APPROPRIATE TREATMENT OF UNCERTAINTY AND AMBIGUITY; A FLEXIBLE SYSTEM FOR CLIMATOLOGICAL CALCULATIONS IN RESPONSE TO AN ON-GOING DEBATE ON THE TRANSFER VELOCITY, K.

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ABSTRACT

Air-sea fluxes of gases, including carbon dioxide, are commonly calculated using an air-sea flux equation. Within this equation, fluxes are proportional to a transfer velocity, k. We can use Earth observation or in situ data for the calculation of the fluxes, only if we adopt a suitable algorithm that typically describes the dependence of k on wind speed and water temperature. Unfortunately, appropriate algorithms for the transfer velocity of carbon dioxide are debated. Since there is a large body of data, but the perceived information is contradictory, more data is unlikely to resolve the debate swiftly. This ambiguity poses a dilemma for estimation of fluxes and their uncertainty. A twofold approach is adopted. Firstly, we examine critically both algorithms and outline an alternative more mechanistic approach. Secondly, we construct an open system for the calculation of air-sea fluxes that enables a very broad range of algorithms to be applied.

1. GAS FLUX CLIMATOLOGIES AND TRANSFER VELOCITIES

1.1. Introduction

The climate of Earth is sensitive to the radiative impact of a number of gases and different types of particles in the atmosphere. The atmospheric concentration of many important gases and particles is sensitive to the air-sea transfer of volatile compounds. These gases can also play a substantial role in the biogeochemistry of the oceans. It is important to quantify contemporary air-sea fluxes of gases and also to provide the understanding necessary to project possible future changes in these fluxes. The air-sea flux of gases can in some cases be inferred indirectly, but most flux estimates depend on a calculation using a standard bulk air-sea gas transfer equation, [e.g., 1]. For each gas, this calculation depends upon both measurements of the gas concentration in both the surface ocean [e.g., 2] and the lower atmosphere and upon formulae and resulting "transfer coefficients" that describe the "rate constants" for transfer across the sea surface. Simple calculations require only a single transfer coefficient, the gas transfer velocity, k, to be used in the air-sea gas flux equation:

$$Flux = k. \ concentration \ difference \qquad (1)$$

The basic processes determining air-sea gas exchange and the exchange rate of carbon dioxide have been known approximately for more than half a century [e.g., 3, 4] Proposed parameterizations for the transfer velocity of all gases have been available for four decades [5, 6]. However, a detailed understanding of processes and rates has been hotly debated and recent interpretations are contradictory [e.g., 7, 8]. A consensus has failed to emerge despite major advances in the understanding of the underlying processes and a burgeoning of data from a wide range of methodologies. A contributing factor to this failure is the broad range of academic disciplines and experimental techniques that can usefully be applied to this subject, together with historical separations between some of those disciplines (notably between geochemistry and meteorology). Most published interpretations appear to be based on quite small subsets of the available data and fairly limited consideration of the processes. A few studies have made a greater effort to describe the wind-driven flux of gases mechanistically and reconcile this description to measured gas transfer velocities [9]. In this paper, we provide a concise report on a broad review of the theory, methods and data relevant to gas transfer velocity parameterization. We conclude that there is a large uncertainty in k, based on contradictory information and interpretation. It is not appropriate to overly restrict the choice of k. We describe a flexible system that facilitates calculations of gas flux with a relatively free choice of k.

1.2. A survey of methods

Within this brief paper, we cannot do justice to the numerous methods and experiments applied to the determination of gas transfer velocities, but it is useful simply to note the wide diversity of methods. The following list of methods is limited to those based on actual measurement of gases in the field

    a) Chamber or dome measurements of CO_2 flux
    b) Micrometeorological measurements of CO_2 flux

c) Budgets of dissolved inorganic carbon (DIC)
d) Modelling of oceanic DIC
e) Carbon isotope methods
f) Oxygen and nitrogen in the atmosphere
g) Oxygen covariance in the ocean and oxygen deficit method
h) Oxygen and nitrogen oceanic time series
i) Triple isotopes of oxygen
j) Noble gas time series
k) Radon deficit method
l) Purposeful tracers (including dual tracer method)
m) Micrometeorological measurements of dimethyl sulphide

In addition, more indirect methods have been applied in the field, for example using heat as an analogue for gases. Also there is a rich literature on laboratory experiments, modelling studies and basic theory.

