Comparison of wind speed-gas exchange parameterizations with upper-ocean radon profiles for biogeochemical applications in the Eastern Tropical South Pacific

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Abstract

The rate of atmosphere-ocean gas exchange remains a key uncertainty in both global and basin-scale oceanic gas budgets. We report upper-ocean ventilation rates in the Eastern Tropical South Pacific obtained from $^{222}$Rn distributions measured during a cruise in February 2010, and we compare these data to six empirical wind-speed-based gas transfer velocity parameterizations. $^{222}$Rn-based results from seven stations were compared with gas transfer velocities calculated from 30-day wind histories obtained from a satellite scatterometer (ASCAT) and a meteorological reanalysis (NCEP) data product. Three different grid scales were used for wind averaging: $0.5^\circ \times 0.5^\circ$, $1^\circ \times 1^\circ$, and $2^\circ \times 2^\circ$. Average wind speeds in the region were 5 – 8 m s$^{-1}$, corresponding to in situ gas transfer velocities of 1 – 3 m d$^{-1}$. We find that the best parameterizations yield gas exchange velocities agreeing with our in situ results within 10%. Differences between grid sizes and wind products are discussed. Averaged over the region, most of the recent gas exchange parameterizations perform similarly, although quadratic parameterizations tended to overestimate gas exchange rates while cubic parameterizations tended to underestimate them. These results have implications for constraining fluxes of O$_2$ and CO$_2$ that reflect biological productivity in the upper ocean.

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1. Introduction

The distribution of biologically relevant gases (e.g., O$_2$, N$_2$, and CO$_2$) and their isotopic composition in the mixed layer is the basis for a powerful class of approaches for studying sea-surface biogeochemistry, and in particular, primary productivity, in the oceans [Bender and Grande, 1987; Craig and Hayward, 1987; Emerson, 1987; Hendricks et al., 2004; Hendricks et al., 2005; Juranek and Quay, 2005; 2010; Luz and Barkan, 2000; Quay et al., 1993; Quay et al., 2010; Reuer et al., 2007; Stanley et al., 2010]. Recent methodological and technological advances [Cassar et al., 2009; Sarma et al., 2005] have made possible in situ studies of primary productivity with high spatial resolution and/or large areal extent. Although free of the potential artifacts that may bias on-deck incubation experiments, in situ methods still have well known uncertainties. Principal among them is the air-sea gas transfer velocity, $k$ (m d$^{-1}$), which is important for understanding the balance between biological activity and the physical transport mechanisms that govern the mixed-layer trace gas budget.

Wind speed is widely recognized as a robust parameter from which the gas transfer velocity can be calculated [Asher and Wanninkhof, 1998; Wanninkhof et al., 2009], so parameterizations of wind speed are often employed to calculate $k$ values. They are convenient for field studies because accurate wind-field data are readily available, e.g., from satellite-based scatterometer instruments or meteorological data, and therefore, wind-speed parameterizations require no additional experimental effort on field campaigns. Other methods to estimate gas transfer velocity exist (e.g., tracer injection [Ho et al., 2006; Nightingale et al., 2000; Watson et al., 1991], direct-covariance flux [McGillis et al., 2001; McGillis et al., 2004], and passive gas flux methods [Sarma et al., 2010; Stanley et al., 2009]), but they generally require a significant experimental effort, optimal field conditions, or both, to obtain accurate $k$ values. Which among
the published wind-speed parameterizations is best for studies involving *in situ* dissolved gas
tracers, or if a “best” parameterization even exists, is not known.

Since the early wind speed-gas exchange relationships developed from wind-wave tank
experiments [Liss and Merlivat, 1986], many other wind speed-*k* relationships have been derived
from direct field studies in lakes and in the open ocean. These parameterizations may differ both
qualitatively and quantitatively. For instance, studies have found both quadratic and cubic
dependences of *k* on wind speed (see Wanninkhof, *et al.* [2009] and references therein); the
cubic dependence is often attributed to wave-breaking, which enhances bubble-mediated gas
transfer [Woolf, 2005]. Furthermore, parameterizations optimized for the global relationship
between gas transfer velocity and wind may not be optimal on smaller spatial scales, where
contributions from e.g., gas exchange-retarding surfactants and gas exchange-enhancing bubble
injection can vary significantly. Ho *et al.* [2006] proposed a parameterization with an associated
uncertainty of ~±15% (2σ) in a study of short-term (1 – 3 days) gas exchange in the Southern
Ocean, but how this and other uncertainties propagate over the longer upper-ocean residence
lifetime of biogeochemically relevant gases (weeks) is not known. An *intercomparison* of gas
exchange parameterizations was made recently using the global GEOSECS gas exchange dataset
[Bender *et al.*, 2011], but that study was limited by a relatively coarse grid of wind-speed
averages (2° × 2°) and could not incorporate wind speeds derived from satellite scatterometer
measurements.

The $^{222}$Rn-deficit method uses a naturally occurring radiogenic isotope to integrate gas
transfer velocities in the upper ocean over a timescale of days to weeks. While the method has
well known and significant uncertainties associated with its estimates of air-sea gas flux [Refs],
the distribution of $^{222}$Rn in the upper ocean resembles those of biogeochemically relevant gases
such as O₂ and N₂; the gas concentration in the ventilated upper layer (i.e., the mixed layer) is
distinct from, but somewhat sensitive to, the concentration of gas in the lower layer (i.e., the
thermocline). However, ²²²Rn is not subject to biological processing. This key difference
suggests that ²²²Rn may be able to constrain the importance of physical factors affecting the
budgets of dissolved gases in the upper ocean (e.g., horizontal advection).

We present new in situ ocean ventilation measurements in the Eastern tropical South Pacific
(ESTP; see Figure 1) obtained by the ²²²Rn method. We compare the results against six wind
speed-gas transfer velocity parameterizations.

