
Ozone deposition to coastal waters

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SUMMARY
The air–sea exchange rate of ozone to a coastal region on the North Sea was measured using the eddy correlation technique at the UK Weybourne Atmospheric Observatory. The average measured surface resistance to ozone uptake, \( r_s[O_3] \), was found to be \( 950 \pm 70 \text{ s}^{-1} \). This exchange rate for coastal waters is very close to that recommended for open ocean conditions by Galbally and Roy of \( 1000 \text{ s}^{-1} \). The results are discussed in the light of currently accepted exchange rates and the rather small micrometeorological measurement database available for trace gas exchange to sea surfaces. Although more data are needed to confirm the observations, a tentative dependence on the surface uptake with friction speed, \( u_* \), was found, given by \( r_s[O_3] \approx -574 \ln(u_*) + 282 \text{ s}^{-1} \), possibly explaining the variation in previous measurements presented in the literature which were mostly obtained using chamber techniques.

KEYWORDS: Air–sea exchange  Coastal waters  Eddy correlation  Flux measurements  Ozone Deposition

1. INTRODUCTION
Dry deposition is an important removal pathway for many trace gas species contributing to net global chemistry budgets and regional-scale problems of pollution. Ozone is a gas species whose removal rate by landmasses and ocean surfaces is important in chemistry general circulation models, influencing the spatial distribution of reactive trace gases (Ganzeveld and Lelieveld 1995; Jenkins 1999). Simple surface-uptake resistances, \( r_s[O_3] \), for ozone based on deposition velocity measurements, have been proposed for a variety of surfaces; however, even for apparently simple surfaces such as snow and water, the measured values show large variations (\( r_s[O_3] \approx 650 \) to \( 9000 \text{ s}^{-1} \); Wesely 1989; Padro 1994; Stocker et al. 1995). Deposition velocities to ocean and snow and ice surfaces are often simply quoted as being identical for use in global climate models, Hauglustaine et al. (1994). Even small uncertainties in ocean exchange rates can have significant consequences for global budgets.

Photochemical models used to predict ozone production in urban plumes transported over water also require accurate loss rates. Sillman et al. (1993) used a photochemical model to simulate abnormally high ozone concentrations often observed at rural coastal sites on Lake Michigan and the Atlantic coast at Maine in the USA. They showed that the observed peak concentrations could only be predicted accurately if a maximum ozone deposition velocity of \( 0.05 \text{ mm s}^{-1} \) is assumed. The peak ozone concentrations predicted could be very sensitive to the loss-rate used; any higher and the simulated concentrations of ozone over water would be significantly lower, although this may not account for other possible removal mechanisms in the near-surface layer as discussed later. This deposition velocity value was also justified by theoretical arguments by Walcek (1987), and is in good agreement with some but not all measurements. Unfortunately, there are very few micrometeorological field measurements for comparison. An additional problem is that large differences in deposition rates for ozone to open freshwater surfaces (Wesely et al. 1981; \( r_s \approx 9000 \text{ s}^{-1} \)), compared to sea water surfaces (Lenschow et al. 1982; \( r_s \approx 1690–1890 \text{ s}^{-1} \)), have been observed, making comparison with such experiments and open-ocean measurements difficult.

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Figure 1. Location of the Weybourne Atmospheric Observatory on the north Norfolk Coast, UK, and local orography.

Here we present for discussion some short-term measurements of fluxes of ozone at a coastal site relevant to coastal water deposition, using the eddy correlation technique. In section 2 the measurement site is described together with the prevailing meteorological conditions. In section 3 the instrumentation used is briefly described, whilst in sections 4 and 5 fetch-height requirements, the eddy correlation technique and the commonly used resistance analogy for surface atmosphere transfer are discussed. The routinely applied coordinate transformations, corrections and uncertainties for the eddy correlation technique are also presented for completeness. The measured results are then presented in section 6, and a discussion in context of the existing but somewhat sparse database is provided in section 7 prior to the summary and conclusions in section 8.

2. The Weybourne Atmospheric Observatory site

In order to study the exchange rate of ozone to coastal sea water, direct flux measurements were made at the UK Weybourne Atmospheric Observatory. This experimental site is located on the north Norfolk coast in the UK (52.951°N, 1.125°E). Measurements were conducted during June 1998 as a component of a larger field experiment described
by Coe et al. (2001). The Weybourne Observatory is operated by the University of East Anglia, School of Environmental Sciences, and was designed for monitoring long-range transport of pollutants in the northern hemisphere; it contributes to the Eurotrac Tropospheric Ozone Research (TOR) network. The site, its instrumentation and infrastructure are described in detail by Penkett et al. (1999). The observatory is located 15 m above sea level, 100 m from the coastal zone. The fetch between the observatory and the sea consists of short grassland (70 m) and a pebble beach (30 m). The site is well removed from the nearest large conurbations (Norwich is 50 km and London 190 km distant), and is surrounded by flat arable land; it is also well away from any large local pollution sources. The site is exposed to clean marine air in northerly winds. Figure 1 shows the location of Weybourne and the variation in elevation of the local terrain, which is relatively smooth and uniform towards the sea. This particular coastal site has the further advantage that there is no tidal zone to complicate interpretation of flux measurements.

During the experiment described here winds from the north occurred on several days. Air trajectory analysis for these periods showed that air masses arriving at the site had been advected southwards at low level over the North Sea with no terrestrial influences or wet deposition effects occurring during the previous five days (Coe et al. 2001). This period afforded us the opportunity to investigate air–sea exchange rates of ozone using the eddy correlation flux measurement technique.

