nature portfolio

Peer Review File

A 37-year record of ocean acidification in the Southern California Current

Web links to the author's journal account have been redacted from the decision letters as indicated to maintain confidentiality

26th Jun 23

Dear Professor Martz,

Your manuscript titled "Ocean Acidification in the Southern California Current: A 37–Year Record" has now been seen by 3 reviewers, and we include their comments at the end of this message. They find your work of interest, but some important points are raised. We are interested in the possibility of publishing your study in Communications Earth & Environment, but would like to consider your responses to these concerns and assess a revised manuscript before we make a final decision on publication.

We therefore invite you to revise and resubmit your manuscript, along with a point-by-point response that takes into account the points raised. Please highlight all changes in the manuscript text file.

Please find below our editorial thresholds:
1) make the whole dataset clearer, and accessible from an online repository, following comments from Reviewer #3
2) clarify the scope/objectives of the study, if it is to remain centred around the dataset itself, in a way that sets the stage to more in-depth analyses

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

Please use the following link to submit your revised manuscript, point-by-point response to the referees' comments (which should be in a separate document to any cover letter) and the completed checklist:
[link redacted]
** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

We hope to receive your revised paper within six weeks; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we may close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Earth & Environment or published elsewhere in the meantime.

Please do not hesitate to contact us if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Olivier Sulpis, PhD
Editorial Board Member
Communications Earth & Environment

0000-0002-6463-3320

Clare Davis, PhD
Senior Editor
Communications Earth & Environment

EDITORIAL POLICIES AND FORMATTING

We ask that you ensure your manuscript complies with our editorial policies. Please ensure that the following formatting requirements are met, and any checklist relevant to your research is completed and uploaded as a Related Manuscript file type with the revised article.

Editorial Policy: Policy requirements (Download the link to your computer as a PDF.)

Furthermore, please align your manuscript with our format requirements, which are summarized on the following checklist:
Communications Earth & Environment formatting checklist

and also in our style and formatting guide Communications Earth & Environment formatting guide .

*** DATA: Communications Earth & Environment endorses the principles of the Enabling FAIR data project (http://www.copdess.org/enabling-fair-data-project/). We ask authors to make the data that support their conclusions available in permanent, publically accessible data repositories. (Please contact the editor if you are unable to make your data available).

All Communications Earth & Environment manuscripts must include a section titled "Data Availability" at the end of the Methods section or main text (if no Methods). More information on this policy, is available at http://www.nature.com/authors/policies/data/data-availability-statements-data-citations.pdf.

In particular, the Data availability statement should include:
- Unique identifiers (such as DOIs and hyperlinks for datasets in public repositories)
- Accession codes where appropriate
- If applicable, a statement regarding data available with restrictions
- If a dataset has a Digital Object Identifier (DOI) as its unique identifier, we strongly encourage including this in the Reference list and citing the dataset in the Data Availability Statement.

DATA SOURCES: All new data associated with the paper should be placed in a persistent repository where they can be freely and enduringly accessed. We recommend submitting the data to discipline-specific, community-recognized repositories, where possible and a list of recommended repositories is provided at http://www.nature.com/sdata/policies/

repositories.

If a community resource is unavailable, data can be submitted to generalist repositories such as figshare or Dryad Digital Repository. Please provide a unique identifier for the data (for example a DOI or a permanent URL) in the data availability statement, if possible. If the repository does not provide identifiers, we encourage authors to supply the search terms that will return the data. For data that have been obtained from publically available sources, please provide a URL and the specific data product name in the data availability statement. Data with a DOI should be further cited in the methods reference section.

Please refer to our data policies at http://www.nature.com/authors/policies/availability.html.

REVIEWER COMMENTS:

Reviewer #1:

The study analyzed a 37-year time series of seawater inorganic carbon collected by the CalCOFI program, specifically focusing on Station 90.90. The analysis revealed a clear signal of ocean acidification, with a decrease in pH of -0.0015 ± 0.0001 per year, driven by temperature and total dissolved inorganic carbon. The unique carbon chemistry signature of Station 90.90, influenced by its proximity to a mid-latitude eastern boundary current upwelling zone, resulted in a reduced uptake rate of CO2 compared to other long-standing time series, highlighting regional differences not captured by existing models.

These results are novel and this type of study is important as they contribute to refining model output for future climate predictions, thus this will be of interest to the community. I think this importance could be better outlined in the introduction, maybe by mentioning the current uncertainty regarding OA trends.

I have very few comments to the authors, as I thought overall it was a well written manuscript. The study could benefit from the addition of context in the introduction (OA uncertainty, model output etc) as well as a better presentation of the comparison with model output and global products (GLODAP, SOCAT). I recommend it be accepted with minor revisions.

Below a few minor comments:
L57 can you provide an uncertainty estimate for the decrease in pH?

L69 it's a bit unclear what the other seven time series are - also having a map locating station 90.90 would be helpful

L71 are they net sources of CO2 all throughout the year or are there seasonal variations?

L98 what's the point of comparing estimates of CT/AT to observations here? I think you mean it the other way around but it doesn't come across that way in text.

L135 Did you propagate the uncertainty for the dissociation constants as well?

L170 how much HgCl was added? Were CO2 best practices followed for the entirety of the timeseries?

L179 wouldn't accuracies differ if two different methods were used in time? Also did you take into account the uncertainty associated with the existence (or not)/availability of CRMs for part of your time series when measuring AT/CT?

L192 were errors propagated in CO2Sys as well? See previous comment, and Python version error propagation by Humphreys et al (2022)

L207 I'm not too sure I understand the point of comparing to climatology products - is it to highlight the importance of high-resolution time series for some areas of the oceans? to better refine model output? In text, it seems like you're trying to have observations match model/big dataset outputs rather than the opposite. These type of long-term time series are definitely a big help to assess the accuracy of models and I think that's what you're trying to show here, but it seems to be clarified a little

L422 Fig 10 I think here the figure should actually show the correction, otherwise it feels a bit meaningless - also, is there should be some sort of uncertainty for the SOCAT climatology

Table 1: p-values of 0.0000 is quite off - is this just a rounding off?

