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REVIEW

of the PhD dissertation by Fernando Aguado Gonzalo entitled "Characteristics of the marine CO_2 system in Arctic Waters"

Subject of the review

The subject of this review is the PhD dissertation by Fernando Aguado Gonzalo, MSc, entitled "Characteristics of the marine CO_2 system in Arctic waters," who is applying for the degree of Doctor of Philosophy in the field of Exact and Natural Sciences, in the discipline of Earth and Environmental Sciences, before the Scientific Council of the Institute of Oceanology of the Polish Academy of Sciences (IO PAN). The supervisor of the thesis is Karol Kuliński, Prof. IO PAN. I have prepared this review based on the decision of the aforementioned Council, which entrusted me with the duties of a reviewer at its meeting on June 16, 2026.

Bibliometric Evaluation

The PhD dissertation submitted for evaluation by Fernando Aguado Gonzalo, MSc, constitutes a thematically coherent series of three scientific articles published between 2024 and 2026 in international journals indexed in the Web of Science database. These publications appeared in recognized scholarly journals such as *Frontiers in Marine Science*, *Marine Chemistry*, and *Oceanologia*, which are characterized by high academic rigor and a significant impact on the advancement of the discipline.

The research cycle was supported by national and international funding. The Polish National Science Center (NCN) provided foundational support through the PROSPECTOR project and other dedicated grants. Bilateral cooperation was facilitated by the GRIEG Programme, co-funded by the Norwegian Financial Mechanism and the NCN. Furthermore, the European Union's Horizon Europe programme supported the studies through the SEA-Quester project, aiding in the contextualization of biogeochemical data. This multi-layered funding framework integrated Polish national resources, Norwegian-Polish collaboration, and broader European research initiatives across all three publications.

In terms of both bibliometrics and substantive quality, this collection of papers is impressive, unequivocally confirming the high scientific value of the research conducted and fully qualifying the candidate to apply for the doctoral degree. In all three articles comprising the dissertation, Fernando Aguado Gonzalo, MSc, is the first author, demonstrating his pivotal role in executing the entire research cycle. Furthermore, in two of these papers, he served as the cor-

responding author, confirming his direct responsibility for the editorial process and the overall coordination of manuscript preparation.

An analysis of the co-authors' statements and the breakdown of percentage contributions indicates the candidate's dominant contribution to each work, with his involvement estimated at a very high level: 60% for the first publication, 75% for the second, and 70% for the third, respectively. According to the attached documentation, Fernando Aguado Gonzalo's engagement encompassed virtually all stages of the scientific process, ranging from conceptualization and methodology development, through active sample collection during research cruises aboard the research vessel *Oceania*, to advanced chemical analyses, data acquisition and interpretation, result visualization, and drafting the initial manuscript versions.

The declared scope of work is entirely commendable—and indeed outstanding—in experimental disciplines where projects are typically carried out by multi-author teams. Serving as the lead author throughout the entire publication cycle conclusively demonstrates that the candidate has mastered the ability to independently plan and conduct complex biogeochemical research under demanding polar conditions.

Taking the above facts into account, it can be asserted with complete confidence that the series of publications constituting Fernando Aguado Gonzalo's dissertation fully meets the criteria required for doctoral theses. It represents a coherent body of published, peer-reviewed scientific work that makes a novel contribution to the knowledge of marine carbonate systems in the Arctic.

General Evaluation of the Subject Matter

The overarching topic of Fernando Aguado Gonzalo's doctoral dissertation addresses a critical issue in marine biogeochemistry: the characterization of the carbonate system in Arctic waters in the context of ongoing climate change. Due to its low water temperatures, the Arctic Ocean exhibits a high capacity for absorbing anthropogenic carbon dioxide, leading to an increase in dissolved inorganic carbon (DIC) concentrations and a decline in seawater pH. Although this region is recognized as pivotal for global carbon sequestration and exhibits extreme vulnerability to ocean acidification, the understanding of the mechanisms controlling these processes remains incomplete due to complex interactions among the cryosphere, freshwater inputs, and biological activity. Within chemical oceanography, there is a clear imperative to quantify the relative contributions of specific physical and biological drivers to carbonate system variability, particularly in the Atlantic sector of the Arctic, where intense heat and water mass exchange further complicate the chemical structure of the surface layer.

In marine carbonate system studies, calculating unmeasured parameters via thermodynamic equilibrium models is widespread practice, driven by logisitical and technical challenges associated with continuous *in situ* monitoring under harsh polar conditions. While this approach is well established for open-ocean environments, a major knowledge gap exists in Arctic coastal areas and fjords—systems subject to strong inputs of glacial meltwater, river runoff, and enhanced primary production. This gap concerns the reliability of thermodynamic calculations in environments with non-standard chemical compositions, where uncharacterized acid-base species can introduce systematic errors in estimating carbonate saturation states. Furthermore, traditional discrete water sampling methods lack vertical resolution, hindering the capture of rapid biogeochemical transformations occurring within the photic zone. Given the importance of high-precision datasets for modelling Arctic ecosystem dynamics, refining analytical methodologies and evaluating the internal consistency of the carbonate system represents a highly justified research endeavour.