3. INSTRUMENTATION

Ozone fluxes were measured using an eddy correlation system comprising a sonic anemometer (Gill UK Model Solent A1012R) and a fast-response ozone fluctuation meter (GFAS Model OSG-2). The sonic anemometer had a resolution of ±0.01 m s⁻¹ and a frequency response of 20.83 Hz. The ozone sensor, its performance and comparison with other measurement techniques is described in detail by Güsten et al. (1992). This instrument comprises a chemi-luminescent disk impregnated with a layer of reactive dye which is placed in front of a photo-multiplier tube (PMT). Sample air, at 10⁻¹ m³ min⁻¹, is drawn down a short corrugated teflon inlet tube 0.6 m in length, collocated with the sonic anemometer measurement volume, between the target disk and the PMT. As ozone in the sample air reacts with the chemical on the disk light is emitted. The PMT measures the intensity of the emitted light, which is then converted by an electronic amplifier to a suitable output signal. The so-called ‘target’ disk must be pre-conditioned by exposure to a high-concentration ozone source for a period of three hours prior to use. The lifetime of the disk is limited, and its longevity has been found to vary somewhat depending on the batch supplied by the manufacturer, but is primarily affected by the storage protocols employed. Its longevity is obviously also limited by ambient ozone concentration and humidity of the sampled air. Typically the disks last 3–5 days over which time the disk calibration is stabilized by heating the disk using a heating element built into the instrument. Although this maintains the instrument’s calibration quite well over the bulk of the disk’s lifetime, absolute calibration is best achieved by comparison with a slower-response absolute instrument. In this case a Thermo Environment Model 49 UV photometric analyser was used, with a detection limit of 1 p.p.b. (part per billion) and a response time of 10 s. This instrument was operated continuously at the observatory by the University of East Anglia as part of the TOR network. Air for this instrument was sampled down a 10 m tall glass pyrex sampling stack mounted directly in front of the observatory (Penkett et al. 1999).
The GFAS ozone meter has a reported resolution of <0.1 p.p.b. and a frequency response of 20 Hz; however this can, again, vary from instrument to instrument (Duyzer, private communication). The response of the analyser used here was determined to be greater than 10 Hz by comparison with high-frequency atmospheric temperature and water-vapour spectra obtained in previous experiments (Walton et al. 1997).

The analogue signal from the ozone analyser was fed directly into the auxiliary input port of the sonic anemometer. This was subsequently digitized and output as a serial RS-422 signal concurrently with the turbulence data at 20.83 Hz. The absolute temperature and humidity was recorded using a slower-response humicap/PRT-100 instrument (Vaisala Model HMP50Y) whose output signals were again fed into the auxiliary port of the sonic anemometer. Water-vapour fluctuations were measured using a Krypton-UV absorption hygrometer (Campbell Scientific Model KH2O) with a frequency response greater than 20 Hz. The measurements of absolute temperature, relative humidity and water-vapour fluxes were subsequently used to correct sonic anemometer sensible-heat fluxes and sonic potential temperature, and to apply density and surface mass-flux corrections to the ozone fluxes as described by Bakan (1978), Smith and Jones (1979) and summarized by Webb et al. (1980).

The sonic anemometer, ozone flux meter and associated instruments were all mounted at the top of a 10 m tall mast located 50 m from the sea between the observatory and the beach. The ozone flux meter was calibrated against the absolute-ozone instrument in the observatory using measurements averaged over ten minutes. For the purposes of this work, although not ideal, we assume that the 50 m horizontal separation does not impose any serious error on the calibration due to spatial variation. Calibration of the ozone flux meter was carried out using successive 10 min averages of signals from both instruments.

Meteorological measurements of wind speed, temperature, humidity and solar radiation were also provided by an automatic weather station mounted on a 10 m tower located north and to seaward of the Observatory as part of the permanent instrumentation at the site. Comparison of the mean wind and temperature data from the eddy correlation mast with those from the weather station showed excellent agreement.

4. METHODS OF MEASUREMENT

(a) The eddy correlation technique

The total vertical flux of an atmospheric scalar such as a gas, $F_1$, is preferably measured using the technique of eddy correlation. This involves the usual Reynolds decomposition of a turbulent time series into its mean and fluctuating components such that:

$$F_1 = \overline{w' \chi'} = \overline{w' \rho \chi'} + \overline{\overline{w} \rho \overline{\chi}},$$  \hspace{1cm} (1)

where $w$ is the vertical velocity, $\chi$ the gas concentration (in this case ozone), and $\rho$ its density. The primes denote fluctuations from the assumed quasi-steady-state mean and the overbar denotes a time average. The additional term in (1) will be discussed later.

The constraints for accurate eddy correlation measurements include a relatively fast-response sensor in order to capture the majority of flux-containing eddies at a given measurement height. At a height of 4 m over a short grass surface, for example, a response time of 1 Hz will capture about 80% of the total flux depending on the local stability. Typically a response time of 5–10 Hz is preferred. There is, of course, no such thing as a perfect eddy correlation sensor and all are subject to a greater or lesser degree
to many potential sources of error. These errors include: imperfect sensor response, turbulence and scalar sensor-response mismatch, spatial separation of turbulence and scalar sensors and scalar path averaging, as well as errors introduced by sample tubes for scalar measurements such as frequency attenuation within the tubes. These sources of error have been discussed in detail by Moore (1986), who derived corrections for flux loss using transfer functions based on model spectra and standard turbulence co-spectra obtained for the atmospheric surface layer (Kaimal et al. 1972). These transfer functions were calculated for the current system but were negligible due to the fast response, 20 Hz, of the sensors involved, the minimal sensor separation used, 0.1 m, and the very short sample line for the ozone sensor, 0.6 m. The ozone sensor was mounted directly on the mast just below the sonic anemometer; cross-correlation analysis of the ozone and vertical velocity time series again revealed negligible loss in flux due to the very small time lag introduced. This type of ozone flux system has been used by many workers with few problems.