Reviewer #2 (Remarks to the Author):

Summary:

Wolfe et al. present and discuss data from a 37 year long timeseries from the California Current System. They show that while the long-term trend at this site is commensurate with that seen at other sites in the global ocean, the magnitude of the seasonal cycle and other features are quite unique.

Evaluation:

The authors present exciting and highly relevant new long-term observations from the California Current System, a system that is particularly vulnerable to the effects of ocean acidification. No doubt, these data are of high interest to the community, since we have very few places in the world's ocean where ocean acidification is documented over nearly four decades. Thus, these data deserve the highest attention. The publication is long overdue!

While I fully support the publication of these data, this paper does not do full justice to their potential. The analysis of the record is very limited, lacking depth and new insight. The majority of the points made by the authors are well known and thus not particularly novel. The authors refer a few times to a number of follow-up studies (e.g. the study of interannual variations), where more detailed analyses will be presented. This indicates to me that they well recognize the potential of these data. As it stands, the paper does not live up to what I expect from a research paper. It would fit very well into a more data-centric journal such as Earth System Science Data (ESSD).

Recommendation:

I really love to these data published. But by providing only a very limited number of new insights, this paper does not realize the potential contained in these data. I thus do not recommend this manuscript to be published in Communications Earth & Environment. There are a number of excellent opportunities whose inclusion could lift this manuscript above the bar. These are namely: "(i) inclusion of the analysis of interannual variability, (ii) stronger consideration of the timeseries in the context of the northeast Pacific, (iii) more detailed analyses of the driver in the trends of pH, Omega, etc. (iv) addition of a more quantitative comparison of this timeseries vis-a-vis exisiting data sets (there are more datasets than just ESPER).

Detailed comments:

page 3, lines 63ff: I find this discussion potentially misleading. Especially the statement on page 4 (line 75ff) "All of the other time series sites are located in areas where either a lower Revelle factor is coupled with a lower ΔpCO2 or a higher Revelle factor is coupled with a higher ΔpCO2, both of which result in a greater rate of CT uptake." is problematic. First, this statement can be read as if there was a connection between DpCO2 and the Revelle factor, which is not correct. Second, and more concerning is the second part of the statement, since the statement that a higher Revelle factor leads to higher CT uptake is incorrect. There are two places where the Revelle factor matters for the uptake of CO2. First with regard to the uptake and storage of anthropogenic CO2: Here, it turns out that the ability of the surface ocean to absorb and store anthropogenic CO2 scales with 1/Revelle factor, i.e., it is a lower Revelle factor that leads to higher storage. Second with regard to the kinetics of the uptake, i.e. a higher Revelle factor indeed would accelerate the equilibration of the surface ocean with a fixed

atmospheric CO2. But it does not lead to a higher flux for a given Delta pCO2. Thus, this statement needs to be revisited. At the same time, I am wondering why this should even be relevant here.

page 4, line 79 "presumably". There are a handful of studies that have looked already at the processes governing the Delta pCO2 and the air-sea CO2 fluxes in coastal regions and especially in the California Current System. For example, Roobert et al. (2019) comes to mind.

page 4, line 92: "While temporal anomalies in this time series may be worthy of further investigation, the goal of this work is to present the 1st order OA trend, mean seasonal cycle, and to finally make the quality-controlled time series publicly available." This statement illustrates my main concern. I fully agree that there is great value in making the time series publicly available, but I also think that in order for a manuscript to be published in Communications Earth & Environment, it also needs to have more substance. I would consider the inclusion of the analysis of the interannual variations as one of the elements that could lift this manuscript above the bar.

page 5, lines 98ff: "This was done using two different sets of predictor variables: first, using only temperature and salinity, and second, using all available predictor variables including temperature, salinity, phosphate, nitrate, silicic acid, and oxygen". It is unclear to me why one would used only T and S when one knows that the quality of the agreement is much lower. Of course, I am aware that T and S are much more widely available, and that it is of interest to know how much one loses by not using the other parameters. If this was the intention here, then I recommend to write it that way. Otherwise, one gets the impression that the authors want to demonstrate that ESPER does not work, while it actually works rather well.

page 6, line 119: "The discrepancy between the OA trend observed and predicted confirms the impact of local Revelle Factor and ΔpCO2 on CO2 uptake rates relative to global trends." I don't understand the basis for this statement. Why should this misfit be caused by differences in the Revelle factor? There are many other potential causes for biases in the ESPER model. Lack of training data is probably the most important issue. I thus recommend to broaden the discussion here.

page 6, line 132: "On a decadal timescale, increasing CT is the only significant driver of pCO2, contributing 93% (Extended Data Fig. 2)." Here, it would be very helpful to learn more about the other parameters of the surface ocean carbonate system. E.g. what is driving pH, Omega, carbonate ion concentrations etc? And what is the role of the relevant sensitivities

del pH/del DIC or del Omega/del DIC in defining the absolute magnitude of these trends.

page 6, line 132: "Although it is beyond the scope of this work, a mixed layer carbon budget at station 90.90 is the subject of a separate manuscript in progress." This is another potential for adding more depth to this manuscript.

page 6, line 137: "The measured seasonal cycle of sea surface pCO2 matches reasonably well with the grid point corresponding to station 90.90 extracted from the climatology made using the Surface Ocean CO2 Atlas (SOCAT) (Extended 140 Data Fig. 10)." These data products (e.g. Fay et al. 2021) provide also estimates of the trends in pCO2, with some of them also providing estimates of other parameters of the surface ocean carbonate system. This provides many opportunities to put this local timeseries into a larger (regional or global) context, again providing a potential for lifting this ms above the bar.

References:

Fay, A. R., Gregor, L., Landschützer, P., McKinley, G. A., Gruber, N., Gehlen, M., et al. (2021). SeaFlux: Harmonization of air-sea CO2 fluxes from surface pCO2 data products using a standardized approach. Earth System Science Data, 13(10), 4693–4710. https://doi.org/10.5194/essd-13-4693-2021

Roobaert, A., Laruelle, G. G., Landschützer, P., Gruber, N., Chou, L., & Regnier, P. (2019). The Spatiotemporal Dynamics of the Sources and Sinks of CO 2 in the Global Coastal Ocean. Global Biogeochemical Cycles, 33(12), 1693–1714. https://doi.org/10.1029/2019GB006239

Reviewer #3 (Remarks to the Author):

General Comments

Time series are important tools for studying the changing status of the marine carbon cycle, including phenomena such as ocean acidification. The commitment needed to sustain such time series means that there are not many of them globally, and so each one is valuable in itself, as well as contributing to a collective which enhances understanding of the changing drivers of marine ecosystems.

