**Ocean Science
Discussions**

Interactive
Comment

Interactive comment on "A numerical scheme to calculate temperature and salinity dependent air-water transfer velocities for any gas" *by* M. T. Johnson

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I thank both referees for their constructive and generally positive reviews of this work, which I feel has led to substantial improvements in the detailing and discussion of the scheme presented. I will respond to their specific points one-by-one below, but there are some general points which I will put forward first to frame the discussion.

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1 General points

i) Intended audience: As pointed out by both referees the scheme put forward does not account for the various effects outside of the standard 'two-phase' model of gas exchange such as bubble mediated transfer, microlayer effects etc. Necessarily, it also utilizes specific parameterisations for each individual component of the transfer velocity calculation. These are limitations which need to be clearly stated in the abstract and further in the main text of the manuscript, although it is important to consider the uncertainties associated with these paramterisations in the context of the uncertainty in the concentration fields used to drive flux calculations for poorly studied / understood trace gases, which are likely to be large. However, this scheme is not intended to replace either the NOAA COARE algorithm (as both referees clearly recognize) or the detailed study of exchange for a particular gas; rather it is envisaged that the intended users of this scheme will be non-experts in air-sea gas exchange who wish to calculate fluxes of their (probably poorly studied) gas of interest, and where they would currently apply e.g. the Nightingale et al 2000 parameterisation, with a fixed Schmidt number, irrespective of solubilty, temperature etc, and would not even consider the effects of bubbles / chemical enhancement etc. If this scheme is adopted by such studies, then they would at least be employing the standard two-phase model in a consistent, applicable and traceable manner.

To highlight the importance of the 'simple' approach to calculating trace gas exchange in the literature, I have conducted a Scopus search on articles since Jan 2008 which cite either Liss and Slater (1974) or one or more of four key papers concerning the NOAA COARE algorithm - Fairall et al 2000, Fairall et al 2003, Hare et al 2004 and Blomquist et al 2006 (Figure 1; not to be included in the paper unless reviewers / editor think it necessary). Although more than 3 times as many articles cite the COARE papers (167 vs 55 for Liss and Slater), only 2 of the citing articles are concerned with non-greenhouse trace gases other than DMS. DMS flux studies account for 16 cita-

tions, GHG or O2/N2 flux studies for a further 17. 9 citing articles are concerned with general gas exchange theory and the remaining 124 cover water vapour / heat or momentum transfer. On the other hand, only 1 of the articles citing Liss and Slater is concerned with transfer of water vapour, 6 with generic gas exchange, 12 with GHGs/ O2 and 36 with the flux of other trace species (of which 5 are concerned with DMS, the remainder spanning organic solvents, pesticides, mercury, oxygenated volatile organic compounds, halocarbons, H2S, ammonia and numerous others). This highlights the large 'tail' of of studies which employ a simple approach to quantifying trace gas exchange. As many of these studies rely on limited observational data, often with substantial measurement uncertainty, it is pragmatic to employ a realtively quick and simple approach to quantifying gas exchange (of course this analysis doesn't account for those which apply simple transfer velocity paramterisations and then amend them with other terms for e.g. bubble-mediated transfer or chemical enhancement, which is how I envisage the scheme under discussion here would ideally be used). However, even as it stands, this scheme, and accompanying software may go some way to reducing the errors commonly made by non-experts when calculating trace gas fluxes. Colleagues and I know of at least one example where published calculated fluxes were more than a factor of 20 overestimated due to the application of kw for an extremely soluble gas. Thus I would argue that a paper bringing together a scheme which provides non-experts with a convenient method for calculating transfer velocities for their gas of interest is of significant value to the field. That said, I accept that the sensible selection of paramterisations and the justification thereof in the text of this paper is of fundamental importance and that some amendments in line with the referees comments below were certainly required.

ii) Selection of parameterisation / flexibility

It is of course important appropriate parrameterisations are selected for this generic scheme and that these selections are adequately justified in the text. I accept that this may not have been executed as well as possible and have taken steps to improve

both the discussion and justification of the selection, including a restructuring of the manuscript to dedicate a section to the selection of both gas and liquid phase transfer velcoity parameterisations. Both refereees comment on the need for flexibility in the R code. Fortunately, the code has been written on a fully functional basis, so adapting it to include new parameterisations is technically simple. Most existing paramterisations (Wanninkhof, Nightingale, Liss and Merlivat, Duce, Mackay and Yeun, Shahin etc) were already available within the scheme, and since receiveing the reviews I have implemented the Woolf '97 physically-based paramterisation which includes bubble effects to provide further choice for end-users of the scheme.