(b) Transformations and corrections to eddy correlation fluxes

Ten-minute averaged micrometeorological and trace gas fluxes were subsequently calculated from the raw data. Each ten-minute block of turbulence and ozone data was treated for the time lag between the ozone and turbulence time series due to the sample tube and instrument response using cross-correlation analysis in conjunction with a circular buffer. The time series were detrended, and fluxes, variances and covariances were rotationally transformed for alignment to the local vertical. The geometrical rotational transformations were developed in-house and confirmed by comparisons: with those originally presented by Tanner and Thurtell (1969); with those of many co-workers in this field over the past three decades, e.g. Bradley (1980); and also with software provided by manufacturers of sonic anemometers, e.g. Gill Solent Instrument Manual, 1998. Sonic anemometer coordinate transforms, to produce zero vertical and transverse mean components, are usually performed, although more complete three-dimensional (3D) rotational schemes are available for flows in complex terrain, e.g. McMillen (1988). A comprehensive discussion of eddy correlation trace gas flux systems and relevant analysis software is provided by Moncrieff et al. (1997); they also provide a summary of a commercial system (Edisol), and a freely available de-facto standard Microsoft Windows software package for use with Gill Solent sonic anemometers which provides all the necessary corrections and transformations (John Moncrieff, private communication, http://helios.bto.ed.ac.uk/ierm/research/edisol/).

Transformations can be applied to the raw time series prior to computation of second-order moments and fluxes or, more efficiently in terms of computer time for on-line display purposes, to the calculated second-order moments, i.e. the variances and covariances based on the detrended time series. As the application of coordinate transformation is standard practice in all presentations of eddy correlation measured micrometeorological fluxes, only the basic equations will be stated below. The basic coordinate transformed or rotated mean longitudinal, transverse and vertical components, \( \bar{u}_{\text{rotated}} \), \( \bar{v}_{\text{rotated}} \), and \( \bar{w}_{\text{rotated}} \), can be given by:

\[
\begin{align*}
\bar{u}_{\text{rotated}} &= \bar{u} \cos \theta \cos \phi + \bar{v} \sin \theta \cos \phi + \bar{w} \sin \phi, \\
\bar{v}_{\text{rotated}} &= \bar{v} \cos \theta - \bar{u} \sin \theta, \\
\bar{w}_{\text{rotated}} &= \bar{w} \cos \phi - \bar{u} \cos \theta \sin \phi - \bar{v} \sin \theta \sin \phi,
\end{align*}
\] (2)
where $u$ and $v$ are transverse velocity components, and the angles $\phi$ and $\theta$ are the vertical and horizontal wind angles defined by

$$
\theta = \tan^{-1} \left( \frac{v}{u} \right),
$$

$$
\phi = \tan^{-1} \left( \frac{\bar{w}}{\sqrt{(\bar{u}^2 + \bar{v}^2)}} \right).
$$

(3)

Similar transformations can be applied to second-order moments or variances and covariances. The momentum flux was determined from the covariance $\sigma_{uw}$, from which the eddy or friction velocity, $u_*$, can be calculated, viz:

$$
u_* = \sqrt{(-u'w')} = \sqrt{-\sigma_{uw}}.
$$

(4)

The sensible-heat flux was calculated using:

$$
H = \rho c_p \sigma_{wT},
$$

(5)

and the latent-heat flux from:

$$
L_v E = \rho L_v \sigma_{wq},
$$

(6)

and the ozone flux from $\sigma_{wO_3}$. Here $c_p$ is the specific heat of air at constant pressure, $L_v$ the latent heat of vaporization of water, and $q$ the specific humidity. $c_p$, $\rho$, and $L_v$ depend on the water-vapour density of the air, $\rho_v$, the air temperature, $T_a$, and the atmospheric pressure, $p$. Using mean values of the latter, the values of $c_p$, $\rho$ and $L_v$ can be corrected using standard meteorological formulations, e.g., Pruppacher and Klett (1980).

The sensible-heat flux measured by the sonic anemometer is based on $\sigma_{wT_s}$ where $T_s$ is the sonic virtual potential temperature (more generally referred to as the sonic temperature) based on the speed of sound which the sonic anemometer measures directly. As this depends on the water-vapour density and ambient pressure, the sonic temperature and associated eddy correlation-derived heat flux must be corrected to take this into account. This correction is generally small but significant, and is usually accounted for by applying the formulae provided by Kaimal and Gaynor (1991).

Sensible- and latent-heat fluxes also affect measured fluxes of trace gases by causing vertical gradients in air density, resulting in a mass flux from the surface. For the ozone fluxes presented here this effect is extremely small, but the correction is applied routinely as it can be significant for certain trace gas fluxes or when the measured fluxes are very small. Wesely et al. (1981), for example, present ozone fluxes an order of magnitude smaller than those presented here, and the mass flux correction term was found to be significant. Webb et al. (1980), following the work of Bakan (1978) and Smith and Jones (1979), developed corrections for these effects which are now applied routinely to micrometeorological fluxes, generally referred to as 'Webb' corrections.

Wesely et al. (1981) discuss the Webb corrections in some detail, showing that the net effect can be likened to the appearance of a non-zero mean vertical velocity, $\bar{\bar{w}}$. This component is, however, removed by the standard application of geometrical transformations. These transformations, therefore, may have the effect of introducing an apparent tilt and a mean vertical transport term. The tilt component is negligible, but the mean transport term may not be, depending on the relative magnitude of the measured fluxes. Typically, it can be shown that for every 100 W m$^{-2}$ of sensible-heat flux the mean vertical velocity introduced by the mass-transfer effect would be
0.3 mm s\(^{-1}\) compared to 0.05 mm s\(^{-1}\) for the latent-heat flux term. These corrections should be compared to the deposition velocities presented later, in the results section.

