96, no. 1-2, pp. 73–85, 2005.
- [108] N. Karousos, L. C. Chong, C. Ewen, C. Livingstone, and J. Davis, “Evaluation of a multifunctional indicator for the electroanalytical determination of nitrite,” *Electrochimica Acta*, vol. 50, no. 9, pp. 1879–1884, 2005.
- [109] Z. H. Xie, X. C. Lin, and G. N. Chen, “Novel phosphate-sensitive fluorescent composite matrix,” *Chemical Research in Chinese Universities*, vol. 19, no. 2, pp. 201–205, 2003.
- [110] D. Thouron, R. Vuillemin, X. Philippon et al., “An autonomous nutrient analyzer for oceanic long-term in situ biogeochemical monitoring,” *Analytical Chemistry*, vol. 75, no. 11, pp. 2601–2609, 2003.
- [111] K. S. Johnson and L. J. Coletti, “In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean,” *Deep-Sea Research Part I-Oceanographic Research Papers*, vol. 49, no. 7, pp. 1291–1305, 2002.
- [112] P. C. Gardolinski, A. R. David, and P. J. Worsfold, “Miniature flow injection analyser for laboratory, shipboard and in situ monitoring of nitrate in estuarine and coastal waters,” *Talanta*, vol. 58, no. 6, pp. 1015–1027, 2002.
- [113] R. T. Masserini and K. A. Fanning, “A sensor package for the simultaneous determination of nanomolar concentrations of nitrite, nitrate, and ammonia in seawater by fluorescence detection,” *Marine Chemistry*, vol. 68, no. 4, pp. 323–333, 2000.
- [114] A. R. J. David, T. McCormack, and P. J. Worsfold, “A submersible battery-powered flow injection (FI) sensor for the determination of nitrate in estuarine and coastal waters,” *Journal of Automated Methods & Management in Chemistry*, vol. 21, no. 1, pp. 1–9, 1999.
- [115] A. R. J. David, T. McCormack, A. W. Morris, and P. J. Worsfold, “A submersible flow injection-based sensor for the determination of total oxidised nitrogen in coastal waters,” *Analytica Chimica Acta*, vol. 361, no. 1-2, pp. 63–72, 1998.

- [116] H. W. Jannasch, K. S. Johnson, and C. M. Sakamoto, "Submersible, osmotically pumped analyzer for continuous determination of nitrate in situ," *Analytical Chemistry*, vol. 66, no. 20, pp. 3352–3361, 1994.
- [117] W. L. Pearce and Faraday Reprint, "Experimental researches in electricity. vols. 1 to 3. Michael Faraday. Dover, New York, 1965. Vols. 1 and 2, 896 pp. (bound as one volume); vol. 3, 602 pp. plates. \$15," *Science*, vol. 150, no. 3696, pp. 598–599, 1965.
- [118] W. Hong, D. Pan, and H. Han, "Electrochemical monitoring of marine nutrients: from principle to application," *TrAC Trends in Analytical Chemistry*, vol. 138, article 116242, 2021.
- [119] G. A. Crespo, "Recent advances in ion-selective membrane electrodes for in situ environmental water analysis," *Electrochimica Acta*, vol. 245, pp. 1023–1034, 2017.
- [120] Z. Liang, J. Wan, J. Li et al., "Fabricating a self-supported electrode for detecting ammonia in water based on electrodepositing platinum-polyppyrrrole on Ni foam," *Journal of the Electrochemical Society*, vol. 167, no. 2, 2020.
- [121] Y. Ding, M. G. Zhao, J. T. Yu, X. M. Zhang, Z. M. Li, and H. Li, "Using the interfacial barrier effects of p-n junction on electrochemistry for detection of phosphate," *Analyst*, vol. 145, no. 9, pp. 3217–3221, 2020.
- [122] M. D. Patey, M. J. A. Rijkenberg, P. J. Statham, M. C. Stinchcombe, E. P. Achterberg, and M. Mowlem, "Determination of nitrate and phosphate in seawater at nanomolar concentrations," *Analytical Chemistry*, vol. 27, no. 2, pp. 169–182, 2008.
- [123] P. Nicolas, "Interferences from oxygen reduction reactions in bioelectroanalytical measurements: the case study of nitrate and nitrite biosensors," *Analytical and Bioanalytical Chemistry*, vol. 405, no. 11, pp. 3731–3738, 2013.
- [124] A. Rafiq, K. S. Bhat, M.-S. Ahn, and Y.-B. Hahn, "Fabrication of a robust and highly sensitive nitrate biosensor based on directly grown zinc oxide nanorods on a silver electrode," *New Journal of Chemistry*, vol. 41, no. 19, pp. 10992–10997, 2017.
- [125] Z. Ke, H. Zhou, H. Ping, and L. Qing, "The direct electrochemistry and bioelectrocatalysis of nitrate reductase at a gold nanoparticles/aminated graphene sheets modified glassy carbon electrode," *RSC Advances*, vol. 9, no. 64, pp. 37207–37213, 2019.
- [126] A. E. Santoro, N. J. Nidzieko, G. L. Van Dijken, K. R. Arrigo, and A. B. Boehm, "Contrasting spring and summer phytoplankton dynamics in the nearshore Southern California Bight," *Limnology and Oceanography*, vol. 55, no. 1, pp. 264–278, 2010.
- [127] F. Monteiro-Silva, P. A. S. Jorge, and R. C. Martins, "Optical sensing of nitrogen, phosphorus and potassium: a spectrophotometrical approach toward smart nutrient deployment," *Chem*, vol. 7, no. 4, p. 51, 2019.
- [128] Z. Elena and E. Bakker, "Potentiometric sensing," *Analytical Chemistry*, vol. 91, no. 1, pp. 2–26, 2019.
- [129] S. A. Jaywant and K. M. Arif, "A comprehensive review of microfluidic water quality monitoring sensors," *Sensors*, vol. 19, no. 21, p. 4781, 2019.
- [130] K. Wanpen, S. Pancharee, C. Puangpila, S. K. Hartwell, S. Lapanantnoppakhun, and J. Jakmunee, "Exploiting an automated microfluidic hydrodynamic sequential injection system for determination of phosphate," *Talanta*, vol. 177, pp. 77–85, 2018.
- [131] K. Guebuem, Y.-W. Lee, D.-J. Joung, K.-R. Kim, and K. Kim, "Real-time monitoring of nutrient concentrations and red-tide outbreaks in the southern sea of Korea," *Geophysical Research Letters*, vol. 33, no. 13, 2006.
- [132] R.-V. M. Victor, J. R. Sempionatto, B. E.-F. de Avila et al., "Delayed sensor activation based on transient coatings: bio-fouling protection in complex biofluids," *Journal of the American Chemical Society*, vol. 140, no. 43, pp. 14050–14053, 2018.