2. A Standard Interpretation

2.1. The "quadratic model"

Early insights into air-sea gas exchange arose from two calculations of a global CO_2 transfer velocity and the first relatively local measurements of gas transfer velocity inferred by some of the first radon deficit methods [5]. It was reported that all these measurements and some earlier laboratory experiments [3] supported a consistent picture where gas exchange was adequately described by the stagnant layer model, the implied global average stagnant layer thickness was approximately 30μm and gas transfer velocity was proportional to the square of wind speed. The influence of the latter conclusion has persisted to the current day. The stagnant layer model, which implies k will be proportional to the molecular diffusivity of the gas in seawater, D, has largely fallen into disuse, instead transfer velocity is widely assumed to vary inversely with the square root of Schmidt number, Sc. Schmidt number is defined as $Sc = \upsilon/D$, where υ is the kinematic viscosity of seawater. These developments are encapsulated in one of the most cited parameterisations for gas transfer velocity [10], which was inferred from preceding global ^{14}C data (natural and bomb):

$$k_w = 0.31 \, U^2 \, (Sc/660)^{-1/2} \qquad (2)$$

The bomb ^{14}C method has been revisited with the benefit of much improved measurements and the inferred global CO_2 exchange has been revised down substantially [11, 12]. As a result, a revised quadratic expression proposed by [12] and given here as Eq. 3 is widely used for calculations, including with a minor recalibration within [1].

$$k_w = 0.27 \, U^2 \, (Sc/660)^{-1/2} \qquad (3)$$

Equation 3 from [12] is included in a summary of parameterizations in Table1.

Table 1. Polynomial relationship of k to wind speed as described by Eq. 4 for various studies.

Study	Short Hint	Method (Sect 1.2)	a0	a1	a2	a3
[12]	Sween	e	0	0	0.27	0
[13]	Night	l	0	0.318	0.212	0
[14]	Ho	l	0	0	0.254	0
[15]	Wann	l	3	0.1	0.064	0.011
[21]	McG	b	3.3	0	0	0.026
[22]	Weiss	b	0	0.46	0.365	0
[24]	Pryth	b	5.3	0	0	0.034
[8]	Edson	b	5.4	0	0	0.029
[26]	Kuss	c	0	0	0.45	0
[26]	Kuss	c	0	0	0	0.037
[29]	Kihm	h	0	0	0	0.029
[31]	Sarma	i	0	0	0.41	0
[36]	Hueb	m	-5	2.4	0	0
[37]	Godd	m	0	1.8	0	0

2.2. Results from Dual Tracer Experiments (DTE)

While there is still occasional reference to results from the radon deficit method, more convincing results have been forthcoming from purposeful tracers and especially Dual Tracer Experiments (DTE). Numerous experiments have been conducted and a recent compendium of the results has been published [7]. We will limit discussion to parameterizations arising from some or all of these experiments, which generally can be described by the polynomial Eq. 4, with coefficients varying according to the study. In most cases, one or more of the coefficients is set to zero or to another theoretical value *a priori*. A normalization to $Sc = 600$ has been used in many studies, but here we have consistently standardized to $Sc = 660$.

$$k_w = (Sc/660)^{-0.5} \, [c_0 \, U + c_1 \, U + c_2 U^2 + c_3 U^3] \qquad (4)$$

Three parameterizations [13, 14, 15] based primarily on DTE are included in Table 1. These three parameterizations, exhibiting variation of ~10% at each wind speed, are displayed in Fig. 1. A similar or slightly greater degree of variation is possible by slightly different interpretations of the same experiments, for example by choosing a different polynomial [16, 7] or preferring a different measurement of wind speed [17]. A transfer velocity constrained to 20% or better is implied, especially considering the almost identical square law relationship found from isotopic data ([12], Eq. 3 and Table 1) and DTE ([14] and Table 1). At least one DTE [18] however implies a substantially different