Once the above transformations and corrections were applied, the ozone and momentum fluxes were used to compute aerodynamic and boundary-layer resistances as well as other micrometeorological variables. These variables were subsequently block averaged over, typically, 30 minutes and one hour for interpretation.

\(c\) Fetch-height requirements

Upon encountering a transition from a sea surface to a rougher land surface, an air parcel experiences a transition turbulence zone above and below which the turbulence levels will be characteristic of the surfaces upwind and downwind of the transition. It is important, therefore, to site flux instrumentation accordingly. Simple flux-footprint models (Horst and Weil 1992, 1994, 1995; Horst 1997) can be used to estimate the influence of this transition on local flux measurements as a function of measurement height. For typical sea-to-land roughness transitions (Garrat 1977; McRae et al. 1982; Kondo and Yamazawa 1986) the height of the transition layer at the mast location would lie between 6.5 and 8 m. Under more unstable conditions the peak of the flux footprint would move closer to the measurement location. Conditions where the land fetch contributed to more than 5% of the total flux were not encountered during this part of the experiment. The bulk of flux measurements made at the mast location should, therefore, be representative of the sea surface for northerly winds at this site except under more unstable conditions.

5. SURFACE FLUXES AND RESISTANCE ANALOGY THEORY

We invoke the classical picture of turbulent transport of a material to a surface in terms of the usual resistance analogy. In this picture, the height-independent bulk transfer process for heat or trace gases is considered to be the sum of the turbulent transfer of the component, from some height, \(z\), above the surface, to the zero plane displacement height, \(d\) (e.g. the sink height for momentum flux), followed by transfer across a laminar sublayer which extends a few millimetres above the surface. These two pathways can be represented by resistances, by analogy with Ohm’s law. This view, of course, assumes no storage error or chemical conversion processes are associated with the trace gas within the measurement height, on time-scales comparable to the transport time-scale (Duyzer et al. 1995).

The aerodynamic atmospheric resistance, \(r_a\), is used to characterize the first pathway, and is calculated assuming gradient transport theory. This resistance will depend on the turbulence intensity, which in turn will be governed by the atmospheric stability. The model then postulates an additional resistance, \(r_b\), representing the near-surface quasi-laminar sublayer, across which transport is governed by molecular diffusion to the surface. This resistance will depend to varying degrees on the nature of the surface. The depth of the layer may be non-constant as a result of shear stresses in non-equilibrium with the flow immediately above it. In this sense the transport is governed by intermittent processes and represents, generally, the main obstacle to deposition. Further, there are indications from a variety of micrometeorological measurements that enhancement of the transport rate across this layer may occur under unstable conditions due to removal of energy from the mean flow above the layer, although this remains to be proved. If we assume for simplicity that for a water surface (not undergoing deformation by wave
motion) the total transport is due simply to these two mechanisms then it follows that:

\[
r_t = r_a + r_b + \ldots = -\frac{\chi(z - d)}{F_t} = -\frac{1}{v_d},
\]

(7)

where \(r_t\) is the total resistance to transport for heat or gases in question. The bracketed term may be applied, if required, to include any additional resistance terms that usually occur for complex surfaces, for example, by chemical or physiological uptake processes. These processes are assumed to take place at a constant level within the surface if it is, for example, a vegetated surface, or at the surface if non-deformation of the surface is occurring. \(F_t\) in (7), therefore, represents the total measured flux at a given reference height. The minus sign is applied by convention to define upward fluxes (emission) as negative and downward fluxes (deposition) as positive, due to the fact that meteorological and sonic vertical velocity is defined as negative downwards towards a surface. \(\chi\) is the air concentration of the gas at some reference height, corrected for the zero-plane displacement height, or sink height if for momentum, which is non-zero for vegetated surfaces. \(v_d\) is the deposition velocity, \(v_d = (r_t)^{-1}\), sometimes called the exchange velocity to allow for both emission and deposition processes. The aerodynamic and laminar boundary-layer transport processes will thus define the maximum rate at which a species will be transferred to that surface, and hence define the maximum possible deposition velocity. Any additional resistance terms, as a result of additional surface processes, may then be inferred from differences between measurements of the total flux and the computed resistance terms.

\(r_a\) may be evaluated using Monin–Obukhov similarity profile functions of the appropriate quantities in the constant surface flux layer. Various empirical expressions for \(r_a\) have been determined for different atmospheric stability conditions applicable for the lowest part of the boundary layer (\(z < 100\) m). The total aerodynamic resistance to transfer for heat and trace gases to the surface can be calculated using the relation derived by Garland (1977):

\[
r_a(z - d) = \frac{u(z - d)}{u_*^2} - \frac{1}{k u_*} \{\psi_H(z/L) - \psi_M(z/L)\},
\]

(8)

where \(L\) is the Monin–Obukhov length, the height above which buoyant energy terms dominate production of turbulence kinetic energy compared to that from the mean wind shear:

\[
L = -\frac{\rho_a c_p T_0 u_*^3}{kg H},
\]

(9)

where \(T_0\) is the surface temperature, \(k\) is Von Karman’s constant (\(\approx 0.4\)), \(\psi_M, \psi_H\) are the height-dependent integrated stability functions for momentum and heat, respectively, and are approximated by the analytical solutions derived by Paulson (1970). For unstable conditions, \((L > 0)\), these are:

\[
\psi_M(z/L) = 2 \ln \left( \frac{1 + x}{2} \right) + \ln \left( \frac{1 + x^2}{2} \right) - 2 \tan(x) + \frac{\pi}{2},
\]

\[
\psi_H(z/L) = 2 \ln \left( \frac{1 + x^2}{2} \right),
\]

\[
x = \{1 - 16(z/L)\}^{1/4},
\]

(10)
whilst for stable conditions, \((L < 0)\) they are given by:

\[
\psi_M(z/L) = \psi_H(z/L) = -5.2(z/L).
\] (11)

Here we will calculate \(r_a\) directly from the sonic anemometer-derived measurement of stress i.e. \((\tau = -\rho_u w' w')\), which have been suitably corrected, and the wind speed and apply the stability corrections using (10) and (11) as appropriate. Henceforth \(r_a\) will be assumed to include this correction when stated. For the dataset presented here the corrections were very small for the stability regimes encountered. Hence, with these corrections applied we have:

\[
\tau_t = r_a + r_b + (\ldots) = U/u_*^2 + r_b + (\ldots),
\] (12)

where \(U\) is the mean wind speed and \((\ldots)\) may again represent additional resistance terms.

