Sulphur dioxide removal by turbulent transfer over grass, snow, and water surfaces

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ABSTRACT

Vertical gradients of sulphur dioxide concentration have been measured over grass, snow, and water surfaces in order to assess the importance of these surfaces as SO_2 sinks. Concentrations were usually found to be lower near the surface indicating that removal occurs there. Vertical concentration gradients, normalized with respect to the concentration at 8 m, were generally greatest over water and least over snow, independent of meteorological conditions, suggesting that a water surface is the strongest SO_2 sink, with grass next, and snow weakest. The turbulent transfer of SO_2 to the interface is discussed in relation to stability of the lower atmosphere and physical and chemical properties of the surfaces. Using a bulk aerodynamic transfer approach similar to that for water vapour, values of SO_2 flux averaged over periods of from one to several hours were found to be of the order of 1 $\mu g\ m^{-2}\ s^{-1}$ to the water and grass surfaces, and an order of magnitude smaller to the snow surface. Deposition velocities were found to be of the order of 1 cm s^{-1}.

1. Introduction

The study of the removal of trace constituents from the atmosphere involves a consideration of the methods of removal and the nature and rate of loading of the sink. Three main processes for depletion are well known: chemical transformation to new substances in the atmosphere, wet removal or precipitation scavenging by rainout and washout, and dry removal processes such as gravitational deposition and sorption at the atmosphere-earth interface. In order to make a quantitative estimate of trace constituent removal over a certain surface, it is necessary to know the magnitude of the contributions from precipitation scavenging and the various dry removal processes.

The purpose of this study was to investigate the removal of a gaseous trace constituent, sulphur dioxide, by grass, snow, and water surfaces, as a result of the processes of turbulent transfer to the interface and subsequent sorption there. There has been insufficient work done on this problem of dry removal of SO_2, considering the abundance of the gas and its potentially harmful effects. Martin and Barber (1971) investigated SO_2 loss near a hedge and concluded that this vegetation is an effective sink for the gas. The uptake rate was found to depend upon the wetness of the leaves and the degree of stomatal opening. Saito et al. (1971) concluded, however, from their measurements of SO_2 flux to a grass surface, that stomatal uptake was unimportant.

Liss (1971) predicted that gas phase resistance is much greater than liquid phase resistance for the transfer of SO_2 to natural waters and Spedding (1972) provided laboratory confirmation in the case of sea water. He suggested that the oceans may be a major sink of SO_2. Other laboratory experiments have identified vegetation and soil as SO_2 sinks. Hill (1971) showed SO_2 uptake by alfalfa to be proportional to the ambient concentration while Spedding (1969) found the uptake rate by barley to be dependent upon degree of stomatal opening and relative humidity. Abeles et al. (1971) and Terraglio & Manganelli (1966) examined SO_2 uptake by various soils and found

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Table 1. *A summary of the five experimental periods*

Period	Date (1972)	Location	Surface	Per cent of time SO_2 present
1	May 2–24	Niagara Bar, Lake Ontario	Freshwater	6
2	June 9–21	Niagara Bar, Lake Ontario	Freshwater	7
3	Oct 3–16	Niagara Bar, Lake Ontario	Freshwater	13
4	Aug 10–Sep 10	Meteorological Research Station, Toronto	Grass ($\sim$10 cm)	10
5	Nov 17–Dec 15	Meteorological Research Station, Toronto	Snow	21

soil moisture content to be an important parameter. Schmitt (1970) examined a variety of substances commonly occurring at the atmosphere–earth interface and found large differences in their ability to absorb SO_2. It is clear from these experiments that the characteristics of the sink are critical to sulphur dioxide uptake rate.

In addition, work done on the transfer of other gases has provided much useful information. For example, Chamberlain & Chadwick (1966) conducted a detailed investigation of the transfer of iodine from the atmosphere to a grass surface; they examined the various transfer resistances and determined deposition velocities for iodine of approximately 0.5 cm s^{-1}. Finally, Kellogg et al. (1972) have recently summarized estimates of SO_2 removal by diffusion to soil and vegetation on a global basis. Such estimates usually assume that all SO_2 reaching the surface is absorbed and that a representative SO_2 concentration and deposition velocity exist.