relationship and we will show contradictory evidence later in this paper.
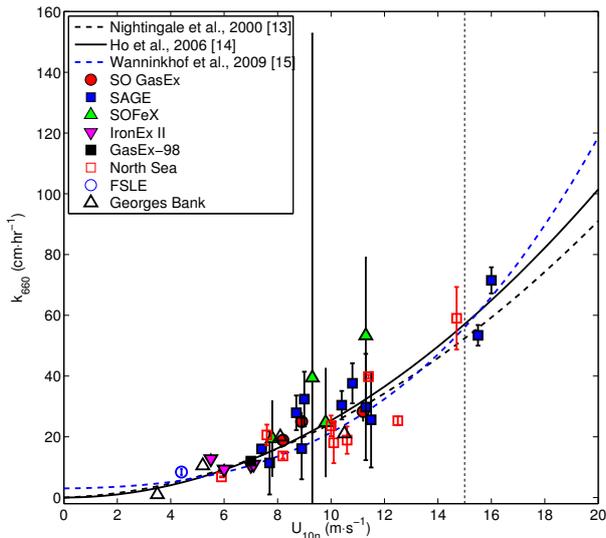

Figure 1. Measurements of transfer velocity by Dual Tracer Experiments and three related parameterizations [13, 14, 15]. Transfer velocities in cm/h have been normalized to a Schmidt number of 660 and are plotted against (neutral stability, 10-metre-elevation) wind speed in m/s.

2.3. The interpretation of isotopic and DIC data

Various isotopic data [e.g., 10, 11, 12, 19] and the distribution of total dissolved inorganic carbon (DIC) in the oceans [e.g., 20] provide some constraint on realistic transfer velocities. The "standard interpretation" of ^{14}C isotopic data has already been discussed in Sect. 2.1. In most cases [10, 11, 12] a square law dependence on wind speed and proportionality to $Sc^{-1/2}$ are presumed and only a coefficient (i.e. 0.31 in Eq. 2 and 0.27 in Eq. 3) is determined. These studies do not test the wind speed or Sc dependence, but only estimate the coefficient contingent upon the presumed statistical model. One study based on isotopic data [19] does provide some genuine insight into the wind-speed dependence.

When dependence of transfer velocity is presumed to be proportional to $Sc^{-1/2}$ and have a power law dependence on wind speed, U, as in Eq. 5, a relatively weak dependence on wind speed is inferred [19]. The exponent, n, is constrained to be $n = 0.5 \pm 0.4$ by a globally optimum fit or $n = 0.6 \pm 0.7$ from a fit of regional transfer velocities, each to oceanic bomb ^{14}C measurements. Similarly two fits of ^{13}C data imply $n = 0$ (0 – 1.1) or $n = 1.2$ (0.3 – 1.9). Additionally a relatively high globally averaged transfer velocity, ~20cm/h, is implied by this study [19] compared to that estimated by [11] (16.7 cm/h) or especially by [12] (14.6 cm/h)

$$k_w = a_n \, U^n \, (Sc/660)^{-1/2} \qquad (5)$$

The constraint of the Schmidt-number dependence is unfortunate since any alternative temperature dependence is thereby excluded. The genuine implication of the isotopic data (contingent on an adequate general circulation model) is that equatorial transfer velocities are not particularly low and high latitude transfer velocities are not particularly high, but the relative importance of wind speed and temperature in determining that outcome cannot be resolved.

