Measurement of gas transfer velocity

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Abstract. Air-sea CO_2 exchange is an important process in the global carbon cycle because a lot of carbon goes from the air into the sea in a year and mitigates global warming. Knowledge of the gas transfer velocity (k) is needed to understand the air-sea CO_2 exchange, since the air-sea gas exchange can be calculated by multiplying k and concentration difference of the gas. To determine k in the field, there are several methods such as mass balance technique, direct flux measurement and estimation from heat flux. There are advantages and disadvantages in these methods. Field research conducted to date does not favour one method above the other.

1 Introduction

Air-sea gas exchange is an important part of the global carbon cycle. According to IPCC (2013), 2.3±0.7 PgC yr^{-1} anthropogenic carbon was transported from air to sea between 2000 and 2009, which is examined by both model and observations (Fig. 1). IPCC (2013) also reported that 9.5±0.7 PgC anthropogenic carbon is emitted in 2011 from land to the atmosphere; therefore, 2.3 / 9.5×100=24% of the annual anthropogenic carbon is transported from air to the sea in 2011, and mitigate the increase of CO_2 in the air.
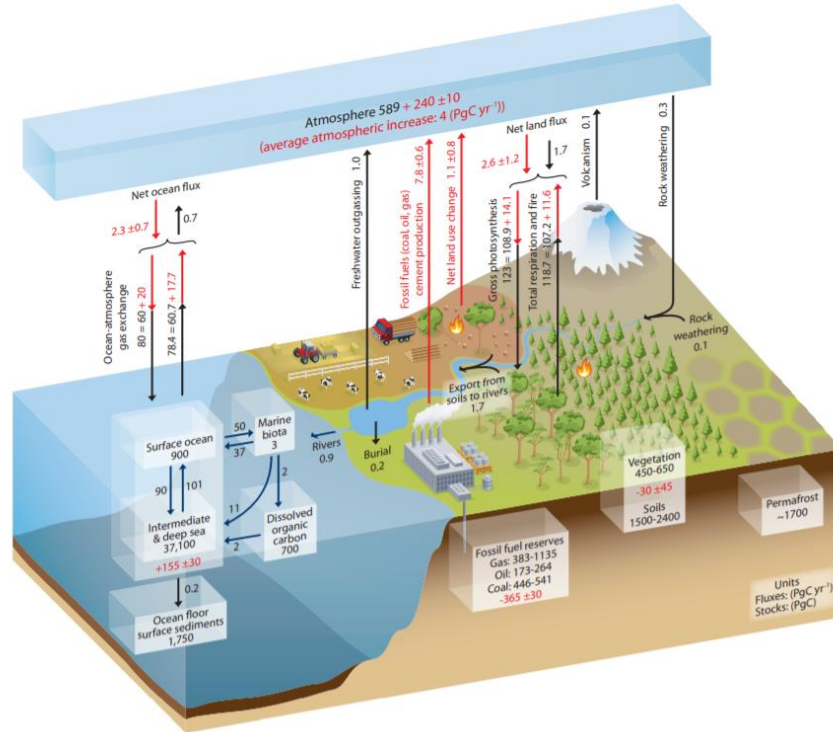

Fig. 1 Schematic figure of Global carbon flux from IPCC (2013). The unit of numbers and arrows are PgC and PgC per year, respectively. Black numbers and arrows represent mass and flux estimated for prior to 1750. Red numbers and arrows represent anthropogenic flux estimated for 2000–2009.

Knowledge of the gas transfer velocity (k) is needed to understand the air-sea

CO_2 exchange, since air-sea gas flux is a function of k and the air-sea difference in concentration (C) of the gas as shown in equation (1).

$$air - sea\ gas\ flux = k(C_{sea} - C_{air}) \tag{1}$$

Since it is difficult to measure k in the field, parameterizations are often used to estimate k (such as Ho et al., 2006).
35   These parameterization predict k well from widely and easily measured parameters such as wind speed in the offshore region. However, fewer studies examined k in coastal regions, polar regions and extreme conditions such as high wind speed. To make better parameterizations and estimate the air-sea CO_2 exchange accurately, we need to measure k in these environments and make better parameterizations. In this paper, I will review several techniques to measure k in the field.