The Eastern tropical Pacific makes up 18% of the total Pacific ocean area and accounts for
23% of the Pacific’s estimated primary productivity, or about 10% of oceanic production
globally [Pennington et al., 2006]. It may be a region where N₂ fixation and denitrification are
spatially coupled, thus playing an important role in regulating the global oceanic N budget over
time [Deutsch et al., 2007; Westberry and Siegel, 2006]. Furthermore, it is linked to the world’s
largest low-oxygen area, which lies in the upper thermocline at depths of only a few hundred
meters [Codispoti et al., 1986; Fiadero and Strickland, 1968]. The ETSP has remained relatively
undersampled by field studies, however, in part because the potential importance of its
biogeochemistry to the global nutrient budgets of the ocean has only recently been recognized.
This study examines an important and understudied region of the ocean, and it constitutes a test
of global and regional-scale wind speed-gas exchange parameterizations and their utility for
local- and regional scale studies of dissolved gas budgets.

2. Theory and Methods
2.1. Boundary-layer diffusion paradigm for gas exchange across the air-water interface.

The boundary-layer diffusion model is a basic physical model for gas exchange across the air-water interface, and it is the conceptual basis for both the \(^{222}\text{Rn}\)-deficit and wind-speed methods. It is based on the assumption that molecular transport dominates mass transport at an interface, while turbulent transport dominates transport away from an interface [Jähne and Haussbecker, 1998; Prandtl, 1925]. In the liquid phase, molecular diffusion is the rate-limiting process for transport, while in the gas phase, molecular diffusion and viscous (momentum) diffusion are comparable. This difference in mass transport properties results in water-side control for exchange of sparingly soluble gases (e.g., \(\text{Rn}, \text{O}_2, \text{N}_2, \text{and Ar}\)) and air-side control for exchange of highly soluble gases (e.g., \(\text{SO}_2\)). Next to solubility, wind is the most important environmental forcing on air-sea gas exchange because of its direct effects on the aqueous diffusive boundary layer.

2.2. In situ gas transfer velocity with the radon-deficit method. The radon-deficit method employed in this study utilizes the radioactive decay of \(^{222}\text{Rn}\) as a ‘clock’ to determine upper-ocean ventilation rates [Broecker and Peng, 1971; Broecker et al., 1967; Peng et al., 1974; Peng et al., 1979; Roether and Kromer, 1978; 1984; Smethie et al., 1985]. Produced by the \(\alpha\)-decay of the well mixed nuclide \(^{226}\text{Ra}\) (mean lifetime = \(\tau \sim 2300\) years) in the water column, \(^{222}\text{Rn}\) in the ocean interior (\(\tau = 5.5\) days) reaches a steady-state concentration at equilibrium such that its activity is equal to that of \(^{226}\text{Ra}\). In the upper ocean, ventilation to a nearly radon-free atmosphere contributes a second loss term to the \(^{222}\text{Rn}\) activity budget, and the magnitude of disequilibrium is directly proportional to the gas transfer velocity. Thus, the \(^{222}\text{Rn}\) activity deficit resulting from ocean ventilation reflects the steady-state gas transfer velocity over several decay lifetimes of \(^{222}\text{Rn}\); in practice, radon depth profiles represent the integrated variable gas transfer velocity over
2 – 3 decay lifetimes (~2 weeks) [Bender et al., 2011; Roether and Kromer, 1984; Smethie et al., 1985]. The gas transfer velocity $k_{Rn}$ can be expressed as:

$$k_{Rn} = \left( \frac{A_E}{A_M} - 1 \right) \lambda h$$  \hspace{1cm} (1)

in the absence of an atmospheric contribution to the upper-layer $^{222}\text{Rn}$ activity. Here, $A_E$ is the $^{222}\text{Rn}$ activity at equilibrium (in the absence of gas exchange), $A_M$ is the measured $^{222}\text{Rn}$ activity in the upper layer, $\lambda$ is the first-order decay constant of $^{222}\text{Rn}$ (0.1813 d$^{-1}$), and $h$ is the equivalent depth of the $^{222}\text{Rn}$ deficit, i.e.

$$h = \int_0^x \frac{(A_E - A_x)dx}{A_E - A_S}$$  \hspace{1cm} (2)

where $A_S$ and $A_x$ are the $^{222}\text{Rn}$ activities measured at the surface and at depth $x$, respectively. This method was used extensively for gas exchange estimates during the GEOSECS program [Peng et al., 1979], as well as for the JASIN, FGGE,[Roether and Kromer, 1984] and BOMEX programs [Broecker and Peng, 1971], and as part of a long-term observational program at Station PAPA [Emerson et al., 1991; Peng et al., 1974]. It has well known limitations that have been discussed at length previously [Bender et al., 2011; Roether and Kromer, 1984]; we have introduced additional constraints in our study to address these limitations and improve the accuracy of our field data (see below).

2.3. $\text{Rn-222 and Ra-226 analyses}$ Radon-222 depth profiles were measured onboard the R/V Atlantis from Niskin casts at seven stations encompassing the oceanic region bounded by 10°–20°S and 80°–100°W during a research cruise in February 2010 (see Figure 1). This region
includes the transition zone between the Eastern Boundary Current regime, influenced by coastal
upwelling along the South American margin, and the South Pacific Gyre. It is primarily
oligotrophic [Pennington et al., 2006], so inhibition of gas exchange due to surfactants is not
expected to be important in this region. Surface currents were generally to the Northwest at 2 –
10 cm s\(^{-1}\) (A. Knapp, private communication).

For each depth profile, we measured 4 – 6 water samples from the mixed layer and 2 – 4
samples from below, between 1 and 250 m. A conductivity-temperature-depth (CTD)/Rosette
system with 24 10-L Niskin bottles was used to collect water from 8 – 10 depths per cast. Two
Niskin bottles were triggered at each depth, and the water from both Niskins was transferred into
a pre-evacuated 19-L glass bottle. Each bottle had been marked with several calibration lines so
that sample volume could be determined from water height. Bottles were sealed on the top with
an o-ring seal to a polyvinyl chloride lid. The lid was penetrated by a long inlet tube, with a
fritted tip attached, and a short exit tube.