The investigation reported here involves the measurement of vertical concentration gradients of SO_2 between the levels of 2 m and 8 m over grass, snow, and water surfaces. The depletion of an atmospheric constituent at the interface may result in a concentration increase with height near the surface. The relative importance of the rate of turbulent transfer and the rate of sorption at the surface in controlling the removal will be reflected in the magnitude of the gradient in the first several meters above the surface. If surface uptake is the rate-limiting process, then there will be an adequate atmospheric supply with a resulting small gradient. However, if turbulent diffusion is rate limiting, this will be reflected in a large atmospheric concentration gradient. Thus there is reason to expect that the nature of a particular sink for a gas will be reflected in the magnitude of the concentration gradient above it, if other factors such as meteorological conditions and ambient concentration are taken into account.

As well as reflecting surface characteristics, gradient measurements provide a means of estimating SO_2 fluxes to the surface without having a detailed knowledge of the surface properties and exchange processes. This enables one to evaluate the rate of loading of a sink by gaseous transfer and provides a means of estimating deposition velocities.

2. Method

Data were collected at two locations in an industrialized region of southern Canada. One location was approximately 2 km offshore on Lake Ontario (area = 19.10^3 km^2) from an anchored barge. (This was part of the Meteorological Aspects of Air Pollution Program of the International Field Year for the Great Lakes, IFYGL.) The other location was the Meteorological Research Station of the Atmospheric Environment Service located approximately 30 km from central Toronto. There were no sources in the immediate vicinity of the measuring

sites to interfere with the gradient measurements. The date and location of the experimental periods, the underlying surfaces, and the percentage of time during which detectable SO_2 was present are given in Table 1.

The primary measurements taken were of sulphur dioxide concentration at two levels, usually 8 m and 2 m above the surface. Air was continuously drawn through sampling tubes mounted on booms extending 2 to 3 m from the supporting tower to two analyzing units (Philips SO_2 monitor PW 9700); measurements were recorded on paper strip charts. Concentration differences were determined by subtraction of values from the two traces and by interchanging input tubes from the two levels to the same analyzing instrument. Frequent calibration and zeroing of the instruments as well as the interchange of input tubes during episodes lead to an expected accuracy in the concentration differences of within ± 6 μg m^{-3} with tube interchange and ± 14 μg m^{-3} without. Concentration and gradient values were determined as consecutive 15 min averages over land and 6 min averages over water during episodes of measurable SO_2 (> 10 μg m^{-3}).

In addition to SO_2 concentrations a variety of meteorological parameters were available at both locations. Hourly values of wind speed and direction, air temperature and water vapour pressure at 4 m, and surface water temperature were available from an automatic IFYGL meteorological buoy on the Lake. Lake water pH and conductivity were also measured. At the Meteorological Research Station continuous recordings of wind speed and direction, and air temperature at 10 m and 50 m were available, as were daily summaries of relative humidity and precipitation.

3. Observations

Monitoring of SO_2 concentration was carried out continuously during the five periods. Sulphur dioxide occurred for periods of time ranging from less than one to several hours in duration. Each such period when the SO_2 concentration was above an arbitrary lower limit (> 10 μg m^{-3} over the Lake and > 20 μg m^{-3} over land) was termed an episode. SO_2 was present for the percentage of each measuring period shown in the last column of Table 1.

Table 2. *Episode average values of SO_2 concentration and gradient for all periods*

Episode	Date	Duration (h)	$\overline{[SO_2]_{8m}}$ ($\mu g\, m^{-3}$)	$\overline{\frac{\Delta[SO_2]}{\Delta z}}$ ($\mu g\, m^{-3}\, m^{-1}$)
1.2	13.05.72	1.5	14	2.3
1.3	15.05.72	0.8	22	0.9
1.4	16.05.72	1.5	104	2.7
1.5	17.05.72	1.2	3	−1.7
1.6 *a*	18.05.72	1.7	38	2.7
b	18.05.72	1.5	14	−0.5
1.8 *c*	23.05.72	0.5	21	−5.3
d	23.05.72	2.0	43	5.4
2.1	10.06.72	2.5	55	4.1
2.2	11.06.72	1.3	28	1.9
2.10	16.06.72	0.8	16	1.3
2.11	16.06.72	0.7	8	0.9
3.7	11.10.72	2.5	56	6.3
3.8	11.10.72	8.5	30	3.2
3.9	12.10.72	1.5	33	3.7
3.11	14.10.72	2.8	19	2.3
3.12	14.10.72	0.3	14	2.3
3.13	14.10.72	5.5	19	2.7
3.14	14.10.72	1.0	30	2.3
3.15	14.10.72	0.5	30	2.7
3.16	15.10.72	1.0	42	4.7
3.17	15.10.72	0.3	62	8.0
3.18	15.10.72	0.5	31	3.3
3.19	16.10.72	5.3	22	1.8
4.1	16.08.72	3.5	273	26
4.2	20.08.72	2.3	37	0
4.3	21.08.72	4.3	44	2.3
4.4	22.08.72	10.0	37	3.6
4.5	24.08.72	7.8	90	6.4
4.6	27.08.72	3.5	27	2.4
4.7	29.08.72	2.8	55	4.1
4.8	30.08.72	6.0	55	2.4
4.9	31.08.72	7.5	165	13
4.10	01.09.72	11.8	84	5.9
4.11	02.09.72	2.5	35	3.7
4.12	06.09.72	6.3	93	7.2
4.13	07.09.72	3.0	30	4.9
4.14	08.09.72	3.5	26	2.4
4.15	10.09.72	4.0	57	1.8
5.1	17.11.72	1.5	40	2.3
5.2	18.11.72	3.8	74	2.3
5.3	20.11.72	4.0	43	0.5
5.4	20.11.72	2.0	49	1.5
5.5	21.11.72	1.0	29	0.5
5.6	22.11.72	6.3	47	1.0
5.7	24.11.72	22	54	1.4
5.8	26.11.72	12.8	37	1.4
5.11	05.12.72	10.4	52	0.5
5.12	08.12.72	30.8	43	1.9
5.14	12.12.72	1.6	41	2.0
5.15	12.12.72	8.2	60	2.4

