Understanding the Current Use and Future Needs of CO_2 in Seawater Certified Reference Materials

NOAA Technical Memorandum OAR-OAP-5

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Photo: Bottled reference materials for ocean CO_2 measurements. Scripps Institution of Oceanography.

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Introduction

Certified reference materials (CRMs) are fundamental for accurate and precise measurements of seawater CO_2 system parameters and research related to ocean acidification and oceanic carbon cycles. Currently, there is a single global source of reference materials for total alkalinity, dissolved inorganic carbon, and pH in seawater and a calibrated HCl titrant for seawater alkalinity analysis (Andrew Dickson Laboratory, Scripps Institution of Oceanography, University of California San Diego). When production of these materials was halted during lab closures due to the Covid-19 pandemic, a shortage of CRMs ensued and highlighted the risks associated with having a single producer of CRMs. Distribution of CRMs was halted from for a year starting in March 2020. The U.S. Interagency Working Group on Ocean Acidification, which is responsible for coordinating U.S. federal activities related to ocean acidification, is engaging in efforts to increase resilience in the production and distribution of reference materials for the quality control of measurements of seawater CO_2 system parameters. Increasing resilience of CRM production includes exploring multiple nodes of production inside the U.S. and whether a country outside of the United States could develop a production site. In parallel with U.S. efforts, the Global Ocean Acidification Observing Network (GOA-ON) is also working to advance efforts to improve international CRM resilience through its program for the UN Decade of Ocean Science for Sustainable Development: OARS, Ocean Acidification Research for Sustainability.

A new model for CRM production and certification, both within the US and internationally, must be informed by an understanding of the current and future use of CRMs. Specifically, it is vital to understand who uses CRMs, how and where CRMs are used, how many CRMs are currently used, and how many CRMs are expected to be used in the future. To better understand these aspects of CRM use, the GOA-ON executive secretariat created a questionnaire on CRM usage in collaboration with the Interagency Working Group on Ocean Acidification. The questionnaire was shared with the carbonate chemistry research community in April 2021. It was released approximately one month after Dr. Andrew Dickson presented a webinar in which he discussed his current reference material production system at Scripps Institution of Oceanography and options for the future of CRM production. The questionnaire was made available on social media platforms, including the Ocean Acidification Information Exchange, and was shared with webinar attendees. Additionally, the Dickson laboratory, GOA-ON, and the Ocean Carbon and Biogeochemistry Program (OCB) shared the questionnaire with their contacts. The questionnaire was made available along with a link to a recording of Dr. Dickson's webinar and a link to an Ocean Acidification Information Exchange post about the webinar which contains questions, discussions, and a pdf copy of the presentation slides. Members of the OA and carbonate chemistry research communities voluntarily elected to participate in the questionnaire. It was encouraged that only one representative from each laboratory or research group provide answers.

A total of 247 individuals voluntarily responded to the questionnaire, although not every participant responded to every question. This document describes the responses that were received. All responses are presented in aggregate form as all individual responses are confidential and will not be released publicly.

Current CRM Usage

Which CRMs Are Used

Improvements and changes to the CRM production model should be informed by an understanding of how CRMs are used. The Dickson Laboratory currently produces three products that are used for seawater carbonate chemistry measurements: a total alkalinity and dissolved inorganic carbon (TA/DIC) reference material, a tris-buffered pH reference material, and a certified HCl titrant solution. Questionnaire respondents indicated which of these products they use. Nearly all use the TA/DIC reference material, around half use the tris-buffered pH product, and about one-quarter use the certified HCl tritant solution (Figure 1-A). Respondents were able to select multiple choices to indicate that they use multiple products. Figure 1-B shows the percent of respondents that use each combination of products. Nearly half use only the TA/DIC reference material.