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2. Basic mechanism of air-sea gas exchange

Broecker and Peng (1974) explained that a classical stagnant film model
45   can be applied to air-sea gas exchange. The schematic view of the film model is shown in Fig. 2. The air-sea gas exchange is limited by
50   the most time-consuming process which is molecular diffusion at a diffusive sublayer in the sea for insoluble gasses such as
55   CO_2 (blue line in Fig. 2). Soluble gasses such as ammonia, on the other hand, is limited by diffusive sublayer in the air for its

Fig. 2 Schematic figure of a classical stagnant film model from Fig. 2 of Wanninkhof et al. (2009). In this paper, C_w and aC_a represent CO_2 concentration in the mixed layer and sea surface, respectively.

60   exchange between air and sea (red line in Fig. 2). The concentration of CO_2 is constant at C_w in the mixed layer and decreases in the film layer toward the surface value of aC_a which is the equilibrium CO_2 concentration with the air.
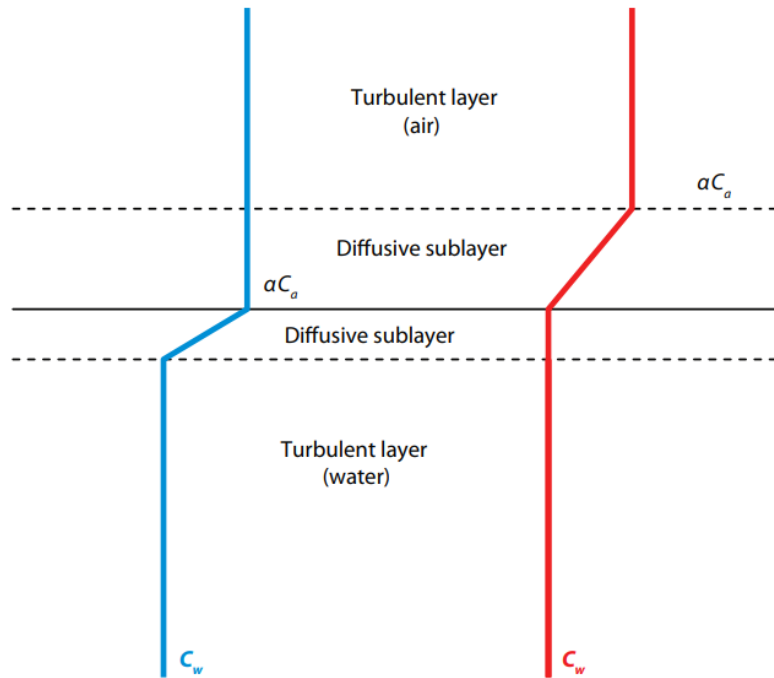
The film layer for CO_2 is estimated to be 46 on global average (Broecker and Peng, 1974). The stagnation film model predicts the CO_2 flux by equation (2) below

$$air - sea\ CO_2\ flux = D\frac{Cw - aC_a}{z} \tag{2}$$

where D and z are molecular diffusivity and film thickness, respectively. From equation (2), it is apparent that air-sea gas flux increases when D is high, Cw minus aC_a is high, or z is thin. By comparing equation (1) and (2), it is apparent that k is calculated by D/z. Note that although the stagnant film model is useful and simple, more recent studies suggest that k is known to be a function of D to the power between 1/3 and 1/2, not 1 (Wanninkhof et al., 2009). Moreover, recent studies argue that k is expressed as follows (e.g., Wanninkhof et al., 2009).

$$k \propto D, z, mixing\ strength, \nu \tag{3}$$

where ν is the kinetic viscosity of water. k is affected not only from D and z but also turbulence and viscosity of water. In the offshore region, k is known to be well parameterized by wind speed because wind mainly controls the sea surface turbulence and bubbles (Wanninkhof et al., 2009). In coastal regions, on the other hand, mixing strength is affected by several other factors in addition to the wind, such as bottom-generated turbulence, fetch limitation and the presence of surfactants.

