Transfer of SO_2 and other reactive gases across the air–sea interface[1]

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ABSTRACT

Using results obtained from experimental studies of the atmospheric transport of sensible heat, water vapour and momentum over the sea, deposition velocities of soluble and reactive trace gases are evaluated. The deposition velocities that result vary with the height of observation; they are nearly linearly dependent upon wind speed and are a function of the prevailing stability regime. In near-neutral stratification, it appears best to take the deposition velocity to be about 0.13 % of the wind speed when observations are made at 10 m height. When data are collected at 1 m height, this factor becomes about 0.2 %. Although the evaluations are intended to apply particularly to the case of SO_2 transfer, consideration of the molecular diffusivities of other gases that are similarly reactive (e.g., NH_3, HCl, NO_2 and SO_3) suggests that less than 10 % error will result from adopting the present results for SO_2 for these gases as well. When the liquid phase resistance is important, as is the case for CO_2 for example, then the deposition velocities are decreased to a limiting lower value specific for each gas. The present model considers only the simpler case in which the liquid phase resistance is negligible.

1. Introduction

Studies of the global budgets of atmospheric contaminants, and the associated schemes intended to predict concentrations near the surface, necessarily incorporate some formulation of the surface deposition. Empirical determinations of the appropriate deposition velocity are often used, applied through the familiar relationship

$$F_p = \varrho v_p p_z \qquad (1)$$

This permits evaluation of the surface flux F_p from the contaminant concentration p_z at observational height z. Clearly, eq. (1) hides a host of effects in its simplicity. Among these are such obvious influences as those of surface roughness, wind speed, atmospheric stability, and the often overlooked though fundamental dependence of v_p on the height at which concentrations are measured. Over water surfaces, the uncertainties involved in applying eq. (1) are compounded by the relative insolubility of some gaseous pollutants, the sensitivity of the liquid-phase reactions of some gases to the pH of the solution, and the presence of surface films (natural and anthropogenic). Furthermore, it does not seem likely that accurate experimental evaluations of v_p are possible in those intractable situations that characterize much of the open ocean. Thus it appears that evaluations of the surface deposition of, say, SO_2 at sea must depend upon estimates of v_p that are obtained in other circumstances or by deduction from some other relationships.

Recent investigations of the chemical behaviour of various pollutants at an air–water interface (e.g. Broecker & Peng, 1974; Liss & Slater, 1974) suggest that the reaction rates in the liquid phase are reasonably well understood. Liss (1971) has considered such matters as the influence of solution pH on the affinity of natural waters for SO_2 and, using rather rudi-

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mentary estimates of the atmospheric transfer coefficients, has derived deposition velocities for SO_2 transfer across the air–sea interface that are in broad agreement with experimental results obtained over relatively calm water and other surfaces (e.g. Garland et al., 1973; Whelpdale & Shaw, 1974). In an alternative approach, Hicks (1974) has derived gross SO_2 deposition velocities by considering the roles of atmospheric stability and wind speed in the deposition process. In this work, SO_2 was assumed to be removed instantaneously upon impact with the water surface, and the deposition velocities that resulted were again found to be in fair agreement with experimental results. The genneral case that incorporates realistic descriptions of both chemical and atmospheric factors has not been thoroughly addressed. It is the present purpose to combine the methods of Liss (1971) and Hicks (1974) in order to derive theoretically-based deposition velocities that are appropriate to a wider range of conditions than have been studied experimentally. In the present analysis, only those gases that are very reactive at the surface will be considered; thus the water-phase resistance will be ignored.

2. The atmospheric turbulent deposition velocity

It is readily shown that integration of the common micrometeorological flux-gradient relationship describing the potential temperature gradient yields

$$T_z - T_0 = (H/\varrho c_p k u_*) \cdot [\ln (z/z_H) - \Psi_H(z/L)] \qquad (2)$$

where symbols are as appended. Here, the function $\Psi_H(z/L)$ is Panofsky's (1963) stability dependent integrated departure from neutral of the dimensionless potential temperature gradient. In keeping with current practice, atmospheric stability is characterized by the ratio z/L, where L is the Obukhov scale length of turbulence. Many experimental studies have been made of the form of the Ψ-function. In the analysis that will follow, the recommendations of Dyer (1974) will be accepted, namely