Radon-222 was analyzed by the method of Mathieu, et al. [1988] with a few
modifications. First, helium carrier gas was circulated through the bottle to extract dissolved
gases; the gas stream was then passed through a CaSO\(_4\) drying column to remove water, ascarite
to extract CO\(_2\), and finally through a column of activated charcoal immersed in a dry
ice/isopropanol bath (−78 °C) to trap radon. At Station 7, the dry ice ran out, so a Thermos of
pre-chilled −80°C isopropanol was used instead as the cold trap throughout the remaining
analyses. During radon extractions, the pre-chilled isopropanol bath stayed below −65°C, which
is sufficient to trap radon with 99.5% efficiency. After 50 – 120 minutes of extraction, the
charcoal trap was heated to 400°C, allowing radon transfer with a helium carrier into a Lucas-
type scintillation cell [Lucas, 1957]. The cell was counted in a radon counter (Applied
Techniques). Radon measurements were corrected to the activity present at the time of sampling considering blanks, ingrowth from $^{226}$Ra in the sample, and the combined efficiency of extraction and counting cells. The combined efficiency was determined from analyzing standards containing $^{226}$Ra prepared by the GEOSECS program and stored in bottles like those used for samples.

Radium-226 was measured by storing selected samples in sealed bottles to allow $^{222}$Rn ingrowth and analyzing the resulting activity. These analyses were repeated until the standard deviation of the mean was less than 4%. The blank for $^{226}$Ra was measured for each bottle used, and these blanks averaged $0.17 \pm 0.07$ dpm (mean $\pm$ sample s. d.). We also identified an additional blank in the analytical system not previously noted by Mathieu, et al. [1988]. In a typical run, about 10 cm of the dessicant column was hydrated, generating a total system blank (dessicant + board) of $0.09 \pm 0.03$ dpm; experiments with silica gel showed a similar blank. If board blanks were run with dry CaSO$_4$ and the charcoal column (with 1 day or fewer of ingrowth), only 0.03 dpm was released. Consequently, a board blank of $0.09 \pm 0.03$ dpm was applied to all $^{222}$Rn and $^{226}$Ra analyses in addition to the bottle blank. The overall relative uncertainty for a single $^{222}$Rn analysis should be about 4%, based on contributions from: (a) counting statistics (2%), (b) scintillation cell efficiency (2%), (c) extraction efficiency (1%), and (d) bottle and board blanks (2%). The $1\sigma$ analytical uncertainty in the $^{222}$Rn deficiency ($A_E/A_M$), therefore, is estimated to be $\pm 6\%$.

To calculate gas exchange velocities from upper-ocean radon depth profiles, a 1-D, two-layer boundary-layer diffusion model was constructed, similar to that derived by Broecker and Peng [1971] and Peng, et al. [1974]. The model calculated best-fit radon depth profiles using Fick’s second law of diffusion:
The eddy diffusivities for the upper and lower layers ($K_1$ and $K_2$, respectively) are determined from the solutions to Eq. 3,

$$K \frac{d^2 A}{dx^2} = -\lambda (A_E - A_x)$$  \hspace{1cm} (3)

The profile was then used to calculate $h$ in Eq. 2, and finally, $k_{Rn}$ in Eq. 1. A full derivation can be found in Peng, *et al.* [1974].

Generally, the upper layer had a high eddy diffusivity (i.e., $K_1 > 10$ cm$^2$ s$^{-1}$), whereas the lower layer had a small eddy diffusivity (i.e., $K_2 \sim 0.1$ cm$^2$ s$^{-1}$). The boundary between these two layers was defined as the depth of the thermocline at each station, which was identified from CTD measurements as the depth at which the water temperature decreased by 0.5°C from its surface value. The depth of the upper layer may be different from that of the homogeneous mixed layer because thermocline entrainment and barrier-layer formation are not uncommon on timescales of days to weeks; however, the vertical integration of the radon deficit is insensitive to vertical exchange of water, so Kromer and Roether [1984] argued that the thermocline depth is the natural length scale of the radon deficit method in the absence of vertical shear in horizontal transport. An important distinction must also be made between the mixed-layer/thermocline depth and $h$: while $h$ is similar to the mixed-layer depth (MLD) in most cases, the two may
diverge when the upper-layer $^{222}$Rn deficit is small and the proportion of high-$^{222}$Rn water from the lower layer entrained into the upper layer becomes larger.

Implicit in this 1-D model were assumptions of horizontal homogeneity, maintenance of steady-state conditions, and an invariant upper-layer depth during the timescale of interest (~2 weeks). Uncertainties related to these assumptions have been discussed and estimated previously to be 20 – 35% \cite{Roether and Kromer, 1984}, resulting from short-term forcing such as internal waves, water mass entrainment/detrainment, and/or a fluctuating MLD. In general, these phenomena limit the accuracy of single $^{222}$Rn depth profiles; consequently, the replicate depth profiles at two stations (5 and 7), 43 hours apart, were measured to provide a window to the short-term reproducibility of $^{222}$Rn-derived gas exchange velocities.

2.4. Wind speed-based gas transfer velocity parameterizations. Many gas exchange parameterizations based on wind speed have been developed, but the ones most often employed in biogeochemical studies are empirical, the data having been acquired at different timescales under varying wind and surface conditions. One goal of this parameterization intercomparison is to evaluate which parameterization(s) are the most accurate in the ETSP, and, perhaps, on basin scales in general. The second goal of this intercomparison is to determine the optimal temporal and spatial scales for averaging remotely sensed and/or modeled wind products. Consequently, we will evaluate wind-speed based gas exchange velocities for six recent parameterizations using winds from two different sources.

A variety of wind speed-gas exchange relationships with quadratic and cubic dependencies on the wind speed at 10 m above the ocean surface, $u_{10}$, were tested. Conceptually, these two classes of wind speed parameterizations represent the dependence of gas exchange on wind stress, which scales with $u_{10}^2$, and bubble injection (surface whitecaps), which scales
roughly with $u_{10}^3$ [Stanley et al., 2009; Woolf, 2005]. Additionally, there is some laboratory
evidence that gas exchange scales linearly with friction velocity, and therefore $u_{10}$, at low wind
speeds [Deacon, 1977; Large and Pond, 1981], and that the buoyancy flux is also nontrivial,
resulting in a nonzero gas transfer velocity at zero wind. Therefore, the generalized functional
form of wind speed-gas exchange parameterizations is {Woolf, 2005 #86;Wanninkhof, 2009
#85}:

