An automated gas exchange tank for determining gas transfer velocities in natural seawater samples

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We would like to thank the reviewers for their valuable suggestions and positive comments. In response to the reviewers' comments, we have provided a detailed reply and incorporated a number of revisions as detailed below.

Reply to reviewers' comments

Reviewer #1: D. K. Woolf
Specific comments

One possible criticism is that the turbulence (and gas transfer) is driven by a convenient method (a baffle) rather than necessarily a realistic mechanism. I do not think this is a major issue and it does seem sensible (as argued in the introduction) to focus on maintaining a sealed tank and achieving reproducible results rather than dwelling on the precise characteristics of the turbulence, wave field and other physical characteristics. It is worth noting also that wave spectra are measured, therefore there is a record of the wave field generated by each setting of the baffle.

The reviewer agrees with our view. We have added a note regarding the wave spectra in the introduction.

Results are described for natural water samples (from various distances offshore of the north east of England). It would be useful to see more results, but those reported here are adequate to demonstrate both the utility of the apparatus and the significant role of surfactants in controlling gas transfer rates.

The aim of this work was to describe, in detail, the method and apparatus we have developed to determine gas transfer velocities in natural seawater samples. We felt that significant detail was required given the complexity of the automation etc. In this context, we felt that more results would have detracted from this aim. Further results will be published in a separate publication which focuses on the processes of gas exchange rather than the method used to determine it.

The abstract is slightly misleading in that 3 gases are mentioned here, but in fact the results for one gas, nitrous oxide are very limited (appearing only in Figure 5). Perhaps there should be some explanation that the apparatus has been designed and tested (in respect to the equilibration component, Figure 5) for 3 gases, but transfer velocities are reported here for only 2 gases?

The apparatus is designed for 3 gases. However, the N_2O chromatography was not fully operational in all our tests. Therefore, we have decided not to include data for this gas. We have added a note in the introduction.

The only major doubt I have about this paper is the contention at line 15 of page 710 that D is approximately Cw for SF6 throughout. Since the system is closed, I'd expect the head space to equilibrate with the water volume during the course of the experiment and sensibly (to get accurate transfer velocities) the experiment should be run long enough for this to occur substantially. Solubility is largely irrelevant to that argument (contradicting lines 15 to 19 of page 710) but will equilibrate less simply because it has a lower transfer velocity. This criticism may be relatively unimportant if the mathematics in Section 4.4.1 has been rigorously applied to all the gases.

As stated in p. 708 l. 3, we have used Eq. (13) for the evaluation of all gases. The text which the reviewer refers to was only meant as a general side note and has been removed from the manuscript to avoid confusion.

Section 4 on experimental procedure is generally good but there a few places where the explanation was inadequate for me, while other material was probably superfluous. The explanation of sample volume calculations at Lines 4-9 of Page 707 mystified me.

We have clarified the description as the reviewer requests.

At line 26 and following of page 707, it would be worth citing one or more sources on the calculation of propagated errors.

We have added references to textbooks and have also added the resulting expressions to the the appendix (c.f. reviewer #2).

There is a disconnection between lines 8-12 of page 708 in Section 4.2 and the description of subsection 4.4.3, if not a contradiction. Were these two sections written by a different person? In my opinion Section 4.4.3 is superfluous and discarded, but there should be some better explanation in 4.2; firstly, why n = 12 is unsurprising for this apparatus and MilliQ; secondly, why (if this is the case ?!) n= 12 was used for normalization throughout.

There is a mistake on p. 708. $n = \frac{1}{2}$ corresponds to a wavy surface as stated correctly in section 4.4.3 and not to a flat surface as incorrectly written on p. 708. We have corrected the text on p.708. $n = \frac{1}{2}$ was used for the normalisation throughout as it has been determined experimentally. We have added more explanation on this to the paper.

With regards the reviewers suggestion to remove Section 4.4.3, although Schmidt number scaling is commonly used, if this section is removed the equation used to scale the data would not be mentioned or explained at all in the paper. Considering that all other equations, even those commonly used, used are also explained, we prefer to keep this section.