3. FIELD ESTIMATES OF CO$_2$ FLUX AND TRANSFER VELOCITY

3.1. Micrometeorological experiments

Micrometeorological measurements are an essential tool of experimental air-sea interaction. Measurements of momentum, (sensible and latent) heat transfer by one or more micrometeorological methods provide detailed knowledge of these transfer processes and underpin bulk parameterizations of these fluxes In many ways, micrometeorological techniques are the obvious choice for determining air-sea CO_2 fluxes. However, relative to heat, gases present a challenging "signal-to-noise" issue. A variety of micrometerological techniques are available including eddy covariance (or "eddy correlation"), relaxed eddy accumulation, gradient flux (based on profile measurements) and inertial dissipation. The eddy covariance method is the most direct measurement of the flux and is also the most widely used. We focus on that method here and only note that while the challenges for the less direct methods are different they are similar in magnitude. The covariance method is simple in principle; it measures a turbulent flux by measuring the covariance of vertical motion and gas concentration. Many studies have introduced significant variants on the basic methodology and the reader is referred to the details of these many studies [e.g., 8, 21-24]. The most obvious challenge is to measure the fluctuations in gas concentration rapidly and accurately. The scales of turbulence determine the necessary sampling rate, which is about 10Hz [25]. While the method is simple in principle, there are numerous pitfalls. The method must be corrected for density (and moisture) variations, flow distortion and motion. Fluxes may be biased by sensor cross-sensitivities or distortion of optical measurements by the action of drops and aerosols. Careful attention must be paid to the statistical sampling of turbulent fluctuations. When a flux at a measurement height is calculated, a transfer velocity can be calculated using the coincident concentration difference, but this assumes the flux at the measurement point and at the sea surface are equal, which can be questioned on grounds of heterogeneity and non-stationarity.

The brief description above summarises the considerable challenge faced by micrometeorological methods. Nevertheless, defensible eddy covariance

measurements of air-sea CO_2 flux and transfer velocity have been published. Individual estimates of flux generally have very large uncertainties. In order to have sensible errors in estimated gas transfer velocities it is necessary to amalgamate or "bin" a large number of individual transfer velocities into a sample with a calculable mean and standard error. This amalgamation can in principle be based on any environmental variable or set of variables, but in practice wind speed has been used to produce estimates of the variation in transfer velocity with wind speed based on the order of 10 sample means over the wind speed range [8].

The results can be broadly separated into weak, moderate (6-12 m/s) and strong winds. There is little consistency between published results for weak winds, as apparent in the comparison of two studies within [24]. In common with almost all field methods it is debatable if eddy covariance has adequate sensitivity for weak winds. Fortunately for most ocean basins the average fluxes will not be particularly sensitive to the precise transfer velocity in weak winds. The results for moderate wind speeds are more consistent but the spread between experiments (e.g. approximately in the range of 30-40cm/h for 10m/s) suggests considerable bias uncertainty and the typical values are quite high in comparison to some other methods (e.g. dual tracer method implies approximately 25cm/h at 10m/s). The moderate wind speeds will dominate most basin averages and it is very important to reduce uncertainties in this wind speed range. Three experiments spanning the Atlantic Ocean, GasEx 98 [21], HiWASE [24] and SO GasEx [8] each provide data in very strong winds (far in excess of 15m/s; see results from GasEx 98 and HiWASE in Fig. 2).
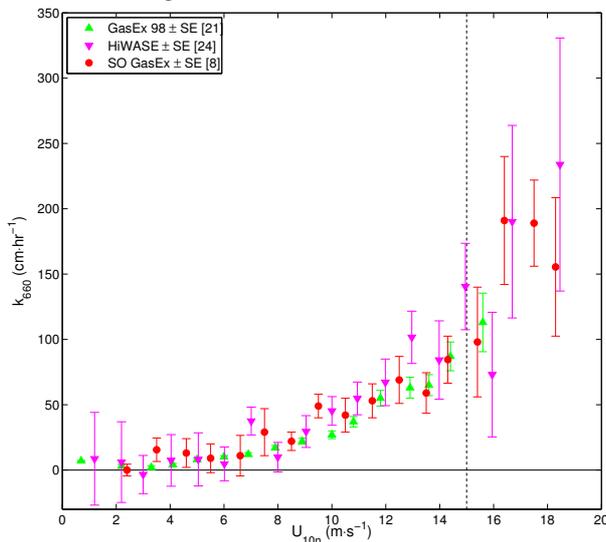

Figure 2. Measurements of the transfer velocity of carbon dioxide by eddy covariance methods in three open ocean studies [21, 24, 8].

