PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Trace Gases and Air-Sea Exchanges

P. S. Liss, A. J. Watson, M. I. Liddicoat, G. Malin, P. D. Nightingale, S. M. Turner and R. C. Upstill-Goddard

Phil. Trans. R. Soc. Lond. A 1993 **343**, 531-541
doi: 10.1098/rsta.1993.0064

Trace gases and air–sea exchanges

By P. S. Liss[1], A. J. Watson[2], M. I. Liddicoat[2], G. Malin[1],
P. D. Nightingale[1, 2], S. M. Turner[1] and R. C. Upstill-Goddard[1, 2]

[1] *School of Environmental Sciences, University of East Anglia,*
Norwich NR4 7JT, U.K.
[2] *Plymouth Marine Laboratory, Prospect Place, The Hoe, Plymouth PL1 3DH, U.K.*

The most widely used approach for calculating the flux of gases across the sea surface is from the product of the concentration difference across the interface and a kinetic parameter, often called the transfer velocity. During the NERC North Sea Community Research Project (CRP) a considerable effort was made to improve our knowledge of both of these terms.

Concentration measurements were made on nine survey cruises (February to October 1989) for dimethyl sulphide (DMS) (and its precursor dimethylsulphonioproprionate DMSP, both dissolved and particulate), as well as for a variety of natural and man-made low molecular mass halocarbons.

To better define the relationship between transfer velocity and wind speed a novel double tracer technique was used on two of the process cruises in the North Sea CRP. The tracers added to the water were SF_6 and ^{3}He and from the measured change in their concentration ratio over time, four estimates of the transfer velocity were made, one at a rather high wind speed (*ca.* 17 $\mathrm{m\,s^{-1}}$). The results are in general agreement with the relationship of Liss & Merlivat (1986) based on laboratory and lake studies and theoretical considerations, and constitute their first real test at sea.

Combining the above results for the transfer velocity with the detailed concentration fields measured in the CRP has enabled us to calculate fluxes across the sea surface for the measured gases with a much finer time and space resolution than was possible hitherto. Some implications of the calculated fluxes for atmospheric chemistry in Europe are discussed.

1. Introduction

The most widely used method for calculating gas fluxes across the air–sea interface is described by the following relationship:

$$F = K_{(\mathrm{T})}\,\Delta C, \tag{1}$$

where F is the flux of gas, $K_{(\mathrm{T})}$ is the overall transfer velocity, $\Delta C = (C_{\mathrm{a}} H^{-1}) - C_{\mathrm{w}}$ is the air-water gas concentration difference; C_{a} is the concentration of gas in air; C_{w} is the concentration of gas in water; H is the Henry's law constant of gas, $(C_{\mathrm{a}}/C_{\mathrm{w}})$, at equilibrium.

A more detailed account of the use of the above equation can be found in Liss (1983). What is clear is that in (1) air–sea gas fluxes are derived from the product of the concentration difference and transfer velocity terms, both of which must be

Phil. Trans. R. Soc. Lond. A (1993) **343**, 531–541
Printed in Great Britain

known for the gases of interest. The North Sea CRP presented an excellent opportunity to significantly advance knowledge of both parameters, and thereby lead to better estimates of gas fluxes across the sea surface.

For this study we chose to measure the trace gas dimethyl sulphide (DMS), which is found ubiquitously in the (surface) oceans (and its precursor dimethylsulphoniopropionate (DMSP) which is formed by marine algae). A major reason for studying DMS is because it is invariably found to be supersaturated in surface seawaters relative to its atmospheric concentration (Andreae 1986) and the resulting net sea-to-air flux of the gas is of importance in several aspects of atmospheric chemistry. Once in the atmosphere the DMS is subject to oxidation by hydroxyl and nitrate free radicals leading to the formation of sulphur dioxide, methanesulphonic acid and sulphate *inter alia* (Plane 1989). These species are generally considered to be the most important natural contributors to the acidity of rain and atmospheric aerosols (Liss 1991). Further, production of submicrometre sulphate aerosols, which act as cloud condensation nuclei, from atmospheric oxidation of DMS plays a significant role in marine cloud formation (Shaw 1987). Charlson *et al.* (1987) have gone further and hypothesized that biogenic DMS production leading to cloud formation may function as an important feedback mechanism regulating climate.