$$\Psi_{M,H,W} = -5.2\, z/L \qquad (3a)$$

in stable conditions (as suggested by Webb, 1970). For unstable conditions the tabulated values of Dyer & Hicks (1970) will be used. The behaviour in unstable conditions can be approximated by

$$\ln (\Psi_M) = 0.032 + 0.448 (\ln (-z/L)) - 0.09 (\ln (-z/L))^2$$

and

$$\ln (\Psi_{H,W}) = 0.598 + 0.390 (\ln (-z/L)) - 0.090 (\ln (-z/L))^2 \qquad (3b)$$

In the case of the transfer of some generalized contaminant p to the surface, the relationship analogous to eq. (2) is

$$p_z - p_0 = (F_p/\varrho k u_*) \cdot (\ln (z/z_p) - \Psi_p(z/L)) \qquad (4)$$

For the case of momentum, this becomes

$$u_z - u_0 = (u_*/k) \cdot (\ln (z/z_0) - \Psi_M(z/L)) \qquad (5)$$

In eq. (5), the constant of integration, z_0, can be interpreted as a length scale associated with the transfer of momentum at the surface, namely the familiar roughness length. The similar parameter appearing in eq. (2) is sometimes termed the "thermal roughness length" for sensible heat transfer. In the same way, in relations of the form of eq. (4), concerning pollutant transfer, it seems appropriate to consider z_p as a diffusive length scale that specifies the rate of uptake of the contaminant p at the surface. The descriptive term "capture length" has been suggested and will be used here for z_p.

It should be noted that T_0 and p_0 are formally the temperature and pollutant concentration at the heights z_H and z_p respectively. It can be shown that there is no loss of generality over oceans by taking these to be the actual surface values. Both experimental and theoretical studies of the surface drift velocity u_0 have shown that $u_0 \simeq u_*$ (Roll, 1965; Hess, 1975), and exact equality will be assumed here.

Specification of the (momentum) roughness length that is appropriate to the open ocean is a problem that has confronted researchers for a considerable time. While much early work tended to suggest that the oceanic drag coefficient was approximately constant, recent experiments utilizing direct measurement of the momentum flux (as summarized by Wieringa, 1973, and by Smith, 1973) support a linear relationship between the drag coefficient and the

near-surface wind speed. A simple means of formulating this increase has been given by Charnock (1955), who uses dimensional arguments to relate the roughness length for a fully developed sea to the surface momentum flux and the acceleration due to gravity. In light winds we will assume that the surface is aerodynamically smooth, although there is some contrary evidence (Sheppard et al., 1972). The form describing the long-fetch oceanic case that is adopted for use here is

$$z_0 = \nu/9.1u_* + 0.016u_*^2/g \tag{6}$$

which is essentially an interpolation formula between the aerodynamically smooth case (with ν being the kinematic viscosity of air) and Charnock's relationship. The factor 0.016 has been determined experimentally (e.g. see Hicks, 1972).

Comparison between eqs. (1) and (4) shows that an *eddy* deposition velocity v_e can be expressed as

$$v_e \simeq ku_*/[\ln (z/z_p) - \Psi_p(z/L)] \tag{7}$$

provided $p_0 \ll p_z$ (essentially requiring that surface uptake of the contaminant be extremely efficient). In the case of particulate transfer, it is clearly necessary to consider gravitational settling as well, but for gaseous transfer this may be ignored.

3. Stability corrections and the capture length

The form of the dependence of Ψ_p upon stability might sometimes be a critical consideration, particularly in the highly stable and unstable situations that often occur in light winds and near shorelines. In this connection, the mass transfer of water vapour has received quite intensive study. Whereas early workers commonly assumed that the atmospheric vertical transport of water vapour was controlled by relationships similar to those appropriate for momentum, later empirical studies showed that this was not the case in unstable conditions (Crawford, 1965; Dyer, 1967). Rather, it appeared (and is now widely accepted) that water vapour is transferred in a manner similar to the flux of sensible heat. There is now some experimental evidence which suggests that the vertical flux of any passive contaminant can also be described in the same way as the transfer of heat. In particular, this is supported by field studies of the atmospheric transport of ozone (Galbally, 1971) and CO_2 (Sinclair *et al.*, 1975). Here, we will assume that the transfer of the gaseous property p is described by the same forms of the Ψ-functions as have been determined empirically for the case of sensible heat. No contrary experimental results are known to us.

