Field Application of Automated Spectrophotometric Analyzer for High-Resolution In Situ Monitoring of pH in Dynamic Estuarine and Coastal Waters

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High quality pH measurements are required in estuarine and coastal waters to assess the impacts of anthropogenic atmospheric CO2 emissions on the marine carbonate system, including the resulting decrease in pH. In addition, pH measurements are needed to determine impacts on carbonate chemistry of phytoplankton blooms and their breakdown, following enhanced anthropogenic nutrient inputs. The spectrophotometric pH technique provides high quality pH data in seawater, and is advantageous for long-term deployments as it is not prone to drift and does not require in situ calibration. In this study, a field application of a fully automated submersible spectrophotometric analyzer for high-resolution in situ pH measurements in dynamic estuarine and coastal waters is presented. A Lab-on-Chip (LOC) pH sensor was deployed from a pontoon in the inner Kiel Fjord, southwestern Baltic Sea, for a total period of 6 weeks. We present a time-series of in situ pH_T (total pH scale) and ancillary data, with sensor validation using discretely collected samples for pH_T and laboratory analysis. The difference between the sensor and laboratory analyses of discrete samples was within ±0.015 pH_T unit, with a mean difference of 0.001 (n=65), demonstrating that the LOC sensor can provide stable and accurate pH_T measurements over several weeks.

Keywords: pH sensor, Lab-on-Chip, spectrophotometric, mCP, Kiel Fjord, coastal carbonate system, ocean acidification

INTRODUCTION

The oceans play a significant role in the global carbon cycle as one of the main reservoirs of carbon. Since the beginning of the Industrial Revolution, anthropogenic CO2 emissions have perturbed the exchange of CO2 between the atmosphere and oceans. Oceans have absorbed about a quarter of anthropogenic carbon dioxide (CO2) emissions (Friedlingstein et al., 2020), a process causing a long-term pH decrease (ocean acidification). To date, several studies have focused on determining the progression of ocean acidification by using long-term ocean observations datasets (Dore et al., 2009; Midorikawa et al., 2010; Hu et al., 2015; Van Dam and Wang, 2019; Ishida et al., 2021). Time-series measurements of surface ocean pH over the past two decades have reported a decrease of about 0.1 units since the pre-industrial era from ca. 8.2 to 8.1 (Orr et al., 2005). An additional
The traditional carbonate chemistry observations in marine systems are based on discrete water sample collection, storage, transportation, and land-based laboratory analysis. Discrete water samples for carbonate chemistry can be collected using dedicated samplers such as Niskin bottles, and then stored following poisoning using mercuric chloride until laboratory analysis for pH, DIC and A$_t$ using standard operational procedures (Dickson et al., 2007). pH can be determined directly using potentiometric or spectrophotometric techniques (Dickson et al. (2007), but also calculated via the CO2Sys software following e.g. A$_t$ and DIC measurements (Lewis and Wallace, 1998; Pierrot et al., 2006). The main limitations of this approach are the inadequate temporal resolution and duration and the high costs associated with the collection, preservation, shipping, and analysis of samples.

Advancements in marine technology and observational oceanography have enabled the development of miniaturized in situ pH sensors that can be integrated into stationary or autonomous platform for monitoring marine environments at a high temporal and spatial resolution (Sastri et al., 2019). To date, a range of pH sensors have been reported for autonomous in situ pH measurements, and are based on three different analytical methods, potentiometry (electrodes), fluorescence (optodes) and, spectrophotometry (indicator dyes). Table 1 presents examples of the current in situ pH sensors and their application in multiple oceanographic studies. Each system has a range of advantages and limitations (Rérolle et al., 2012; Rérolle et al., 2018; Sastri et al., 2019). Potentiometric pH sensors for seawater (i.e., Honeywell DuraFet Ion-Sensitive Field Effect Transistor (ISFET), SeaFET, SeapHOx) do not require chemical reagents and have a fast sampling frequency (6 seconds per measurement), but measurements are limited to a salinity range between 20 and 40 (Sea-Bird Electronics, Inc.). Besides, Honeywell DuraFet based pH sensors may be prone to drift (potentially more than 0.02 pH unit/week) (Rérolle et al., 2016), therefore require preconditioning of the electrode for 5 to 10 days and frequent calibrations (Sabine et al., 2004; Martz et al., 2010; Bresnahan et al., 2014; Mclaughlin et al., 2017; Miller et al., 2018). To date, the Deep Sea DuraFet sensor has been deployed on a range of profiling floats, and the assessment and correction for any potential drift to reduce bias in the pH measurements have been comprehensively evaluated by Johnson et al., 2016. Recent work introduced a self-calibrating SeapHOx system for seawater, periodic flushing of the sample cell with a calibration solution of Tris buffer in artificial seawater (Bresnahan et al., 2021), which is yet limited to seawater applications. The main limitations of fluorescent-based pH measurements are the interfering compounds of natural seawater (i.e., chlorophyll-a), drift with time, and the sensor spot is also light sensitive (Clarke et al., 2015). Staudinger et al. (2018) presented a stand-alone optode sensor system for pH, oxygen, and carbon dioxide with an integrated battery and logger and its short-term applications in the Baltic Sea and mentioned the need for drift correction and assessment of biofouling for long-term deployments.