This manuscript presents the first analysis of a 37 year long marine carbon time series in the South California Current, part of the Calcofi programme, and much of these data have not been publicly available previously. The data are interpreted through the lens of ocean acidification and reveal a long term trend similar to that seen at other sites, and in line with uptake of anthropogenic atmospheric carbon dioxide. The seasonal drivers are teased out, and the stage is set for a more in

depth analysis including a mixed layer carbon budget.

These data, and this analysis are an important contribution to marine carbon science, including ocean acidification. I note that the full dataset is not yet available (manuscript line 237), DIC and alkalinity data from 2008 to 2015 are downloadable, however earlier and later data are not. An update on the status of this is required, given that it is explicitly stated (line 168) that the observations will be published.

It appears that the work has formed part of a PhD thesis, so congratulations to W Wolfe for a nice piece of work.

I recommend that this manuscript be published, with only a few minor edits, as detailed below.

Specific Comments
Abstract nicely written and gives a good summary of the main findings of the manuscript.
Line 28 specify "… the mean surface ocean pH has decreased…"
Line 36 This is a bit confusing, implying that carbonate chemistry observations at Calcofi began when time series observation started in Bermuda. Maybe use "at the same time as.."
Line 56,57 This is a key finding and I think should be expressed more rigorously in the text as well as in Table 1 and Fig 1. ie state the error in the slope instead of "~", and state the time period.
Lines 63-73 This paragraph is very clunky, its not clear what is meant by "distinct carbonate chemical signature" (line 66), "unique among all longstanding time series (lines 66 and 67), "exists in a gap not covered by …" (line 68), "naturally poised" (line 72),
Line 73 pCO_2 is not close to the atmosphere (Ex Fig 9), as claimed but can be up to +/- 40 uatm from the values shown from Mauna Loa. (estimated by eye).
Line 103 add in the word "concentrations"
Lines 98 -126 For a concise paper such as this, I found that this section was unnecessarily long, certainly in the detail. I suggest that it is re-written to emphasis the main point that estimating the carbon parameters using global climatologies, relationships and models, does not capture the variability at Station 90.90, therefore emphasizing the need for direct measurements.
Line 180 indicate how the accuracy was estimated (presumably via the use of reference material)
Line 183 specify the pH scale used,
Table 1 In the caption state the time period for which the regression analyses were done

Kim Currie
NIWA,
Dunedin,
New Zealand.

Response to Review of Manuscript COMMSENV-23-0564-T

9 Aug 2023

We thank the reviewers and editors for the valuable feedback that has resulted in an improved manuscript. We appreciate the opportunity to submit this revised version for further consideration. Below, in red, is a point-by-point response to each comment received.

Reviewer #1:
The study analyzed a 37-year time series of seawater inorganic carbon collected by the CalCOFI program, specifically focusing on Station 90.90. The analysis revealed a clear signal of ocean acidification, with a decrease in pH of -0.0015 ± 0.0001 per year, driven by temperature and total dissolved inorganic carbon. The unique carbon chemistry signature of Station 90.90, influenced by its proximity to a mid-latitude eastern boundary current upwelling zone, resulted in a reduced uptake rate of CO2 compared to other long-standing time series, highlighting regional differences not captured by existing models.

These results are novel and this type of study is important as they contribute to refining model output for future climate predictions, thus this will be of interest to the community. I think this importance could be better outlined in the introduction, maybe by mentioning the current uncertainty regarding OA trends.

I have very few comments to the authors, as I thought overall it was a well written manuscript. The study could benefit from the addition of context in the introduction (OA uncertainty, model output etc) as well as a better presentation of the comparison with model output and global products (GLODAP, SOCAT). I recommend it be accepted with minor revisions.

Below a few minor comments:
L57 can you provide an uncertainty estimate for the decrease in pH?
Added uncertainty (0.0001) from table 1.

L69 it's a bit unclear what the other seven time series are - also having a map locating station 90.90 would be helpful
A station map has been added as Extended Data Figure 1.

L71 are they net sources of CO2 all throughout the year or are there seasonal variations?
The sentence was changed to read:
“Station 90.90 is also one of two time series locations that appear to be annual net sources of CO_2 to the atmosphere”

L98 what's the point of comparing estimates of CT/AT to observations here? I think you mean it the other way around but it doesn't come across that way in text.
We used ESPER to estimate C_T & A_T to compare to the direct observations. The difference between estimates and observations of C_T & A_T aims to emphasize the value of direct observations.

L135 Did you propagate the uncertainty for the dissociation constants as well?

We did not propagate uncertainty for the various equilibrium constants (and borate value) involved in the CO2SYS calculations, but some text has been added (see reply to reviewer #1 comment below, "L192…") regarding propagation of errors through CO2SYS. We used the set of constants recommended by the Guide to Best Practices for Ocean CO2 Measurements. The Matlab version of CO2SYS used in this work did not have error propagation options. Propagating errors through CO2SYS will will not change the reported slopes or how they compare to various products, however, as addressed in the added text (see below), using different sets of constants within CO2SYS can lead to bias in the derived parameters and this is the subject of ongoing research.

L170 how much HgCl was added? Were CO2 best practices followed for the entirety of the timeseries?
Added "to final concentration of 50 µM". Best practices were followed as indicated by the statement and reference at the end of the sentence.

L179 wouldn't accuracies differ if two different methods were used in time? Also did you take into account the uncertainty associated with the existence (or not)/availability of CRMs for part of your time series when measuring AT/CT?