The main objective of the thesis was to advance the understanding of the structure and variability of the marine carbonate system in understudied, bio geochemically complex Arctic waters, with a particular emphasis on coastal domains. Achieving this aim required characterizing the spatiotemporal variability of carbonate parameters in the Fram Strait and identifying key driving mechanisms, including net primary production, temperature, and water mass mixing induced by sea ice melt. The research also sought to identify the limitations of applying thermodynamic models to both open-ocean and coastal waters, establishing methodological guidelines to guarantee high-quality data generation. Additionally, a central component of the dissertation involved developing and field-validating a high vertical resolution sampling system to enable precise characterization of fine-scale processes in strongly stratified Arctic waters subject to freshwater discharge. Ultimately, the work aims to couple chemical dynamics with physical and biological processes, which is essential for quantifying the Arctic's role in the global carbon cycle and assessing ocean acidification impacts on this sensitive region.

Objectives, goals and hypotheses

The strategic objective of the doctoral dissertation was to provide new insights into the structure and variability of the marine carbonate system in understudied Arctic waters, with a particular focus on the biogeochemically complex coastal domains of the Atlantic sector. Achieving this goal focused on providing high-quality datasets that allow for coupling the dynamics of carbonate parameters with the impacts of river discharge, sea ice and glacial melt, primary production, and temperature. Specific secondary objectives included characterizing the interannual and spatial variability of the carbonate system in the surface waters of the Fram Strait, alongside identifying and quantifying the primary physical and biological drivers governing these transformations. Furthermore, the author sought to identify data quality limitations in the application of ion-pairing thermodynamic equilibrium models for calculating carbonate system parameters in Arctic waters, and to formulate concise guidelines for obtaining high-quality data. The third specific objective was to develop an innovative technical solution enabling the simultaneous sampling of all four measurable carbonate system parameters at high vertical resolution within strongly stratified and biogeochemically complex coastal waters.

In the course of the research, three hypotheses were formulated and subsequently verified within the individual scientific publications constituting the dissertation.

The first hypothesis posited that, despite the direct impact of sea ice meltwater on total alkalinity (TA) and dissolved inorganic carbon (DIC), net primary production (NPP) represented the primary driver governing pH variability in the surface layer of open Arctic waters during the summer season. This hypothesis was confirmed in Publication 1, which demonstrated that NPP was the key process controlling pH and pCO_2 variability, whereas water mass mixing primarily determined TA and DIC levels.

The second hypothesis postulated that the accuracy of carbonate system parameters calculated using thermodynamic models was lower in Arctic coastal areas compared to open-ocean waters, thereby constraining the quality of ocean acidification research. The validity of this assumption was proven in Publication 2, which highlighted significantly higher absolute calculation uncertainty in coastal regions resulting from the presence of acid-base active substances not accounted for in the model.

The third hypothesis assumed that high vertical resolution measurements and sampling of the marine carbonate system would reveal fine-scale biogeochemical variability in the surface layer driven by riverine discharge as well as sea ice and glacial melt. This hypothesis was confirmed in Publication 3 using a custom-designed "carbonate profiler" system, which en-

abled precise identification of sharp chemical gradients in strongly stratified fjord and estuarine waters. Following an analysis of the specific hypotheses and planned research tasks mapped to the individual publications, I can unequivocally state that the candidate proposed a well-conceived and logical research strategy that fully enabled the verification of the overarching hypothesis.

Substantive Evaluation

The first publication provides a comprehensive quantitative decoupling of physical and biological drivers in a highly dynamic Arctic region. The research utilized underway continuous measurements of temperature, salinity, pCO_2 via cavity ring-down spectroscopy (CRDS), and pH through spectrophotometry, alongside discrete sampling for total alkalinity (TA) and dissolved inorganic carbon (DIC) during the summers of 2019, 2020, and 2021. The findings demonstrate that while TA and DIC are primarily governed by the conservative mixing of Atlantic Water and sea ice meltwater, with a zero-salinity TA end-member of approximately 420 μmol kg^{-1}, it is net primary production (NPP) that acts as the dominant regulator of spatial and temporal pH variability. Numerically, NPP was responsible for pH changes ranging from 0.10 to 0.22, whereas the effects of temperature and salinity were secondary, accounting for changes up to 0.14 and 0.10, respectively. The study concludes that interannual shifts in sea ice extent—which varied from 49.9% in 2019 to 18.7% in 2021—significantly alter phytoplankton community structures and the position of the chlorophyll maximum, which is crucial for predicting the Arctic's future capacity as a carbon sink. The overall conclusions as well as methodology are correct; **however I would like to ask if the primary role of the NPP and secondary role of the temperature in regulation of the pH would also be valid for various scenarios proposed by the IPCC involving the global increase (slight, average and high) of the temperature according to the CO_2 emission?**