The spectrophotometric method for pH, developed in the 1980s (Robert-Baldo et al., 1985), provides many advantages for marine studies as it is robust, stable, calibration-free
and not prone to drift (Rérolle et al., 2012). Under oceanic conditions, spectrophotometric pH measurement systems have demonstrated excellent performance (Clayton and Byrne, 1993; Bellerby et al., 2002; Aßmann et al., 2011; Rérolle et al., 2016). Commercially available, submersible spectrophotometric sensors (see Table 1, Lab-on-Chip (LOC) and SAMI-pH) have been successfully tested for fine-scale, autonomous and in situ monitoring of pH in a wide variety of environments, from freshwater (Martz et al., 2003) to seawater (Seidel et al., 2008; Rérolle et al., 2018; Yin et al., 2021). Indicator impurities and wavelength accuracy of spectrophotometers are some of the potential sources of uncertainty in spectrophotometric pH measurements, which DeGrandpre et al. (2014) has reported in detail. The quality of the pH data is related to how well the molar extinction coefficients and the second dissociation constant of an indicator dye have been determined as a function of sample temperature and salinity. To date, the experimental characterization and modelling of a meta-Cresol Purple (mCP) for estuarine (S ≤ 20, Mosley et al., 2004; Lai et al., 2016; Douglas and Byrne, 2017; Lai et al., 2017; Müller and Rehder, 2018) and hypersaline (35≤S ≤ 100, Loucaides et al., 2017) waters have been reported.

Recently, the capabilities of the LOC pH sensor have been successfully demonstrated on fixed and moving platforms under different environmental conditions, including deployments in surface waters of Southampton (S>24) for several months, and in deep ocean waters (~4820 m) (Yin et al., 2021). However, the performance of this LOC pH sensor in estuarine and coastal waters has not yet been thoroughly investigated.

The aim of this study was to evaluate the performance of an automated spectrophotometric analyzer, a LOC sensor, for high-resolution in situ pH determinations in dynamic estuarine and coastal waters, and expand the applicability of the sensor to waters with a wide salinity range (13.2-21.8). The sensor was deployed from a floating pontoon at GEOMAR Helmholtz Centre for Ocean Research (Kiel, Germany) in the southwestern Baltic Sea between summer and autumn 2018 for a total period of 6 weeks. Ancillary data were obtained to assess the control of pH dynamics at the sampling site. Additional spectrophotometric pH_T measurements were conducted in the laboratory on discretely collected samples, and the measurements were validated with certified reference material (DIC-A2, CRM, Batch-151, obtained from Prof. A. G. Dickson at Scripps Institute of Oceanography, USA).

### Table 1: Examples of the current in situ pH sensors used in oceanographic studies.

| Model, Manufacturer | Analytical method | pH Monitoring Applications |
|---------------------|-------------------|----------------------------|
| Honeywell Durafet ISFET, SeaFET and SeapHOx (Sea-Bird Electronics, USA) | Potentiometric | Deployment of ISFET pH sensor on vertical profiling platforms from 2000 m to the surface over several months (Johnson et al., 2016); <0.010 pH units accuracy. Deployment of ISFET pH sensor in coastal waters over months periods (Bresnahan et al., 2014) 0.030 pH units accuracy. Commercially available SeaFET and SeapHOx sensors based on ISFET technology: ± 0.050 pH units accuracy (https://www.seabird.com/seafet-v2-ocean-pH-sensor/product-details?id=54627921732&callback=0). SeaFET pH sensor deployment in coastal waters of south-central Alaska, USA for a period of 3 to 5 months (Miller et al., 2018): <0.025 pH units accuracy.|
| pH optodes (Custom-made) | Fluorescent optode | Shipboard surface seawater measurements in the Southern Ocean, over a month (Clarke et al., 2015): accuracy is not reported, 0.0074 pH units precision. Profiling on a pier in Southampton, UK, for 6 days (Staudinger et al., 2018): 0.020 pH units accuracy. Coastal waters, deployment at the pier at Scripps Institution of Oceanography for about 22 days (Seidel et al., 2008): ± 0.0017 pH units accuracy. Commercially available SAMI-pH sensor: ± 0.003 pH units accuracy (http://www.sunburstsensors.com/products/oceanographic-pH-sensor.html).|
| SAMI-pH (Sunburst Sensors, LLC, USA) | Spectrophotometric | Shipboard measurements in the North Sea over 6 weeks period (Aßmann et al., 2011): 0.0081 pH units accuracy compared to CRM and 0.0005 pH units to a reference system, short-term precision: ± 0.0007. Note: The sensor is a benchtop unit, not yet submersible.|
| CONTROS HydroFIA-pH (4H-Jena engineering GmbH, Germany) | Spectrophotometric | Deployed in surface waters of northwest European shelf seas for about a month period (Rérolle et al., 2018): 0.004 pH units accuracy compared to CRM. Deployed on fixed and moving platforms over varying environmental salinity, temperature, and pressure condition (Yin et al., 2021): <0.003 ± 0.022 pH units accuracy compared to discrete validation seawater samples.|
| National Oceanography Centre, University of Southampton, UK, Lab-on-Chip pH (ClearWater Sensors, Southampton, UK) | Spectrophotometric | |
MATERIALS AND METHODS