$$k_{660} = a + bu_{10} + cu_{10}^2 + du_{10}^3 \quad (6)$$

where $k_{660}$ is the gas transfer velocity normalized to a Schmidt number, $Sc$, of 660 (i.e., for CO$_2$
at 20°C in seawater). The Schmidt number is defined as the ratio of the water’s kinematic
viscosity to the solute gas’ molecular diffusivity ($Sc = \nu/D$), and can be calculated as a function
of temperature for seawater (assuming $S = 35\%$) from empirical relationships reported in
Wanninkhof [1992] with a reported uncertainty of 3 – 10%. To convert $k_{660}$ to $k_{Rn}$, a scaling
factor of $(Sc_{Rn}/660)^n$ was applied to Eq. 6, where $n = 1/2$. The exponent $n = 1/2$ is commonly
used because the diffusive boundary layer is assumed to have a rough surface, in which the gas
transfer resistance scales with $D^{1/2}$. In the limit of a smooth surface, $n = 2/3$ [Jähne and
Haussbecker, 1998]. Under most oceanic conditions, $n = 1/2$, whereas if surfactant coverage is
important (rendering the surface smoother) $n$ may increase towards 2/3 [Goldman et al., 1988].
At 20°C, the upper limit of error in converting $k_{660}$ to $k_{Rn}$ associated with this range in $n$ is 7%.

Table 1 shows the values for coefficients $a$, $b$, $c$, and $d$ for the parameterizations tested: the
quadratic parameterizations of Wanninkhof [1992] (W92), Nightingale, et al. [2000] (N00), Ho,
et al. [2006] (H06), and Sweeney, et al. [2007] (S07), and the cubic parameterizations of
Wanninkhof and McGillis [1999] (W99) and Wanninkhof, et al. [2009] (W09). Note that for the
N00 parameterization we have chosen their reported best fit to their dual-tracer data and not the
composite fit to theirs and others’ dual tracer-data. Other wind speed-gas exchange
parameterizations have been developed for specific conditions, i.e., those derived from the
GasEx studies [McGillis et al., 2001; McGillis et al., 2004] and recent short-term oxygen triple-
isotope study [Sarma et al., 2010], but they are not applicable to the present study.

Three wind products were utilized: Shipboard measurements (24-h station averages),
winds from the Advanced Scatterometer (ASCAT;
http://manati.orbit.nesdis.noaa.gov/products/ASCAT.php), and winds from the NCEP/NCAR
meteorological reanalysis ([Kalnay et al., 1996];
http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.html). These data products were
chosen because they are most often used to interpret mixed-layer gas budgets; other wind
products employing the same operating principles (i.e., light scattering or reanalysis of weather
data) were not investigated, but they are expected to yield similar results. Winds from the 30
days prior to the radon casts, taken as 6-h averages, were obtained from each of the satellite wind
products. This approach is appropriate because the surface radon deficit likely reflects the wind
history integrated over a ~2 week time period. Wind values from ASCAT were averaged in grids
of $0.5^\circ \times 0.5^\circ$, $1^\circ \times 1^\circ$, and $2^\circ \times 2^\circ$ around each relevant station. For the winds obtained from the
NCEP reanalysis, the minimum grid size was $2^\circ \times 2^\circ$. We note that wind values were generally
only available at two different times daily in the ASCAT data product; for all other 6-hour
blocks, the winds were interpolated linearly; no additional accounting of wind variability was
undertaken.
The 30-day wind histories were integrated into a predicted gas transfer velocity, $k_{\text{wind}}$, by weighting the 6-hour averages according to their proximity to the $^{222}$Rn sampling time at a given station: winds further in the past were weighted less than those immediately preceding a radon cast. The weighting factor depended on the wind speed parameterization, the upper-layer depth, the station’s wind history, and the $^{222}$Rn decay constant, which were all used to calculate the fraction of the upper layer ventilated, $f_t$, during each time-step, $\Delta t$. For instance, if the gas transfer velocity on the first 6-h interval is 2 m d$^{-1}$ and the thermocline depth is 40 m, then 1.25% of the mixed layer is ventilated during that time. Over that same time period, 4.4% of the initial $^{222}$Rn decayed radioactively. Weighting factors ($\omega_t$) are then calculated according to the equation: $\omega_t = \omega_{t-1} \times (1 - f_{t-1}) \times e^{-\lambda \Delta t}$. Given that $\omega_0 = 1$ and $f_0 = 0.0125$, then $\omega_1 = 0.9875 e^{-\lambda \Delta t} = 0.9438$; this equation is re-evaluated for each time step for 30 days and 120 time blocks, by when $\omega_t$ is sufficiently close to zero. The final expression for the integrated $k_{\text{wind}}$ value was:

$$k_{\text{wind}} = \frac{\sum_{t=1}^{120} k_t \omega_t}{(1 - \omega_{120}) \sum_{t=1}^{120} \omega_t} \quad (7)$$

This weighting scheme was used by Bender, et al. [2011], and is a version of the mixed-layer ventilation model in Reuer, et al. [2007] modified to include the radioactive decay of $^{222}$Rn. The factor $(1 - \omega_{120})$ in the denominator of Eq. 7, whose value was always very close to 1, accounts for the residual, unventilated portion of the mixed layer. For this study, we assumed that the MLD was equal to that measured by the CTD at each station and was constant during the previous 30 days. In this idealized case, Reuer, et al. [2007] found that the weighting scheme yielded accurate gas transfer velocities in their box model simulations using winds of 1 – 20 m s$^{-1}$. 


3. Results and Discussion

3.1. Radon-222 measurements. All $^{222}\text{Rn}$ depth profiles are shown in Figure 2, along with their fits from the two-layer upper-ocean ventilation model. Measured $^{226}\text{Ra}$ activities at all stations were near 7.0 dpm/100L, with no significant variation with depth, except at Station 1* (see Table 2). At Station 1*, the $^{226}\text{Ra}$ activity in the mixed layer was significantly lower than that in the thermocline, i.e., $A_E = 7.3$ vs. 8.1 dpm/100L at 18 m and 55 m, respectively. We attribute this difference to either steady-state upwelling with some $^{226}\text{Ra}$ removal (e.g., particle association) or horizontal advection at Station 1*. Consequently, we use an $A_E$ profile with a ‘step’ in $^{226}\text{Ra}$ activities; this stepped profile will lead to a lower-limit estimate of the gas transfer velocity because vertical transport of high-$^{222}\text{Rn}$ waters from the thermocline into the upper layer will tend to increase the measured $A_M$ relative to the value set by ventilation in Eq. 1. At all other stations, $A_E$ was estimated by averaging the $^{226}\text{Ra}$ activity in the upper 10 m with the apparent equilibrium $^{222}\text{Rn}$ activities below the thermocline, whose values were not significantly different. We verified that atmospheric $^{222}\text{Rn}$ was negligible by conducting replicate analyses of 40-L bottles of air at (10°S,95°W); based on these analyses, the activity of $^{222}\text{Rn}$ in the upper ocean due to atmospheric $^{222}\text{Rn}$ would be 0.2 dpm/100L, or ~3% of $A_M$.