The Analytical Methods section has been revised as follows:

"Bottle samples were analyzed for total alkalinity (A_T) and dissolved inorganic carbon (C_T). A_T was measured using a closed cell titration[30] until 1992 and an open cell titration[31] after 1992. C_T was measured using vacuum extraction and manometry[32,33] until 1992, coulometry[34] from 1992–2015 and an infrared (IR) analyzer[35,36] after 2015. Throughout the record, C_T has been traceable to a Scripps manometer (either directly or via Certified Reference Materials[37] after 1992) which, in parallel with NOAA, defines the WMO mole fraction scale for CO_2 in air. A_T has been measured using the traceable practices (acid standardization, weighing) and data processing that now define the A_T of Certified Reference Materials[31]. The various methods used over the years for both A_T and C_T differ primarily in their precision and therefore accuracy of A_T and C_T is estimated to range from 2-5 µmol kg^{-1} and 1-3 µmol kg^{-1}, respectively, over the dataset, reflecting the range of precisions of instruments used with the low end of the range representing the uncertainty of the reference material or method."

L192 were errors propagated in CO2Sys as well? See previous comment, and Python version error propagation by Humphreys et al (2022)
Measurement errors have been propagated and reported. Following this and the comment above, the paragraph beginning on L200 in the revised MS has been expanded as follows:

"The partial pressure of CO_2 in seawater (pCO_2), pH (total scale), carbonate ion concentration ($[CO_3^{2-}]$), saturation states of aragonite and calcite ($\Omega_{aragonite}$, $\Omega_{calcite}$), and Revelle Factor ($\partial \ln[CO_2]/\partial \ln C_T$), were calculated in MATLAB using CO2SYS[38] from A_T, C_T, temperature and salinity with carbonic acid equilibrium coefficients reported in Lueker et al.(2000)[33] and other constants as recommended by the Guide to Best Practices[29] along with the borate-salinity relationship of Lee et al. (2010)[39]. Based on propagation of error through CO2SYS, the measurement uncertainty in C_T and A_T may lead to an error in pCO_2 in the range 6-10 µatm. The choice of input constants (or choice of uncertainty one assigns to the constants) used in CO2SYS presents a significant source of bias in derived values that would negligibly affect the reported slopes in Table 1, but significantly affect the mean pCO_2 and other derived parameters in Fig 1, 3, and 4. Resolving such biases in derived vs measured CO_2 system parameters has long been a central focus of marine carbonate chemists[40–42] and may indeed prove to be part of the apparent ~15 µatm bias between the pCO_2 derived from CalCOFI bottle data and products based on of underway pCO_2 (Fig. 3, Fig. 4). A_T and C_T were salinity normalized (indicated by nA_T and nC_T,) to the average salinity of the time series (33.3, n = 107)."

L207 I'm not too sure I understand the point of comparing to climatology products - is it to highlight the importance of high-resolution time series for some areas of the oceans? to better refine model output? In text, it seems like you're trying to have observations match model/big dataset outputs rather than the opposite. These type of long-term time series are definitely a big help to assess the accuracy of models and I think that's what you're trying to show here, but it seems to be clarified a little
Based on this comment and others echoing it. The following sentence has been added to the discussion section.
"The higher and more variable pCO2 of the time series relative to the data products highlights the continued need for direct measurements."

L422 Fig 10 I think here the figure should actually show the correction, otherwise it feels a bit meaningless - also, is there should be some sort of uncertainty for the SOCAT climatology
A correction for the difference in mean year was added to the figure and uncertainty was added to the climatology.

Table 1: p-values of 0.0000 is quite off - is this just a rounding off?
Yes, it was rounding. p-values revised to read "< 0.0001", indicating a highly significant correlation.

Reviewer #2 (Remarks to the Author):

Summary:
Wolfe et al. present and discuss data from a 37 year long timeseries from the California Current System. They show that while the long-term trend at this site is commensurate with that seen at other sites in the global ocean, the magnitude of the seasonal cycle and other features are quite unique.

Evaluation:
The authors present exciting and highly relevant new long-term observations from the California Current System, a system that is particularly vulnerable to the effects of ocean acidification. No doubt, these data are of high interest to the community, since we have very few places in the world's ocean where ocean acidification is documented over nearly four decades. Thus, these data deserve the highest attention. The publication is long overdue!

While I fully support the publication of these data, this paper does not do full justice to their potential. The analysis of the record is very limited, lacking depth and new insight. The majority of the points made by the authors are well known and thus not particularly novel.
The authors refer a few times to a number of follow-up studies (e.g. the study of interannual variations), where more detailed analyses will be presented. This indicates to me that they well recognize the potential of these data. As it stands, the paper does not live up to what I expect from a research paper. It would fit very well into a more data-centric journal such as Earth system Science Data (ESSD).

Recommendation:
I really love to these data published. But by providing only a very limited number of new insights, this paper does not realize the potential contained in these data. I thus do not recommend this manuscript to be published in Communications Earth & Environment. There are a number of excellent opportunities whose inclusion could lift this manuscript above the bar. These are namely: "(i) inclusion of the analysis of interannual variability, (ii) stronger consideration of the timeseries in the context of the northeast Pacific, (iii) more detailed analyses of the driver in the trends of pH, Omega, etc. (iv) addition of a more quantitative comparison of this timeseries vis-a-vis exisiting data sets (there are more datasets than just ESPER).