For each of these three studies a simple wind-speed-parameterisation of the form $k_{w,\,660} = (Sc/660)^{-0.5} [c_0 +$

$c_3 U^3]$ is fitted (see Table 1 and Fig. 3). Strong winds are infrequent and these winds also raise greater challenges with vessel motion correction and sea spray effects. Nevertheless, all three experiments provide a rather consistent result that transfer velocities increase rapidly with wind speed (approximately 100cm/h at 15m/s, even higher in HiWASE). These results are contradictory to the few available dual tracer results that imply a transfer velocity of approximately 60cm/h at 15m/s (see also comparison to [14]; "Ho" in Fig. 3). If transfer velocities of 100cm/h occurred 10% of the time, this would contribute 10cm/h to the basin-wide average, which is very substantial. Thus the behaviour in strong winds is important and needs to be established. A more coastal study [22] reports a less non-linear response to wind speed (among the higher reported values at 10m/s, but slightly lower at 15m/s).
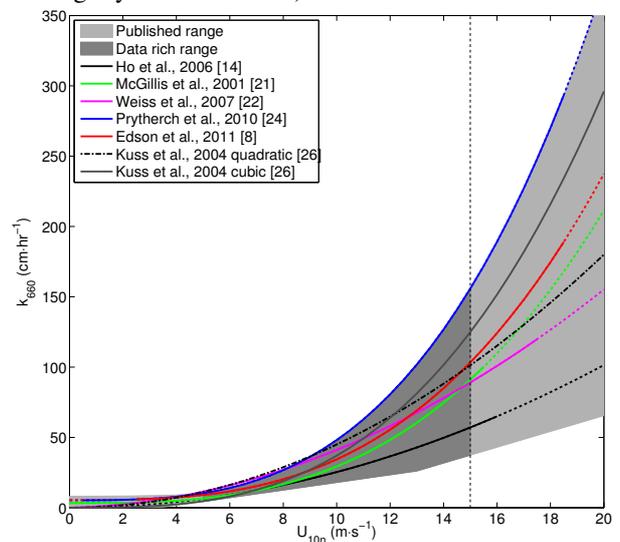

Figure 3. Several empirical fits to estimated transfer velocities of carbon dioxide (see text). The "Ho" parameterisation [14] is also included for comparison.

3.2. Carbon budgets and other methods

We have listed 5 methods (*a* to *e*) directly involving carbon dioxide in Sect. 1.2. Isotopic (*e*) and to a lesser extent DIC modelling methods (*d*) have been discussed in Sect.2 and we have just discussed micrometeorological methods (*b*, Sect 3.1). Other methods include chamber methods (*a*) and DIC budgets (*c*). All of the methods are generally useful and in combination provide some direct insight into transfer velocities for carbon dioxide. Most results do not greatly help to resolve between the contradiction of DTE results (Sect. 2.2) and micrometeorological results (Sect. 3.1). One study based on budgets for part of the Baltic Sea [26]. The inferred transfer velocities are high compared to most efforts, reasonably consistent with eddy covariance values, but much higher than inferred from the dual tracer method (Table 1 and Fig. 3, "Kuss").

4. OTHER GASES

4.1. Oxygen, nitrogen and noble gases.

Another 5 methods listed in Sect. 1.2 (*f* to *j*) apply to oxygen, nitrogen and noble gases. These gases are conveniently grouped together firstly because they are all less soluble than carbon dioxide and secondly, because similar methods can be applied to each (e.g. inversion of oceanic or atmospheric data to a surface flux). Again, we review these methods with a view to whether they contradict or affirm inferences from DTE (Sect. 2) or carbon methods (Sect. 3). It should be noted that since these gases are relatively insoluble they should theoretically (see Section 5) be more likely to exhibit greatly enhanced transfer in high wind speeds. The picture from various studies is rather mixed. A study using neutrally buoyant floats during Hurricane Frances [27, 28] supports relatively low transfer velocities at high wind speeds (MD-07 in Fig. 4).
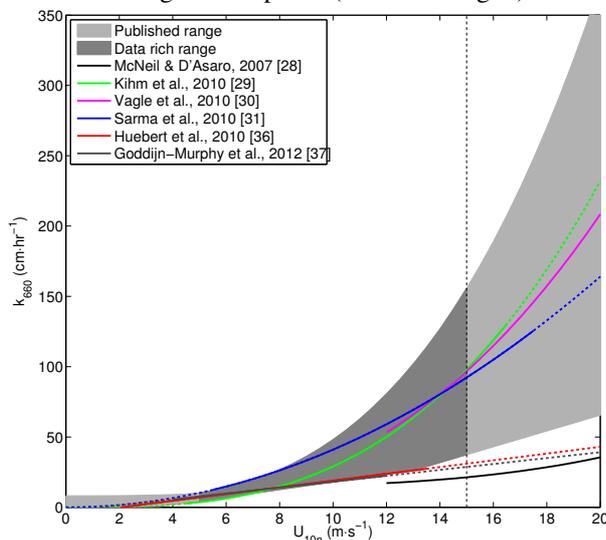