Section 4.4.4 on wave spectra seems to me slightly misjudged and could be omitted. For those (including me) familiar with wave spectra generally and the particular explanation given by Phillips, the material is recognisable and superfluous. For those less interested, the material is unnecessarily mathematical and pedantic. I suggest that it is sufficient to state that the 400 Hz time series of elevation is used to calculate a power spectrum in frequency. The only other things worth noting are that the baffle frequency and its harmonics are readily evident in the power spectra (this has been done in the caption of Figure 9) and the tail above an angular frequency of 100Hz is almost certainly affected by noise. Section 4.4.4 could be omitted and the final paragraph of 4.2 used to provide sufficient explanation.

For the used measurement frequency of 400 Hz, the Nyquist frequency is 200 Hz = 1257 rad/s. However, we agree that the data is influenced by noise at frequencies lower than this. Therefore, the result plots only go up to 500 rad s^{-1} ≈ 80 Hz. We have added this explanation to the paper.

In addition to the figure caption, we have also mentioned the baffle frequency and its harmonics at the end of Section 5.2. As suggested by the reviewer, we have removed section 4.4.4.

The figures are generally well drawn and clear, though some of the text (especially in Figure 4) strained by tired eyes.

We have increased the size of Fig. 4.

Reviewer #2
Specific comments

Section 3.1 I agree with the other reviewer that the simulation of turbulence via a baffle does not represent a natural mechanism, but it is absolutely sensible to use it for this kind of setup. I believe reproducing natural turbulence in a small tank is not possible at all, and the described tank with baffle is still useful to gain new insights in the fundamentals of air-sea gas exchange.

Again, the reviewer agrees with us.

Section 4.1 A minor critism in the sampling of real samples is the use of a bucket to collect subsurface samples, as it would also collect material from the microlayer. But it does not affect the assessment of the tank setup.

Actually, the sampling procedure has not been described precisely enough. Water has been collected with a bucket, and then the sampling tubes have been opened below the water surface of the bucket, filled, and immediately closed, using nitrile gloves. Thus, while there is still SML in the bucket, it is not sampled with the tubes. We have updated the description of this in the paper. (This procedure has been chosen for operational reasons, as it is very difficult to fill the tubes outboard.)

Section 4.2 I could imagine that it is extremely difficult to reduce the surfactant activity in the tanks's microlayer to that of DI water as tiny amounts of DOM would change it. It would be good to show some data how close the authors came to the surfactant activity of DI water.

It is difficult, but with our cleaning method, we managed to get the SML samples to the level of fresh MilliQ within between ± 0.02 eq. mg/l T-X-100 and max. ± 0.04 eq. mg/l T-X-100. We have added these values to the paper.

Filling the tank is described well, but I do not see where the microlayer samples, collected with screen during field sampling, come into the play.

These are used for surfactant activity (SA) measurements as described in sections 4.1 ("Additional samples for the measurement of surfactant activity ...") and 4.3, see also Fig. 10.

Page 15, Line 25: I think it would be nice to provide (potentially young) readers a description how to do the calcultion of Gaussian error propagation. Section 4.4 For me as a more practical scientist a little too long and hard to read. The manuscript describes well a labortory setup, and the authors should think to put the paper into a more practical content (i.e. hands-on in the assessment of uncertainities like error propagation).

We have added references to textbooks and put the final expressions for the uncertainties into the appendix.

Section 5 Presentation of results and discussion very short.For example, I do not understand Fig. 10, and it seems to me the authors compare gas transfer velocities from the laboratory tank with surfactant activity of microlayers in the field. That would be hard to interpret, and should be at least described in a way that the readers understand what was done. Did the authors fill microlayer samples into the tank, too?

We are comparing the laboratory measured transfer velocities of water samples collected in the field to SA measurements of SML samples collected at the same time and place. At no point were SML samples added to the tank. The aim was to compare the transfer velocities of the water samples to the in situ SML in order to learn something about the influence of surfactants.