We thank the reviewer for pointing out the work by Fay et al (2021). We have incorporated the “SeaFlux” data product into our analysis and as a result, moved two figures (Fig. 3, Fig. 4) from the Extended Data to the main body of the paper. The SeaFlux products provide an additional comparison which is based on a different set of data, independent of ESPER. In essence, there are two existing datasets that provide the grounds for comparison: the global bottle dataset (aka GLODAP) and the global underway pCO2 dataset (aka SOCAT). In our original analysis, we compared our data to products based on these two datasets: for GLODAP we used the ESPER product and for SOCAT, we used the Landschützer climatology product. We put a greater emphasis on the comparison to ESPER because it allowed comparison in the domain of our measurements (C_T and A_T) and was recently updated with a time component that allowed seamless comparison to our time series across any choice of CO_2 variable. Reviewer #2 points

out that around the same time that ESPER was released, Fay et al also released a product that included adding a time component to the Landschützer climatology product. This new product "SeaFlux" is based on a temporal forcing of the Landschützer climatology product and, accordingly, is limited to only pCO_2. We agree that it adds to our analysis to display the SeaFlux pCO2 covering 1990-2000 in Fig. 3. Text reflecting this change has been added/modified as follows:

The relevant paragraph (L142) introducing Fig 3 & 4. Has been heavily revised to read:

"The measured sea surface pCO_2 trend matches the atmospheric CO_2 trend over the same timeframe, although the sea surface pCO_2 has significantly greater variability than atmospheric pCO_2, a feature common to all ocean time series (Fig. 3)[27,28]. The mean sea surface pCO_2 seasonal cycle derived from the CalCOFI bottle data is also exhibits a greater amplitude (42 vs. 29 µatm) and a phase shifted maximum (July vs. September) compared to the climatological sea surface pCO_2 (Fig. 4, based on the Landschützer climatology[23] and SeaFlux products[24]). Perhaps most importantly, the measured sea surface pCO_2 at station 90.90 is, on average, 17 µatm higher than the products derived from the Surface Ocean CO_2 Atlas (SOCAT) database[21], a discrepancy large enough to lead to characterization of this location as a CO2 source (when using the measured data) rather than a sink (when using e.g, the SeaFlux data products) to the atmosphere (Fig. 3). "

We believe that these additions are a meaningful improvement to the manuscript. In regard to other concerns expressed by Reviewer #2, we respectfully disagree with the suggestion that the manuscript is too shallow. The best supporting evidence for this disagreement is found in the overwhelmingly positive comments of Reviewer #1 and Reviewer #3, who both find the paper to be compelling upon its initial submission and do not express concerns over the depth of the analysis. As we stated, adding a mixed layer carbon budget is complex and really deserves a dedicated paper of its own. In our opinion a mixed layer carbon budget would not only significantly lengthen the manuscript, but would also be out of place in context of a trend analysis and comparison to existing products. Simply put, a mixed layer carbon budget is beyond the scope of this work.

In regard to iii above, we would argue that we have provided compelling evidence that the driver in the trends of pH, Omega, etc. is quite clear and in fact we have quantified this in Extended Data Figure 3, where we show unambiguously that it is C_T. The following sentence has been added to clarify that this extends to the other CO2 variables mentioned by the reviewer.

"On a decadal timescale, increasing CT is the only significant driver of pCO2, contributing 93% (Extended Data Fig. 3). Similarly, CT is responsible for > 90% of the trends in the other carbonate variables shown in Fig. 1 and Table 1. Although it is beyond the scope of this work, a mixed layer carbon budget at station 90.90 is the subject of a separate manuscript in progress."

Detailed comments:
page 3, lines 63ff: I find this discussion potentially misleading. Especially the statement on page 4 (line 75ff) "All of the other time series sites are located in areas where either a lower Revelle factor is coupled with a lower ΔpCO2 or a higher Revelle factor is coupled with a higher

ΔpCO2, both of which result in a greater rate of CT uptake." is problematic. First, this statement can be read as if there was a connection between DpCO2 and the Revelle factor, which is not correct. Second, and more concerning is the second part of the statement, since the statement that a higher Revelle factor leads to higher CT uptake is incorrect. There are two places where the Revelle factor matters for the uptake of CO2. First with regard to the uptake and storage of anthropogenic CO2: Here, it turns out that the ability of the surface ocean to absorb and store anthropogenic CO2 scales with 1/Revelle factor, i.e., it is a lower Revelle factor that leads to higher storage. Second with regard to the kinetics of the uptake, i.e. a higher Revelle factor indeed would accelerate the equilibration of the surface ocean with a fixed atmospheric CO2. But it does not lead to a higher flux for a given Delta pCO2. Thus, this statement needs to be revisited. At the same time, I am wondering why this should even be relevant here.

After re-reading this we agree that the sentence was potentially misleading. The text has been revised as follows:
"All of the other time series sites are located in areas with either a lower Revelle or a a higher ΔpCO_2, both of which result in a greater rate of C_T uptake."

page 4, line 79 "presumably". There are a handful of studies that have looked already at the processes governing the Delta pCO2 and the air-sea CO2 fluxes in coastal regions and especially in the California Current System. For example, Roobert et al. (2019) comes to mind.

Added citation to Roobaert et al (2019)

page 4, line 92: "While temporal anomalies in this time series may be worthy of further investigation, the goal of this work is to present the 1st order OA trend, mean seasonal cycle, and to finally make the quality-controlled time series publicly available." This statement illustrates my main concern. I fully agree that there is great value in making the time series publicly available, but I also think that in order for a manuscript to be published in Communications Earth & Environment, it also needs to have more substance. I would consider the inclusion of the analysis of the interannual variations as one of the elements that could lift this manuscript above the bar.

The following sentence was adjusted to read:
Power spectral density (PSD) analysis of the detrended time series showed the presence of a strong annual signal in temperature and C_T, as well as in all calculated carbonate system variables, but did not resolve interannual features within the timeseries (Extended Data Fig. 5).

page 5, lines 98ff: "This was done using two different sets of predictor variables: first, using only temperature and salinity, and second, using all available predictor variables including temperature, salinity, phosphate, nitrate, silicic acid, and oxygen". It is unclear to me why one would used only T and S when one knows that the quality of the agreement is much lower. Of course, I am aware that T and S are much more widely available, and that it is of interest to know how much one loses by not using the other parameters. If this was the intention here, then I recommend to write it that way. Otherwise, one gets the impression that the authors want to demonstrate that ESPER does not work, while it actually works rather well.