Figure 4. Some proposed parameterisations of transfer velocity against wind speed based on oxygen (or oxygen and nitrogen) measurements and modelling (see text; [28-31]) and on eddy covariance measurements of dimethyl sulphide ([36, 37]; see Sect. 4.4).

Most other studies support relatively high transfer velocities at high wind speeds. (For example, using oxygen time series [29] ("Kihm" in Fig. 4), oxygen and nitrogen time series [30] ("Vagle" in Fig. 4), or oxygen triple isotopes [31] ("Sarma" in Fig. 4)). The support from these studies for transfer velocities of ~100cm/h at 15m/s superficially validates similar values for carbon dioxide (Sect. 3), but there remains a theoretical difficulty given that carbon dioxide should be less efficiently transferred by bubbles (Sect. 5).

4.2. Radon

Radon is slightly less soluble than carbon dioxide, but more soluble than the tracers considered in Sect. 4.1. As already mention the radon deficit method is historically important. A large recent study [32] re-evaluates many historical data sets, also using reanalysis products in order to calculate weighted transfer velocities and weighted wind speeds. This reanalysis helps to discriminate a wind-speed dependence in transfer velocities (a dependence was not readily apparent in some of the original studies). The reanalysed data still exhibits strong scatter. They [32] conclude that the data supports [12], but their results are reasonably consistent with a wide variety of parameterizations. The maximum weighted mean wind speed in the study is less than 12 m/s, therefore the study provides little insight into gas transfer in strong winds.

Two systematic errors in the calculation of transfer velocity are apparent [32], both of which bias the calculated value below the true value. The first and smaller (<5%) follows from neglecting atmospheric concentrations of radon. A more significant bias (~10%) is related to a net entrainment of radon from below the mixed layer. Note also that the method measures a "mixed layer transfer velocity" that should in principle be significantly lower than an interfacial transfer velocity [33].

Another data set has been published [34], which gives transfer velocities for a stormy winter in the western North Pacific, they report transfer velocities varying from 2.1 to 30.2 metres/day (or 9 to 126 cm/h) with a mean of 9.4m/d (39cm/h). These values are interesting since the inferred transfer velocities greatly exceed the expectation from DTE, but are consistent with the higher transfer velocities reported for carbon dioxide, oxygen and nitrogen in high winds.

4.4. Dimethyl sulphide and other gases

Relatively soluble gases are interesting since bubbles should in principle be ineffective in transferring these gases [35]. Highly soluble gases are a different case however, since these are controlled by different ("air-side") processes [6]. Dimethyl sulphide is a very useful gas, first because air-side processes are only marginally important, secondly since bubbles will be fairly ineffective and also it is quite tractable to micrometeorological methods. Analysis of measurements of dimethyl sulphide ([36, 37] and Fig. 4) suggest a fairly linear relationship of transfer velocity with wind speed, suggesting higher transfer velocities observed for other gases in strong winds may be a result of bubble-mediated transfer [40].

5. DISCUSSION

5.1. A mechanistic approach

While discussing various empirical results earlier in this paper we have anticipated that a more detailed understanding of processes may inform interpretation. In particular, we may understand variation among gases and across a range of temperatures by considering how