Each parameter (e.g. Schmidt number in air) is called as a 'wrapper' function which then calls a specific parameterisation so to implement a new parameterisation it is a simple as coding it in as a function (if not already there) and calling it as the default from the wrapper function. The modularity of the code will be highlighted in the main body of the text (in a new section called "Implementation") and is detailed in the R script itsself.

iii) Restructuring of manuscript

In order to respond to the requirements of the reviews it has useful to restructure the manuscript somewhat, to fit new sections in and to amend the way some information is presented. This has led to a restructuring as follows:

Section on 'new derivations' has been split up - extended evaluation of ka (gas phase transfer velcotiy) paramterisations and selection thereof has been put into a new section along with the same for kl (liquid phase transfer velocity). The novel empirical salinity-solubility relationship is presented subsequently in its own section.

The scheme is then described in full, followed by sensitivity analysis and comparison / validation sections.

As a result of this restructuring and in response to the specific comments made by the reviewers the prose in the manuscript has changed substantially. Rather than copy it

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out verbatim below, I refer the editor / reviewers to the resubmitted manuscript.

iv) Scientific change

As a result of the deeper assesment of transfer velocity parameterisations encouraged by the reviewers, I have changed the default selection of the gas phase transfer velocity paramterisation to one which better reproduces the observations of gas phase transfer velocoity of trace gases of different diffusivities as observed in the wind tunnel study of Mackay and Yeun (1983) (See Section "Selecting transfer velocity parameterisations"). This changes the gas phase transfer velocity only slightly for most gases and at most by +/-10% for those with most extreme values of diffusivity.

2   Response to reveiwers' comments

2.1   Referee 1 (D. Woolf)

...We do not all have to agree each selection (and that is not going to happen anytime soon), but as part of this review process I'd like to reach a point where the most relevant evidence is presented clearly, concisely and fairly. I think you have tried to do this and largely succeeded, but I do have some specific criticisms. The sub-model for liquid phase transfer velocity, kw, is the part I am most familiar with. The "Nightingale et al" model would not be my first choice, but that is not my criticism, I am more concerned that there is a more rounded discussion of "kw models".

This is addressed in the new section assessing and selecting a kw paramterisation (see revised manuscript) and in notes to further comments below.

In the case of "ka", I am concerned that some of the most relevant information has not been used in the selection of the ka sub-model. I have to admit considerably less familiarity with "ka", but even with my limited knowledge it is apparent that there are

major omissions, particularly field evidence on water vapour transfer(a peculiar, but very important and well-measured soluble gas) and the formulations proposed within the NOAA COARE model (Fairall et al., 2003).

I have avoided including a detailed review of such experimental data as it would rather overwhelm the rest of the manuscript, and focus instead on experimental data for trace gases specifically, and the duce et al paramterisation, which effectively synthesises the experimental data on water vapour fluxes. However, a modified version of the COARE model ka term has been included in the analysis, which is very similar to the Duce et al paramterisation as they are based on the same underlying theory of water vapour transfer.

The latter point raises another criticism: The NOAA COARE model is already available as a general tool applicable to gases of all solubilities and should reasonably be introduced at a much earlier stage. At present it is only mentioned with respect to GASEX-98 CO2 data, which it can only be fitted to with unusual (I am tempted to say "unrealistic", but that may be premature with the paucity of evidence at present) tuning constants. Since NOAA COARE can be fitted to other CO2 and DMS results with more consistent tuning constants, the presentation of GASEX-98 alone gives a rather unrepresentative view of NOAA COARE. Note also that DMS falls into the class of gases where liquid phase transfer is more important but the gas phase transfer is significant; thus, some inclusion of recently published field studies of DMS transfer would be appropriate.

The new section considering selection of a kw scheme covers much of this, by synthesising a wide range of data, empirical parameterisations, and physically-based models of kw-windspeed relationships, which are presented in a new figure (Fig. 5 in new manuscript). This has led to the removal of the original Fig 6. and associated comparison of Hare et al 2004 COARE tuning with the scheme for CO2. This subsection of the 'validation' section has been replaced with one which reproduces the analysis of observed DMS presented in Huebert et al 2010 (their analysis using the NOAA

COARE algorithm), where there is apparent linearity of response to windspeed and this is attributed to the absence of a significant bubble effect for DMS. The total and liquid phase transfer velocities are calculated using the scheme presented here using the Woolf 1997 bubble-mediated transfer velcoity model for CO2 and DMS and good agreement is seen with the analysis of Huebert et al 2010.

I do accept the point at line 2 of page 270 that the scheme presented here is simpler than "NOAA COARE" and "MESSY AIR-SEA" but it would be better if you acknowledged their existence specifically in the Introduction, rather than only referring to "More detailed approaches [p.254, l 7]".