2 Mass balance technique

This technique measures k for easily-measured gas and converts it to k for other gasses. Since D is the only specific parameter each gas (equation 3) affecting k, k for one gas can be derived from k for other gases using a function of D if the environment is the same (c.a. same z, mixing strength, temperature and salinity). For example, k_{SF6} can be converted to other gas transfer velocities such as k_{CO2} by using equation (4) below (e.g., Jähne et al., 1984).

$$k_{CO2} = k_{SF6}\left(\frac{Sc_{CO2}}{Sc_{SF6}}\right)^n \tag{4}$$

where Sc_{SF_6} and Sc_{CO2} are the Schmidt numbers (i.e., ν divided by D) for SF_6 and ^3He, respectively. n is between -3/2 and -1/2 depending on the wind speed. Note that (4) can be applied if the two gasses are insoluble, since the limiting process of the air-sea gas exchange is air-side diffusive sublayer if the gas is soluble.

2.1 Natural perturbations

Radon has been used extensively for determination of air-sea gas exchange over the ocean because it has only a single loss term due to radioactive decay (Emerson and Hedges., 2008). The parent Radium, ^{226}Ra has a half decay time ($t_{1/2}$) of 1620 years, while 3.85 days in the case of the daughter Radon of ^{222}Rn.

If there is no air-sea gas exchange, the decay of ^{222}Rn will be in equilibrium with the production which is decay of its parent, ^{226}Ra. This equilibrium is observed below the mixed layer (below ~30 m in Fig. 3). Within the water mixed

layer (between 0 and 30 m in Fig. 3), some of the ^{222}Rn will escape due to the air-sea gas exchange; therefore, the disequilibrium of ^{222}Rn and ^{226}Ra in the mixed layer is related to the gas transfer velocity. The mass balance of ^{222}Rn in the mixed layer can be written as follows.

$$\int_{z=0}^{z=MLD} \frac{d}{dt}\, ^{222}\text{Rn}_{water}\, dz = \int_{z=0}^{z=MLD} \lambda_{Ra}\, ^{226}\text{Ra}_{water}\, dz - \int_{z=0}^{z=MLD} \lambda_{Rn}\, ^{222}\text{Rn}_{water}\, dz - F_{air-water} \tag{5}$$

where λ_{Ra} and λ_{Rn} are the decay constants of ^{226}Ra and ^{222}Rn, respectively. The temporal change in ^{222}Rn at the surface (left-hand side term) is the sum of production term (1st right-hand side term), decay term (2nd right-hand side term) and air-sea gas exchange term (3rd right-hand side term). The air-sea gas exchange term can be written as follows.

$$F_{air-water} = k_{Rn}\{^{222}\text{Rn}_{water} - ^{222}\text{Rn}_{air}\} = k_{Rn}\, ^{222}\text{Rn}_{water} \tag{6}$$

Since the ^{222}Rn$_{air}$ in offshore region is negligible, we can set ^{222}Rn$_{air} = 0$ and $F_{air-water}$ becomes a product of ^{222}Rn$_{water}$ and k_{Rn}. Therefore, if vertical profile of ^{222}Rn and ^{226}Ra is determined with time, k_{Rn} is the only unknown term in equation (5).