In addition to DMS, a series of low molecular mass organo-halogen trace gases were also measured. In most water samples at least 15 organo-halogen gases were identified, of which the more common were: Freons 11 and 113 (CCl_3F and CCl_2FCClF_2), methyl iodide (CH_3I), chloroform ($CHCl_3$), methyl chloroform (CH_3CCl_3), carbon tetrachloride (CCl_4), trichloroethene (Cl_2CCHCl), dibromomethane (CH_2Br_2), dichlorobromomethane ($CHCl_2Br$), tetrachloroethene (Cl_2CCCl_2), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$). Some of these compounds are thought to be formed in seawater by biological and/or photochemical processes, while others are known to come from man-made sources. Again they have importance in atmospheric chemistry, particularly in regard to ozone destruction in both troposphere (Barrie *et al.* 1988) and stratosphere (Soloman 1990). A further trace gas studied in the North Sea CRP was methane and the results of this work are reported in Scranton & McShane (1991).

2. Concentration measurements

(*a*) *Dimethyl sulphide*

Measurements of sulphur and organohalogen gases were made on nine survey cruises in the North Sea CRP (as described in Howarth *et al.*, this symposium) from February to October 1989 (RRS *Challenger* Cruise Numbers 45 to 61 inclusive, odd numbers only). These cruises were selected to cover both the biologically active spring and summer months as well as the less active autumn and winter seasons. Approximately 100 surface water samples were analysed for trace gases on each cruise. Atmospheric measurements were not made since for many of the gases (including DMS and CH_3I) it is the water concentration which principally drives the sea-to-air flux, i.e. for such gases the surface seawater is heavily supersaturated relative to atmospheric concentrations, which are thus numerically unimportant in the flux calculation.

The measured monthly concentration fields for dimethyl sulphide are shown in figure 1. An obvious seasonal cycle is apparent with maximum concentrations in

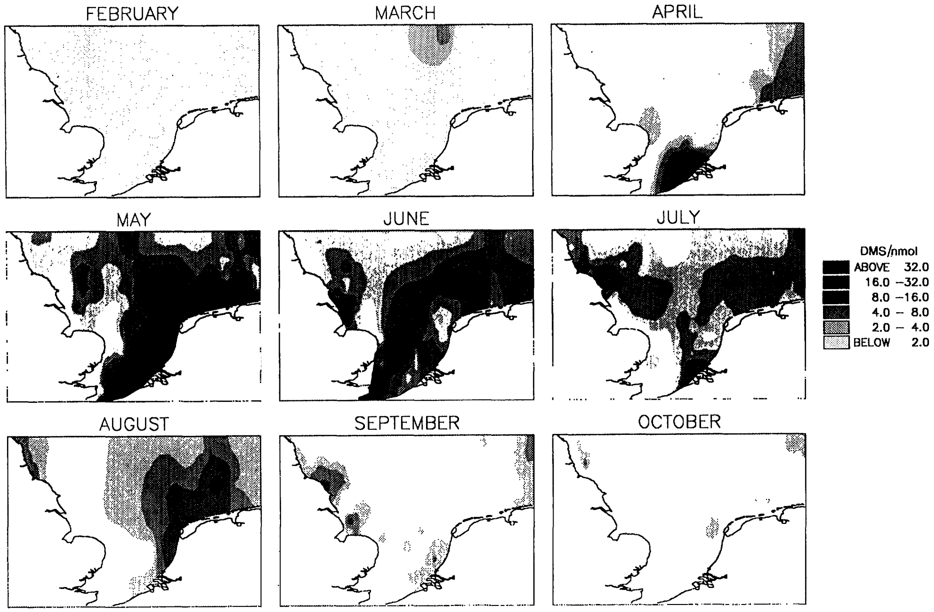


Figure 1. Spatial distribution of DMS in surface waters in the southern North Sea for months of February to October 1989.