"More detailed approaches..." has been replaced by the following:

More detailed approaches than empirical relationships between windspeed and transfer velcoity are often used e.g. NOAA COARE (Fairall et al. 1996; Fairall et al. 2003 or MESSY AIR-SEA (Pozzer et al.2006). However, such generally physically-based schemes require extensive information on the physical properties of the gas and/or more detailed physical forcing data than windspeed alone and are thus more appropriate for well studied gases such as CO_2, O_2 or DMS (dimethylsulfide), where concentration uncertainty is better constrained and physical characteristics of the gases have been determined experimentally, or where detailed study of physical parameters is commonly undertaken e.g. in eddy-covariance or other 'micrometeorological' flux studies. Furthermore such schemes contain tuneable parameters which are poorly quantified due to a paucity of data and may vary for different gases due to unquantified or unaccounted for gas-specific effects. While a simpler, broadly emprical scheme cannot hope to address these issues, there is a good case for a generalised scheme which will allow the quick and simple quantification of trace gas fluxes given concentration data, wind speed, temperature and salinity and the minimum physico-chemical information about the gas possible, to fulfil the requirements of a long 'tail' of studies covering a wide range of poorly-studied trace gases (from e.g. ammonia to mercury vapour to long-chain hydrocarbons), which are often conducted by biogeochemists or

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microbiologists rather than experts in quantifying air-water fluxes.

Elements of the numerical calculation, e.g choice of ka and kw models, are currently a matter of interpretation and the favoured sub-models may alter in the future. Thus, I'd suggest a "modular approach" to the code, allowing substitutions to be made easily. I haven't investigated the R code, so apologies if this has already been addressed.

See general comments (ii) and new section "Implementation". Furthermore it has been made clear in the text that while certain parameterisations have been set as defaults in the software, alternatives can easily be selected for individual calculations as required.

Specific Comments It may be pedantic, but I do not recognize the presented model as a "thin film model". Indeed, the assumed Schmidt number (or molecular diffusivity) dependences of both the ka and kw sub-models are directly contradictory to a "thin film model" as usually defined. If transfer in each phase is controlled by molecular diffusion across a thin film, then necessarily ka is proportional to Sc_a Ë̦-1 and kw is proportional to Sc_w Ë̦-1. What is presented here is a more generic "two phase model". It is certainly reasonable to refer to Liss and Slater for the model of serial transfer across layers in the gas and liquid phases, but avoid using the term "thin film model".

I fully accept this and have changed all ocurrences of 'thin film' to 'two-phase' or removed them entirely.

Similarly, Figure 1 is misleading in implying linear variation in gas concentration either side of the interface. I'd suggest borrowing the "resistance model" drawing of transfer from one of Peter Liss's later papers (incidentally this might be useful in explaining "NOAA COARE + bubbles" where a parallel pathway (and resistance) in the liquid phase is proposed).

A resistance type diagram does seem more appropriate in light of the changes made following this reviewer's comments. However, numerous other tables and diagrams

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have been added to the mnanuscript so I suggest removal of Figure 1 completely as it doesn't add much to the paper (and both concentration profile and resistance model diagrams are common in the literature).

I am not qualified to comment in detail on Section 2.1, but for what it is worth I found it interesting and convincing. Perhaps it should be clearer that this is a "fall back", where the solubility of the gas in seawater has not been directly measured?

The folllowing text has been added: "Note that where reliable data for the solubility of a gas of interest at the required salinity is available, this data should be used in preference over this predictive equation."

However, it is important to note that the paramterisation presented here is applicable at any temperature and salinity, and to my knowledge no studies have presented such a range of solubility data for a gas - the studies used to derive this relationship almost all present freshwater and seawater (S=35) solubilities over a limited range of (or single) temperatures. This is fine for open-ocean flux caluclations, but of limited use for coastal / estuarine and brackish etc waters.

I found Section 2.2 interesting and informative. It is clearly a matter of concern that a range in values from different parameterisations of greater than 4. What I think is missing from this section is a critical review of the experimental data that underlies the parameterization. As far as I am aware the best field experimental data available for the parameterization of ka is measurements of the air-sea transfer of moisture (see Fairall et al. [2003] J. Climate, 16, 571-591, for a review).