The difficulty in this method to determine k is that we need to estimate the change in the mixed layer depth. Changes in mixed layer depth will change the range of vertical integralation. Also, changes in the mixed layer depth affect the vertical profile of ^{222}Rn and ^{226}Ra due to entrainment. The horizontal advection of ^{222}Rn and ^{226}Ra can affect the right had side of equation (5) as well, and so spatial variability should be concerned.
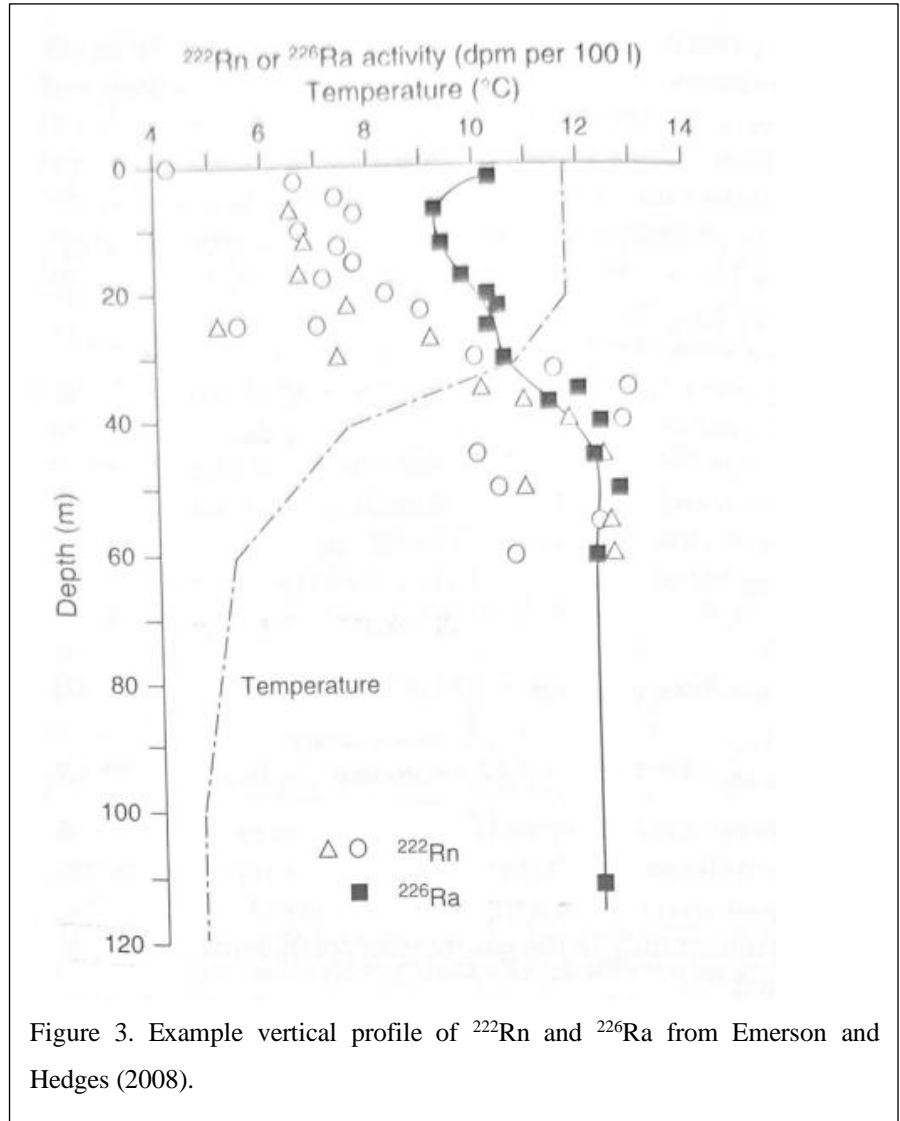

Figure 3. Example vertical profile of ^{222}Rn and ^{226}Ra from Emerson and Hedges (2008).

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2.2 Dual tracer technique

This method injects tracers such as Sulfur hexafluoride (SF$_6$) and light isotope of helium (^{3}He) into the ocean and estimates k by measuring the change in ratio of the two tracers with time.