Gas transfer velocities obtained from the $^{222}\text{Rn}$ distributions ranged from $k_{\text{Rn}} = 1.1 - 3.1$ m d$^{-1}$, or $k_{\text{Rn,660}} = 1.2 - 3.4$ m d$^{-1}$ for $Sc = 660$ (see Table 3); best-fit uncertainties for each cast were ~17% ($2\sigma$) on average. No dependence of gas transfer velocity on latitude or longitude was observed, despite a factor-of-ten range in surface chlorophyll concentration ($0.01 - 0.1$ mg m$^{-3}$; [Pennington et al., 2006]). The mean gas transfer velocity at $Sc = 660$ ($2.5 \pm 0.8$ m d$^{-1}$) is similar to that observed in the Pacific during the GEOSECS mission in the same latitude range ($2.8$ m d$^{-1}$).
Upper-layer eddy diffusivities ($K_1$) in the ETSP were similar to those reported previously in the North Atlantic [Peng et al., 1974], ranging from 14 to 263 cm$^2$ s$^{-1}$. Describing the upper layer with a single eddy diffusivity appears justified because the buoyancy gradients calculated from hydrographic measurements were constant to within several meters of the upper-layer/lower-layer boundary. Best-fit thermocline eddy diffusivities ($K_2$) were between 0.1 – 0.7 cm$^2$ s$^{-1}$, though they were not well constrained due to the few $^{222}\text{Rn}$ data available from the 10 m immediately below the mixed layer. Furthermore, the buoyancy gradients increased with depth below the mixed layer, indicating that $K_2$ was likely decreasing [Sarmiento et al., 1976]. The best-fit $K_2$ values, however, are similar to previous estimates in the North Pacific and Atlantic [Roether et al., 1970; Rooth and Ostlund, 1972]. Gas exchange velocities were not sensitive to changes in the $K_2$ value.

Radon-$^{222}\text{Rn}$ depth profiles at Stations 1, 9, and 1* showed $A_M$ minima at depth rather than at the surface (see Figure 2), indicating horizontal transport may be important at those stations. In those cases, the gas transfer velocity was still calculated using the two-layer model because the results are believed to be sufficiently accurate. The best-fit $A_M$ in the upper layer was a constant, equal to the average mixed-layer $^{222}\text{Rn}$ activity, and piecewise integration of the radon deficit using the trapezoidal rule yielded similar gas exchange velocities. We note that the best-fit $K_1$ for these profiles was unrealistic and reflected the model’s assumptions; the 1-D model cannot account for horizontal advection or other external transport affecting the vertical steady-state, so we do not report $K_1$ obtained for those profiles. The uncertainty in the resulting gas
transfer velocity was calculated considering only the uncertainty in the best-fit surface $^{222}$Rn activity.

Repeat radon casts at Stations 5 and 7 yielded different gas exchange velocities. Agreement between best-fit $k$ values for the two radon depth profiles at Station 5 was poor (1.1 and 2.3 m d$^{-1}$), whereas agreement between repeat radon depth profiles at Station 7 was quite good (2.7 and 3.1 m d$^{-1}$). Shipboard winds for the 24 hours immediately preceding each cast at Station 5 were similar and similar to those at Station 7 (~3 – 10 m s$^{-1}$), so wind variability is unlikely to be the principal cause of the factor-of-two disagreement in $k_{Rn}$ values at Station 5. Horizontal advection and other transport-related effects at Station 5 cannot be ruled out; indeed, fluctuations in MLD occurring at timescales shorter than the lifetime of $^{222}$Rn can cause the $k_{Rn}$ value obtained from a single depth profile to deviate from its true value [Bender et al., 2011; Roether and Kromer, 1984]. For instance, a CTD cast at Station 5 showed a significant density inflection at 38 m, and a similar hydrographic anomaly was identified at Station 3, at 25 m. These density anomalies may reflect additional, although perhaps short-lived, shallow transport barriers. Such a transport barrier would inhibit ventilation of waters in the lower portion of the upper layer, thereby increasing $A_M$ and decreasing the measured $^{222}$Rn deficit ($A_E/A_M$) there.

While the vertical integration of the radon deficit to determine $h$ (Eq. 2) is not sensitive to the presence of this barrier layer if the eddy diffusivity is constant, setting the upper-layer depth at 38 m reduces the best-fit $k_{Rn}$ by ~30% because the modeled depth profile has changed. We note that the wind-history weighting scheme used in this study assumes a homogeneously ventilated upper-ocean layer, so it may overestimate the $^{222}$Rn-based gas transfer velocity in a stratified upper layer.
3.2. Comparison of field data with wind-speed parameterizations. A comparison was made between shipboard winds and satellite winds to test the accuracy of each averaging-grid size and wind-speed product. Averaged shipboard winds at stations for the 24 hours immediately preceding each radon cast ranged from 4.6 to 7.7 m s\(^{-1}\), and corresponding winds derived from ASCAT agreed well (see Figure 3 and Table 4). The best agreement among these winds, judged by its mean accuracy and root-mean-squared (RMS) deviation from the shipboard averages across all stations, was observed for the ASCAT 0.5° × 0.5° grid (0.1 ± 0.5 m s\(^{-1}\) on average). Larger grids showed larger mean and RMS deviations, but none of the mean errors were significantly different than the shipboard measurements. The agreement with 2° × 2° grids, using both ASCAT and NCEP reanalysis winds, is significantly better than that reported in the recent reanalysis of GEOSECS data by Bender, et al. [2011], who used the NCEP wind product and the same grid size. Wind histories were generally consistent between the wind grids and data products at each station (±2 m s\(^{-1}\), the stated uncertainty), although larger grids tended to estimate higher winds, on average. The wind histories showed high variability, generally ranging from 4 to 10 m s\(^{-1}\), during the 30 days prior to each radon cast.