The second publication offers a critical merit-based assessment of thermodynamic modelling using the CO2SYS program. The methodology involved comparing calculated parameters against in situ measurements from 110 stations to determine absolute uncertainties, reported as the 68th percentile to reflect dispersion around "true values" rather than just arithmetic means. A significant finding is that absolute uncertainty in coastal regions is 1.7 to 3.8 times higher than the theoretical uncertainty derived from error propagation, likely due to unparameterized substances like organic alkalinity. The study establishes clear quality thresholds (10 μmol kg^{-1} for TA/DIC, 0.020 for pH, and 7 μatm for pCO_2) and concludes that while oceanic calculations are generally reliable, coastal data are often of lower quality. Crucially, the authors prove that the pair of pH and pCO_2 should be strictly avoided as input variables, while a newly developed linear relationship for salinity-derived TA combined with pCO_2 can accurately calculate pH with an uncertainty of only ±0.007 to ±0.012. This publication provides the scientific community with essential guidelines for conducting high-quality ocean acidification research in biogeochemically complex Arctic environments, however **I would expect some more detailed explanation concerning the impact of the including/excluding of phosphates and silicates to/from the total carbonate system parameters according to data quality thresholds. Is it reasonable to propose some confidence intervals of bad/good quality data according to variation of other parameters, such as phosphates and silicates as well as according to uncertainties of their analytical determinations? Did the authors consider some non-linear models to estimate components of the carbonate system?**

The third publication introduces a novel technological solution for sampling stratified waters. The materials and methods involve a PUMP-CTD system that integrates a submersible pump

with a standard CTD profiler and an underway equilibrator unit, allowing for simultaneous high-resolution profiling of all four carbonate system variables down to a depth of 60 meters. The merit of this system is proven by its ability to achieve a vertical resolution of 0.5 meters, capturing steep gradients that are invisible to traditional Niskin bottle sampling. In oceanic tests, the system showed excellent agreement between measured and calculated pCO_2 with a mean difference of only 0.9±4.5µatm. Application in the Vistula River estuary revealed a very high freshwater TA end-member of 4069±12 µmol kg^{-1}, while measurements in Arctic fjords identified end-members between 790 and 1240 µmol kg^{-1}. These numerical results prove that continental runoff in the Svalbard archipelago drastically reduces the seawater's buffering capacity, thereby accelerating local ocean acidification. This innovative sampling approach fills a significant technological gap, enabling more precise quantification of carbon inventory and air-sea CO_2 fluxes in stratified coastal and polar waters.

The content of the publications unequivocally demonstrates that the candidate possesses highly developed research skills, having ensured the proper application of specialized instrumentation and conducted a substantively sound data analysis.

Summary

In summarizing the execution of the individual research tasks, I state with complete confidence that the objectives of Fernando Aguado Gonzalo's doctoral dissertation have been fully achieved. The candidate successfully designed and validated an innovative technical solution—a so-called "carbonate profiler"—which enabled simultaneous measurements of pCO_2 and pH alongside discrete sampling for TA and DIC at an unprecedented vertical resolution of 0.5 m. The execution of such an ambitious sampling strategy in strongly stratified Arctic waters and estuaries would not have been possible using traditional water sampling methods.

I consider the quantitative decoupling of the physical and biological drivers governing the summer CO_2 system in the Fram Strait to be the most significant element of scientific novelty. The author demonstrated that net primary production (NPP), rather than water mass mixing or temperature, serves as the primary regulator of pH variability in the photic layer. An equally important achievement is the comprehensive evaluation of the internal consistency of the CO2SYS thermodynamic model. The author demonstrated that calculation uncertainties in Arctic coastal regions are 1.7 to 3.8 times higher than in the open ocean, enabling the formulation of the first precise methodological guidelines regarding the selection of input parameter pairs for this region.

The overall conclusion derived from the thesis confirms that freshwater runoff from glaciers and rivers drastically impairs ocean buffering capacity, directly accelerating ocean acidification (OA) processes in the Arctic. These findings constitute a valuable contribution to the advancement of chemical oceanography and marine biogeochemistry.

Final conclusion

I conclude that the evaluated dissertation meets the conditions specified in Article 187 of the Act of July 20, 2018 – Law on Higher Education and Science (consolidated text: Journal of Laws of 2024, item 1571, as amended), and I move for admitting Fernando Aguado Gonzalo, MSc, to the further stages of the doctoral procedure.

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Dokument podpisany
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