Likewise, we will take the capture length for soluble and reactive gases to be given by the same relationship that has proved to be sufficiently accurate for the thermal roughness length in the case of sensible heat transfer,

$$z_p \simeq D_p/ku_* \tag{8}$$

where D_p is the molecular diffusivity of the quantity p. This simple relationship follows formally from the assumption that eddy and molecular diffusivities are additive. The validity of this assumption has been examined by Garratt & Hicks (1973). The results of many field experiments conducted over water verify the general form of eq. (8) for the specific case of sensible heat transfer (Hicks, 1975). Although it might be expected that eq. (8) would be inappropriate in high wind speed situations such as those which normally characterize much of the ocean, it appears that the approximation is sufficiently accurate for most purposes, up to a wind speed of about 15 m s^{-1}. No direct examination of the applicability of eq. (8) to the case of the surface deposition of a particular pollutant has yet been made, but the overall agreement between predicted and observed water vapour transfer coefficients suggests that extrapolation of the relationship to the case of gas transfer is justified.

4. The surface reaction resistance

From consideration of the solubility and chemical reactivity of SO_2, Liss (1971) has evaluated the gas and liquid phase components of the total resistance to exchange of this gas across an air-water interface. Subsequently, Liss & Slater (1974) have extended the analysis to the transfer of many gases, including the environmentally important trace constituents N_2O, CO, CCl_3F and CCl_4. In most cases, the

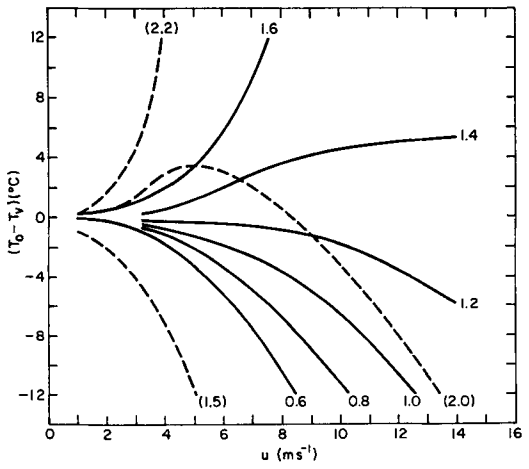

Fig. 1. Isopleths of the ratio $(v_e/u) \times 10^3$ relevant to observations made at 10 m height (solid lines) and 1 m height (broken lines) over open ocean. $T_0 - T_v$ is the virtual potential temperature difference between the surface and the height of observation and u is the wind speed at the same level.

gas solubility is such that the net transfer to or from the overlying air is largely controlled by processes in the liquid phase. An important exception is SO_2, whose exchange for solution pH > 4 is almost totally dominated by the gas phase resistance. Thus for sea water (pH = 8.0 ± 0.2), transfer of SO_2 from the atmosphere will be controlled solely by atmospheric processes. Similarly, the exchange of other gases of high solubility or rapid aqueous phase reaction rate (e.g. NH_3, NO_2, SO_3 and HCl) is almost certainly also controlled by resistance in the gas phase. The treatment derived in this paper would seem to be applicable to all such gases, but not to those for which liquid phase resistance (i.e. transport in the water) plays an appreciable role. This is because turbulence in the liquid and gaseous phases cannot be specified in the same way, e.g. in wind tunnel experiments the exchange rate for gases under liquid phase control varies approximately as the square of the wind speed, whereas in the case of gases for which gas phase resistance is controlling the rate of exchange it is nearly proportional to the wind speed (Liss, 1973).

5. Net deposition velocities for SO_2

The procedures outlined above have been combined to give the net deposition velocities illustrated in Fig. 1. Since both wind speed and atmospheric stability are important considerations, the results are presented as isopleths on a velocity–potential temperature difference plane. In the present considerations of over-water fluxes, it is clear that the buoyancy of water vapour cannot be neglected in specifying the stability regime, and hence virtual potential temperature differences are employed in Fig. 1.