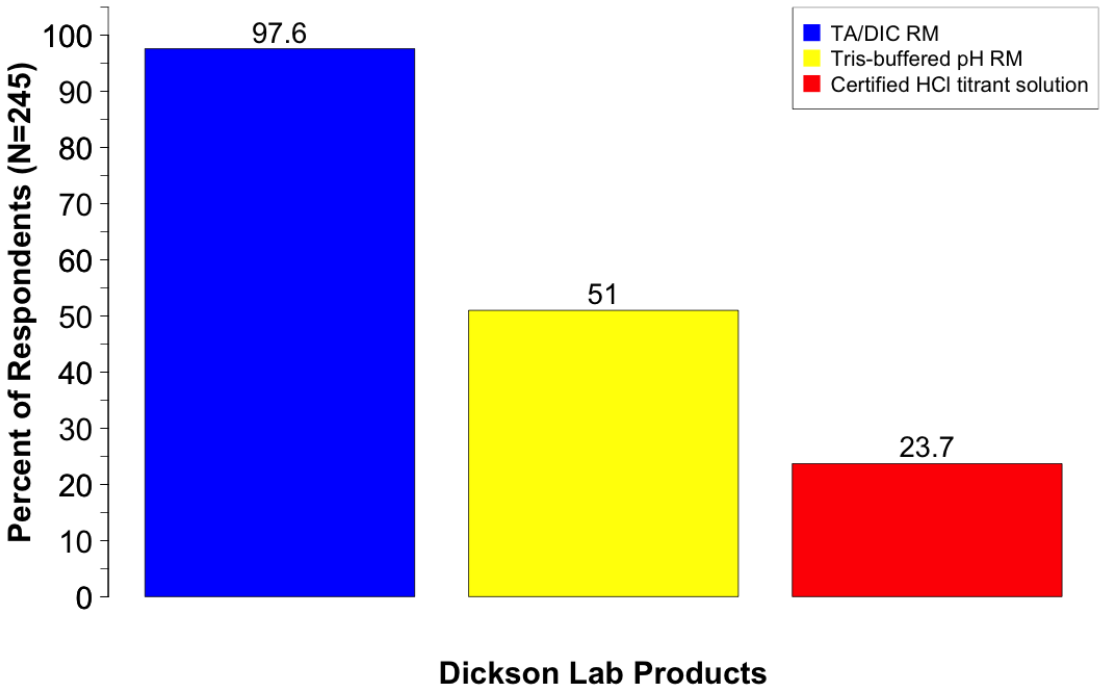

Figure 1-A. *The percentage of respondents that use the three products produced by the Dickson lab*.

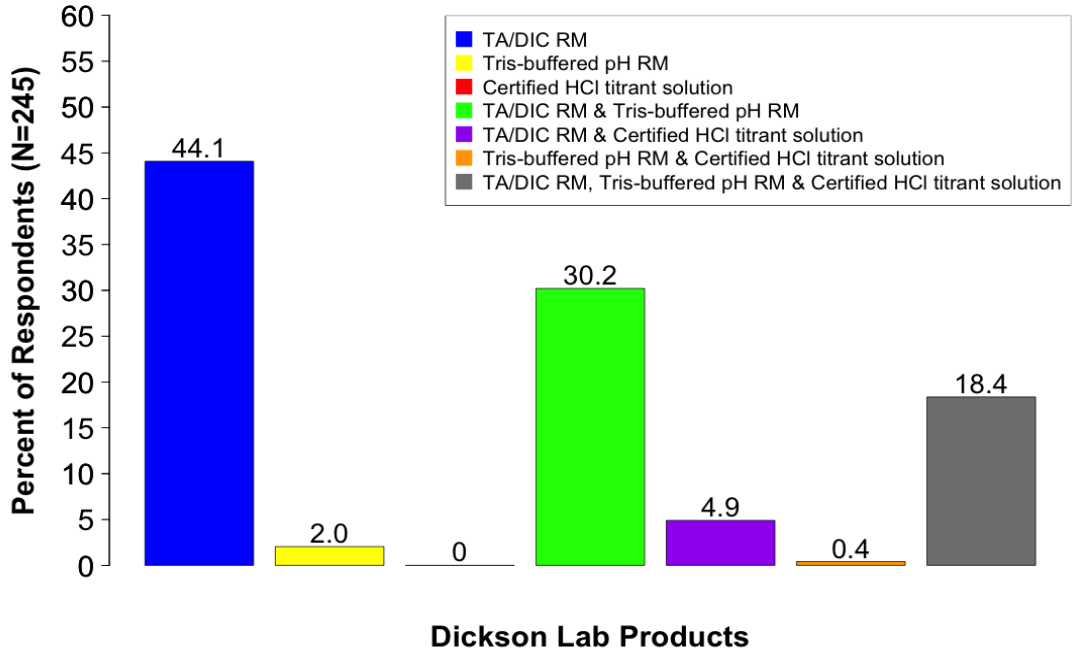

Figure 1-B. *Respondents indicated which of the three reference materials they use; respondents could select multiple choices. This figure represents the percentage of users that use each combination of reference materials.*

What Parameters CRMs Are Used to Verify

The questionnaire asked what measurement(s) of the carbonate chemistry system respondents use TA/DIC reference materials to verify. Nearly all respondents measure total alkalinity, with over half measuring pH or DIC (Figure 2-A). Figure 2-B shows the percent that measure each combination of the four carbonate chemistry parameters.