125 The tracer of SF$_6$ was started to be used solely in a fixed water volume exposed to the atmosphere such as lakes and rivers (e.g., Ho et al., 2002). SF$_6$ is a good gas for a tracer because it has low detection level and it is easy to be measured (Wanninkhof et al., 2009). SF$_6$ is an inert gas and exists in water at very low concentrations; therefore, it has low noise/signal. After injecting large amount of SF$_6$ into the water, the concentration of SF$_6$ will decrease solely by air-sea SF$_6$ exchange as shown in equation (7):

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$$h \cdot \frac{d(SF_{6water})}{dt} = \text{air-sea } SF_6 \text{ Flux} \tag{7}$$

where h is the water depth. If we combine equations (1) and (7), we can show the change in the concentration of SF$_6$ with time in the water can be written as shown below.

$$\frac{d}{dt}(SF_{6water}) = -\frac{k_{SF_{6water}}}{h}(SF_{6water} - SF_{6air}) \tag{8}$$

SF$_{6air}$ is often considered as 0 due to its low concentration in the air compared with the injected concentration. The

135 equation above can be solved to determine $k_{SF_{6water}}$ as shown in the equation below.

$$k_{SF_{6water}} = -\frac{h}{t_2 - t_1}\left(lnSF_{6water,t2} - lnSF_{6water,t1}\right) \tag{9}$$

Using SF$_6$ can examine k in a small area such as lakes, but we cannot determine k by using solely SF$_6$ in the open ocean where the patch of injected tracer is significantly smaller than the field, and so the decrease in (SF$_{6water}$) will occur not only through air-sea gas exchange and but also by advection and dispersion in the water. In these cases, a

140 second tracer is necessary to be used. Two gases with different diffusion coefficients are often used in open ocean experiments, which are ^{3}He and SF$_6$ (e.g., Ho et al. 2006). ^{3}He is often used because it meets the same criteria of inertness, low background concentration, and low detection limits as SF$_6$ (Wanninkhof et al., 2009). After the two gases are injected in a constant ratio into the ocean, their concentration decrease in the water column due to dispersion which will be the same, but the loss due to gas exchange will be different between the two tracers and this difference

145 will be proportional to the inverse square root of the ratio of their Sc: (Sc$_{3He}$/Sc$_{SF6}$)$^{-1/2}$ (equation 5). I omit the calculation process, but the k_{3He} can then be expressed as follows if we use the dual tracer technique.

$$k\,^3{}_{He} = -\left(1 - \left(\frac{Sc_{SF_6}}{Sc\,^3{}_{He}}\right)^{-\frac{1}{2}}\right)^{-1} h\frac{d}{dt}\left(\ln\left(\frac{^3He}{SF_6}\right)\right) \tag{10}$$

Successful ^{3}He/SF$_6$ studies have been performed in several different ocean basins under a range of conditions, and k is well parameterized by wind speed (e.g., Ho et al. 2006). The disadvantage of this method is a low time resolution. The time interval to determine k is one to four days, depending on the rate of gas exchange and h.

3. Direct flux measurement

The covariance or eddy correlation technique determines the air-sea CO_2 flux directly. By measuring the air-sea CO_2 flux and CO_2 concentration both in the sea and air, k_{CO2} can be derived from equation 1. Air-sea CO_2 flux can be directly measured from the CO_2 concentration, c, and the vertical velocity, w, in the atmospheric boundary layer using the expression:

Figure 4. Eddy covariance system for methane in Baltic sea. Photo from Gutiérrez-Loza et al., 2019.

$$\text{air} - \text{sea } CO_2 \text{ flux} = (c'w') + \overline{cw} \tag{11}$$

where the primes indicate fluctuations from a mean value. The 2nd term in the right hand side of the equation is the CO_2 flux carried by mean vertical velocity, which is estimated from other fluxes such as latent and sensible heat flux. The raw data from a covariance flux system is the 1st term in the right hand side of the equation. The covariance flux systems have been used extensively to measure the air-sea CO_2 flux (for instance, Fairall et al. 1997; Figure 4 shows the system set up). The sonic anemometer measures the velocity at the edge of this system and the gas analyzer behind the anemometer measures c. One of the advantages of this method is the high time resolution as written below, which enables it to capture the small changes in air-sea gas exchange.