Evaluations have been performed relative to an assumed height of observation of 10 m, as is commonly employed in meteorological work at sea. The property illustrated in Fig. 1 is the ratio v_e/u_{10}, chosen in order to emphasize the influence of atmospheric stability. The procedure by which the values of v_e/u_{10} have been derived is relatively straightforward, and follows immediately from the various relationships that have been presented. Specifically, for a series of assumed values of the friction velocity u_* and of the atmospheric stability z/L, corresponding wind speeds at 10 m height have been evaluated using eqs. (3), (5) and (6). Then eqs. (7), (8) and (3) have been used to determine the appropriate deposition velocities and the desired ratios have been constructed. To locate each value obtained in this way in the plane of Fig. 1, corresponding surface to air temperature differences have been calculated from eq. (2). It is obvious that evaluation of deposition velocities appropriate to measurements made at some other height can be derived with ease. The dashed isopleths of Fig. 1 illustrate the results that apply to measurements made at a height of 1 m above the sea. Deposition velocities applicable to measurements made at 1 m height are seen to be about double those appropriate at 10 m.

It is immediately apparent, in Fig. 1, that strong atmospheric stability effects must be expected to occur in light wind situations, when effective deposition velocities for SO_2 transfer may change by a factor of more than three in constant winds. Moreover, the fundamental role of wind speed underlines the requirement that atmospheric conditions be carefully specified in any thorough study of the fluxes of SO_2 or similarly reactive gases. In neutrally stratified conditions, the SO_2 deposition velocity may be taken to be about 0.13% of the wind speed when measurements are made at 10 m height, or about 0.2% of the wind speed when measurements are at 1 m.

6. Discussion

Comparisons between the predicted deposition velocities indicated by Fig. 1 and experimental data are quite difficult and the results are often misleading. For example, many of the empirical values that appear in the literature are derived from studies conducted in wind tunnels, with obviously constrained surface wave structure. Any method of extrapolating such results to the case of open ocean is of doubtful value. Direct determinations of v_p over large water surfaces are exceedingly rare; however, the often quoted value of about 1 cm s^{-1} for the SO_2 deposition velocity is in good agreement with the present predictions in moderate winds. In higher winds, such as normally occur in high southern latitudes, the present model suggests that substantially greater deposition velocities are appropriate.

The behaviour of other highly soluble trace gases, such as NH_3 and NO_2, should be well described by the present model. Each of these gases exhibits an atmospheric diffusivity that differs from that of SO_2 by less than a factor of about 2. The inherent insensitivity of the predicted deposition velocity to changes in the capture length (since it appears within a logarithmic term in eq. (7)) suggests that the present evaluations may be sufficiently accurate for relatively general application. In fact, the errors involved in applying the results of Fig. 1 to the case of NH_3, for example, should not exceed 10%. Table 1 allows a comparison of the predicted values of $v_e/\bar{u}$ for a range of sufficiently reactive gases, evaluated for two wind speeds and for various heights of applicability. For purposes of this tabulation, the atmosphere is assumed to be neutrally stratified.

Table 1. *Predicted values of the ratio of the deposition velocity to the wind speed for several trace gases*

The atmosphere is assumed to neutrally stratified. The height of observations is specified as z

		$(v_e/\bar{u}) \times 10^3$					
	z (m)	NH_3	H_2O	HCl	NO_2	SO_2	SO_3
$\bar{u} = 10$ m s^{-1}	10	1.4	1.4	1.3	1.3	1.3	1.3
	5	1.6	1.6	1.5	1.5	1.5	1.5
	2	1.9	1.9	1.8	1.8	1.8	1.7
	1	2.2	2.2	2.1	2.1	2.1	2.1
$\bar{u} = 5$ m s^{-1}	10	1.3	1.3	1.3	1.2	1.2	1.2
	5	1.5	1.5	1.4	1.4	1.4	1.4
	2	1.8	1.8	1.7	1.7	1.7	1.6
	1	2.1	2.1	2.0	1.9	1.9	1.9