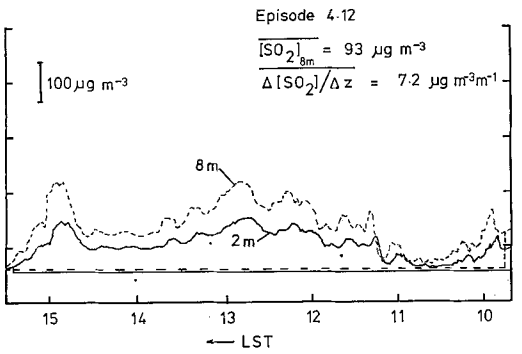

Fig. 1. Sulphur dioxide concentration chart record of episode 4.12.

A summary of the results of the five measuring periods is given in Table 2. For each episode the following information is given: the date, the duration of the episode in hours, the average SO_2 concentration during the episode at 8 m, and the average value of the concentration gradient during the episode. The 8 m concentration is taken to be representative of the ambient level and is used as a reference value. Some episodes from periods 1, 2, and 3 were rejected because of aerodynamic interference caused by the barge. Some of the period 5 episodes were not used because of an insufficient snow cover.

Table 2 reveals interesting characteristics of the different periods. Over the water the average concentration during each episode is usually less than 60 $\mu g\ m^{-3}$, although individual 6 min averages often exceeded 100 $\mu g\ m^{-3}$. These values are typical of locations tens of km downwind of urban areas. The duration of episodes is relatively short indicating that SO_2 is from an urban plume and is not a regional background value. Individual 15 min average SO_2 values during period 4 were often as high as 100 $\mu g\ m^{-3}$ and episode averages are highest during this period reflecting the proximity to the city; in fact the very high values are thought to be from the plume of a large power generating station some 20 km distant. Winter concentrations are generally lower than summer values although episodes are of longer duration. Wind direction is a significant factor in determining ambient SO_2 concentrations. It is seen that concentration gradients usually range from approximately 1–5 $\mu g\ m^{-3}\ m^{-1}$ and, in all but three cases over the Lake which are discussed later, are directed downward indicating that atmospheric SO_2 is depleted near the surface.

An example of a chart record from a typical episode, 4.12, is shown in Fig. 1. The concentration of SO_2 at two levels is shown as a function of time progressing from right to left. The 8 m concentration is the difference between the upper trace and the broken horizontal line (zero value) and the 2 m concentration is the difference between the lower trace and the solid horizontal line; the upper trace is displaced in time to the left by the amount shown. During this episode the ambient SO_2 concentration at 8 m was 93 $\mu g\ m^{-3}$ and the average gradient value was 7.2 $\mu g\ m^{-3}\ m^{-1}$.

4. Discussion

The results shown in Table 2, demonstrating that vertical concentration gradients always existed when measurable SO_2 concentrations were present, are very good evidence that this gas is removed by the three surfaces investigated. Average gradients during episodes over water ranged in magnitude from 1 $\mu g\ m^{-3}\ m^{-1}$, the lower limit of detection, up to 8 $\mu g\ m^{-3}\ m^{-1}$; over grass they were found to range up to 26 $\mu g\ m^{-3}\ m^{-1}$; and over snow up to 2.4 $\mu g\ m^{-3}\ m^{-1}$. Typical values were approximately 3, 6, and 1.5 $\mu g\ m^{-3}\ m^{-1}$, respectively. Although surface sinks for SO_2 by this mechanism have usually been assumed in global sulphur budget studies, this has often not been the case in attempts to parameterize diffusion of this pollutant from large point and urban sources, on local and regional scales, respectively. These results provide strong field confirmation that such depletion does occur and indicate that it must be accounted for in budget studies on all scales.