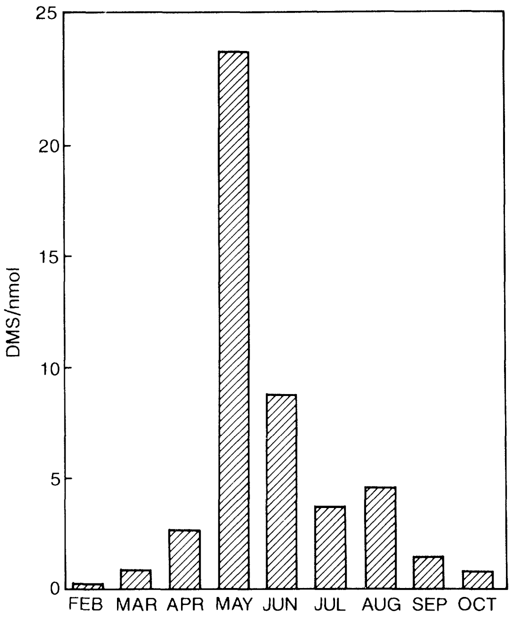
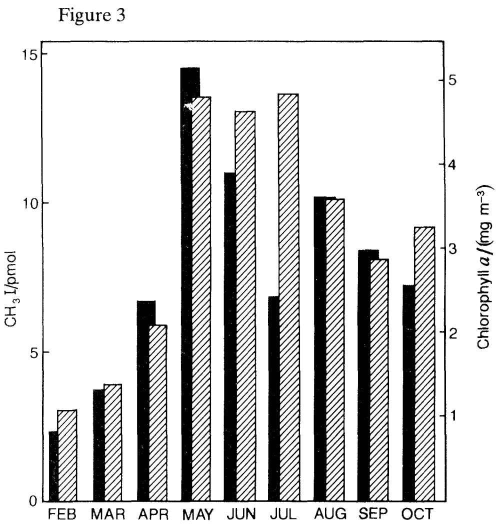


Figure 2. Monthly mean DMS concentrations in surface water of the southern North Sea for February to October 1989.

spring and summer, although the relationship with general measures of biological production, such as chlorophyll *a*, is not strong. This is clearly demonstrated in figure 2 where the monthly average values are plotted. The winter to summer mean values span two orders of magnitude. The maximum monthly average value is found in May, a point to which we will return later.



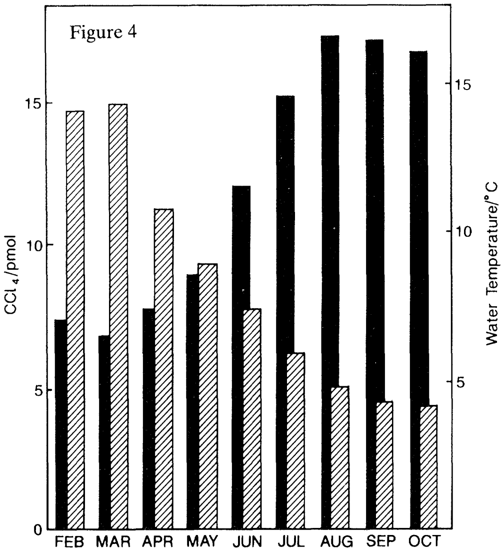


Figure 3. Monthly mean methyl iodide (shaded bars) and chlorophyll a (full bars) concentrations in surface waters of the southern North Sea for February to October 1989.

Figure 4. Monthly mean carbon tetrachloride concentrations (shaded bars) and water temperature (full bars) for surface waters of the southern North Sea for February to October 1989.