The challenge in applying this technique is that high sampling rate and high precision are required for measurement of c, which typically requires sampling at 2 times at 1 second or greater and precision of c in at least two orders of magnitude greater than that of the air-sea gradient (Wanninkhof et al., 2009). As well as this requirement for c measurement, corrections are required against platform motion.

4. Estimation from heat flux

k can be estimated from the transfer velocity of heat by hypothesizing that the *k* and transfer velocity of heat are related by their diffusivities. The estimated *k* from heat flux is often written as k_H.

Heat could be a tracer of air-sea gas exchange because temperature can be measured with high accuracy and very good temporal resolution, thus letting us study the air-sea exchange in detail. Based on the fact *k* is determined by the molecular diffusion at the diffusive boundary

Figure 5. Schematic figure showing the location of diffusive boundary layer and thermal boundary layer from Emerson and Hedges (2008)

layer (Fig. 5) and that *k* for one gas can be derived from *k* for other gas (equation 4), Atmane et al. (2004) assumed that they can derive *k* from heat flux since heat exchange is also limited at the thermal boundary layer (Fig. 5; equation 12).

$$k_{CO2} = k_H \left(\frac{Sc_{CO2}}{Pr}\right)^{-\frac{1}{2}}$$ (12)

where Pr is ν divided by molecular diffusivity of heat. The result of the experiment is shown in figure 6. The estimated k_H overpredict the actual *k* which is determined from He and SF_6. Atmane et al. (2004) explain this difference as a result of the interplay between the distance at which water-side turbulence eddies approach the interface (the layer between 0.03 cm and 0.3 cm in Fig. 5). In fact,
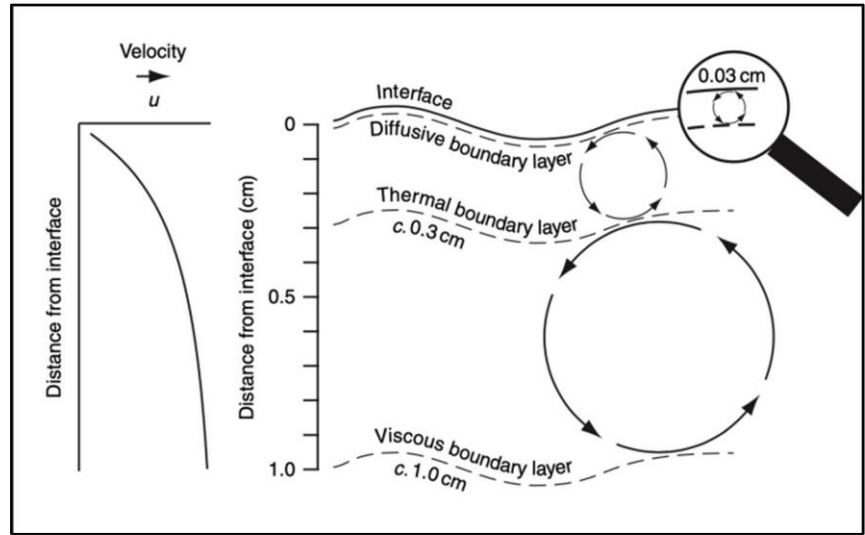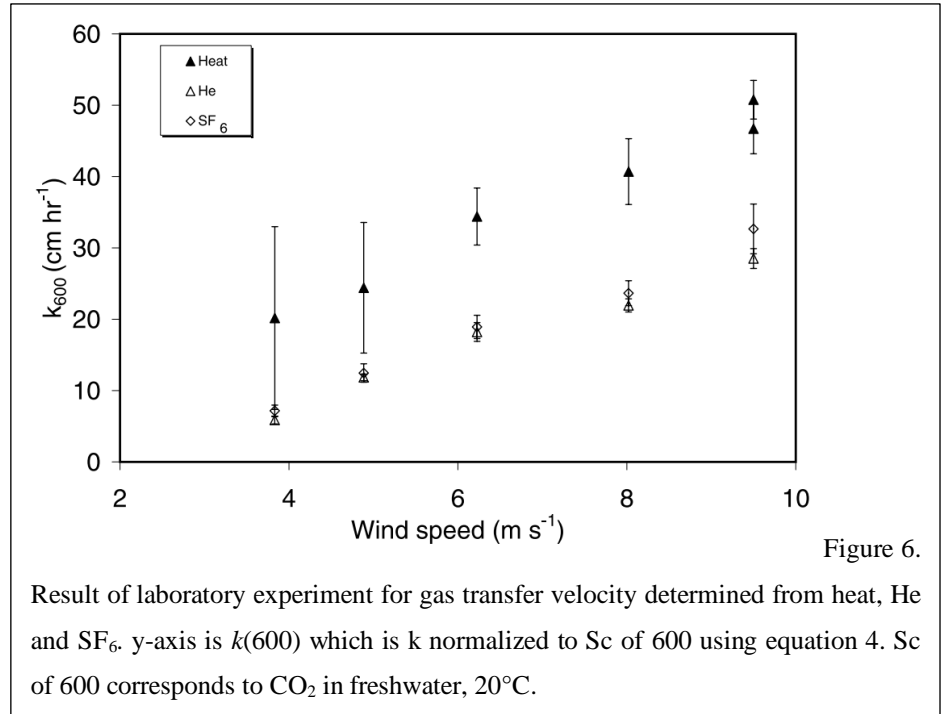