We calculated an effective, weighted average wind speed for each station from the wind-history weighting scheme in Eq. 7, which was used to make a conventional \(k_{660}\) vs. wind speed plot. Figure 4 shows a comparison between in situ \(k_{660}\) values and the parameterizations with a 0.5° × 0.5° grid. For all but one station, the gas transfer velocity predicted by W92 was at or above the 2σ uncertainty limits of the in situ data, suggesting that W92 overestimates gas exchange in this region. Similar results were observed at the 1° × 1° and 2° × 2° grids, although the effective wind speeds tended to increase with grid size (see Figure S1).
A comparison of the ASCAT-derived gas transfer velocities for each grid size is shown in Figure 5, and the tabulated values for the 0.5° × 0.5° grid are shown in Table 5 (values for other grids can be found in Tables S1-S3). We will compare the relative deviations, \( \delta_k \), station-by-station, defined according to the relationship:

\[
\delta_k = \left( \frac{k_{\text{wind}}}{k_{\text{Rn}}} - 1 \right) \times 100
\]  

(8)

with \( \delta_k \) being reported in percent. The relative deviation \( \delta_k \) is similar to the absolute deviation, i.e., \( k_{\text{wind}} - k_{\text{Rn}} \); a notable advantage is that station comparisons will not be sensitive to the wind speeds used to calculate \( k_{\text{wind}} \). Thus, one can compare the average agreement across all stations with the expected value of zero to evaluate gas exchange parameterizations on the regional scale.

For analysis on the station scale, we will use the statistical range and standard deviations in \( \delta_k \) values, as they reflect the limits of accuracy expected from a single spot measurement/calculation of gas transfer velocity. We note that short-term entrainment and detrainment of water masses may cause the radon-deficit method to underestimate true gas exchange velocities by ~10% [Bender et al., 2011], so \( \delta_k \) values on that order are not unexpected for accurate parameterizations. The observed differences in agreement between parameterizations, however, are robust with respect to this possible error source. \( \delta_k \) from cast #1 at Station 5 (\( k_{\text{Rn}} = 1.1 \text{ m d}^{-1} \)) was a statistical outlier in this dataset, so it was removed from quantitative comparisons.

Generally, the purely quadratic wind speed-gas exchange parameterizations (W92, H06, and S07) tested in this study overestimated the \textit{in situ} data, yielding \( \delta_k > 0 \), while the cubic parameterizations (W99 and W09) generally underestimated the \textit{in situ} data, i.e., \( \delta_k < 0 \) (see
Figure 5). No significant dependence of $\delta_k$ on wind-grid size was found, although both the $\delta_k$ averages and standard deviations increased at larger grid sizes. The gas exchange velocities calculated using the W92 parameterization were higher and significantly different from the in situ dataset with >95% confidence in $\delta_k$ for all grid sizes. Other authors have also noted that W92 may overestimate gas exchange relative to more recent wind-speed parameterizations [Müller et al., 2008; Naegler et al., 2006].

At any given station, the agreement between our in situ and ASCAT wind-derived gas exchange velocities (i.e., 1σ s.d.) was near ±20% for all parameterizations (except for W92) and grid sizes, consistent with the predicted reproducibility of a single $^{222}$Rn depth profile [Roether and Kromer, 1984]. Averaged across all stations, however, the linear-quadratic N00 parameterization showed the best agreement, with an average $|\delta_k| < 5\%$ for all grid sizes. The quadratic H06 parameterization showed similar agreement, with an average $|\delta_k| < 15\%$ ($|\delta_k| \leq 10\%$ for the $0.5^\circ \times 0.5^\circ$ and $1^\circ \times 1^\circ$ grids). The S07, W99, and W09 parameterizations performed the least well, but none were particularly inaccurate (i.e., average $|\delta_k| \leq 20\%$). These results are different from, although not inconsistent with, those of Bender et al. [2011]; using the global GEOSECS dataset, they found that the W92, N00, and S07 parameterizations all performed similarly, whereas W99 was not as accurate as the quadratic parameterizations. They did not test the H06 parameterization, but suggested that its results would be similar to those of S07.

$\delta_k$ values derived from the $2^\circ \times 2^\circ$ NCEP reanalysis-derived winds were similar to, but more variable than, those from ASCAT winds across all parameterizations (see Figure 5 and Tables S2 and S3). For instance, the standard deviations in $\delta_k$ values for the parameterizations showing the best agreement, W99 and W09, were 34% and 30%, respectively, whereas they were 20% and 19%, respectively, for the ASCAT $2^\circ \times 2^\circ$ grid. The origin of this variability is
not known at present: the two data products have the same stated accuracy and agree to a similar
degree with the 24-hour shipboard wind averages. The stated ±2 m s⁻¹ accuracy of each wind
product, however, could lead to increased variance in gas transfer velocity at low wind speeds.
The largest disagreement in wind histories was observed at Station 11, wherein the NCEP
reanalysis-derived winds were higher than ASCAT winds at low speeds (i.e, \( u_{10} < 5 \) m s⁻¹) and
lower than ASCAT winds at high speeds. Differences in spatial resolution may be a factor, as the
ASCAT wind data product had higher spatial resolution than the NCEP product (e.g., 54 vs. 4
data points within the first 24 hours in the 2° × 2° grid at Station 11). ASCAT data, however,
were only available at two different times during the first 24-hour period, whereas the NCEP
data product had data every six hours.

Calculated gas exchange velocities, \( k_{\text{wind}} \), were not sensitive to the MLD. For instance,
halving or doubling the MLD for the ASCAT 0.5° × 0.5° winds changed \( k_{\text{wind}} \) by < 0.3 m d⁻¹ and
the \( \delta_k \) average by \( \leq 5\% \). This observation is somewhat counterintuitive, considering that a factor-
of-two change in the MLD yields a factor-of-two change (in the opposite direction) in the
fraction of the mixed layer ventilated during each time-step, \( f_t \). Stable winds in the days
immediately preceding a radon cast, however, would yield \( k_{\text{wind}} \) values insensitive to the MLD.
Although the wind histories showed high variability over 30 days, the winds during the 48 hours
immediately preceding each radon cast typically varied within a 1-m s⁻¹ range. The choice of
wind-speed parameterization, therefore, appears to be the primary control on \( k_{\text{wind}} \) values in this
study.