Although there are a number of regions which may pose varying amounts of resistance to the transfer of a gaseous substance to earth (for example the turbulent boundary layer or the interface region), the approach taken here has been to observe whether the overall resistance to transfer will be reflected in the concentration structure in the turbulent boundary layer as shown by gradient magnitudes. It is felt that this approach may provide a sufficiently good indication of the efficiency of various sinks to be of practical use.

The transfer of a pollutant depends upon

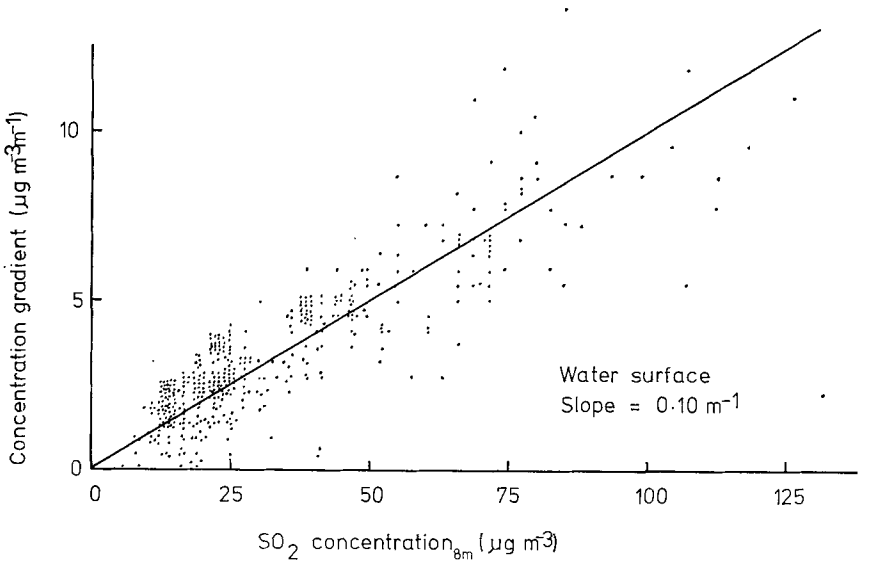

Fig. 2. Vertical SO_2 concentration gradient as a function of ambient (8 m) SO_2 concentration over a water surface. Points are experimental measurements; line with slope 0.10 m^{-1} is best linear fit through origin.

three things: first, the source strength, which in this case is represented by the ambient SO_2 concentration at 8 m; second, the nature of the transfer process in the atmosphere which is a function of meteorological conditions; and third, the nature of the sink which includes the efficiency of the surface exchange processes and the capacity of the sink. In order to assess the characteristics of the sink it is necessary to eliminate the first two, the effect of source strength and the variability of atmospheric transfer. This is done in the following way. Individual vertical concentration gradients from all episodes over the water surface were plotted against their respective ambient concentrations in Fig. 2. Although there is a considerable amount of scatter to the points the results can be represented by a linear fit through the origin with slope 0.10 m^{-1}. The slope of this line gives an average gradient for the surface which is

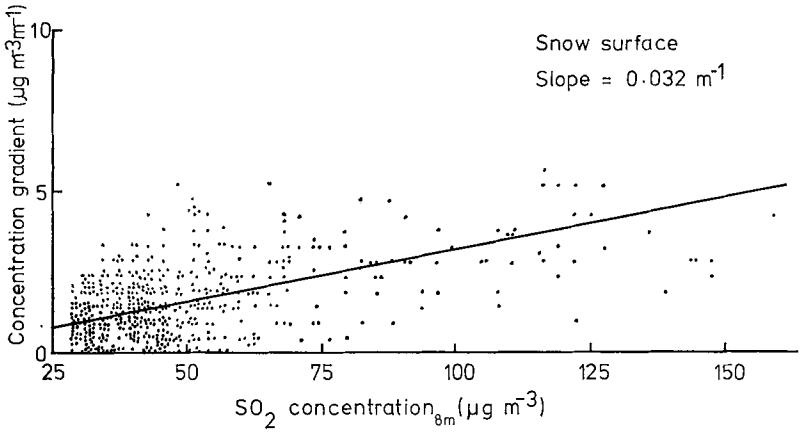

Fig. 3. Vertical SO_2 concentration gradient as a function of ambient (8 m) SO_2 concentration over a snow surface. Points are experimental measurements; line with slope 0.032 m^{-1} is best linear fit through origin.