Sensor Overview

The LOC pH sensor is a submersible unit that performs autonomous in situ pH analysis with a spectrophotometric technique using microfluidic components and was initially developed in 2012 by the Ocean Technology and Engineering group at National Oceanography Centre (NOC) and University of Southampton, UK (Rérolle et al., 2013). It is now (since 2021) commercially available from ClearWater Sensors, Southampton, UK. A schematic diagram of the fluidic design of the sensor is shown in Figure 1. All components were mounted on a three-layer microfluidic chip made from tinted poly(methylenemacrylate) (PMMA, (Floquet et al., 2011; Perez et al., 2016), and together with the electronics placed in a mineral oil-filled (M3516 from Merck, viscosity ≤ 30.0cps) pressure compensated, watertight cylindrical polyvinylchloride housing (15 cm diameter, 56 cm height, 920 g weight in air). Detailed information of the sensor housing and microfluidic chip unit can be found in (Grand et al., 2017).

The operation of the sensor is explained in brief here. A sample and indicator dye are injected by two separate syringe pumps, controlled by valves, and mixed in a static mixer before entering a 10 mm optical cell. The change in the intensity of light transmitted by a Light Emitting Diode (LED, Roithner Lasertechnik, Austria) at 435 nm (15 nm full width at half maximum (FWHM)) and 590 nm (15 nm FWHM) through the optical cell is recorded by a photodiode detector (TSL257, TAOS Inc., USA) (Floquet et al., 2011; Rérolle et al., 2013; Perez et al., 2016). To account for slight discrepancies between the wavelengths of the LED’s emission and the mCP’s absorption maxima (434 and 578 nm) the pH sensor is calibrated post-manufacture according to Yang et al. (2014). The ratio of absorbances at the absorbance maxima of the acidic and basic forms of the indicator dye is then used to assess the pH value of a sample (Clayton and Byrne, 1993). In continuous operation mode, the sensor requires low power about 3 W or 1300 J per measurement and one measurement takes approximately 8 minutes (Yin et al., 2021). For each measurement, 3 µL of indicator dye is added to 700 µL of sample according to a pre-programmed measurement routine stored internally on the sensor unit. Approximately 0.4 mL of indicator is consumed per day when the sensor operates in continuous mode. Stock solutions of mCP are stored in 50 mL gas impermeable Flexboy bags (Sartorius Stedim Biotech, UK), wrapped in black tape to protect from light and avoid photo bleaching. The mCP stock solution remains stable for several months up to 2 years, when stored appropriately (Takeshita et al., 2021). It is possible to conduct up to 16.666 analyses with one reagent bag of 50 mL, which was attached externally to the LOC pH unit. Waste was collected into an additional external bag attached to the sensor. The WetChem Graphical User Interface (GUI) was used to operate the sensor and visualize intensity values, measurement time, pump position, internal temperature in real-time.

Analytical Principle and Data Processing of the LOC pH Sensor

The analytical principle of spectrophotometric pH determination is based on an addition of a pH-sensitive diprotic sulfonephthalein indicator dye (H2I) to a water sample. The dye changes color according to the pH of the seawater sample, i.e., the color changes from pink to yellow when it is in the acidic [HI+] form and to purple when it is in the more basic [I2-] form (Clayton and Byrne, 1993). Chemical equilibria between three dissociation forms of the dye can be expressed as follows:

\[ K_1 = \frac{[H^+] \cdot [I^-]}{[H I]} \]  \hspace{1cm} (1)

\[ K_2 = \frac{[HI^-] \cdot [I^-]}{[H I]} \]  \hspace{1cm} (2)

where [] indicates concentration, \( K_1 \) and \( K_2 \) are first and second dissociation constant of the indicator, respectively. The \( pK_2 \) (in other terms \( -\log(K_2) \)) of mCP is close to the pH of seawater, which is typically between 7.6 to 8.3 (Dickson et al., 2007). The pH of a seawater sample (\( pH = -\log([H^+] \) ) can then be quantified as:

\[ pH_I = -\log(K_1) + \log\left(\frac{[I^-]}{[HI^-]}\right) \]  \hspace{1cm} (3)

According to the Beer-Lambert Law, the amount of \([I^-] \) and \([HI^-] \) can be calculated using their distinct absorption properties at 434 and 578 nm:

\[ A_\lambda = (\varepsilon_{434} \cdot [I^-] + \varepsilon_{578} \cdot [HI^-]) \cdot l \]  \hspace{1cm} (4)

where \( A_\lambda \) is the absorbance, \( \varepsilon \) is the molar absorptivity values at wavelength \( \lambda \), and \( l \) is the optical path length.