water properties and dissolved gas properties affect bubble-mediated gas transfer [35, 38]. We may also understand how sea state may cause a variation in transfer velocity at a fixed wind speed [39, 40]. In relation to the first, we note that the expected variation of the efficiency of bubble-mediated transfer with solubility complicates interpretation significantly [41]. In relation to the second, in a wind-driven sea we may expect bubble-mediated transfer velocity to increase with fetch (Fig. 5, [39]) or duration, though swell may complicate matters [40].
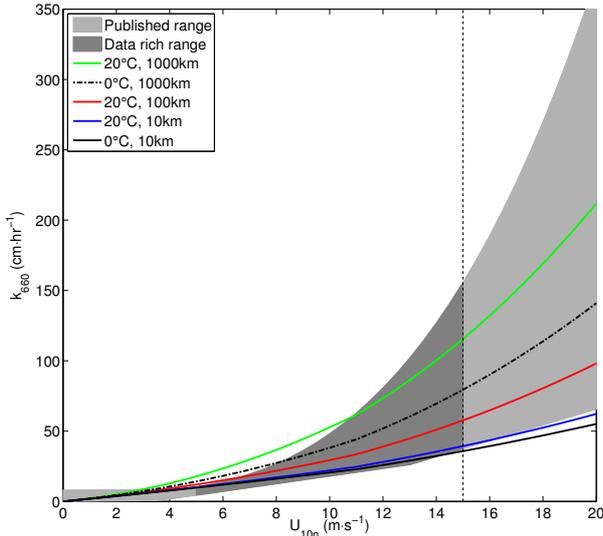

Figure 5. The variation of transfer velocity with fetch (km) in a wind-driven sea and with water temperature (^{o}C)based on a simple model [39]. The dependence on water temperature is limited to a theoretical effect on wave breaking and neglects other bubble kinetics.

5.2. A framework for uncertainties

A conclusion from our review is simply that a number of interpretations are reasonable. In other words, various experts can come to entirely different conclusions about the preferred parameterization for transfer velocity; thus "ambiguity" is entirely genuine and our evaluation of air-sea fluxes should allow for ambiguity. A proposed solution is an accessible processing system that enables "qualified users" to propose their own transfer velocities while sharing data sources and computing facilities.

6. A FLEXIBLE PROCESSING SYSTEM

6.1. Representation of transfer velocities

A limited range of transfer velocities can be calculated by allowing all polynomial relationships to wind speed, Eq. 4. The polynomial expression is also convenient since fluxes are strictly additive. Thus, once four sets of computations are completed (respectively for a constant, linear, quadratic and cubic variation) the flux can be calculated for any wind-speed relationship that can be fitted by a general cubic relationship. For example, a

polynomial approximation to a more mechanistic model (e.g. [42]) is relatively practical.

More general relationships are necessarily more difficult to implement, but some options are relatively straightforward. For example, a part of the transfer velocity may be assumed to be proportional to whitecap coverage. Whitecap coverage may then be sourced separately from wind speed, for example on the basis of a retrieval from satellite instruments or a wave model. Also the constant of proportionality might be assumed to depend on the gas and water temperature using an existing model [e.g., 41].

6.2. A processing system

The final requirement is to design a computing architecture capable of processing. One key is the top-level processing that enables a flexible calculation of transfer velocity (Fig. 6). Other key features include the preparation and serving of input data sets including products based on satellite-borne instruments and key in situ data, notably dissolved gas data. The central philosophy is to allow expert users to direct the process.
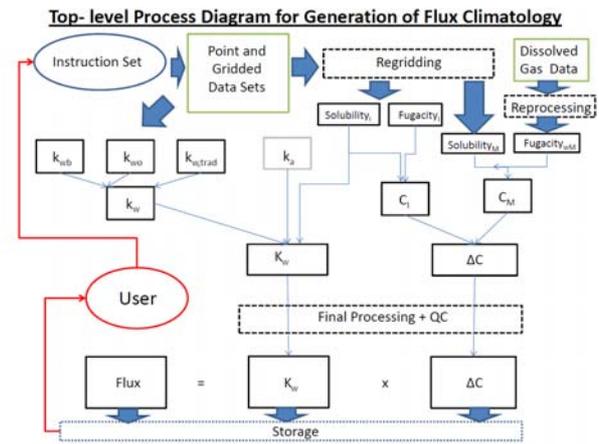

Figure 6. A processing system for user-specified parameterisations of transfer velocity.

7. CONCLUSION

It is not appropriate to calculate air-sea gas flux climatologies on the basis of narrow assumptions of the relationship of transfer velocity to wind speed and Schmidt number. We have designed a more flexible system that enables a broader range of environmental dependencies to be tested.

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