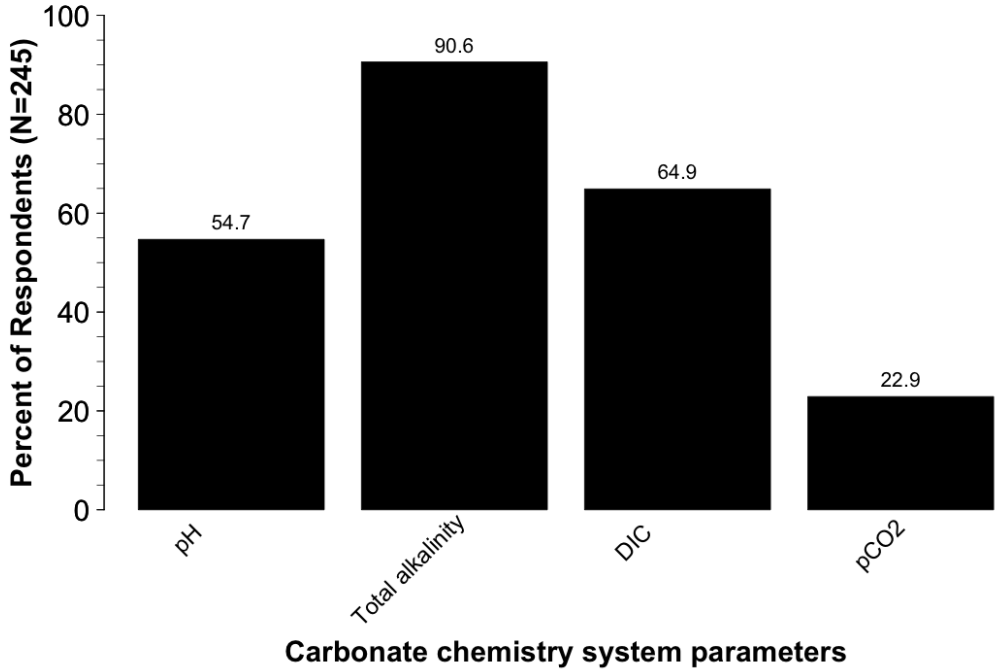

Figure 2-A*: Respondents indicated which of the four carbonate chemistry system parameters they measure using TA/DIC reference materials; respondents could select multiple choices.*

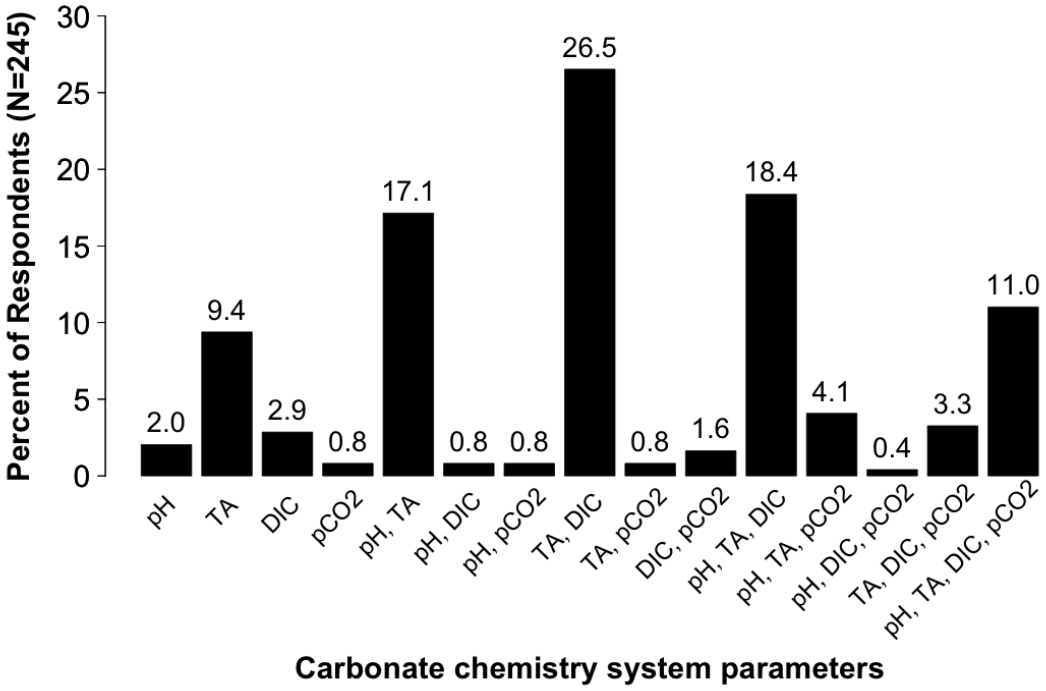

Figure 2-B: *The percentage of respondents that measure each combination of the four carbonate chemistry parameters using TA/DIC reference materials.*

Where Are CRMs Being Used

Respondents were asked to provide short answer responses with details about the locations where their research, and therefore their CRM usage, takes place. To broadly understand the geographic distribution of CRM usage, the data were coded by ocean (Figure 3-A). Most respondents indicated that they use CRMs to conduct research in the Atlantic (59.2%) and/or Pacific (38.1%) oceans. Far fewer respondents stated that they conducted CRM-required research in the polar oceans (Arctic: 8.1%, Southern: 6.7%) and/or the Indian ocean (6.3%). Figure 3-B displays the percentage of respondents that conduct research exclusively in each ocean or in multiple oceans. Slightly less than one-quarter of respondents (22.9%) stated that they use CRMs to conduct research in more than one ocean. No respondent stated that they solely conducted research in the Arctic and only two exclusively conduct research in the Southern Ocean.