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**FIGURE 1** | The schematic diagram of the fluidic design of the LOC pH sensor.
Then, the equation used to quantify pH can be rearranged as follows:

\[
\text{pH}_I = -\log(K_e) + \log \left( \frac{R - e_I}{1 - R e_I} \right)
\]

where \( e_I = e_{434}^{[HI^-]} - e_{434}^{[I^-]} \), \( e_2 = e_{434}^{[HI^-]} - e_{434}^{[I^-]} \), and \( e_3 = e_{434}^{[HI^-]} - e_{434}^{[I^+]} \).

where \( R \) is the ratio of absorbance at 578 (maximum peak for \([I^-]\)) to 434 nm (maximum peak for \([HI^-]\)), \( R = A_{578}/A_{434} \) (Clayton and Byrne, 1993; Liu et al., 2011).

A recent study reports on the characterization of a range of sulfonephthalein indicator dyes in detail, including mCP, for a broad range of environmental conditions (Hudson-Heck et al., 2021). Data processing of the LOC sensors raw data involves computation of molar extinction coefficients (in terms of \( e_1, e_3/e_2 \)), and second dissociation constant value \( (pK_a) \) of mCP at sample temperature and salinity using the equations and coefficients obtained from the literature (\( e_1, e_3/e_2 \)) were computed from (Liu et al., 2011) and \( pK_a \) was computed from Müller and Rehder, 2018, which is valid for salinity range 5-20 and temperature range 5-35°C. In situ temperature and salinity data of the sample range were collected in parallel by external sensors (see section 2.3).

In this study, a purified mCP (Acros Organics, 99%) indicator dye was used as its \( e_1 \) and \( pK_a \) are well-established for estuarine waters (Lai et al., 2016; Lai et al., 2017; Müller and Rehder, 2018). The purification of mCP was done by following the protocol described in Liu et al. (2011) and Loucaides et al. (2017). A 4 mM mCP reagent solution adjusted to pH 8.0 ± 0.1 at 25°C was prepared and verified by a glass pH electrode.

Field Deployments: Sampling Site and Ancillary Data

In situ field demonstration of the LOC pH sensor was performed on a floating pontoon facility of GEOMAR (Kiel, Germany; 54°19’48.78”N, 10°8’59.44”E) for a period of 6 weeks between August 1st to 13th and October 20th to November 19th, 2018. The sampling site is surrounded by dockyards and cruise ship terminals, and the city of Kiel with a population of ca. 250,000. The Kiel Fjord has a length of 9.5 km, an inner width of 250 m with depth of 10 to 12 m, an outer width of up to 7.5 km with depths greater than 20 m (Nikulina et al., 2008). The fjord drains into the southwest Baltic Sea. The waters in the inner fjord are homogeneous mixed, except during the summer period following water column stratification. Most of the freshwater delivered to the system is from rainwater and the Schwentine River on the eastern shore (Nikulina et al., 2008).

The LOC sensor was programmed to sample at hourly intervals (except for the first 5 days in August: 20 min intervals). A 0.45 µm Milllex HP PES in-line filter (Millipore, Merck, Darmstadt, Germany) was placed at the sample inlet of the LOC sensor to prevent particles from entering the microfluidic channels (Rérolle et al., 2013). The filter surface area is relatively large compared to the volume of sample withdrawn and therefore no significant underpressure is required to draw sample through. The sensor was powered externally by a 12 V power supply.