It is not always the case that using more predictor variables is better. In the surface ocean in particular it can be argued that CO2 parameters are less likely to correlate with the additional variables (nutrients and oxygen). For example, this is the reason that predecessors of ESPER (Juranek et al., 2009 and Alin et al., 2012) excluded the shallowest surface waters and, for alkalinity in particular, found that the fit was improved when excluding oxygen (using only T & S). With the development of ESPER the predictor functions can be used at the surface, yet, the limitations of ESPER at the surface are mentioned by Carter et al (2021) who state that, in regard to C_T, "estimates within the surface ocean should be treated with caution". The limitations are due to a combination of limitations of the training dataset of bottle samples not having seasonal resolution and due to other processes, such as the difference in gas exchange rates between CO2 and O2 at the surface that would cause a divergence in the relationship between O2 as a predictor variable for CO2. To clarify, we have added a sentence with the two additional references (Juranek et al 2009 and Alin et al 2012) to this paragraph as follows:

"…including temperature, salinity, phosphate, nitrate, silicic acid, and oxygen (in addition to latitude, longitude, depth, and year in both cases). Depending on the "preformed" nature of surface water, additional variables such as oxygen and nutrients may not correlate with carbonate parameters in the surface ocean, hence the use of T and S only as one set of predictors[25,26]. Using only temperature…"

page 6, line 119: "The discrepancy between the OA trend observed and predicted confirms the impact of local Revelle Factor and ΔpCO2 on CO2 uptake rates relative to global trends." I don't understand the basis for this statement. Why should this misfit be caused by differences in the Revelle factor? There are many other potential causes for biases in the ESPER model. Lack of training data is probably the most important issue. I thus recommend to broaden the discussion here.

This sentence was re-written as follows:

"The discrepancy between the OA trend observed and predicted confirms may be due to the use of the simplified steady-state assumption used by ESPER to predict anthropogenic CO2 as a function of time via a simple exponential equation with one coefficient applied globally."

page 6, line 132: "On a decadal timescale, increasing CT is the only significant driver of pCO2, contributing 93% (Extended Data Fig. 2)." Here, it would be very helpful to learn more about the other parameters of the surface ocean carbonate system. E.g. what is driving pH, Omega, carbonate ion concentrations etc? And what is the role of the relevant sensitivities del pH/del DIC or del Omega/del DIC in defining the absolute magnitude of these trends.

A following sentence was added:

"Similarly, C_T is responsible for > 90% of the trends in the other carbonate variables shown in Fig. 1 and Table 1."

page 6, line 132: "Although it is beyond the scope of this work, a mixed layer carbon budget at station 90.90 is the subject of a separate manuscript in progress." This is another potential for adding more depth to this manuscript.

Addressed above in reply to reviewer #2 summary comment.

page 6, line 137: "The measured seasonal cycle of sea surface pCO2 matches reasonably well with the grid point corresponding to station 90.90 extracted from the climatology made using the Surface Ocean CO2 Atlas (SOCAT) (Extended 140 Data Fig. 10)." These data products (e.g. Fay et al. 2021) provide also estimates of the trends in pCO2, with some of them also providing estimates of other parameters of the surface ocean carbonate system. This provides many opportunities to put this local timeseries into a larger (regional or global) context, again providing a potential for lifting this ms above the bar.

As discussed above in reply to reviewer #2 summary comment, the Fay et al data and reference provided by the reviewer have been incorporated into our analysis.

References:

Fay, A. R., Gregor, L., Landschützer, P., McKinley, G. A., Gruber, N., Gehlen, M., et al. (2021). SeaFlux: Harmonization of air-sea CO2 fluxes from surface pCO2 data products using a standardized approach. Earth System Science Data, 13(10), 693–4710. https://doi.org/10.5194/essd-13-4693-2021

Roobaert, A., Laruelle, G. G., Landschützer, P., Gruber, N., Chou, L., & Regnier, P. (2019). The Spatiotemporal Dynamics of the Sources and Sinks of CO 2 in the Global Coastal Ocean. Global Biogeochemical Cycles, 33(12), 693–1714. https://doi.org/10.1029/2019GB006239

Reviewer #3 (Remarks to the Author):

General Comments
Time series are important tools for studying the changing status of the marine carbon cycle, including phenomena such as ocean acidification. The commitment needed to sustain such time series means that there are not many of them globally, and so each one is valuable in itself, as well as contributing to a collective which enhances understanding of the changing drivers of marine ecosystems.

This manuscript presents the first analysis of a 37 year long marine carbon time series in the South California Current, part of the Calcofi programme, and much of these data have not been publicly available previously. The data are interpreted through the lens of ocean acidification and reveal a long term trend similar to that seen at other sites, and in line with uptake of anthropogenic atmospheric carbon dioxide. The seasonal drivers are teased out, and the stage is set for a more in depth analysis including a mixed layer carbon budget.

These data, and this analysis are an important contribution to marine carbon science, including ocean acidification. I note that the full dataset is not yet available (manuscript line 237), DIC and alkalinity data from 2008 to 2015 are downloadable, however earlier and later data are not. An update on the status of this is required, given that it is explicitly stated (line 168) that the observations will be published.
C_T and A_T data from the full timeseries used in this manuscript are now available at https://calcofi.org/data/oceanographic-data/dic/

It appears that the work has formed part of a PhD thesis, so congratulations to W Wolfe for a nice piece of work.
It was indeed, thank you very much!

I recommend that this manuscript be published, with only a few minor edits, as detailed below.

Specific Comments
Abstract nicely written and gives a good summary of the main findings of the manuscript.
Line 28 specify "… the mean surface ocean pH has decreased…"
Added.

Line 36 This is a bit confusing, implying that carbonate chemistry observations at Calcofi began when time series observation started in Bermuda. Maybe use "at the same time as.."
Added.

Line 56,57 This is a key finding and I think should be expressed more rigorously in the text as well as in Table 1 and Fig 1. ie state the error in the slope instead of "~", and state the time period.
The sentence has been revised as follows:
"The time series exhibits an unambiguous ocean acidification signal in agreement with the global surface ocean showing a decrease in pH of 0.0015 ± 0.0001 yr-1 from 1984–2021, (Fig. 1, Table 1), as well as a distinct seasonal cycle (Fig. 1, right column)."