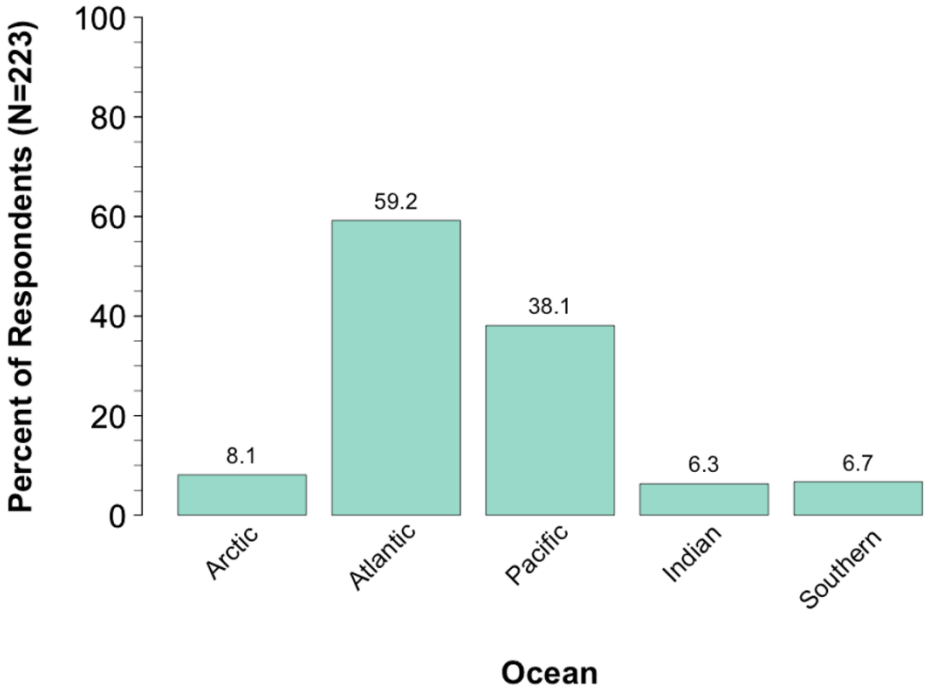

***Figure 3-A**: The percent of respondents who use CRMs in each ocean, along with the percent who use CRMs in multiple oceans.*

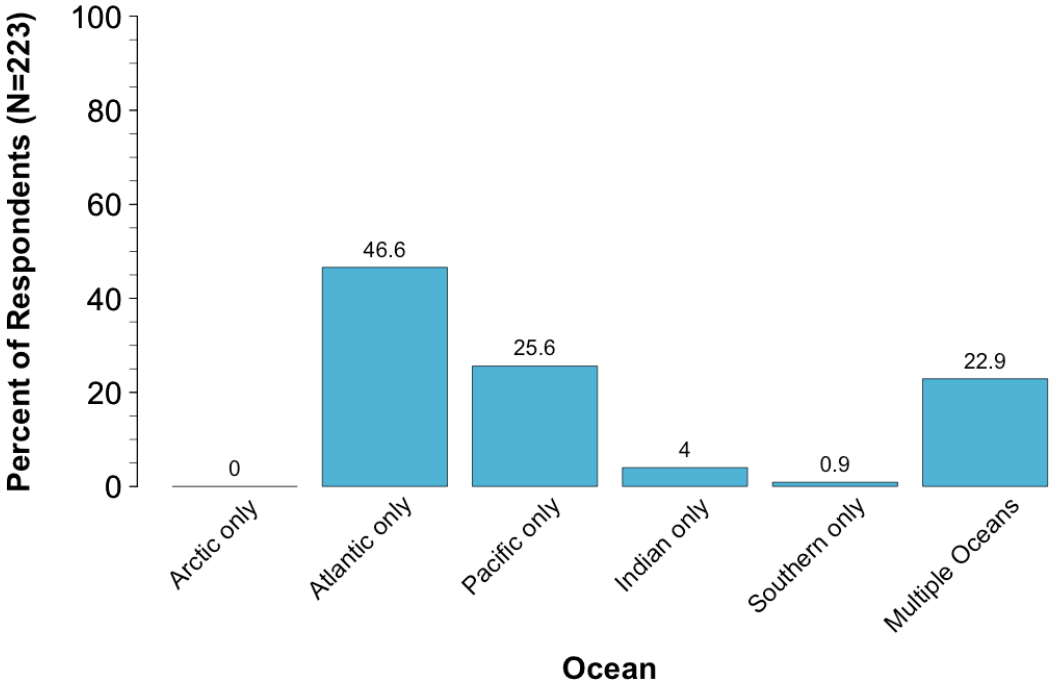

***Figure 3-B**: The percent of respondents who use CRMs exclusively in each ocean or who use CRMs in multiple oceans.*

How Many CRMs Are Being Used

Respondents to the questionnaire could indicate how many bottles of TA/DIC reference materials they use in a typical year by selecting one of the options in Table 1. The most common range of reference material use was 11 to 50 bottles a year, though over 10% of respondents use more than 100 bottles a year.

Table 1: This table displays the percentage of respondents that selected different choices about how many bottles of CRMs they use per year.

Choice (bottles of TA/DIC reference materials)	Number of Responses	Percent of Total Responses (N=243)
1-5	57	23.5%
6-10	43	17.7%
11-50	82	33.7%
51-100	34	14%
101-200	18	7.4%
201-500	7	2.9%
>500	2	0.8%

How Are CRMs Being Used

Questionnaire respondents were able to indicate activities for which they used TA/DIC reference materials. Multiple options could be selected from the following list:

- Measurements of the **open ocean** for the purpose of detecting long-term, anthropogenically driven changes in the ocean CO_2 system.
- Measurements of **coastal waters** for the purpose of detecting long-term, anthropogenically driven changes in the coastal CO_2 system.
- Measurements of the **open ocean** to support species or ecosystem studies focused on the impacts of changes in the ocean CO_2 system or to understand short-term variations in the ocean CO_2 system.
- Measurements of **coastal waters** to support species or ecosystem studies focused on the impacts of changes in the coastal CO_2 system or to understand short-term variations in the coastal CO_2 system.
- Characterizing seawater composition in biological experiments.
- Technology development.
- Education activities

Figure 4-A displays the percent of respondents that use TA/DIC reference materials for each activity. The TA/DIC reference material is most commonly used in coastal areas, either to study short-term trends and biology or to study long-term trends. Almost half of respondents use materials to characterize seawater for biological experiments. The least number of respondents used the materials for technology development or education or instruction. Figure 4-B shows the percent of respondents that chose each activity after they were separated into two groups:

respondents that use over 100 bottles of the TA/DIC reference material annually and those that use less than 100 bottles annually. A higher percent of those using over 100 bottles annually study long-term trends in carbonate chemistry.