This is a fair criticism and evaluation of the experimental data has been undertaken, particularly for the 'outlier' data of Shahin et al, which can be explained by their experimental setup and the resistance model they apply to validate their data. This is described and their paramterisation discounted as not applicable to the open water situation. Mackay and Yeun (1983) present the only reliable data therefore on the transfer velocity of a range of trace gases rather than water vapour, but they are thought to be

overestimated due to wind tunnel effects. The duce et al paramterisation is modified as before to use the Smith (1980) drag coefficient term and this is then compared with the COARE-derived transfer velocity presented by Jeffrey et al (2010) (also using the Smith(1980) drag term). These agree rather well (because they both use the same underlying theory to derive the relationships), and seem to 'sit' in a reasonable place relative to Mackay and Yeun (i.e. below them). Because Jeffrey et al 2010 does a better job of representing the sensitivity to changes in Schmidt number (assuming Mackay and Yeun's sensitivity to Schmidt number is correct), the Jeffrey et al 2010 formulation is adopted for the scheme, but the 'still air' transfer measured by Mackay and Yeun is included. (See section on gas phase transfer velocity in resubmitted manuscript)

It is also important to use sensible drag coefficients and this is dealt with adequately, but a greater issue is the actual data on transfer of volatiles. I have some misgivings myself about applying results for water vapour to all other gases (there might be different behaviour), but I am not convinced that there is adequate experimental data on other soluble gases to pursue any other path. As far as I understand, water vapour measurements underpin the "NOAA COARE" parameterization of ka and this is significantly different to the parameterizations presented in this manuscript. It is significant that Fairall et al. [2003] conclude that the bulk parameter "Ce" for moisture increases slightly but significantly with wind speed (above a minimum at low wind speeds), which would imply a weak non-linearity in ka.

It is certainly a potential problem that our paramterisations of ka for trace gases is based almost entirely on water vapour, although the Mackay and Yeun study gives reasonable validation, particularly when accounting for the wind tunnel effects. Applying the drag coefficient presented by Fairall et al 2003 has a substantial effect on the calculated gas phase transfer velcoity (reduction by a factor of 3 at u10=6m/s relative to the same scheme applying the Smith 1980 formulation). This is highlighted in the text as a potential problem but the assumption is make that an empirical relationship with windspeed alone is more approriate for a wind-only dirven scheme for the transfer

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velocity.

I note that unlike "KH" and "ka" there is not a new derivation for "kw" but I am concerned that kw is treated robustly. I have read much worse summaries of kw parameterizations than the beginning of Section 3.3, but I am compelled to quibble. There is a danger that Sweeney et al (2007) will be regularly misinterpreted and I would rather that did not start here. The bomb 14 C data considered by Sweeney et al.(2007) provides no evidence that gas transfer velocities follow a square law dependence on wind speed. Sweeney et al. do derive a very useful estimate of the global average exchange coefficient of CO_2 and chose to assume square-law dependence.

This is a very good point and has been elucidated in the section discussing different parameterisations of kw.

It is clear that Nightingale et al (2000; "N") is consistent with the global coefficient. Also, N. is clearly a fairly good fit to both the dual-tracer data that they originally considered and to data from subsequent dual tracer studies. Thus, I think there is a reasonable case for choosing this model. However, this model does not fit all data and particularly it is rarely consistent to micrometeorlogical estimates of the transfer of CO_2 and DMS. For completeness, these studies and the apparent discrepancies should be mentioned.

Comparing Nightingale 2000 kw with observed k660 fluxes of CO_2 and DMS from Hare et al. 2004 and Huebert et al. 2010 respectively, there is rather a good fit (i.e. there is a large spread in the data and Nightingale fits broadly in the middle of it all...). In light of the analysis my Asher 2009 which suggests that 50% of the variability in kw observations can be explained by potential measurement error, I would suggest apparent inconsitencies with micromet studies are rather minor.

Also, N is an empirical model and the absence of any substantial theoretical underpinning should be mentioned. The main practical importance of "the weakness of theory" is that it is not clear that N (both the wind-speed dependence and the assumed dependence on Schmidt number) can be applied to all gases. At least one interpretation

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is that it is not reasonable to apply it to gases much more soluble than helium; and that is backed up by the experimental evidence for DMS (see e.g., B. J. Huebert, B. W. Blomquist, M. X. Yang, S. D. Archer, P. D. Nightingale, M. J. Yelland, J. Stephens, R. W. Pascal, and B. I. Moat. 2010. Geophys. Res. Lett., 37, 1, doi:10.1029/2009GL041203, 2010).

The bubble effect is discussed in the new section on selecting a kw paramterisation and the Woolf 1997 kw scheme including the bubble effect has been implemented in the R program. In the section "Application / comparison" (previoulsy calles "Comparison/ validation") the analysis conducted by Huebert et al 2010 using the COARE algorithm to asses the bubble effect (or lack of it for their DMS measurements) has been effectively and relatively closely reprodcued using the scheme presented here.

Personally, I wouldn't make a virtue of N "[sitting] roughly in the middle" –unless you consider a herd instinct beneficial – though clearly N is more acceptable for being far from extreme.

Agreed - this is no longer used as the justification for selecting Nightingale as the default kw paramterisation.

At low wind speeds, rain or free convection may be important and the model may underestimate kw.

This has been mentioned in the new kw section, but no attempt to quantify these have been made.