Lines 63-73 This paragraph is very clunky, its not clear what is meant by “distinct carbonate chemical signature” (line 66), “unique among all longstanding time series (lines 66 and 67), “exists in a gap not covered by …” (line 68), “naturally poised” (line 72),
The section has been revised to read:

“Several features make station 90.90 unique compared to other multi-annual longstanding oceanic inorganic carbon time series[8]. Station 90.90 is the oldest traditional hydrographic inorganic carbon time series location in the Pacific, it is also the furthest from land globally. The observed C_T, $\Omega_{aragonite}$, Revelle Factor, sea surface temperature and salinity at station 90.90 have average seasonal ranges not covered by the other seven time series[8]. Station 90.90 is one of two located within an eastern boundary current, shown in Extended Data Fig. 1 (alongside European Station for Time series in the Ocean at the Canary Islands i.e. ESTOC)[8]. Station 90.90 is also one of two time series locations that appear to be annual net sources of CO_2 to the atmosphere (alongside CArbon Retention In A Colored Ocean i.e. CARIACO)[8,14]. Station 90.90 has a mid-range Revelle Factor, and a mean pCO_2 close to that of the atmosphere (Fig. 3), resulting in a nominal to low mean ΔpCO_2, where ΔpCO_2 is the difference in the partial pressure of CO_2 between the sea surface and atmosphere.”

Line 73 pCO2 is not close to the atmosphere (Ex Fig 9), as claimed but can be up to +/- 40 uatm from the values shown from Mauna Loa. (estimated by eye).
Clarified that the mean is relatively close to the atmosphere

“Station 90.90 has a mid-range Revelle Factor, and a mean pCO_2 close to that of the atmosphere (Fig. 3)…”

Line 103 add in the word “concentrations”
Added.

Lines 98 -126 For a concise paper such as this, I found that this section was unnecessarily long, certainly in the detail. I suggest that it is re-written to emphasis the main point that estimating the carbon parameters using global climatologies, relationships and models, does not capture the variability at Station 90.90, therefore emphasizing the need for direct measurements.
Based on this and other reviewer comments these paragraphs have been updated.

Line 180 indicate how the accuracy was estimated (presumably via the use of reference material)
Addressed above in response to Review #1’s comment (referenced to L179).

Line 183 specify the pH scale used,
pH total scale specified.

Table 1 In the caption state the time period for which the regression analyses were done
Time range (1984–2021) added to table caption.

20th Sep 23

Dear Professor Martz,

Your manuscript titled "Ocean Acidification in the Southern California Current: A 37–Year Record" has now been seen by our reviewers, whose comments appear below. In light of their advice we are delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Earth & Environment under the open access CC BY license (Creative Commons Attribution v4.0 International License).

We therefore invite you to revise your paper one last time to address the remaining concerns of our reviewers. At the same time we ask that you edit your manuscript to comply with our format requirements and to maximise the accessibility and therefore the impact of your work.

EDITORIAL REQUESTS:

Please review our specific editorial comments and requests regarding your manuscript in the attached "Editorial Requests Table".

*****Please take care to match our formatting and policy requirements. We will check revised manuscript and return manuscripts that do not comply. Such requests will lead to delays. *****

Please outline your response to each request in the right hand column. Please upload the completed table with your manuscript files as a Related Manuscript file.

If you have any questions or concerns about any of our requests, please do not hesitate to contact me.

SUBMISSION INFORMATION:

In order to accept your paper, we require the files listed at the end of the Editorial Requests Table; the list of required files is also available at https://www.nature.com/documents/commsj-file-checklist.pdf .

OPEN ACCESS:

Communications Earth & Environment is a fully open access journal. Articles are made freely accessible on publication under a CC BY license (Creative Commons Attribution 4.0 International License). This license allows maximum dissemination and re-use of open access materials and is preferred by many research funding bodies.

For further information about article processing charges, open access funding, and advice and support from Nature Research, please visit https://www.nature.com/commsenv/article-processing-charges

At acceptance, you will be provided with instructions for completing this CC BY license on behalf of

all authors. This grants us the necessary permissions to publish your paper. Additionally, you will be asked to declare that all required third party permissions have been obtained, and to provide billing information in order to pay the article-processing charge (APC).

Please use the following link to submit the above items:
[link redacted]
** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

We hope to hear from you within two weeks; please let us know if you need more time.

Best regards,

Olivier Sulpis, PhD
Editorial Board Member
Communications Earth & Environment

Clare Davis, PhD
Senior Editor
Communications Earth & Environment

www.nature.com/commsenv/
@CommsEarth

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

This manuscript on is an invaluable contribution. The dataset is thorough, and while the authors' interpretations are insightful, the data's potential for broader application stands out. I'm pleased with the revisions made in response to previous feedback and believe this work should be published as it is. It will undoubtedly serve as a foundation for diverse future research. I eagerly anticipate its reception and application by the wider scientific community.

Reviewer #2 (Remarks to the Author):

Evaluation:

Wolfe et al. revised aspects of their manuscript in response to the
comments by this reviewer, thereby substantially improving the text.
But the authors did not take the recommended big
step. I was informed by the editor that this ms is supposed to be

short and that a focus on the results without a deep analysis is perfectly within the purview of the journal. While I continue to think that the lack of a deeper analyis is a missed opportunity, I am perfectly happy to accept this position and support the publication of this ms. And as stated in my first review, "The publication is long overdue!"

I have a few remaining comments that I would like the authors to take into consideration before preparing the final version of their manuscript.

Recommendation:

I recommend acceptance of this manuscript after minor revision.

Detailed comments:

p2, line 30. You may want to consider to add a reference to the reconstructions of Osborne et al. (2020).

p3, line 57. "in line with the global surface ocean". Which study is this comparison based upon? Please cite.

p4, line 75ff: "with either a lower Revelle or a a higher ΔpCO2, both of which result in a greater rate of CT 76 uptake.". I still find this statement confusing. A low Revelle factor permits the surface ocean to take up and store more anthropogenic CO2, while a high (negative) Delta pCO2 enhances the uptake of natural AND anthropogenic CO2. I suggest to separate this more clearly.

p5, line 100ff: "SOCAT data are the basis of two products used in this 101 study23,24 that estimate the sea surface pCO2 at station 90.90." Please be more precise here. Landschützer et al. describes a single pCO2 product, while Fay et al. describe an ensemble of 6 methods, including the estimate of Landschützer et al. Thus one cannot write "two products". I recommend to just use the Fay et al. products, but indicate the spread in your figures.

p5, line 102ff: "Using ESPER we estimate CT and AT, where CT and AT are derived from local data 103 collected independent of CalCOFI (see methods)" Here, it would be helpful to make the link to the ocean acdification parameters, i.e., pH and saturation state. In this context, you may want to take a look also at the recently published OA trend analyses of Ma et al. (2023).

p8, line 165ff: "we found that widely used empirical proxy relationships introduced a 40% bias in the rate of CO2 uptake". What is the basis of this statement? Is this the 15 muatm discrepancy?