\(r_b\) for particular surfaces can be written in terms of a variety of parameters describing the characteristic flow close to that surface, e.g. Wesely (1989). Other relationships have been suggested, e.g. Owen and Thompson (1963), Thom (1972) and Garratt and Hicks (1973). The most common expression is that suggested by Thom (1972) as a first approximation:

\[
r_b = (Bu_*)^{-1},
\] (13)

where \(B\) is the sublayer Stanton number suggested by Owen and Thomson (1963). It can also be thought of as the dimensionless resistance for ozone, a function of the molecular diffusivity of ozone and friction speed. \(r_b\) may also be written in terms of the Schmidt number, \(Sc\), as:

\[
r_b = A Sc^{2/3} u_*^{-1},
\] (14)

where \(A\) is a constant, typically quoted as having a value of five (Wesely 1989). Many alternative formulations are employed for vegetated surfaces, e.g. Garland (1977). The Schmidt number is related to the effective surface transfer-scale length, \(z_s \approx D_s/(ku_*)\), where \(D_s\) is the molecular diffusivity of the scalar quantity \(s\), in air (Hicks and Liss 1976) and is usually calculated for vegetated surfaces as \(Sc = v_a/D_s\) where \(v_a\) is the kinematic viscosity of air. For water, however, work by Deacon (1977) and Wesely (1979) showed that the resistance by the quasi-laminar surface tension layer to ozone transfer by dissolving and diffusion processes is very large. Expressions for this resistance, usually referred to as \(r_w\) to differentiate it from vegetated surfaces, have been derived by the above workers as follows: \(r_w \approx h A Sc^{2/3}(\tau/\rho_w)^{-1/2}\), and \(r_w \approx 15 h Sc^{1/2}(\tau/\rho_w)^{-1/2}\), respectively, where \(h\) is the Henry’s law constant for sea water (4.17 moles m\(^{-3}\) atm\(^{-1}\); Liss and Slater 1974). \(A\) is a constant with a suggested value of 11.7 (Wesely 1979). However, both these relationships yield resistance values far in excess of those observed. For the Weybourne data set \(r_w\) was computed using values for these expressions of \(\approx 5.8 \times 10^5\) and \(3.3 \times 10^5\) s m\(^{-1}\), respectively, for an average \(u_*\) value of 0.21 m s\(^{-1}\). For the freshwater lake measurements made by Wesely et al. (1981), \(r_w\) was found to range from \(8 \times 10^5\) to \(3 \times 10^5\) s m\(^{-1}\). This large discrepancy in predicted and observed resistance values has been attributed to surface chemical reactions acting as significant additional sinks for ozone. The measurements presented here, therefore, also support the existence of surface chemical sinks for sea water that are an order of magnitude greater than for freshwater surfaces.
The additional resistance terms appearing in the brackets in (12) may represent various sea surface chemical-uptake processes. We will denote these using $r_s[O_3]$, or the 'surface' resistance for ozone uptake. However, these terms may simply represent uncertainties or complexities in the physical transport mechanisms arising from surface deformation processes not fully accounted for by $r_a$ and $r_b$. The 'surface' deposition velocity, $v_{ds}$, can also then be calculated to denote the surface velocity transfer rate, independent of the atmospheric turbulent component, a variable often used in model studies, i.e.

$$v_{ds}[O_3] = (r_s)^{-1}. \quad (15)$$

6. Results

Figure 2 shows a diurnal cycle of ozone flux to the sea surface measured at the Weybourne Observatory during a period of northerly winds. Ozone concentrations ranged from 33 to 68 p.p.b. with an average concentration of 56 p.p.b. The full line in Fig. 2 shows the ozone flux with the full range of Webb corrections applied, while the dashed line shows the uncorrected fluxes. The corrections were generally small throughout the experiment. A statistical summary of the measured deposition velocity data is then presented in Fig. 3 in the form of a normalized frequency histogram. After quality control and rejection of non-stationary periods (where advection terms may contribute to the error in measured fluxes (Fowler and Duyzer 1989)) there remained 208 half-hour periods characteristic of the sea fetch. The mean deposition velocity based on these data was $v_d[O_3] = 1.48 \text{ mm s}^{-1}$ with a standard error of $\pm 0.06 \text{ mm s}^{-1}$. The mean was statistically significant: 0.13, at the 95% confidence level. This was despite a relatively large sample deviation of 0.92 mm s$^{-1}$. The median value for the dataset was 1.30 mm s$^{-1}$. The mean surface resistance to ozone uptake, $r_s$, again from the
208 individual $r_s$, values, was found to be $r_s[O_3] = 950 \text{ s m}^{-1}$ with a standard error of $\pm 70 \text{ s m}^{-1}$ (the standard deviation was large at 1089 s m$^{-1}$ primarily due to large variations observed at low wind speeds).

The mean aerodynamic resistance for ozone, $r_a$, for the dataset was 190 s m$^{-1}$ (the standard error was 14 s m$^{-1}$). Friction speeds ranged from 0.02 to 0.56 m s$^{-1}$ with an average of 0.21 m s$^{-1}$.