I do not see mention of whether any of the selected sub-models are inappropriate for some reactive gases (e.g kw of SO2, or of CO2 at very low wind speeds). I think this should be added.

This is mentioned briefly in the conclusions section as an effect which should be considered by users of the scheme for their particular gas of interest. I am currently preparing a manuscript which will provide the tools to enable researchers to do this in a rela-

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tive simple and accessible way. To describe it further in this manuscript would be too
lengthy.

As noted in the general comments, I am concerned that taking GASEX-98 and the tun-
ing of NOAA COARE to that single dataset gives a rather unrepresentative view of both
data and theory. I suggest looking at a few of the most recent publications of microm-
eteorological data (e.g. Miller et al. [2009] GEOPHYSICAL RESEARCH LETTERS,
VOL. 36, L15816, doi:10.1029/2009GL038907; Huebert et al. [2010], GEOPHYSICAL
RESEARCH LETTERS, VOL. 37, L01605, doi:10.1029/2009GL041203) and a recent
theoretical and modelling development of NOAA COARE (Jeffery et al. [2010];Ocean
Modelling, 31(1- 2), 28-35. doi: 10.1016/j.ocemod.2009.09.001)and working back-
wards. I am not suggesting a major revision here, but you might end up with a different
"Figure 6" that gives a more rounded view of both data and theory.

The old Figure 6 has been moved to the section describing selection of a kw parame-
terisation and considerable extended to cover various empirical, physically based and
tuned paramterisations along with global bomb 14C estimates and observational data
from various studies(see Fig 2. in this response document). I believe that this, along
with the discussion of kw parameterisations in the new document, has significantly im-
proved the scientific overview - many thanks to both reviewers for the impetus to make
these improvements.

Technical and typographical:

It would be more consistent to use small letter "a" consistently for gas phase, and "w"for
liquid phase. E.g. Why capital A in the Schmidt number for air?

agreed. capitalisation removed for all subscripts referring to air and water phases

Typo "gaess" at p.262, line 14

corrected

Is equation A1 correct? I ask because there are two linear coefficients in "S"; "A" and

"C"; perhaps there is a missing symbol?

Have checked back with source manuscript - yes equation A1 is correct. The reviewer may have missed the coefficient B which, which is included in A1 and described in A3

Typo "alond" at p.271, line 7

Amended

3 Reviewer 2 (anonymous)

The paper includes a new parameterization for the Henry's law constant as a function of solubility and a modification of the parameterization for calculating the air-side of gas transfer velocity. Although the author calls these both new parameterizations, they seem to me (especially the gas transfer velocity one) to really be modifications of existing parameterizations. Nonetheless, they seem to offer improvement and therefore are a worthwhile contribution. Additionally, the author supplies code in the language R that can be used to calculate the fluxes of any gas. I think the two new/modifications to the parameterizations are a useful contribution. Additionally, I think the idea of clearly assembling the different parameterizations needed to calculate air-sea gas exchange fluxes could be helpful. However, I am worried that some readers may leap upon this scheme as the "answer" for calculating air-sea gas exchange fluxes without looking in detail at the different choices. It is not always obvious which parameterization is the best one to choose and I am concerned that this scheme might actually be a detriment to the field because it might prevent people from using more appropriate parameterizations. This latter fear could be addressed if the author made it clear that other parameterizations (especially ones that might come along in the future) might be improvements over the ones chosen. In general, the language employed should be more cautionary.

It has been made clear in the revised manscript that the selected paramaterisations for ka and kw are simply the 'defaults' in the associated R program, and an example has been given of using the scheme with different kw paramaterisations for analysis of the bubble effect in the DMS data of Huebert et al 2010 (discussed above). Hopefully it is clear to the reader that different approaches may be more or less appropriate for a particular application of the scheme but I would say that the intended users of the scheme as a whole are those who currently use e.g. Nightingale 2000 or Wanninkhof 1992 as the "answer" to calculate the transfer velcoity for their gas of interest and as such I hope the default parameterisations can help at least with these studies.

Additionally, it would be very helpful if the numerical code included could easily be extended to include other parameterizations as they become available or for readers who disagree with the author's choices. Perhaps the code already can do this – I am not familiar with R so I could not check the code.

See general comments (ii), response to similar point by reviewer 1 and 'Implementation' section of revised manuscript.

Finally, it would be very useful to see a detailed error analysis which would include the estimated uncertainty with estimating each term/process in the parameterizations (i.e. molar volume, salinity dependence, air-side transfer velocity, water-side transfer velocity, etc) and ultimately the final gas transfer flux. Such an error analysis would highlight which parameterizations might need to be replaced soonest and would be very useful for any researchers planning on using calculated air-sea gas exchange fluxes.