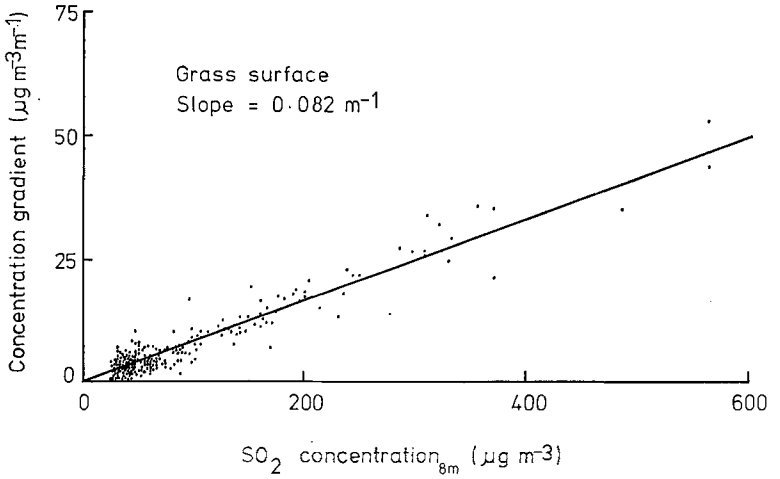

Fig. 4. Vertical SO_2 concentration gradient as a function of ambient (8 m) SO_2 concentration over a grass surface. Points are experimental measurements; line with slope 0.082 m^{-1} is best linear fit through origin.

normalized by ambient concentration. The individual values are for an assortment of meteorological conditions which are representative of those encountered over the Lake. Therefore, the effect of source strength on the gradient is removed and the effect of meteorological variability is averaged over, leaving only the effect of sink strength. This average normalized gradient, 0.10 m^{-1}, is representative of the water surface; its value relative to those of other surfaces is of particular interest. In Fig. 3 results are shown for the snow surface. Although there is even greater scatter, it is clear that for a given ambient concentration the gradient is smaller than for the water surface. The best linear fit through the origin here has a slope of 0.032 m^{-1}. Fig. 4 shows the results over grass. There is an excellent linear relationship evident here although it should be noted that the range of concentrations covered is greater by a factor of four. The slope is 0.082 m^{-1}.

A comparison of the 3 values shows that surface uptake is most efficient relative to atmospheric transport for a water surface, and least efficient for a snow surface. A surface which did not absorb any SO_2 would have a zero concentration gradient above it. In view of the recent laboratory results of Beilke & Lamb (1974) on the very efficient uptake of SO_2 by water with high pH, such as the oceans, it is probable that the water surface investigated here, freshwater with a pH near 8, is as close to a perfect sink for SO_2 as can be found naturally. Table 3 lists the values of normalized gradient obtained for the three surfaces. It should be emphasized that it is the relative and not the absolute magnitude of these values that is important.

It is now of interest to examine briefly the characteristics of the three surfaces which were used. As mentioned above the Lake is a freshwater one with a pH of between 8.0 and 8.3 depending on the time of the year. During the measurement periods the surface temperature varied between 7 and 15° C. The most important characteristic of this surface in the present context is the extremely high solubility of SO_2 in it. Any gas reaching the surface will be im-

Table 3. *A comparison of average normalized gradients which represent the efficiency of surface removal relative to turbulent transport to the surface*

Surface	$\frac{\Delta[SO_2]}{\Delta z} \Big/ [SO_2]_{8m}$ (m^{-1})
Water	0.10
Grass	0.082
Snow	0.032
No removal	0

Table 4. *Episodes for period 4 over grass comparing gradients when the surface is wet and dry*

Episode	Surface condition	Time (LST)	$\frac{\Delta[SO_2]}{\Delta z}/[SO_2]_{3m}$ (m^{-1})
1	Wet, rain	11–14	0.095
2	Dry	14–16	0
3	Dry	11–15	0.052
4	Dry, (dew)	7–15	0.097
5	Dry, (dew)	9–17	0.071
6	Wet, rain earlier	1–2	0.089
7	Dry	12–14	0.075
8	Dry	14–18	0.044
9	Dry, (dew)	8–17	0.079
10	Dry, (dew)	8–17	0.070
11	Wet, dew	7–9	0.11
12	Dry	10–15	0.077
13	Wet, dew	7–8	0.16
14	Wet, rain earlier	15–16	0.092
15	Dry, (dew)	8–13	0.032

mediately taken up. In contrast, the results in Fig. 3 indicate that physical adsorption of SO_2 by the snow is considerably less efficient. The characteristics of the surface will vary depending on the age of the snow surface (new to about 12 days), as shown by Galbally & Allison (1972) for ozone, its temperature, and the amount of SO_2 already scavenged by the snow while falling through the atmosphere. It is probable that these all contribute to the scatter of the results in Fig. 3.