Salinity, temperature and oxygen were measured with a sampling interval of one minute using a SBE 37-SMP-ODO MicroCAT CTD and dissolved oxygen (DO, dO2) sensor (Sea-Bird Electronics, USA). The LOC, CTD, and DO sensors were mounted on a stainless steel sensor frame that was lowered from the side of the pontoon and positioned at a depth of ca. 2 m. Discrete water samples were collected daily, once in the morning and/or once in the evening, using a peristaltic pump (Cole Palmer, Masterflex L/S series) placed on the floating pontoon. The inlet of an acid cleaned (with 1 M HCl) 6.4 mm ID C-Flex tubing (Cole Palmer Masterflex) was attached to the frame close to the sample inlet of the LOC pH sensor. Discrete seawater samples for direct spectrophotometric laboratory analysis of pHf (Yin et al., 2021) were pumped into 250 mL borosilicate bottles and sealed with a ground stopper. Analyses of unpreserved samples were performed within few hours in the laboratory using a benchtop spectrophotometric CONTROS HydroFIA pH analyzer (4H-Jena engineering GmbH, Aßmann et al., 2011). Measurements of the LOC sensor and HydroFIA analyzer were validated using the DIC-A2 CRM (Batch-151, pHf, 7.862 at temperature 25°C and salinity 33) from Prof. A. G. Dickson ( Scripps Institute of Oceanography, USA) before and after deployments. The correction of sample pHf was done using equations described in section 2.2 and in situ temperature and salinity values. Seawater samples of inorganic nutrients (NO3−, PO43− and SiO2(4)−) were collected after filtration through an AcroPak 500 ( Pall GmbH, Germany) in acid-cleaned (1 M HCl) 50 mL polypropylene centrifuge tubes ( Jet Bio-Filtration Co., Ltd., Guangzhou, China) and stored at -20°C for about a month until the wet-chemical colorimetric laboratory analysis using a Seal QuAAtro autoanalyzer (Becker et al., 2019).

The GEOMAR pontoon facility is used for continuous time-series measurements of various biogeochemical and physical parameters in Kiel Fjord as part of the KIMOCC environmental data monitoring program. Here, we used the one-minute interval post-processed pCO2 data of the installed CONTROS HydroC CO2 sensor (4H-Jena engineering GmbH, Germany). An overview of the analytical principle of the CO2 sensor and data processing can be found in Fietzek et al. (2014). CO2Sys was used to calculate concentration of dissolved CO2 gas in the water sample. Throughout the study, in situ pCO2 levels are in µatm and dissolved CO2 gas levels are in µmol·kg−1 SW.

Weather data (wind speed, rainfall, solar irradiation) were obtained from the GEOMAR weather station, and were available for every 8 min. The tide gauge water level (meter) measurements at Kiel Fjord were obtained from the IOC Sea Level Monitoring Facility (http://www.ioc-sealevelmonitoring.org/station.php?code=kiel). All sensors and ancillary data presented throughout this study were examined and processed using Python software (version 3.7.4).
RESULTS AND DISCUSSION

Validation of In Situ pH Sensor Measurements

A total of 65 individual samples were collected during deployments that were analyzed employing a benchtop spectrophotometric analyzer to ensure the accuracy of pH values reported using the LOC sensor. The LOC sensor and discrete water samples pH data followed a consistent pattern throughout both deployments (Figure 2A) and were significantly indifferent (a paired t-test, \( p \leq 0.05 \)) for a total of 65 samples. No offset was applied to the sensor data and both sensor and discrete pH results were calculated independently. The average difference between the sensor and discrete samples pH (\( \Delta pH_T = LOC \) sensor-discrete water samples) was 0.001 pH units, but ranged from -0.015 to 0.015 over the duration of the summer and autumn deployments (Figure 3). No clear correlation was found between \( \Delta pH_T \) and ancillary data (\( T, S, dO_2 \)), however, the relationship between pH, and ancillary data will be detailed in the next section. Additional validation of the sensor pH measurements was done by calculating pH from salinity-derived A and in situ pCO₂. Computational details of salinity-derived A will be clarified in section 3.2. pH data from the summer and autumn deployments pooled together and for a total pH value of 978, a linear regression analysis resulted in \( R^2 = 0.86 \), with an equation of \( y=1.030x-0.217 \) (Figure 2B).

Both the LOC sensor and HydroFIA analyzer measurements were validated by consecutive measurements of DIC-TA Certified Reference Material (CRM) (Batch-151, pH₇₅=7.862 at T=25°C, S=33) before and after the field deployments. The mean pH values obtained from ten consecutive CRM measurements in July, September, and November 2018 were 7.858 ± 0.002, 7.860 ± 0.002 and 7.859 ± 0.001 pH units for the LOC pH sensor and 7.861 ± 0.001, 7.862 ± 0.002 and 7.860 ± 0.001 pH units for the HydroFIA pH analyzer. Both analyzers had a precision of about 0.001 pH units, and the accuracy of the measurements were slightly better with the HydroFIA analyzer (<0.002 pH units).

Statistical Distribution and Diel Variations of In Situ pH and Ancillary Data

The main focus of this work was to demonstrate the capability of the LOC pH sensor in a highly dynamic system, and analysis of the biogeochemical data was completed to investigate the biogeochemical processes influencing carbonate dynamics in the Kiel Fjord. The statistical distribution of all data (seawater temperature, salinity, pH₇₅, dO₂, pCO₂, NO₃⁻, PO₄³⁻ and SiO₄⁴⁻) is presented in Table 2 and allows a closer examination of the summer and autumn data. The seawater temperature and salinity, characterizing the hydrographic situation, showed marked changes; the mean salinity values were about 4 units higher and the mean temperature values were about 10 units lower in autumn, indicating saltier and colder water intrusion in the fjord, with fresher waters in summer. Highly dynamic salinity conditions for Kiel Fjord ranging from 2.6 to 22.4 have been reported, with a mean of 14.3 (Schories et al., 2006). During our summer deployment the salinity values ranged between 13.2 and 18 (mean 15.7), and in autumn deployment within 19.6 to 21.8 (mean 20.7). Enhanced seawater temperatures ranging between 18.1 and 24.2°C (mean 22.1°C) characterized the summer deployment. In autumn, temperature dropped to a minimum value of 8.7 and ranged up to 14.1°C (mean 11.5°C).