Gas transfer depends on a number of factors other than wind speed, however. Surfactants,
rain, surface insolation, and/or wave breaking can affect not only the wind-speed dependence of
gas exchange, but also its Schmidt number dependence, so a given empirical relationship
between gas exchange and wind may only be applicable in certain environments. For instance, McGillis and coworkers found, during the Gas-Ex missions, that whitecap-driven gas transfer was best described by cubic wind-speed relationships that were different from the W99 parameterization [McGillis et al., 2001; McGillis et al., 2004]. In our dataset, the best parameterizations formulated with global constraints (S07 and W09) and those formulated during local studies (N00, H06 and W99, from the coastal North Sea, the Southern Ocean, and the North Atlantic, respectively) performed similarly. Our results, however, apply only to a narrow, albeit globally important, range of wind speeds, 4 – 8 m s\(^{-1}\). At higher wind speeds, mechanisms such as wave-breaking can enhance gas exchange [Woolf, 2005], while possible saturation of sea-surface aerodynamic roughness can inhibit gas exchange [Donelan et al., 2004]; both can alter its dependence on wind speed. The wind histories in this study included winds as high as 11 m s\(^{-1}\), but we saw no evidence for either effect.

Finally, we note that the apparent discrepancy between our \textit{in situ} gas exchange velocities and the calculated values of Krakauer et al. [2006] may be resolved by accounting for the W92 overestimate with $\delta_k$. Using monthly distributions of root-mean-square wind speeds derived from the Special Sensor Microwave/Imager (SSM/I) instrument in 2.5° × 2.5° grids, Krakauer et al. [2006] calculated an average gas transfer velocity of 3.4 m d\(^{-1}\) (Sc = 660) in the Eastern tropical Pacific. Our $\delta_k$ values for the 2° × 2° grids suggest that their regional average may be higher than the equivalent \textit{in situ} average by ~40%; reducing their average by a factor of 1.4 yields a regional gas exchange average of 2.4 m d\(^{-1}\), which agrees well with our average \textit{in situ} value for the ETSP ($<k_{Rn,660}>$ = 2.5 m d\(^{-1}\)). The Krakauer et al. [2006] average encompasses a larger region of the Pacific than our study (i.e., 20°N – 20°S, 70°W – 160°W vs. 10°S – 20°S, 80°W – 100°W), but other measurements of gas transfer velocity suggest that the regional average may
be closer to our in situ value [McGillis et al., 2004; Peng et al., 1979]. A full wind-history reanalysis can test this hypothesis further.

4. Conclusions

We have shown quantitative agreement between the in situ $^{222}$Rn tracer and recent wind-speed parameterizations of gas transfer in the ETSP by integrating the 30-day wind history into the calculation of gas transfer velocity. Agreement between in situ data and calculated gas transfer velocities at individual study stations was best when the spatial grid from which winds were taken was small (0.5° × 0.5°). Still, the best agreement between the $^{222}$Rn-derived gas transfer velocity and the best wind-speed parameterizations was close to the expected single-profile accuracy of the $^{222}$Rn method, i.e., ~20% vs. 20 – 35% [Roether and Kromer, 1984]. Averaged over the entire ETSP study area, gas transfer predictions based on the Wanninkhof [1992] parameterization were significantly higher than the in situ results; the Nightingale, et al. [2000] parameterization showed the smallest relative deviations, regardless of wind-speed grid used, while other parameterizations showed slightly larger deviations, on average. Winds from the NCEP reanalysis yielded gas transfer velocities similar to, but more variable than, those derived from the ASCAT satellite at the same spatial scale.

While the optimal wind-speed parameterizations reported here may not be directly transferrable to other ocean basins, the $^{222}$Rn-deficit method, as it has been employed herein, should be a reasonable approach to constraining gas exchange of other biogeochemically important gases whose transport is limited by the aqueous boundary layer; these gases are subject to the same physical factors affecting the upper-ocean $^{222}$Rn budget. For instance, using an average MLD of 45 m and $<k_{Rn,660}> = 2.5$ m d$^{-1}$ in this region, O$_2$, N$_2$, and Ar (Sc = 589, 670,
and 576 at 20 °C) have residence times of ~18 days. The same mixed-layer fluctuations, wind
variability, surface temperature, and possible non-steady-state transport that would bias the 222Rn
budget of the mixed layer over this time period would also affect the budgets of these other
gases, although the radioactive decay of 222Rn reduces its mixed-layer residence time to about
four days. Future comparisons in other ocean basins with different surfactant concentrations,
wind speeds, mixed-layer climatologies, and wind-wave properties can further investigate the
general applicability of this approach.

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Rick Schwartz for assistance with lab work. The authors especially appreciate the assistance of
Guy Mathieu in constructing new, low-background, high-efficiency cells for this project, and the
ongoing legacy of Guy and Bob Lupton in developing and maintaining the equipment used. This
work was supported by the National Science Foundation Awards #OCE–0961207 and OCE–
0850801.
References


Table 1. Parameters for the wind speed-gas exchange relationships studied, as defined in Eq. 6.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>W92</td>
<td></td>
<td>0.074</td>
<td></td>
<td></td>
<td>Wanninkhof [1992]</td>
</tr>
<tr>
<td>N00</td>
<td>0.024</td>
<td>0.053</td>
<td></td>
<td></td>
<td>Nightingale, et al. [2000]</td>
</tr>
<tr>
<td>H06</td>
<td></td>
<td>0.068</td>
<td></td>
<td></td>
<td>Ho, et al. [2006]</td>
</tr>
<tr>
<td>S07</td>
<td></td>
<td>0.065</td>
<td></td>
<td></td>
<td>Sweeney, et al. [2007]</td>
</tr>
<tr>
<td>W99</td>
<td></td>
<td></td>
<td>0.0068</td>
<td></td>
<td>Wanninkhof and McGillis [1999]</td>
</tr>
<tr>
<td>W09</td>
<td>0.72</td>
<td>0.024</td>
<td>0.015</td>
<td>0.0026</td>
<td>Wanninkhof, et al. [2009]</td>
</tr>
</tbody>
</table>
Table 2. Summary of $^{226}$Ra measurements. Reproducibility of external replicates was ±0.3 dpm/100L (1σ s.e.).