Hill (1971) and Martin & Barber (1971) have found SO_2 uptake by vegetation to be dependent upon both its physical (wetness) and physiological (stomatal state) characteristics. Only one of our episodes, 4.6, occurred at night and we are therefore unable to comment on the importance of stomatal activity. It was possible, however, to examine the observations over grass for the effect of moisture. Table 4 lists for each episode, the state of the grass surface, the time of day, and the value of $(\Delta[SO_2]/\Delta z)/[SO_2]$. The average value of this parameter for episodes 2, 3, 4, 5, 7, 8, 9, 10, 12, and 15 when the grass was judged to be mostly dry was 0.60 m^{-1}; whereas, for the other five episodes when the grass was wet, the value is 0.11 m^{-1}, which is close to the value for the water surface. It appears that the wet grass surface is as good a sink as the Lake. The increased small-scale turbulence over the grass caused by its greater roughness would enhance the exchange.

As a last comment on the gradients, the three episodes over water in which upward-directed gradients were measured should be noted. All three occurred under the following conditions: relatively high concentrations of SO_2 were present for some time and then an abrupt shift in wind direction brought cleaner air over the site. SO_2 concentrations were then found to be higher at the 2 m level. These episodes did not occur under conditions of unusually high stability nor was such an effect always observed with a similar change in meteorological conditions. It is tempting to think of desorption of SO_2 occurring from the Lake; but, in view of the high pH of the water, very little SO_2 is expected to be in a physically-dissolved state and available for desorption. At this time we have no further explanation for these observations.

5. SO_2 flux and deposition velocity

Once a surface has been identified as a sink for SO_2, the rate of deposition can be found by calculating the turbulent flux through a layer above the surface. For the following calculations it is assumed that steady state conditions exist, the surfaces are of a uniform nature, and vertical flux divergence is insignificant. There are a number of methods available for estimating fluxes from gradient data; in the absence of profile data for wind speed or humidity we have used the bulk aerodynamic transfer approach, outlined by Deacon & Webb (1962) for example. This is a general approach often used to estimate water vapour transfer between the sea and the atmosphere with parameters from a reference level of 10 m. Assuming that there is a constant flux through the lower several meters of the atmosphere, the flux F of SO_2 is given by

$$F = C_{SO_2} \bar{u}_{10} \Delta[SO_2]_0^{10}. \quad (1)$$

C_{SO_2} is the bulk transfer coefficient, $\bar{u}_{10}$ the average wind speed at 10 m, and $\Delta[SO_2]_0^{10}$ is the vertical SO_2 concentration difference between 10 m and the surface. C_{SO_2} is assumed to equal that for water vapour, since both involve the transfer of mass, and to have the representative values of 0.0025 over grass, 0.0015 over snow, and 0.00135 over water for neutral

Table 5. *Average values of flux and deposition velocity for the three surfaces under three stability classes*

Surface	Stability	No. of cases	SO_2 flux ($\mu g\ m^{-2}\ s^{-1}$)	Deposition velocity ($cm\ s^{-1}$)
Grass	Lapse	10	0.84	2.4
	Neutral	3	0.29	2.6
	Stable	2	0.015	0.5
Snow	Lapse	1	0.17	1.6
	Neutral	3	0.051	0.52
	Stable	8	0.005	0.05
Water	Lapse	7	0.59	4.0
	Neutral	7	0.27	2.2
	Stable	4	0.05	0.16

stability conditions. (These values correspond to roughness lengths of 3, 0.5, and 0.2 mm, respectively.) The variation of the bulk transfer coefficient with stability given by Deardorff (1968) is used in the following calculations. As a measure of atmospheric stability the bulk Richardson number, Ri_b, defined by