A series of hypothetical 'test gases' of varying molar volume and solubility have been used to compare the effect of increasing each parameter in turn by an amount representative of the estimated uncertainty in quantifying that parameter under normal conditions (Table 4 and 5 of revised manuscript). The reviewer is right that this has revealed useful information on the relative importance of different parameterisations

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and will help to focus future work, by this author at least.

Specific Comments

1) Abstract, Line 14: "to improve comparability." I'm not convinced that having a standard scheme for parameterizations would really improve comparability. If the parameterizations were perfect, then it would. But since they clearly are not, and some parameterizations might have more severe problems for certain gases (for example, neglecting bubbles is more severe for studying oxygen than for CO2), using a blanket scheme without paying attention to which gas it is for will not necessarily improve comparability.

This statement was really referring to 'traceability' in the calculations of gas exchange. For example, trace gas flux studies often do not state how or what value for diffusivity / schmidt number they use for their particular gas, or whether they accound for salinity / temperature etc. By using this scheme, even if the values are not correct or true to the real world, they would be fully reproducible in future works. Nonetheless I have removed reference to compatibility.

2) "significant improvements under certain conditions" I wasn't convinced that the new scheme offers significant improvements. This sentence has been removed.

3) End of abstract: In the paper, the author mentions that some of these parameterizations (such as the one for diffusion coefficients) should only be used if direct data is not available. It would be good to state that as the final sentence of the abstract too.

The following has been added as the final line of the asbtract: "It is suggested that the various components of this numerical scheme should be applied only in the absence of experimental data providing robust values for parameters for a particular gas of interest."

4) Section 2 is title "New derivations introduced for this scheme". I don't think the word "new" is accurate – maybe the salinity-dependence parameterization could be

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considered new. But the air-side transfer velocity parameterization is not new – it rather is just a modification of the existing parameterization, i.e. it substitutes an existing parameterization for Cd for a constant in the standard Duce et al parameterization. Thus this section should have a different title.

I would argue that the solubility-dependent salinity/solubility relationship is a novel empirical relationship. To my knowledge no attempt to correlate the salting out effect with both Henry's law solubility and molar volume has been previously attempted, in seawater or any other medium. And whilst the gas phase transfer velocity term is far from novel (a term I have avoided), it is certainly 'new' to the field in that it brings together aspects of various studies to produce a current 'best estimate' of ka given the available data. Irrespective of this, in the restructuring of the manuscript the section named "New derivations..." has been split up and no longer exists anyway.

5) P.254, line 20: I think the author means a blanket 20% solubility decrease has been applied compared to the freshwater solubility but could the author please clarify if that is indeed the case. As it is written, statement begs the question of 20% decrease from what?

The reviewer correctly surmises that this refers to a 20% decrease from the freshwater case and this has been clarified in the text.

6) P. 256, line 20: "we find closest fit to the Ks data . . ." It would be nice to include a figure that shows the data as a function of Vb and shows the fit.

This is effectively shown in Fig. 2 - where the molar volume is corrected for for each gas in order to calculate theta. The only way to show the molar volume relationship is to plot it against Ks with each gas theta-corrected, which is rather circular. I have reworded this sentence: "A close fit to the Ks data for real and synthetic seawater is found by assuming that Ks is a function of the natural logarithm of the molar volume Eq. 8 and a solublity-dependent constant of proportionality, θ."

7) P. 258, equation 11 (now equation 7.): u* should be defined the first time it is used – later in the paper, it is stated that u* is wind stress but that should be moved to here, the first time u* is used.

u* is now defined directly following the series of equations describing gas phase transfer velocity parameterisations staring with Eq. 7.

8) It would be useful to have more explanation of why certain parameterizations were chosen. This is really essential because the author is in some sense asking the reader to believe that these parameterizations are the ones that should be used in all cases. In other words, the author is expecting the reader to trust the author's opinions on all these parameterizations. In order for the reader to do so, the reader needs to be informed about why they were chosen. In some cases, the author explains his reasons and that is laudable. But in some cases, he does not. For example, on p.262, line 8, why should the scheme of Tsilingiris be used? What are other options? What makes that one the best? I would also like to see more information for choice of parameterization for molar volume and for choice of diffusion coefficient parameterization.

In some cases these paramterisations were selcted becuase they were the only appropriate selections,particularly as the idea is to limit the amount of gas-specific input data required e.g. for molar volume. Where this is the case it has been stated and the reasons given. Where there has been a choice, the most recent / applicable paramterisation has been chosen. Where calculated transfer velocities are less sensitive to certain parameters, the selection of those paramterisations is of less importance, and thus less detail is required. It doesn't seem reasonable to provide an in-depth review of e.g. air viscosity paramterisations in this work (the paper would get extremely long!), although where possible I have referred the reader to other articles containing reviews / overviews of the field.