7. Conclusions

The evaluations that are illustrated in Fig. 1 are derived from three basic assumptions regarding the behaviour of SO_2 in the vicinity of an air–water interface. Firstly, it is noted that the gas is highly soluble and chemically reactive in the water and hence the surface transfer is primarily controlled by the resistance in the gas phase. Secondly, the effective capture length for SO_2 transfer is assumed to be described by a relationship similar to that which has been shown to be sufficiently accurate in the cases of sensible heat and water vapour (eq. 8). Thirdly, transfer within the air near the surface is assumed to be governed by the same flux-gradient relationships that have been well documented in the cases of sensible heat and water vapour transfer; this is also supported by recent data on surface fluxes of both O_3 and CO_2. It appears that the assumption most susceptible to error is the second. Obviously, careful field experiments designed to evaluate the capture lengths relevant to the transfer of trace gases should be conducted.

Although limited by the accuracy of the assumptions involved, the present model allows estimation of the commonly required deposition velocity as a function of wind speed, atmospheric stability, and height of observation. The well-established near-linear dependence upon wind speed is confirmed, as is the experimental finding that deposition velocities are considerably smaller in stable than in unstable conditions. The model appears to be applicable to all trace gases for which liquid phase resistance can be ignored. Moreover, the deposition velocities of such gases seem to be quite similar, with differences rarely exceeding 10%. On the whole, the most appropriate value of the gaseous deposition velocity for oceanic application that is suggested by the analysis is about 0.13% of the wind speed when observations are made at 10 m height, increasing to about 0.2% for measurements at 1 m.

Experimental testing of the predictions de-

rived from the present model is obviously required, particularly in steady-state, long-fetch, near-neutral situations. Furthermore, the assumptions adopted regarding the physical processes involved need to be verified. Since the roles of surface roughness and of atmospheric stability are quite important, it appears that the experimental resolution of the obvious questions that arise from the present treatment will require rather thorough micrometeorological support in the form of accurate measurements of the surface momentum flux and heat transfer as well as of the fluxes and concentrations of the gases of particular interest.

Appendix

c_p Specific heat of air at constant pressure
D_p Molecular diffusivity of the trace property p in air
F_p Flux to the surface of the property p
H Sensible heat flux
k von Karman's constant (about 0.4)
L The Obukhov length scale
p_z Concentration of the property p in air at height z
T_z Potential temperature at height z
T_v Virtual potential temperature
u_z Wind speed at height z
u_* Friction velocity
v_e The deposition velocity directly associated with atmospheric eddies
v_p The total (net) deposition velocity of the property p
z Height above the surface
z_H Roughness length associated with sensible heat transfer
z_0 The conventional, momentum, roughness length
z_p The roughness length associated with the vertical flux F_p
ν Kinematic viscosity of air
ϱ Density of air
Ψ_i Panofsky's stability correction function for the cases identified by the subscript i.

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ПЕРЕНОС SO_2 И ДРУГИХ РЕАГИРУЮЩИХ ГАЗОВ ЧЕРЕЗ ГРАНИЦУ РАЗДЕЛА АТМОСФЕРА-ОКЕАН

При использовании результатов, полученных в экспериментальных исследованиях переноса тепла, водяного пара и количества движения в атмосфере над морем, оцениваются скорости осаждения растворимых и реагирующих трассерных газов. Получаемые скорости осаждения меняются с высотой наблюдения; они приблизительно линейно зависят от скорости ветра и являются функцией превалирующего режима устойчивости. При стратификации, близкой к нейтральной, наилучшим представляется брать скорость осаждения равной приблизительно 0,13 % от скорости ветра, измеренной на высоте 10 *м*. Если данные собираются на высоте 1 *м*, то эта величина становится равной примерно 0,2 %. Хотя эти оценки предназначены в первую очередь для случая переноса SO_2, рассмотрение коэффициентов молекулярной диффузии других газов, реагирующих подобным образом (напр., NH_3, HCl, NO_2, SO_3), дает основание предположить, что применение результатов, полученных для SO_2 и к другим газам, даст ошибку, меньшую 10 %. Когда существенно сопротивление жидкой фазы, как в случае CO_2, например, то скорости осаждения уменьшаются до предельной меньшей величины, характерной для каждого газа. В настоящей модели рассматривается только более простой случай, когда сопротивлением жидкой фазы можно пренебречь.