$$Ri_b = \frac{g}{T}\Delta z \frac{\Delta\theta}{(\Delta\bar{u})^2} \tag{2}$$

was determined for the layer of interest. g is the acceleration of gravity, T the ambient absolute temperature, Δz the thickness of the layer, $\Delta\theta$ the potential temperature difference across the layer, and $\Delta\bar{u}$ the wind speed difference across the layer. $\Delta[SO_2]_0^{10}$ was estimated as follows: the 10 m value was determined by assuming a power law relationship to hold between the 1 m and 10 m levels based on measured 2 m and 8 m values. $[SO_2]_{10}$ is reasonably insensitive to whether a power law or logarithmic profile is used. $[SO_2]_0$ is assumed to be zero at the lake surface in view of its efficiency as a sink. Over land the following approach was used. The concentration was extrapolated linearly from 2 m to 1 m to the surface to yield a maximum concentration and zero was used as a minimum. The average of these two was used as the surface concentration over grass and snow. Values of $\Delta[SO_2]_0^{10}$ obtained in this way are thought to be accurate within 50 %. Another useful concept for discussing deposition of gaseous constituents is by deposition velocity. This is defined as the ratio of the flux to the surface, to the concentration difference between a reference level and the surface,

$$v_d = F/\Delta[SO_2]_0^2 \tag{3}$$

Deposition velocities cannot be determined independently here because fluxes and gradients were not measured independently. However, within the limits of the assumptions used to calculate the fluxes, they were calculated according to eq. (3). The reference level was 2 m and the surface concentration was determined as above.

Fluxes and deposition velocities for each surface were subdivided into three stability classes: lapse for $Ri_b < -0.02$, neutral for $-0.02 < Ri_b < 0.02$, and stable for $Ri_b > 0.02$. Average values for each surface and stability class, as well as the number of cases are given in Table 5. The flux values are estimated to be representative of the conditions investigated with an accuracy of about a factor of two. Fluxes are seen to be greatest over the grass surface, a consequence of both the higher concentrations encountered there and the increased turbulence over the rougher surface as reflected in C_{SO_2}. There is slightly less transfer to the Lake, but considerably less to the snow. The dependence of transfer on atmospheric stability is evident over all surfaces; fluxes are reduced by a factor of 10 to 50 in stable conditions as compared to lapse conditions. A stable atmosphere has the effect of suppressing transfer between different layers whereas in an unstable one there is a great deal of turbulent exchange. During individual episodes fluxes ranged from .01 to 2.8 $\mu g\ m^{-2}\ s^{-1}$ to grass, 10^{-4} to 0.17 $\mu g\ m^{-2}\ s^{-1}$ to snow, and 10^{-4} to 0.94 $\mu g\ m^{-2}\ s^{-1}$ to water. Deposition velocities are greatest over water, the best sink, and least over snow. These also show a decrease with increasing stability; average values range from less than 0.1 $cm\ s^{-1}$ during stable conditions up to 4.0 $cm\ s^{-1}$ during lapse conditions. These are in reasonable agreement with gaseous deposition velocities determined by Chamberlain & Chadwick (1966).

In summary, it is seen that representative values of deposition rates for lapse conditions are several tenths to 1 $\mu g\ m^{-2}\ s^{-1}$ of SO_2 and an order of magnitude less for stable conditions. Deposition velocities are typically 0.5

to 2.5 cm s^{-1}. Such deposition rates would account for amounts of SO_2 of approximately 5 mg m^{-2} being deposited on water or grass during a typical 3 h episode. Recent measurements of Shaw & Whelpdale (1973) have shown that approximately 40 mg m^{-2} of SO_4^{--} are deposited over the same region during a 10 h period of precipitation. Thus gaseous transfer of SO_2 must account for a significant fraction of the total sulphur deposited into the region.

5. Conclusions

These investigations have shown that it is possible to detect vertical concentration gradients of sulphur dioxide within the first several meters above grass, snow, and water surfaces. The existence of gradients is taken as confirmation of the ability of these surfaces to take up SO_2, thus removing it from the air. Gradients of 6, 3, and 1.5 $\mu g\ m^{-3}\ m^{-1}$ were typically found over grass, water, and snow surfaces respectively.

The strength of the sink is reflected in the magnitude of the average concentration gradient, normalized against ambient SO_2 concentration. On this basis the Lake is found to be the most efficient sink for SO_2 removal. This is undoubtedly a characteristic shared by all natural waters with a high pH value. Grass surfaces are also efficient for the removal of this gas. Normalized gradients were found to be approximately 80% of those for water and in the case of a wet grass surface they were as large as for water. Snow surfaces were least efficient of the three, average gradients over them being only 30% of those over water.