9) P. 264, line 18: Although the Nightingale parameterization is probably a reasonable choice, choosing it because it sits in the middle of other parameterizations is not a

very good reason. If most of the existing parameterizations are wrong, then choosing one in the middle doesn't make it right! There are newer parameterizations that would be better choices, including some for example that explicitly include bubble processes (Stanley et al, 2009). This is one place where it would be very useful to include more information on newer gas exchange parameterizations and to make the code flexible enough that different users of the scheme could make their own decisions about which to use.

Agreed - as mentioned above in the response to the previous reveiwer, the 'middling' nature of Nightingale et al 2000 has been removed as a justification. The parameterisation of Stanley et al is a very interesting development in the field, particularly in that it considers the partial pressure of the gas as well as its solubility as part of the bubble scheme. However, this requires further input data, specific to both the gas and the environment in question and as such it is not compatible with the 'generalist' approach applied here. Moreover it has only been validated for a series of extremely insoluble gases (for which tuned values of free parameters appear to vary) so its applicability to e.g. soluble trace gases is currently unknown. Nonetheless, reference is made to Stanley et al 2009 in the context of quantifying bubble effects in the section on selection of kw paramterisations.

10) P. 269, line 25: "case by case" basis. I don't agree with the term case-by-case basis. Microlayer effects, such as surfactants, are important for all gases with water side gas transfer velocity and thus need to be applied much more widely than on a case by case basis (see Guitart et al, 2010, as well as several papers by Frew). It would be OK with me if the model doesn't include those effects since I'm not sure if a parameterization exists for them. However, to say "case by case basis" makes it sound like they are only important some of the time. Additionally, bubble effects have been shown to be important for many gases and thus need to be included with a wide range of gases and thus again used on more than simply a case by case basis.

The reference to 'case by case basis' has been removed and replaced with the follow-

ing:

"Like most field-based studies of trace gas fluxes calculated from concentration measurements, this scheme does not currently account for processes of chemical enhancement (e.g.Liss and Slater 1974), or microlayer effects (e.g. Guitart et al. 2010), which are important in many cases and should be carefully considered by future users of the scheme for their gas / environment of interest. "

11) P. 269, line 26: "suggested that this scheme should be adopted". This is another place where the caveat should be made that if some of the data is directly available for a gas, then the data should be used instead of parameterization. P. 270. Line 1 "standard and intercomparable method." I don't think it is right to promote this scheme to become the standard one when the parameterizations are likely to be quickly outdated. Some sentence should be added that as improved parameterizations are published in the literature, the improvements should be used in the scheme. Essentially, I think language should be more cautionary, both here and earlier.

The final paragraph of the conclusions now reads:

"It is hoped that the scheme presented here and associated software will provide a basis for improved, traceable transfer velcoity paramaterisations for poorly-studies gases (i.e. not CO_2, DMS, N_2O, CH_4, O_2, N_2 and the noble gases). It is envisaged that users would override default parts of the scheme for their gas of interest where robust measurement data is available to replace paramaterised components of the scheme and furthermore that key further uncertainties in quantifying gas fluxes would be considered outside of the scheme presented here (e.g. surfactants and other microlayer effects, chemical enhancement etc.)"

13) P. 287, Fig.4: It is hard to tell the dashed lines representing Duce et al Sc and Duce et al with Large and Pond CD apart in the legend. Also, it would be nice to see an inset that blows up the region of wind speeds less than 7 m/s to see what differences are in that region.

Each of figs 3 4 and 5 have been replaaced with double panels, the second showinf 0-7 m/s range in each case. Colour / patterns have been changed to enhance readability. The contents of these figures have changed slightly due to the change in assesment and selection of ka paramterisations (see responses to reviewer 1)

Technical Details

1) In many cases, when terms in the equation are explained, the phrase starting with "Where" on the line following the equation is capitalized whereas I don't think it should be. In any case, the author should at least be consistent and either always capitalize "Where" or never do.

all instances of line follwing equation starting "Where" have been changed to lower case. Can change to all upper case at editor's discretion.

2) P.257, line 26: "methanal" should be "methanol"

This does actually refer to methanal - but a number of other readers have suggested that this is in error. Have added 'formaldehyde' in parentheses to clarify. Methanal is the IUPAC standard name.

3) P.261, line 8: "veloicites" should be "velocities"

corrected

4) P. 262, line 9: "represetative" should be "representative"

corrected

5) P. 263, line7: "reccommended" should be "recommended"

corrected

6) P.265, line 16: "vs" should be "vs."

corrected

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Comment

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7) P. 280, caption: The second time that "Vb" is mentioned, it should be formatted the same as the first time.

corrected

8) P. 282: Table A1: could the headings of the columns be moved a bit so it is more clear which heading goes with which column?