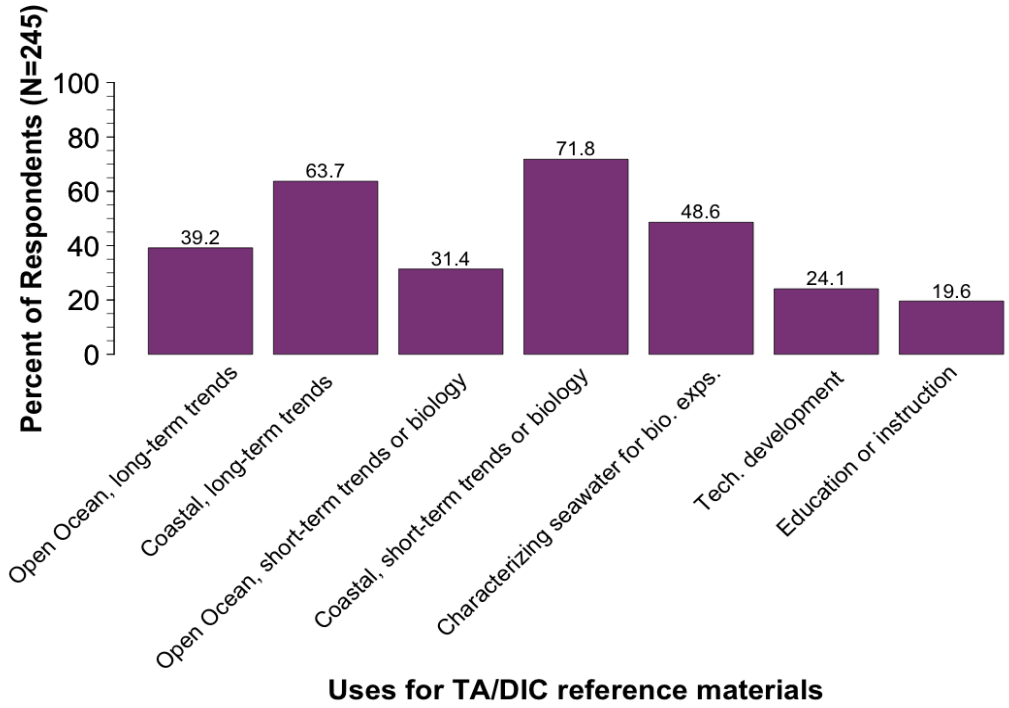

***Figure 4-A**: Respondents indicated which activities they use TA/DIC CRMs for, with some respondents selecting multiple options.*

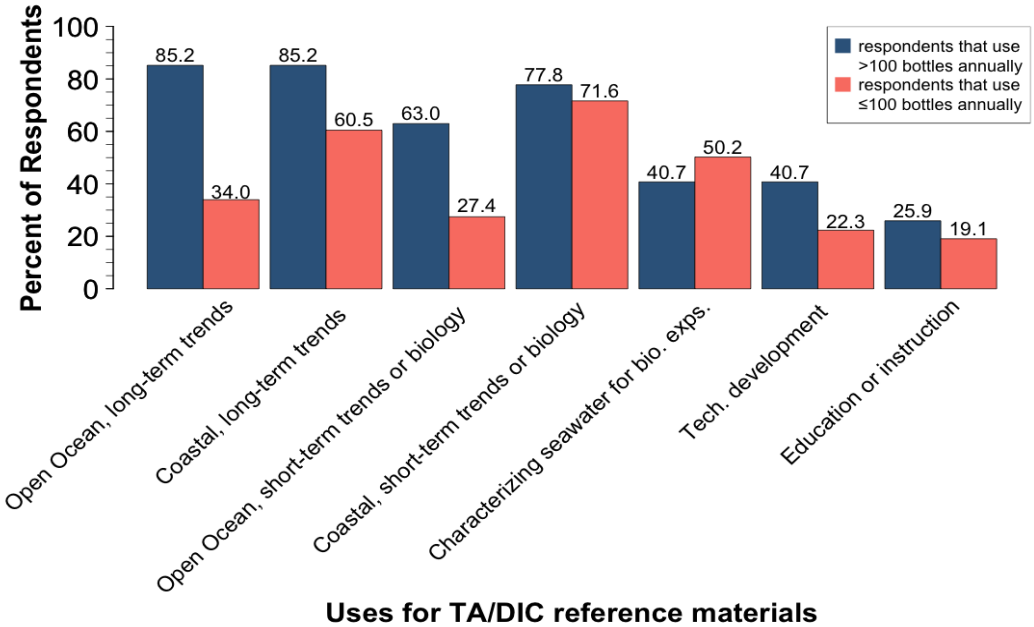

***Figure 4-B**: Respondents were broken into two groups: those that use over and under 100 bottles of CRMs annually. This figure displays the percentage of each group that uses CRMs for each of the seven activities included in the questionnaire. A greater percentage of the respondents that use over 100 bottles annually use CRMs to study long-term trends in the open ocean and short-term trends or biology in the open ocean.*