The DMS concentration data in figure 1 also show very considerable spatial variability. This is to be expected for a biogenic trace gas, since the distribution of the phytoplankton is also patchy (see Howarth *et al.*, this symposium). Such patchiness is almost certainly emphasised for DMS since there is mounting evidence that different algal species show a considerable range of abilities to form DMSP and therefore DMS (Liss *et al.* 1992). For example, the high levels measured along the Dutch/German coasts in April and May are very likely due to the presence of *Phaeocystis pouchetii*, an organism well known to be a prolific producer of DMS. This species variability in terms of DMSP production is one reason for the rather poor relationship between DMS and chlorophyll a.

(*b*) *Organohalogens*

Space does not allow a proper display of the concentration data obtained for the large number of halocarbons measured on the nine cruises (full details will be published elsewhere and can also be found in Nightingale (1991)). We have instead chosen two representative gases, methyl iodide and carbon tetrachloride, and their monthly average concentrations are shown in figures 3 and 4. These compounds were selected to illustrate the range of behaviours of organohalocarbon gases; methyl iodide is thought to be wholly formed in seawater by biological (or possibly photochemical) processes with a net flux from sea to atmosphere, whereas carbon tetrachloride is considered to be man-made with a net flux from the atmosphere into the oceans.

The results for methyl iodide (figure 3) show a marked temporal cycle, with highest values in the summer, although the extent of the seasonality is not as strong as that for DMS (figure 1). Corresponding data for chlorophyll ‘a’ are also plotted in figure 3 and show a similar pattern to that of methyl iodide, with the exception of the month of July, where CH_3I remains high in spite of a substantial drop in the level of chlorophyll. The general agreement between methyl iodide and chlorophyll levels is evidence for, but not conclusive proof of, a biological origin for this gas.

In contrast, the monthly average water concentrations of carbon tetrachloride (figure 4) exhibit maximum values in the two winter months sampled (February and March), with concentrations dropping continuously from then. Also shown in figure 4 is the temperature of the surface water. The anti-correlation between temperature and carbon tetrachloride suggests that concentration levels of this particular gas are controlled, at least in part, by its aqueous phase solubility, with colder water being able to dissolve more atmospheric CCl_4. Calculations by Nightingale (1991) indicate that approximately 50 % of the seasonal variation can be explained by the solubility effect. Possible reasons for the remainder include seasonal changes in the atmospheric concentration of the gas, and/or lack of equilibration between air and sea, and/or uncertainties in our knowledge of the temperature dependence of the Henry's Law constant for the dissolution of CCl_4 in seawater.

3. Measurement of air–sea transfer velocity

For the gases of interest here it is processes on the seawater side of the air–sea interface which control their rate of exchange. This arises from their relatively high Henry's Law constants and lack of chemical reactivity in water (Liss 1983). Our understanding of the processes which control the transfer velocity of gases of this type has been summarized by Liss & Merlivat (1986), who proposed a three-line relationship to describe the behaviour of the transfer velocity as a function of wind speed (as shown by the dashed lines in figure 5). The equations developed by Liss & Merlivat (L & M) are as follows:

$$k_w = 1.17u, \qquad \text{for} \quad u \leqslant 3.6, \tag{2}$$

$$k_w = 2.85u - 9.65, \qquad \text{for} \quad 3.6 < u \leqslant 13, \tag{3}$$

$$k_w = 5.9u - 49.3, \qquad \text{for} \quad u > 13, \tag{4}$$

where k_w is the water phase transfer velocity (cm h^{-1}), and u is the wind speed (m s^{-1}) at a height of 10 m. Equation (2) describes exchange when the water surface is smooth or with only few waves, (3) is for the situation where the surface is covered with waves but not sufficiently rough for wave breaking to be common, and (4) covers the case of a surface with breaking waves and resultant bubble formation.