I will check this on proofs of any future manuscript to ensure that these are correct (when I compile the latex document locally, headings are correctly aligned with columns)

9) p. 290, Fig 7: Axis labels should not use slashes but instead us negative exponents,i.e. pmol m-2 s-1

amended

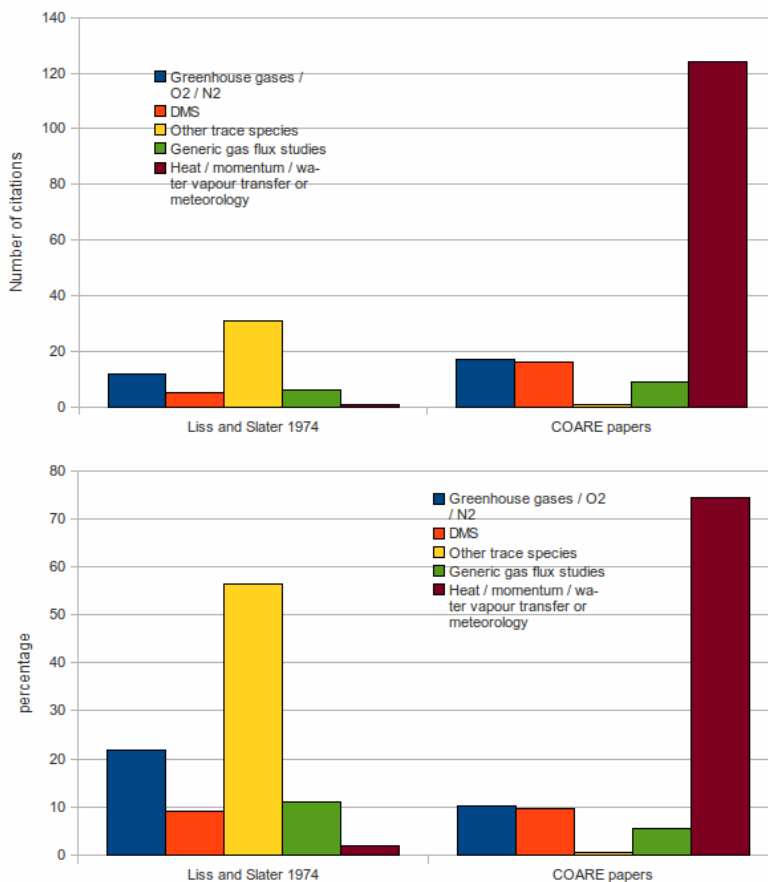Interactive comment on Ocean Sci. Discuss., 7, 251, 2010.

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Fig. 1. Comparison of content of works citing Liss and Slater 1974 vs key NOAA COARE papers, highlighting the popularity of the 'simple' approach to quantifying air-sea fluxes for studies of trace gases
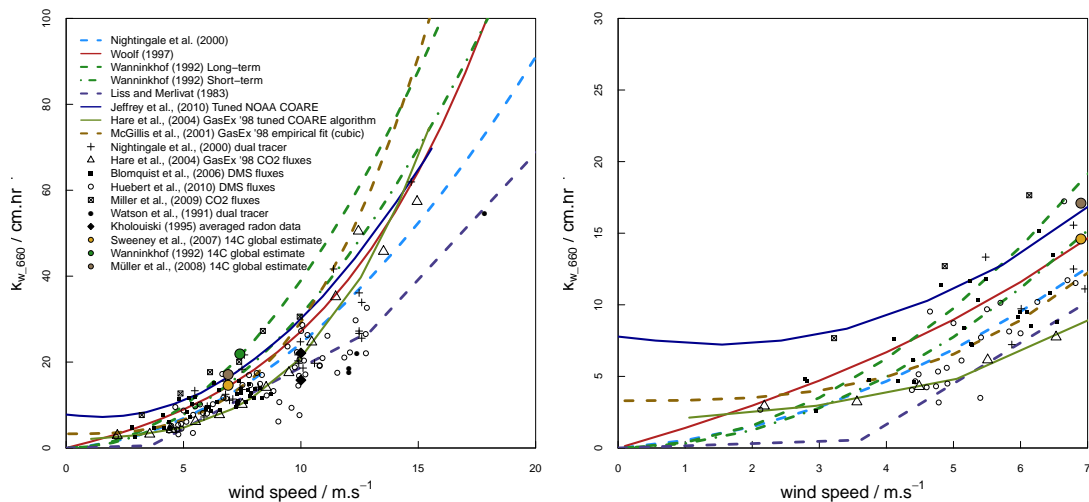
Fig. 2. New Fig 5. for manuscript summarising kw paramaterisations and studies