Future CRM Usage

Future Quantity of CRMs Needed

The questionnaire included questions to elucidate how usage of CRMs may change in the future. Respondents were asked if they expect to use an increased amount of TA/DIC reference materials in the future, and, if so, how many they expect to use. The majority of respondents indicated that they do expect to use more materials in the future (Table 2). The respondents that indicated increased future use were then asked to estimate how many bottles of TA/DIC reference materials they expected to use per year in the future (Table 3). Figure 5 depicts the relationship between respondents' current CRM use and their anticipated future use.

***Table 2**: Out of 245 responses, the majority (70.6%) indicated that yes, they expect to use an increased amount of TA/DIC reference materials in the future.*

Choice	Number of Responses	Percent of Total Responses (N=245)
Yes, I expect to use more bottles of reference materials in the future	173	70.6%
No, I don't expect to use more bottles of reference materials in the future	72	29.4%

***Table 3**: Respondents who thought they would use more bottles of TA/DIC reference materials in the future estimated how many bottles they expected to use in future years. The most common response was that they expected to use between 11-50 bottles per year.*

Choice (bottles of TA/DIC reference materials)	Number of Responses	Percent of Total Responses (N=184; 11 more than expected from Question 9a)
1-5	21	11.4%
6-10	30	16.3%
11-50	69	37.5%
51-100	35	19%
101-200	14	7.6%
201-500	10	5.4%
>500	5	2.7%

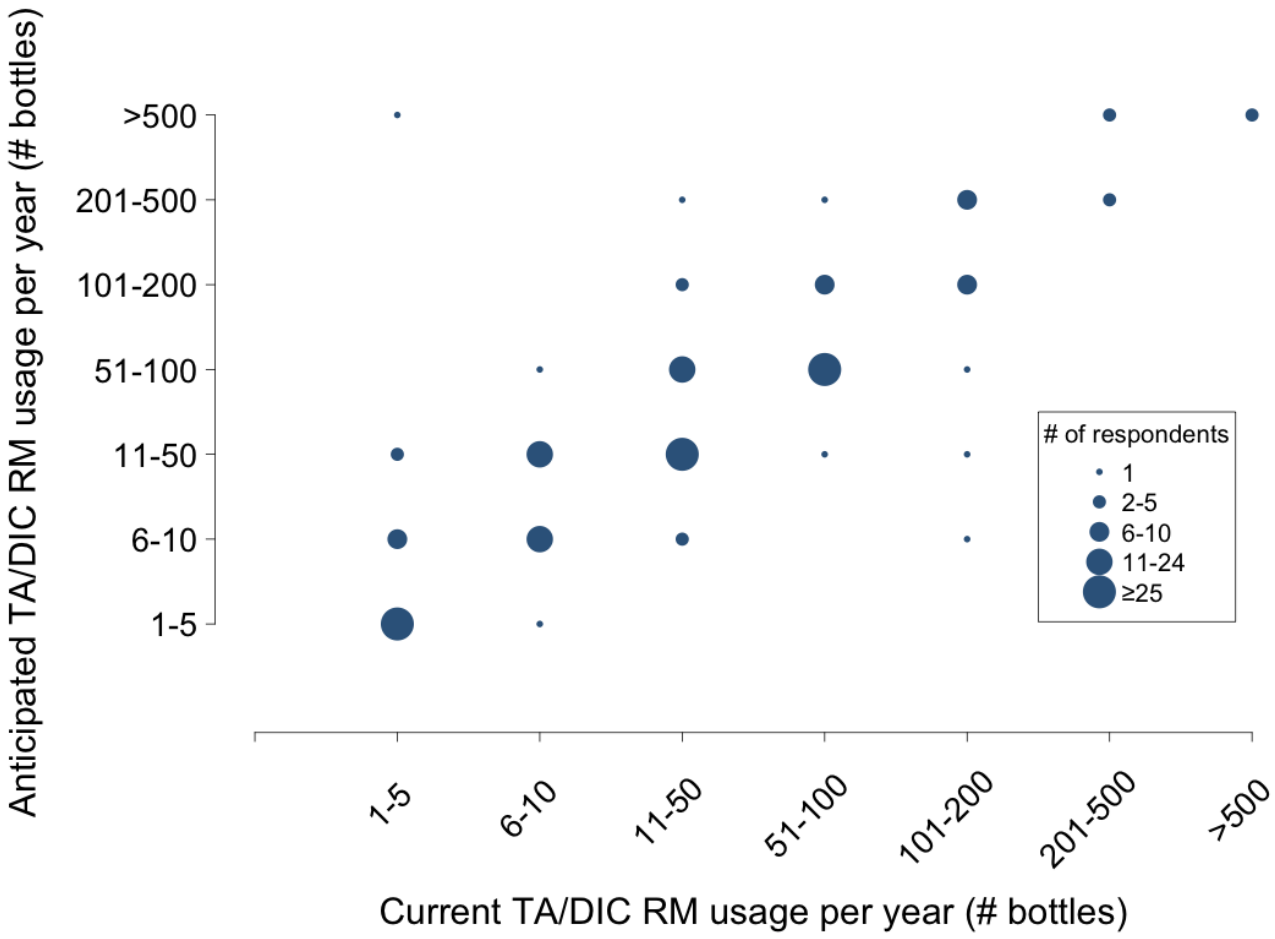

Figure 5*: This graph displays respondents' current usage of TA/DIC reference materials plotted against their anticipated future use. The majority of respondents expect to use the same amount or more of reference materials; very few expect to use less.*