Figure 6. Result of laboratory experiment for gas transfer velocity determined from heat, He and SF_6. y-axis is $k(600)$ which is k normalized to Sc of 600 using equation 4. Sc of 600 corresponds to CO_2 in freshwater, 20°C.

it is still controversial whether estimation of k from heat flux provides k, and a clear resolution to this problem is not available at present (Wanninkhof et al., 2009).

Van dam et al. (2020) estimated k_H using equation 12 at seagrass ecosystem in Florida Bay, and found that k_H is lower than k which is estimated from published parameterization such as from Ho et al. (2006) who determined the parameterization based on the result from dual tracer technique in offshore region. This result contradicts the result of Atmane et al. (2004) who found that k_H tends to overestimate actual k (Fig. 6). Van dam et al. (2020) suggested that stratification is large in the shallow Florida Bay ($\sim$ 2 m), which suppressed the air-sea gas exchange. Dobashi and Ho. prep conducted the dual tracer release experiment at the Florida bay to examine the air-sea gas exchange in the seagrass ecosystem, and we also found smaller k compared with the other coastal and offshore regions which is the same result with Van dam et al. (2020). However, we found a weak relationship between stratification and k. We argue that the smaller k in seagrass ecosystem is probably due to limited wind fetch and wave attenuation by seagrasses.

5. Summary

Gas transfer velocities are determined mainly by mass balance technique, direct flux measurement and heat flux in the field. The advantages and disadvantages of these methods are summarized in Table 1. Improvement is needed for better time resolution and precision to make better parameterization and calculate air-sea CO_2 exchange more accurately.

Table 1. advantages and disadvantages of different techniques to determine gas transfer velocity

	mass balance technique		direct flux measurement	heat flux
	^{222}Rn	Dual tracer technique		
Advantages	I think dual tracer technique is more precise than using ^{222}Rn.	High precision	Long-term measurement High time resolution	Easily measured
disadvantages	Need to consider	Low time resolution	Large noise/signal and so needs many corrections	Tend to overestimate the actual gas transfer velocity

	spatial variability and changes in mixed layer depth	(time resolution is 1 day at the lowest case)		

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