The LOC sensor determined in situ pH values were within 7.520-8.275 (mean 7.954) and within 7.560-7.932 (mean, 7.742) in summer and autumn, respectively. High mean pCO₂ levels were observed related to lower pH values towards autumn. The pCO₂ values ranged between 264-1446 µatm (mean 845 µatm) in summer and between 521-1402 µatm (mean, 904 µatm) in autumn. The dO₂ observations showed values between 4.5-9.5 mg·L⁻¹ (mean 7.3 mg·L⁻¹) in summer, and 5.8-8.7 mg·L⁻¹ (mean, 7.7 mg·L⁻¹) in autumn, respectively. Although, the mean dO₂ levels were almost identical in two seasons, dO₂ levels were about...
two times more dynamic in summer (ΔdO$_2$ was 5 mg·L$^{-1}$ in summer and 2.9 mg·L$^{-1}$ in autumn, respectively).

Discretely analyzed samples of nutrients exhibited that NO$_3^-$ concentrations in summer were depleted with values between 0.08 and 0.81 µM (mean 0.31 µM), and was followed by an increase in autumn, with concentrations between 0.84 and 3.83 µM (mean 2.09 µM). Mean PO$_4^{3-}$ and SiO$_4^{4-}$ concentrations were also higher in autumn. In summer, the concentration range for PO$_4^{3-}$ was 0.16-1.51 µM (mean 0.47 µM) and for SiO$_4^{4-}$ 1.7-23.3 µM (mean 9.12 µM), whilst in autumn PO$_4^{3-}$ concentrations varied from 1.1 to 1.55 µM (mean 1.30 µM) and SiO$_4^{4-}$ from 19.9 to 28.6 µM (mean 24.3 µM). The wind speed was maximum 11 m·s$^{-1}$ in summer (mean 3.2 m·s$^{-1}$), and 13 m·s$^{-1}$ in autumn (mean 4.1 m·s$^{-1}$).

Diel variations of seawater temperature, salinity, pH$_T$, and ancillary variables (pCO$_2$, A$_T$, dO$_2$, nutrients, water level, solar irradiance and wind speed) obtained during the first deployment in summer 2018 are presented in Figure 4. A total of 346 LOC sensor measurements and 21 discrete seawater samples for pH and 32 for nutrients were collected from August 1 to August 13 on the GEOMAR pontoon facility in Kiel Fjord. The 3-day gap in the dataset, between August 5 and 8, was associated with an electrical failure of the power supply to the sensor. The ranges of all variables and the number of samples measured are presented in Table 2.

Co-located deployment of independent sensors facilitated the validation of the time-series data at a higher spatial and temporal resolution than can be achieved by analysis of discrete samples (Martz et al., 2015). Considering the high diel variability in temperature, salinity, pH$_T$, and the ancillary data presented in Figure 4, there was a clear difference between the waters sampled at the beginning and end of the deployment. At the beginning of the deployment period until about August 9, 2018, it can be stated that there was not much activity in the water, referring to tidal ranges (difference between high tide and low tide) below 0.3 m and relatively stable ancillary data.

A rapid decrease in pH$_T$ from 8.249 to 7.573 (determined by the LOC sensor), increase in pCO$_2$ from 292 to 1029 µatm and
A typical tidal range for the Fjord is ±1 m (Geißler et al., 2021). The water level, temperature and salinity measurements presented in Figure 4 illustrate the impact of the storm on the sampled waters. The surface waters of the Kiel Fjord are characterized by enhanced temperature and low salinity, as opposed to the bottom waters of low temperature and high salinity. Shifts in seawater temperature (approximately 3°C decrease) and salinity (approximately 2 units increase) values were observed during the storm. Nutrients were in a trend consistent with pCO$_2$, and both increased in response to increased wind speed and decreased temperatures (Figure 4). Enhanced biological activity was evidenced as while nutrients and pCO$_2$ were increasing, A$_T$ and dO$_2$ were in decreasing trend. The in situ determined pH$_T$ values were a reflection of pCO$_2$ and dO$_2$ levels.