Using a bulk aerodynamic transfer approach, fluxes of SO_2 were estimated over the three surfaces under lapse, neutral, and stable atmospheric conditions. Fluxes were approximately 0.2, 0.6, and 0.8 $\mu g\ m^{-2}\ s^{-1}$ to snow, water, and grass surfaces respectively under lapse conditions and at least an order of magnitude less under stable conditions over all surfaces. Fluxes of this magnitude can account for a significant fraction of the input of sulphur from the atmosphere to sinks in the region. Deposition velocities determined were in good agreement with those of other workers and it appears that a reasonable value of this parameter for SO_2 is between 0.5 and 2.5 cm s^{-1}.

REFERENCES

Abeles, F. B., Craker, L. E., Forrence, L. E. & Leather, G. R. 1971. Fate of air pollutants: removal of ethylene, sulphur dioxide, and nitrogen dioxide by soil. *Science 173*, 914–916.

Beilke, S. & Lamb, D. 1974. On the absorption of SO_2 in ocean water. *Tellus 26*, 268–271.

Chamberlain, A. C. & Chadwick, R. C. 1966. Transport of iodine from atmosphere to ground. *Tellus 18*, 226–237.

Deacon, E. L. & Webb, E. K. 1962. Small scale interactions. In *The Sea*, vol. 1 (ed. M. N. Hill). Interscience, New York.

Deardorff, J. W. 1968. Dependence of air-sea transfer coefficients on bulk stability. *J. Geophys. Res. 73*, 2549–2557.

Galbally, I. & Allison, I. 1972. Ozone fluxes over snow surfaces. *J. Geophys. Res. 77*, 3946–3949.

Hill, A. C. 1971. Vegetation: a sink for atmospheric pollutants. *J. Air Poll. Control Ass. 21*, 341–346.

Kellogg, W. W., Cadle, R. D., Allen, E. R., Lazrus, A. L. & Martell, E. A. 1972. The sulphur cycle. *Science 175*, 587–596.

Liss, P. S. 1971. Exchange of SO_2 between the atmosphere and natural waters. *Nature 233*, 327–329.

Martin, A. & Barber, F. R. 1971. Some measurements of loss of atmospheric sulphur dioxide near foliage. *Atmospheric Environment 5*, 345–352.

Saito, T., Isobe, S., Nagai, Y. & Horibe, Y. 1971. Transport of SO_2 gas to grass. *The Journal of Agricultural Meteorology* (Tokyo) *26*, 177–180.

Schmitt, R. 1970. *Modellversuche zur Deposition von Schwefeldioxid.* Diplomarbeit, Institute for Meteorology and Geophysics, Frankfurt, 63 pp.

Shaw, R. W. & Whelpdale, D. M. 1973. Sulphate deposition by precipitation into Lake Ontario. *Water, Air, and Soil Pollution 2*, 125–128.

Spedding, D. J. 1969. Uptake of sulphur dioxide by barley leaves at low sulphur dioxide concentrations. *Nature 224*, 1229–1231.

Spedding, D. J. 1972. Sulphur dioxide absorption by sea water. *Atmospheric Environment 6*, 583–586.

Terraglio, F. P. & Manganelli, R. M. 1966. The influence of moisture on the adsorption of atmospheric sulphur dioxide by soil. *Air and Water Pollution 10*, 783–791.

УДАЛЕНИЕ ДВУОКИСИ СЕРЫ ТУРБУЛЕНТНЫМ ПЕРЕНОСОМ НАД ТРАВОЙ, СНЕГОМ И ВОДНОЙ ПОВЕРХНОСТЬЮ

Были измерены вертикальные градиенты концентрации двуокиси серы над травой, снегом и водной поверхностью с целью оценить важность этих поверхностей в качестве стоков SO_2. Как правило, концентрации оказывались меньшими вблизи этих поверхностей, указывая, что удаление действительно имеет место. Вертикальные градиенты концентрации, нормированные на значение концентрации при 8 *м*, обычно оказывались наибольшими над водой и наименьшими над снегом, независимо от метеорологических условий, показывая тем самым, что водная поверхность является самым интенсивным стоком SO_2, трава — помежуточным, а снег — самым слабым. Турбулентный перенос SO_2 к поверхности анализируется в зависимости от устойчивости нижнего слоя атмосферы, а также физических и химических свойств поверхности. Используется аэродинамический подход к изучению потока аналогично тому, как это делается для водяного пара. Значения потоков SO_2, осредненные за периоды от одного до нескольких часов, оказались порядка 1 *мкг* $м^{-2}$ $сек^{-1}$ для водной и травяной поверхности и на порядок меньше для снежной поверхности. Скорости оседания были найдены порядка 1 *см* $сек^{-1}$.