Use of Mercuric Chloride

The questionnaire included two questions related to mercuric chloride ($HgCl_2$), a toxic substance currently used as a preservative in TA/DIC reference materials. The use of mercuric chloride presents potential challenges for some users. The questionnaire inquired if it is challenging for respondents to receive shipments containing mercuric chloride. While less than a quarter of respondents indicated that it is challenging, finding an alternative, less-hazardous preservative may make it easier to distribute reference materials in the future (Table 4). Respondents had the opportunity to provide short answer responses describing their challenges. For many international customers, it is difficult for reference materials containing mercuric chloride to clear customs. Similarly, international customers encounter issues with shipping restrictions from carriers, challenges around disposing of the materials, and other logistical problems. A second question asked if the countries where respondents use TA/DIC reference materials have procedures in place for safely disposing of $HgCl_2$ laboratory waste. While the majority responded "yes", nearly one-in-five respondents indicated "no" or that they were unsure of their country's disposal procedures (Table 5). This is problematic, since mercuric chloride is

hazardous and must be disposed of properly to prevent the substance from causing harm to human and environmental health.

***Table 4**: Respondents were asked if it is challenging to receive shipments containing mercuric chloride. 18% responded yes, and 82% responded no.*

Choice	Number of Responses	Percent of Total Responses (N=245)
Yes	44	18%
No	201	82%

***Table 5:** Respondents were asked if the countries where they use TA/DIC reference materials have procedures in place for safely disposing of mercuric chloride laboratory waste; the majority (81.3%) responded yes.*

Choice	Number of Responses	Percent of Total Responses (N=246)
Yes	200	81.3%
No	16	6.5%
I am not sure	30	12.2%

Future Production of CRMs

The questionnaire asked respondents if they were confident in their laboratory's ability to produce a secondary standard for their laboratory's CO_2 system measurements in seawater. If labs are able to produce secondary standards, this would greatly alleviate demand for certified reference materials from Dickson's lab. Over half of respondents indicated they were not confident in this, indicating an opportunity for investment, training, and capacity building (Table 6).

***Table 6**: Respondents were asked if they are confident in their laboratory's ability to produce a secondary standard for their laboratory's carbonate chemistry measurements in seawater. 57% said no while 43% said yes.*

Choice	Number of Responses	Percent of Total Responses (N=242)
Yes	104	43%
No	138	57%

Finally, the questionnaire asked respondents to indicate whether a government, university, NGO, or industry laboratory in their country or region was capable of and willing to bottle or verify carbonate chemistry conditions with the accuracy and precision required to produce a reference material for the four carbonate system parameters. Out of those that responded (N=53, or about one fifth of total respondents), most selected that they knew someone or some organization who was capable of doing this for total alkalinity, and the fewest thought someone or some organization could do this for calibrated HCl (Table 7). Knowing who is capable of producing various reference materials is important for identifying potential partners for future production. Respondents who answered affirmatively were also asked to share the contact information for whomever they believed could carry out this work, so GOA-ON and the IWG-OA could gather more information.

Table 7*: Respondents were asked to select for which products (TA, DIC, pH, and calibrated HCl) there is a government, university, NGO, or industry laboratory in their country/region capable of and willing to bottle or verify conditions with the accuracy and precision required to produce a reference material. Over half of respondents indicated that someone or some organization in their country or region could do this for a TA, DIC, or pH reference material.*

Choice	N responses	percent of total responses (N=53)
Total alkalinity	48	90.6%
Dissolved inorganic carbon (DIC)	38	71.7%
pH	35	66%
Calibrated HCl	15	28.3%

Conclusion

The community's robust engagement with this questionnaire provided important information about the current and projected future usage of seawater carbonate chemistry system reference materials. A second questionnaire in the future may be useful in collecting even more information; the majority of respondents (79.6%) indicated they would be willing to fill out a more detailed questionnaire related to their use of reference materials. The most important conclusions from this questionnaire are described below:

1. About 75% of respondents use less than 50 bottles of CRMs each year.
2. The total demand for CRMs is expected to increase over the next five years.
3. Respondents who reported using more than 100 bottles annually are more likely to study the open ocean; long-term trends in coastal systems; and technology development.
4. The vast majority of respondents (more than 80%) use CRMs to conduct work in the Atlantic and/or Pacific oceans.

5. About 20% of respondents find it challenging to receive shipments containing mercuric chloride, a key ingredient in Dickson's CRM. Similarly, nearly 20% of respondents either live in a country that does not have procedures in place for safely disposing of mercuric chloride or are unsure of such procedures.
6. Less than half of respondents are confident in their laboratory's ability to produce a secondary standard for CO_2-in-seawater measurements.