Please provide the calculations. I also think it is important to add the expression "local" to uptake.

Figure 3: I am very happy that you moved this figure to the main text. But please add the uncertainty ranges from the different products here. And please show only the waterside estimateas of pCO2.

Cited references:

Ma, D., Gregor, L., & Gruber, N. (2023). Four Decades of Trends and Drivers of Global Surface Ocean Acidification. Global Biogeochemical Cycles, 37(7), 1–19. https://doi.org/10.1029/2023GB007765

Osborne, E. B., et al. (2020). Decadal variability in twentieth-century ocean acidification in the California Current Ecosystem. Nature Geoscience, 13(1), 43–49. https://doi.org/10.1038/s41561-019-0499-z

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

This manuscript on is an invaluable contribution. The dataset is thorough, and while the authors' interpretations are insightful, the data's potential for broader application stands out. I'm pleased with the revisions made in response to previous feedback and believe this work should be published as it is. It will undoubtedly serve as a foundation for diverse future research. I eagerly anticipate its reception and application by the wider scientific community.

Reviewer #2 (Remarks to the Author):

Evaluation:

Wolfe et al. revised aspects of their manuscript in response to the comments by this reviewer, thereby substantially improving the text. But the authors did not take the recommended big step. I was informed by the editor that this ms is supposed to be short and that a focus on the results without a deep analysis is perfectly within the purview of the journal. While I continue to think that the lack of a deeper analyis is a missed opportunity, I am perfectly happy to accept this position and support the publication of this ms. And as stated in my first review, "The publication is long overdue!"

I have a few remaining comments that I would like the authors to take into consideration before preparing the final version of their manuscript.

Recommendation:

I recommend acceptance of this manuscript after minor revision.

Detailed comments:

p2, line 30. You may want to consider to add a reference to the reconstructions of Osborne et al. (2020).
Citation added

p3, line 57. "in line with the global surface ocean". Which study is this comparison based upon? Please cite.

Sentence updated to read:
“The time series exhibits an unambiguous ocean acidification signal in pH of -0.0015 ± 0.0001 yr^{-1} from 1984–2021, in agreement with the global surface ocean average[14] of -0.0017 yr^{-1}…”

Where 14 is the Ma et al., 2023 citation.

p4, line 75ff: "with either a lower Revelle or a a higher ΔpCO2, both of which result in a greater rate of CT 76 uptake.". I still find this statement confusing. A low Revelle factor permits the surface ocean to take up and store more anthropogenic CO2, while a high (negative) Delta pCO2 enhances the uptake of natural AND anthropogenic CO2. Isuggest to separate this more clearly.

Line 75 has been expanded into two sentences to incorporate this comment.

“All of the other time series sites are located in areas with either a lower Revelle Factor or a higher greater ΔpCO2. A lower Revelle Factor allows for greater up take and storage of anthropogenic CO2 and a greater (negative) ΔpCO2 increases the uptake of both natural and anthropogenic CO2.”

p5, line 100ff: "SOCAT data are the basis of two products used in this 101 study23,24 that estimate the sea surface pCO2 at station 90.90." Please be more precise here. Landschützer et al. describes a single pCO2 product, while Fay et al. describe an ensemble of 6 methods, including the estimate of Landschützer et al. Thus one cannot write "two products". I recommend to just use the Fay et al. products, but indicate the spread in your figures.

Text on L101 was modified to clarify that it is really only one product: the Landschützer climatology. We think it is worth keeping the two different scalings shown in Figure 4 as this indicates that temporal scaling of the pCO_2 is likely not the major source of error.

p5, line 102ff: "Using ESPER we estimate CT and AT, where CT and AT are derived from local data collected independent of CalCOFI (see methods)" Here, it would be helpful to make the link to the ocean acdification parameters, i.e., pH and saturation state. In this context, you may want to take a look also at the recently published OA trend analyses of Ma et al. (2023).

The following sentence was added at L104: “While ESPER can also serve as the basis to estimate pCO2, (as well as pH and Ω) products based on SOCAT provide a more robust comparison for pCO2 due to the higher density of surface data in their training set.”

p8, line 165ff: "we found that widely used empirical proxy relationships introduced a 40% bias in the rate of CO2 uptake". What is the basis of this statement? Is this the 15 muatm discrepancy? Please provide the calculations. I also think it is important to add the expression

"local" to uptake. Figure 3: I am very happy that you moved this figure to the main text. But please add the uncertainty ranges from the different products here. And please show only the waterside estimateas of pCO2.

L170: Added “local”

L127 was modified to read: “C_T trend was 40% higher (a residual slope of 0.3 higher than the measured slope of 0.7 µmol kg^{-1} yr^{-1})”

The following text was added to the Figure 3 caption: “From Table 2 in Ref. 25, the reported bias ± RMSE (relative to the training data) in the product used to generate $SeaFlux_{sea}$ is 0.1 ± 13.7 µatm.”

It is necessary to show atmospheric pCO2 in this figure in order to support the statement on L155 that the 90.90 site would be characterized as a CO2 source based on the bottle data. Therefore we will keep both the atmospheric and waterside pCO2 lines in this figure.

Cited references:

Ma, D., Gregor, L., & Gruber, N. (2023). Four Decades of Trends and Drivers of Global Surface Ocean Acidification. Global Biogeochemical Cycles, 37(7), 1–19. https://doi.org/10.1029/2023GB007765

Osborne, E. B., et al. (2020). Decadal variability in twentieth-century ocean acidification in the California Current Ecosystem. Nature Geoscience, 13(1), 43–49. https://doi.org/10.1038/s41561-019-0499-z