Figure 4 shows the observed deposition velocity for ozone, $v_d[O_3]$, for the diurnal period corresponding to Fig. 2. The error bars represent the standard error of the mean flux within each one-hour period. During this period the wind direction backed from 070° at midnight to between 335 and 355° during the morning, and remained in this direction for most of the rest of the day. A further backing from 340 to 290° occurred during the night, where the wind remained for the rest of the experimental period. Data from this period were rejected from the dataset as being uncharacteristic of sea surface conditions. The apparent diurnal variation in $v_d$ may be due to the slight backing in wind direction, however, over all these directions the fetch was representative of the sea. The behaviour may be due to changes in wind speed, and subsequent surface roughness changes at the sea surface.

Some care must be taken when treating flux data from sloping terrain. Figure 5 shows the mean vertical wind angle recorded by the sonic anemometer over the entire experiment at this site. The significant positive up-slope angle of attack, 5–7°, for winds in the 300–360° sector is obvious. The change in this wind angle across this sector is also relatively large (several degrees), although consistent with many micrometeorological sites from which data have been published, and confirms the magnitude of the local slope between the observatory and the sea indicating good vertical alignment of the sonic anemometer. The winds from sector 000–060° have a relatively constant vertical wind angle. It is interesting that the slight increase in $v_d$ corresponds to a change in wind direction during the morning from 330 to 030°. The departure of the flow from the horizontal and its influence on the local fluxes should be accounted for by the geometrical transformations that were applied. These will however only account for
Figure 4. The diurnal sea surface ozone deposition velocity $v_d(O_3)\,(\text{mm s}^{-1})$ observed for 15 June at Weybourne.

Figure 5. The mean vertical wind angle ($^\circ$) for all wind directions measured at 10 m by the sonic anemometer during the Weybourne Atmospheric Gas-Aerosol Characterization Experiment (WAGACE), June 1998, at the Weybourne Observatory.

the geometry of the flow, and not for any perturbations to the local stress profile due to a nearby slope change. The perturbations to the stress profile at the measurement height due to the smooth slope change should be relatively small, based on literature reports, e.g. Peterson et al. (1979), Panofsky et al. (1982), Bradley (1983) and Smedman and Bergstrom (1984). Only more detailed measurements at different heights would be able to resolve this issue at this particular site.
TABLE 1. Compilation of surface uptake rates for ozone to water surfaces

<table>
<thead>
<tr>
<th>Reference</th>
<th>$r_a$ (s m$^{-1}$)</th>
<th>$r_b$ (s m$^{-1}$)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galbally and Roy (1980)</td>
<td>See text</td>
<td>1000</td>
<td>Compilation of laboratory and in situ measurements (no eddy correlation), recommended for open ocean</td>
</tr>
<tr>
<td>Galbally and Roy (1980)</td>
<td>N/A</td>
<td>1100–4000</td>
<td>Laboratory chamber decay method</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3100)</td>
<td></td>
</tr>
<tr>
<td>Aldaz (1969)</td>
<td>N/A</td>
<td>2400–3400</td>
<td>Laboratory chamber measurements using sea water</td>
</tr>
<tr>
<td>Regener (1974) based on</td>
<td>See Fig. 6</td>
<td>650–1250</td>
<td>Flux gradient over ocean</td>
</tr>
<tr>
<td>Tiefenau and Fabian (1972)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Garland and Penkett (1976)</td>
<td>N/A</td>
<td>2400</td>
<td>Laboratory wind-tunnel/chamber decay method</td>
</tr>
<tr>
<td>Garland (1980)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wesely et al. (1981)</td>
<td>Not presented</td>
<td>9000</td>
<td>Eddy correlation over a freshwater lake; 16 half-hour measurements</td>
</tr>
<tr>
<td>Lenschow et al. (1982)</td>
<td>129</td>
<td>1800</td>
<td>Airborne eddy correlation over</td>
</tr>
<tr>
<td></td>
<td>109</td>
<td>1890</td>
<td>North Pacific and Gulf of Mexico; three flights</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1690</td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>190</td>
<td>952</td>
<td>Eddy correlation, North Sea coastal site</td>
</tr>
</tbody>
</table>

7. REVIEW AND DISCUSSION

Micrometeorological and, in particular, eddy correlation flux measurements, of trace gas exchange to sea or freshwater surfaces are surprisingly rare. Table 1 summarizes measurements of ozone exchange to water surfaces reported in the literature to date. The mean value of $r_a$[O$_3$] measured at Weybourne was very close to that of 1000 s m$^{-1}$ recommended by Galbally and Roy (1980). Their figure was based upon a compilation of laboratory and in situ chamber measurements, and some gradient measurements (none was made by eddy correlation). Wesely et al. (1981) reported eddy correlation measurements, using propeller and fast cup anemometers, of ozone exchange made at the coast of Lake Michigan, USA, on a 10 m tall tower, very similar to the experimental arrangement described in this work. However, Lake Michigan is a freshwater lake, and the value for $r_a$[O$_3$] obtained was significantly larger than reported elsewhere, at 9000 ± 300 s m$^{-1}$. This value was actually based on 16 half-hourly averaged values using a logarithmic average, which the authors justified because of an observed near log–normal distribution in the $r_a$ values (the measurements were also performed during evening or nocturnal periods). If a linear average is presented (as is the case for most of the work listed in Table 1 and that presented here) the average is 10 550 s m$^{-1}$. The standard deviation in their dataset is, like the other data presented in Table 1, large at ±6400 s m$^{-1}$. This large variation was attributed to the vertical fluxes of ozone being so small that minute drifts in ozone sensor output and horizontal inhomogeneities caused significant errors. The mean friction speed reported for the Michigan dataset was 0.16 ± 0.03 m s$^{-1}$ with a deposition velocity of $v_{ds} = 0.13$ (with a standard deviation of ±0.09) mm s$^{-1}$ and a standard error of ±0.02 mm s$^{-1}$. Sensible-heat fluxes were small and conditions were neutrally stable for the dataset reported. Their peak ozone concentrations were higher than reported here, ranging from 33 to 93 p.p.b., although the mean was comparable at 59 p.p.b.