Anomalous characteristics of the Baltic Sea waters with respect to major ions and hence alkalinity do not allow a straightforward calculation of alkalinity using salinity that applies to all regions of the Baltic Sea in general (Hammer et al., 2014; Müller et al., 2016). Müller et al. (2016) describes the temporal alkalinity trends in the Baltic Sea using long-term historical datasets and shows the relationship between alkalinity and salinity at four different basins. Instead, we have theoretically calculated A$_T$ using in situ salinity data from our deployments and the equation for the Atlantic waters (0°C<T<20°C, 31<S<37) from Lee et al. (2006) to compute pH$_T$ using CO2Sys and have a view of A$_T$ values for our study site. During the summer deployment, salinity-derived A$_T$ values ranged between 2205 and 2427 µmol·kg$^{-1}$ with a mean of 2267 µmol·kg$^{-1}$. Although the salinity-derived A$_T$ values are not exactly suitable for our study area, when the pH$_T$ values calculated using these A$_T$ and in situ pCO$_2$ data are compared with the sensor pH$_T$ values, a significant relationship is seen (Figure 2B).

The second deployment at the same location took place in autumn 2018, from October 20 to November 19.
632 LOC sensor measurements were conducted, and discrete seawater samples for discrete seawater samples for pH (n=44) and for nutrients (n=75) were collected. Diel variations of the seawater pH and ancillary data are shown in Figure 5 and the corresponding value ranges are provided in Table 2. The tide gauge water level measurements at Kiel Fjord corresponding to our measuring period indicated that during a heavy storm (wind speed up to ca. 13 m·s⁻¹, Figure 5E), the water level increased by about 1 m (from 4.46 to 5.46 m, Figure 5D).

During the autumn deployment a further notable weather event occurred starting from October 26th, a storm flood approached at the sampling site, followed by successive winds (speed >10 m·s⁻¹) for about 3 days. Over the same period, daily rain intensities (precipitation) of ca. 10 mm were captured, which is a threshold of a heavy rainfall event for Germany (Deumlich and Gericke, 2020), and reductions in water temperature and salinity of about 2 units were observed with additional responses in pH_T, pCO₂, dO₂ and NO₃⁻ levels. Strongly variable increases in pH_T values were observed, presented in the yellow circle in Figure 5B, and were not included in Table 2. This was likely due to the variations in the physical conditions of the fjord waters with winds and tides. The in line filter of the LOC sensor was changed on November 1, 2018, to avoid possible clogging after dynamic water conditions. The gaps (couple of hours) in the LOC sensor dataset between October 25 and 26, as well as November 11 and 12, were related to the power cuts.

The salinity-derived A_T values ranged between 2075 and 2130 µmol·kg⁻¹ with a mean of 2099 µmol·kg⁻¹ in autumn, much lower than those reported in summer. Compared to the first deployment (Figure 4), the time series data presented in Figure 5 were relatively uniform with small differences between maximum and minimum values of all parameters (as indicated by low Δ values, Table 2). An increase in NO₃⁻ concentrations, from 1.70 to 3.83 µM, was noticed over a one-day period, between November 5 and 6, 2018. The dO₂ levels decreased from 8.5 to 7.9 mg·L⁻¹, whilst pCO₂ levels increased from 704 to 961 µatm. The acidification
process was evidenced with decreasing pH values from 7.858 to 7.752. This event can be ascribed to supply of subsurface waters enriched in DIC due to organic matter respiration process (see also section 3.3).

**Carbonate Chemistry Dynamics in Kiel Fjord**

Estuarine and coastal waters feature complex hydrological conditions, often including strong variations in surface salinity (Castelao et al., 2010). Carbonate chemistry in coastal waters is regulated by variety of factors, including biological metabolic (photosynthesis, respiration, and calcium carbonate precipitation or dissolution), and physical processes (ocean currents, tide, weather conditions) (Kristiansen et al., 2001; Feely et al., 2010; Stokowski et al., 2020; Huang et al., 2021). A change in the mass balance of the carbonate system or thermodynamic conditions of the waters affect the surface pCO$_2$ levels, consequently the pH dynamics (Dai et al., 2009).

pH$_2$, and ancillary data, presented in this study, exhibited clear diel variations (Figures 4, 5), and the patterns were different in the two seasons, suggesting that distinct internal processes may be involved in regulating these variations. At our deployment site, observations indicated that in the nearshore surface waters of Kiel Fjord were colder, saltier, and more acidic in autumn compared to summer (Figure 6). The $\Delta$pH$_2$ was 0.372 units in autumn and 0.755 units in summer, respectively.

pH$_2$, pCO$_2$ and dO$_2$ are important indicators for characterizing water masses and biological processes (Orr et al., 2005; Staudinger et al., 2018). An increase in dO$_2$ concentrations corresponded to an increase in pH and decrease in pCO$_2$ levels in waters, due to enhanced photosynthetic activity of algae. The mean differences in dO$_2$ between summer and autumn can also be attributed to the fact that the effect of wind mixing on the water was sharper in our summer distributions, as the waters are generally not well mixed in the summer. The increase in nutrient concentrations and pCO$_2$ while the dO$_2$ decreases are evidence of the biological life in the environment. The pH time-series data mirrors that of pCO$_2$ and dO$_2$, when fit to a linear regression yielded $r^2$ = 0.85 and $r^2$ = 0.77 in summer and yielded $r^2$ = 0.46 and $r^2$ = 0.70 in autumn, respectively (Figure 7). Besides, pCO$_2$ data can be considered as a form of validation of the pH data, as in situ measurements were conducted using two different sensors; CONTROS HydroC and LOC.