<table>
<thead>
<tr>
<th>Station</th>
<th>Depth (m)</th>
<th>$^{226}$Ra activity (dpm/100L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>150</td>
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<td>10</td>
<td>7.4</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>6.9</td>
</tr>
<tr>
<td>1*</td>
<td>18</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>8.1</td>
</tr>
</tbody>
</table>
Table 3. Best-fit model parameters for $^{222}$Rn depth profiles and the resulting gas exchange velocities in the field ($k_{Rn}$) and normalized to Sc = 660 ($k_{Rn,660}$).

<table>
<thead>
<tr>
<th>Station</th>
<th>Location (°S/°W)</th>
<th>MLD (m)</th>
<th>$T_{surface}$ (°C)</th>
<th>$h$ (m)</th>
<th>$K_1$ (cm² s⁻¹)</th>
<th>$K_2$ (cm² s⁻¹)</th>
<th>$A_E$ (dpm/100L)</th>
<th>$k_{Rn}$ (m d⁻¹)</th>
<th>$k_{Rn,660}$ (m d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20/80</td>
<td>35</td>
<td>19.8</td>
<td>34</td>
<td>-</td>
<td>0.1</td>
<td>7.7</td>
<td>1.5 ± 0.2</td>
<td>1.8 ± 0.3</td>
</tr>
<tr>
<td>3</td>
<td>20/90</td>
<td>63</td>
<td>20.7</td>
<td>25</td>
<td>21</td>
<td>0.1</td>
<td>7.5</td>
<td>2.3 ± 0.6</td>
<td>2.7 ± 0.7</td>
</tr>
<tr>
<td>5</td>
<td>20/100</td>
<td>80</td>
<td>21.0</td>
<td>22</td>
<td>14</td>
<td>0.1</td>
<td>7.0</td>
<td>1.1 ± 0.2</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>7</td>
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<td>48</td>
<td>22.7</td>
<td>43</td>
<td>114</td>
<td>0.5</td>
<td>7.0</td>
<td>2.7 ± 0.4</td>
<td>3.0 ± 0.5</td>
</tr>
<tr>
<td>9</td>
<td>10/90</td>
<td>35</td>
<td>23.8</td>
<td>36</td>
<td>-</td>
<td>0.2</td>
<td>7.0</td>
<td>2.8 ± 0.5</td>
<td>2.9 ± 0.5</td>
</tr>
<tr>
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<td>25.8</td>
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<td>263</td>
<td>0.1</td>
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<td>1.8 ± 0.3</td>
<td>1.8 ± 0.3</td>
</tr>
<tr>
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<td>40</td>
<td>21.1</td>
<td>40</td>
<td>-</td>
<td>0.1</td>
<td>7.3/8.1*</td>
<td>2.9 ± 0.4</td>
<td>3.3 ± 0.5</td>
</tr>
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</table>

*Upper/lower layer in stepped $A_E$ profile.
Table 4. Comparison of wind averages ($<u_{10}>$ in m s$^{-1}$) for the 24-hour period immediately preceding each radon cast. Also shown is the average difference between wind product-derived wind speeds and shipboard wind speeds, $<u_{10} - u_{10,\text{Shipboard}}>\text{ (m d}^{-1})$, and the associated RMS deviation across all stations.

<table>
<thead>
<tr>
<th>Station</th>
<th>Shipboard</th>
<th>ASCAT $0.5^\circ \times 0.5^\circ$</th>
<th>ASCAT $1^\circ \times 1^\circ$</th>
<th>ASCAT $2^\circ \times 2^\circ$</th>
<th>NCEP $2^\circ \times 2^\circ$</th>
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<td>5.4</td>
<td>5.5</td>
<td>5.6</td>
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</tr>
</tbody>
</table>

$<u_{10} - u_{10,\text{Shipboard}}>\text{ \quad 0.1} \pm 0.5 \quad 0.4 \pm 0.7 \quad 0.6 \pm 0.8 \quad -0.1 \pm 0.7$
Table 5. Gas exchange velocities ($k_{\text{wind}}$ for direct comparison with $k_{Rn}$ in m d$^{-1}$) derived from wind parameterizations using ASCAT winds in a 0.5° × 0.5° grid around each station, shown with average relative ($<\delta_k>$, in %, as defined by Eq. 8) and absolute ($<k_{\text{wind}} - k_{Rn}>$, in m d$^{-1}$) deviations ± 1σ s.d.

<table>
<thead>
<tr>
<th>Station</th>
<th>$k_{Rn}$</th>
<th>W92</th>
<th>N00</th>
<th>H06</th>
<th>S07</th>
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<th>W09</th>
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<td>1.8</td>
</tr>
<tr>
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<td>2.9</td>
<td>2.6</td>
<td>2.0</td>
<td>2.1</td>
<td>2.3</td>
<td>1.6</td>
<td>1.8</td>
</tr>
</tbody>
</table>

$<\delta_k>$ (%)  
31 ± 21  
7 ± 17  
14 ± 18  
−13 ± 18  
−10 ± 16

$<k_{\text{wind}} - k_{Rn}>$ (m d$^{-1}$)  
0.7 ± 0.8  
−0.1 ± 0.4  
0.1 ± 0.4  
0.3 ± 0.5  
−0.3 ± 0.6  
−0.3 ± 0.5
Figure 1. Map of study area and steaming directions in the Eastern Tropical South Pacific. Station numbers are noted.
Figure 2. Radon-222 depth profiles (with 1σ counting uncertainties), their best-fit model results, and station temperature profiles.
Figure 3. Comparison of shipboard wind averages with those obtained from satellite measurements for the 24 hours immediately preceding the radon casts. The line denotes a 1:1 correspondence.

Figure 4. Comparison of gas transfer velocity parameterizations with \textit{in situ} measurements. Gas exchange rates obtained from the radon-deficit method (circles) are plotted against effective wind speed, the weighted average of the 30-day wind history (0.5° × 0.5° grid; see main text). Standard deviations (2σ) of the best-fit \textsuperscript{222}Rn depth profiles are shown. The open circle is a statistical outlier, and is discussed in the main text.
Figure 5. Average relative deviations, $<\delta_k>$, across all stations, shown with 95% confidence intervals.