Lenschow et al. (1982) reported airborne eddy correlation measurements obtained from three aircraft flights, two over the Gulf of Mexico and one over the North Pacific.
They concluded from their measurements that the surface resistance value obtained by Galbally and Roy (1980) was too small. This conclusion seemed to be based primarily on the fact that the eddy correlation technique was not used. They further concluded that the resistance value reported by Wesely et al. (1981) was much too low, due to the fact that freshwater and salt-water surface resistance to ozone uptake may have significantly different surface chemical uptake processes. Interestingly, Galbally and Roy (1980) do not draw this latter conclusion despite presenting chamber measurements from both freshwater and salt-water surfaces. This was due probably to the large variation that existed in their datasets.

An important finding in the Galbally and Roy (1980) study, not often referred to, is that when the water surface was disturbed in their chamber experiments the resistance to uptake declined significantly, typically by a factor of two. This decreasing surface resistance with increased surface roughness probably explains a significant fraction of the variation in most observations; however, this is not presently included in models. It is not clear whether this observation was an artefact that can occur in chamber measurements where turbulent flow conditions are not used or whether it is real. Galbally and Roy (1980) eventually recommended a value of \( r_s = 1000 \text{ s m}^{-1} \) as discussed below for open ocean conditions, a figure in very good agreement with the data presented here. However, we suspect that our measurements may be yielding resistance values that are too low due to coastal-specific effects. Measurements, however, have either not been reported over a wide enough range of conditions or in sufficient detail by the appropriate micrometeorological techniques to evaluate any wind speed or momentum flux dependence on the exchange process with sufficient confidence.

Although the dataset reported here is less than extensive with regard to addressing the last point, some interesting features were observed in the Weybourne dataset. Figure 6, shows the variation of friction speed with ozone sea surface resistance (the data were sorted as a function of friction speed, not wind speed, a point we will return to in a later paper). The bars represent standard deviations within the selected ranges and are large. The term \( r_s \) in this figure, as indicated on the axis label, has not had the \( r_b \) term removed, i.e. we are less than confident in assuming a particular relationship for \( r_b \) for a sea surface, which of course is difficult to measure. We therefore assume the contribution by \( r_b \) to be small for the purposes of this discussion, although this remains to be shown. Also included in Fig. 6 are the actual chamber data reported by Galbally and Roy obtained at a coastal site. Friction speed values for their data for 'calm' conditions were assumed to be less than 0.05 m s\(^{-1}\), and for the wind speeds quoted for the 'rough' sea state, a typical neutral drag factor, \( C_{DN} \), relationship with wind speed was assumed, after Garrat (1977), to determine \( u_* \). These assumptions may of course be unjustified given the nature of the measurement techniques used.

A simple logarithmic fit to this dataset produced the result \( r_s[O_3] = -574 \ln(u_*) + 282 \text{ s m}^{-1} \). Unfortunately the correlation is not ideal, \( r^2 = 0.89 \), primarily due to the large variance in the sample at low values of friction speed. A logarithmic fit is, however, a somewhat crude representation of the actual behaviour of \( r_s \) which is more likely to show sudden changes, possibly as a result of the onset of wave-breaking processes at particular wind speeds. A detailed discussion of these processes are at present beyond the scope of this work.

Interestingly, the actual \( r_s \) data obtained by Galbally and Roy (1980) from their chamber measurements (1390–1560 s m\(^{-1}\)) agree quite well with the aircraft data reported by Lenschow et al. (1982; 1690–1890 s m\(^{-1}\)). It should be noted however that Lenschow et al. also reported large scatter in their individual flux measurements which could not be explained. The \( r_s \) data reported here are approximately 50% of
those reported by Lenschow et al., but they are very close to the open-ocean value recommended by Gabally and Roy. This recommendation was based primarily on the analysis of open-ocean flux-profile data provided by Regener (1974; see Table 1), whose values for $r_s$ ranged from 650 to 1250 s m$^{-1}$.

Roughness length changes at the air–sea interface may also play an important role in the laminar sublayer resistance to ozone transfer. For open water, Charnock’s relationship, as suggested by Wesely et al. (1981), and that of Hicks and Liss (1976) for smooth surface flow is suggested in order to determine roughness length over a water surface. This is given by $z_0 = 0.014 \frac{u_*^2}{g} + \frac{V}{(9.1 \; u_*)}$ (Wesely 1979), where $g$ is the acceleration due to gravity and $V$ is the kinematic viscosity of air. For the work presented here, with typical $u_*$ values of 0.21 m s$^{-1}$, this yields $z_0 \approx 0.07$ mm. However, the coastal site at Weybourne is somewhat different from true open-ocean conditions, in that there is an extensive shallow coastal shelf where breaking waves are common, even under light winds. The usual wind or friction-speed relationship with roughness length, and hence air–sea exchange rates for gases, may, therefore, not be entirely consistent with open-ocean conditions with enhanced gas uptake possibly occurring at lower wind speeds. More data across a range of wind speeds are required to investigate this further.