The observed Redfield ratios, defining the stoichiometry of the photosynthesis and respiration reactions (Redfield et al., 1963), are shown in Table 3. The molar ratios between carbon, nitrogen, and phosphorus from simultaneous measurements on the deployment site indicated that the C:N ratio was largely above the proposed Redfield ratio of 106C:16N, which may be related to N loss processes due to denitrification (Gruber, 2008). The N:P ratio in our data was below the Redfield ratio of 16N:1P, which may again be related to N loss through denitrification and additional benthic P supply from anoxic sediments (Lenton and Watson, 2000).

Our data from the Kiel Fjord shows strongly elevated in situ pCO$_2$ (maximum of 1420 µatm) levels, even higher than reported for other estuaries. For example the Polish Oder Estuary which also drains into the Baltic Sea has reported pCO$_2$ values of<1200 µatm (Stokowski et al., 2020). Higher CO$_2$ levels were related to nutrient enrichment in the system (Figure 8), with respiration resulting in O$_2$ consumption and CO$_2$ production (Figures 4, 5).

The physical mixing and enhanced remineralization of organic substances in estuaries, promoted by high nutrient loads from land, determine the chemical composition of the system (Bauer et al., 2013; Stokowski et al., 2020). While it is beyond the scope of this study to precisely quantify the intensity of photosynthesis/respiration processes, studies from different estuaries have suggested that intensity levels of biological activities are modulated by wind-driven inputs of nutrients from subsurface waters (Gazeau et al., 2005; Saderne et al., 2013; Li et al., 2020).

Given our in situ data and the main biological and physical drivers of the carbonate chemistry of the estuarine systems, the carbonate system in Kiel Fjord is regulated by i) respiration, and ii) wind-driven mixing. During the deployment periods storm

**FIGURE 6** | In situ (A) temperature-salinity and (B) pH$_2$-salinity diagram of the period investigated, illustrating different hydrological periods in summer (black, green circles) and autumn (red, orange circles).
Lab-on-Chip pH Sensor

events were captured, in which subsurface waters (with enhanced pCO$_2$ and nutrient levels) were transferred to the surface, evidenced by temperature and salinity observations.

**CONCLUSION**

Understanding spatial and temporal changes in pH in association with environmental variables is essential for a sustainable management of marine systems. Hydrodynamic and biogeochemical processes in coastal estuaries change rapidly from minutes to days, triggering acidification in the system (Xu et al., 2017; Wright-Fairbanks et al., 2020). Those sudden changes often cannot be resolved through sampling and analyses of discrete water samples. The automated real-time observation of carbonate chemistry dynamics with sensors like LOC offer a potentially substantial improvement in that regard. While the performances of the LOC sensor for high-resolution spectrophotometric pH
measurements has been demonstrated in surface waters of shelf seas with salinities above 24 (Rérolle et al., 2018; Yin et al., 2021), this is the first report on deployments of the sensor in dynamic estuarine waters (S<20).

Our study shows the effects of respiration and wind-driven mixing of water masses leading to consecutive impacts on the carbonate chemistry of the Kiel Fjord. The presented in situ data from observations conducted within a period of six weeks in two seasons (summer and autumn) showed the suitability of the LOC pH sensor for revealing the strong dynamics in highly dynamic estuarine waters on a fine temporal scale. The applicability of the sensor is broad, it was integrated on a Seaglider (iRobot/Kongsberg) (Possenti et al., 2021), on an Autosub Long Range AUV (Yin et al., 2021), and on an ROV (Mork et al., 2021). The unique depth rating (6000 m), low power and reagent consumption, low cost, high portability, and ease to use without calibration for long-term monitoring make the LOC sensor a good choice for autonomous pH observations on various monitoring platforms. Work is currently underway for integration of the LOC pH sensor on other AUVs (pers. comm. Socratis Loucaides). The measurement frequency (~8 min) is the main weakness of the sensor when deployed on fast-moving and profiling platforms such as gliders and floats. Future works should focus on optimizing the measurement duration of the sensor to achieve better performance on such platforms.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

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AUTHOR CONTRIBUTIONS

MN performed the laboratory and field work, statistical analysis and data visualization. ME performed the installation of the sensors on the deployment platform. MN wrote the first draft of the manuscript. All authors contributed to the article and approved the submitted version.

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