Information collected from this questionnaire is guiding the efforts of the U.S. Interagency Working Group on Ocean Acidification and the international community work to build resiliency around certified reference material production and create new models of production.

Appendix A: Questionnaire

CO2-in-seawater Reference Materials Community Survey

Privacy statement:
Individual responses to this survey are confidential. Data from this survey linked to respondents' identities will never be released publicly. Rather, data for public release will be presented in aggregated forms.

Timeline:
While the survey will not close on a specific date, we request that you complete it by May 21, 2021.

Rationale:
Reference materials are fundamental for accurate and precise measurements of seawater CO2 system parameters and research related to ocean acidification and oceanic carbon cycles. Currently, there is a single source of reference materials for total alkalinity, dissolved inorganic carbon, and pH in seawater and a calibrated HCl titrant for seawater alkalinity analysis (A. Dickson Laboratory, Scripps Institution of Oceanography, UC San Diego). The U.S. Interagency Working Group on Ocean Acidification is engaging in efforts to increase the resilience of the production and distribution of reference materials for the quality control of measurements of seawater CO2 system parameters. This survey is the second community engagement in this larger effort, the first being a webinar by Andrew Dickson entitled, "CO2-in-seawater reference materials: yesterday, today, and tomorrow" which can be viewed using Link #1 (below). A pdf of the slides and a conversation thread resulting from the webinar are available by accessing Link #2 (below).

Link #1 - "CO2-in-seawater reference materials: yesterday, today, and tomorrow"
https://www.youtube.com/watch?v=eajzkNxei6w

Link #2 - Questions, conversations, and a pdf of the Dr. Dickson's webinar slides
https://www.oainfoexchange.org/members/updates/50051

* Required

1. Email address *

2. What is your first (given) name?

3. What is your last (family) name?

4. What laboratory, institution, or organization are you affiliated with? Please coordinate with your colleagues to prevent duplicate submissions from the same laboratory.

5. Which products from the Dickson Lab do you use? Select all that apply.

Check all that apply.

- [ ] Total alkalinity/dissolved inorganic carbon (TA/DIC) reference material
- [ ] Tris-buffered pH reference material
- [ ] Certified HCl titrant solution

6. In which oceanographic region(s) do you use TA/DIC reference materials (i.e., the location where the materials are actually used, not necessarily the location of your home institution)?

7. What do you use TA/DIC reference materials for? Select all that apply.

Check all that apply.

- [ ] Measurements of the open ocean for the purpose of detecting long-term, anthropogenically driven changes in the ocean CO2 system.
- [ ] Measurements of coastal waters for the purpose of detecting long-term, anthropogenically driven changes in the coastal CO2 system.
- [ ] Measurements of the open ocean to support species or ecosystem studies focused on the impacts of changes in the ocean CO2 system or to understand short-term variations in the ocean CO2 system.
- [ ] Measurements of coastal waters to support species or ecosystem studies focused on the impacts of changes in the coastal CO2 system or to understand short-term variations in the coastal CO2 system.
- [ ] Characterizing seawater composition in biological experiments.
- [ ] Technology development.
- [ ] Educational activities/instruction.

8. How many bottles of TA/DIC reference material do you use in a typical year?

Mark only one oval.

- ◯ 1-5
- ◯ 6-10
- ◯ 11-50
- ◯ 51-100
- ◯ 101-200
- ◯ 201-500
- ◯ >500

9. Do you anticipate needing to use more bottles of TA/DIC reference material in the future?

Mark only one oval.

- ◯ Yes
- ◯ No

10. If yes, please estimate how many bottles of TA/DIC reference material you will use per year in the future?

Mark only one oval.

- ◯ 1-5
- ◯ 6-10
- ◯ 11-50
- ◯ 51-100
- ◯ 101-200
- ◯ 201-500
- ◯ >500

11. Is it challenging for you to receive shipments containing mercuric chloride (HgCl2)?

Mark only one oval.

- ◯ Yes
- ◯ No

12. If yes, what are the challenges? Please limit your response to 5 sentences.

13. Does the country where you use TA/DIC reference materials have procedures in place for safely disposing of HgCl2 laboratory waste?

Mark only one oval.

- Yes
- No
- I am not sure

14. Which measurement(s) of the carbonate chemistry system do you use TA/DIC reference materials to verify? Select all that apply.

Check all that apply.

- pH
- Total alkalinity
- Dissolved inorganic carbon
- pCO2

15. Are you confident in your laboratory's ability to produce a secondary standard for your laboratory's CO2 system measurements of seawater?

Mark only one oval.

- Yes
- No

16. Please select all applicable boxes. A government, university, NGO, or industry laboratory in my country/region is capable of and willing to bottle or verify conditions with the accuracy and precision required to produce a reference material suitable for:

Check all that apply.

- [ ] Total alkalinity
- [ ] Dissolved inorganic carbon
- [ ] pH
- [ ] Calibrated HCl

17. If you selected any of the boxes above, please give the name of the organization and a good point of contact (including their email address).

_____

_____

_____

_____

_____

18. Are you willing to fill out a more detailed questionnaire related to your use(s) of seawater CO2 system reference materials?

Mark only one oval.

- ◯ Yes
- ◯ No