Additional reported measurements that we might draw on as indicators of the expected magnitudes for $u_{\text{dil}}[O_3]$ are those of Jacob et al. (1992), who used eddy correlation to measure ozone fluxes to a mixed dry upland and wet tundra with small lakes during the ABLE (Arctic Boundary Layer Experiment) 3A. Deposition velocities ranged from 1.2 mm s$^{-1}$ during the night to 2.4 mm s$^{-1}$ during daytime. Surface reactivity and turbulence accounted for the day–night variation, so these results can be seen as an upper limit for water surfaces. The question of the chemical activity of these water surfaces remains open if one compares them to the freshwater fluxes measured by Wesley et al. (1981). Interestingly, the deposition velocities to sea surface
are comparable to, or smaller than, those measured to desert sand, which have typical mean values of 0.65 mm s\(^{-1}\) and maximum daytime values of 1.50 mm s\(^{-1}\) (again measured by eddy correlation; Güsten et al. 1996). Güsten et al. (1996) recommended values of 1 mm s\(^{-1}\) for daytime and 0.4 mm s\(^{-1}\) for night-time values, much larger than for freshwater, but again emphasizing the importance of surface chemical reactions for sea water surfaces.

8. Conclusions

Measurements have been made at the Weybourne Atmospheric Observatory of air–sea exchange of ozone to coastal waters for winds carrying air parcels over anthropogenically unaffected sea surface regions using the eddy correlation technique. Surface resistance values for ozone were found to be 950 ± 70 s m\(^{-1}\) for average friction speeds of 0.21 m s\(^{-1}\). This resistance value is very close to that recommended by Galbally and Roy (1980) of 1000 s m\(^{-1}\) for open-sea conditions, considering the very different techniques employed. The coastal water value is, however, approximately 50% lower than those values reported by Lenschow et al. (1982) from airborne eddy correlation for true open-ocean conditions. Perhaps the possible sources of error alluded to in previous discussions may also explain this discrepancy, or different surface deformation processes are acting.

There is some indication of a dependence on wind speed of the ozone exchange rate, approximately a factor of three or more increase occurring as friction speeds decreased from 0.2 to 0.05 m s\(^{-1}\). This dependence was approximated by \(r_5[O_3] = -574 \ln(u_*) + 282 \text{ s m}^{-1}\). This result is again, in qualitative agreement with the chamber measurements presented by Galbally and Roy (1980). At present, however, this finding remains tentative due to the large scatter in the measurements and the correspondingly larger contribution by various error terms to the flux measurements in this wind speed range. The details of this process, therefore, require further investigation over a greater range of wind and sea conditions at this particular site than obtained to date. The deposition velocity, \(v_{dep}[O_3] = r_5[O_3]^{-1}\), obtained here of 1.0 mm s\(^{-1}\) is about twice that usually quoted in most models, e.g. Hauglustaine et al. (1994) quote a value of 0.7 mm s\(^{-1}\), and Lenschow et al. (1981) a value of 0.53 mm s\(^{-1}\). Much of this variation is, no doubt, primarily due to wind speed, momentum flux dependencies and subsequent surface-roughness related effects.

There are, as shown by Wesely et al. (1981), significant chemical removal mechanisms over water for ozone which appear to be enhanced by up to almost an order of magnitude for sea water compared to freshwater surfaces. It has been suggested that this enhancement may be due to the presence of thin layer organic surfactant films (Schwartz 1992), such as humic acids that may originate from phyto and zooplankton (Hunter and Liss 1977). There is strong evidence that organic emissions can significantly enhance surface ozone uptake to certain types of vegetated surfaces but not others, so this should not be surprising. These surfactants may also influence aerosol production processes via bubble bursting (Cloke et al. 1991). In addition there are further physical removal processes that are wind speed dependent. Breaking waves (particularly at sites with extensive shelf zones) will for example enhance the sea surface roughness and so reduce the surface resistance, although very different exchange rates will probably occur under higher wind speed regimes where spray generation occurs. The wind speed range for the data herein is not yet sufficient to examine gas transfer enhancements, due to the onset of various breaking-wave and bubble entrainment processes, which are thought to occur
within particular wind-speed regimes. These wind speed regimes are currently being debated, e.g. Liss and Merlivat (1986) suggest transitions occur at 3.6 and 13 m s\(^{-1}\) (measured at 10 m), respectively, based on data from the tracer experiments of Wanninkhof (1985) and the laboratory work of Broeker and Siems (1984).

Although wind speed does have a major influence on gas exchange rates to ocean surfaces, it is likely that many other contributing processes are not linked to wind speed in a simple manner, and application of such links may be dubious (Wanninkhof \textit{et al.} 1992). Due to the difficulty in determining second-order turbulence moments over the ocean, wind speed as a governing variable will, however, continue to be used. Rather than attempt to resolve this difficult question using this limited dataset we simply present the wind speed dependence for \(v_d[O_3]\), observed at this site, Fig. 7. The full error bars for \(v_d[O_3]\) represent the standard deviations within each wind speed range, whilst the smaller error bars represent the standard error. There is some evidence of an enhancement in surface uptake between 2.5 and 3 m s\(^{-1}\). If an enhancement in breaking-wave processes occurs at this wind speed then momentum flux transfer and hence trace gas exchange could also increase slightly, however the deposition then decreases between 5 and 6 m s\(^{-1}\) which may be related to roughness length influences as waves become more developed. Unfortunately the variation in the data is large, and no firm conclusions can yet be drawn, although suitable experimental design should be able to resolve these issues.

The surface resistance for ozone to sea water surfaces under typical wind conditions can be constrained according to the micrometeorological data to a value between 950 and 1890 s m\(^{-1}\).

We finally conclude that the Weybourne observatory site appears to be a reasonable location for measuring air–sea exchange rates by the eddy correlation technique, the flux measurements presented being representative for coastal waters in the appropriate wind sectors. Further investigation of turbulence and stress profile behaviour at the site is, however, needed for absolute confidence in this respect, and to improve the absolute accuracy of micrometeorological parameters.
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