Also shown on figure 5 are average transfer velocities obtained at sea using the radon deficiency technique and the global mean value derived from bomb $^{14}CO_2$. Both of these techniques give estimates of the transfer velocity averaged over periods of several days to months, so that any relationship with wind speed can be easily obscured. In spite of this, all but one of the radon data points lie quite close to the part of the L & M line for wind speeds 3.6–13 m s^{-1}. However, one radon point and the mean bomb $^{14}CO_2$ value lie significantly above the line.

Since wind strength over the ocean is highly variable over short timescales, it would clearly be advantageous, in the context of trying to relate gas transfer to wind speed, to have a technique which measured the transfer velocity with a time resolution of the order of a day. It should also be noted from figure 5 that there are no radon or ^{14}C data to test the uppermost line (for $u > 13$ m s^{-1}) given by (4).

The North Sea CRP gave us the opportunity to deploy a new purposeful tracer

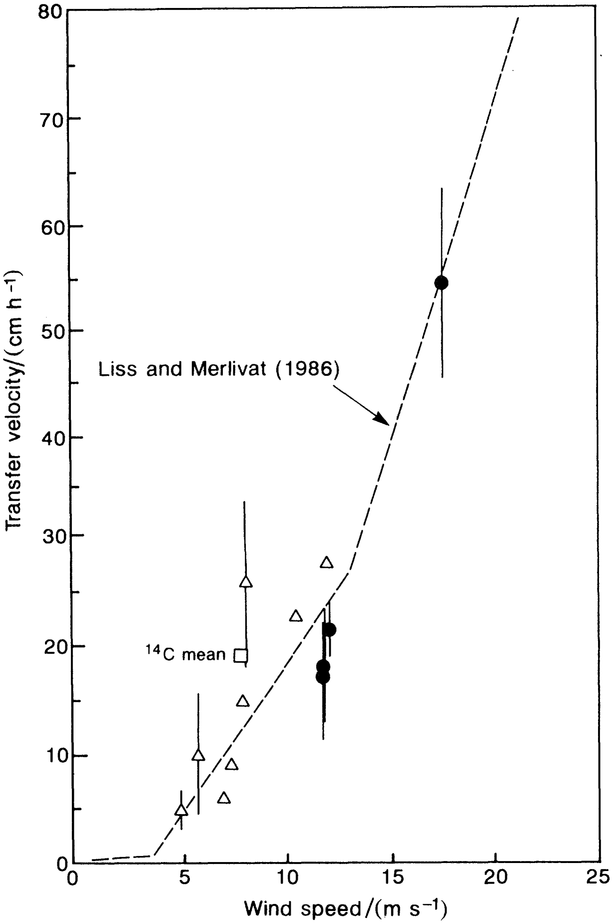


Figure 5. Transfer velocity for a gas of $Sc = 600$ as a function of wind speed. The Liss & Merlivat (1986) predictions are shown by the dashed lines. Open triangles are mean values from the radon deficiency method, the open square is the global mean value from bomb ^{14}C measurements. Full circles are the four data points obtained in the North Sea CRP using the ^{3}He/SF$_6$ purposeful tracer technique (1σ errors are indicated by vertical bars).

technique to measure *in situ* transfer velocities over periods of tens of hours. It consisted of adding two gaseous tracers (SF$_6$ and ^{3}He) simultaneously to a patch of seawater and measuring the change in their concentration ratio with time, as they escaped at different rates to the atmosphere (C_a for both gases assumed to be zero). The technique is described in more detail in Watson *et al.* (1991) and the governing equation is as follows,

$$\frac{1}{R}\frac{\mathrm{d}R}{\mathrm{d}t} = -\frac{k_{\mathrm{He}} - k_{\mathrm{SF_6}}}{D}, \tag{5}$$

where R is the ratio of ^{3}He to SF$_6$ in the water at time t, k is the transfer velocity of the gas indicated and D is the water depth; D is assumed constant at 30 ± 2 m for the well-mixed, flat-bottomed study area selected. This region is called the 'Broad Fourteens' and is about 60 km off the Dutch coast (52° 15′–52° 30′ N, 3° 20′–3° 40′ E).

It is clear from (5) that by using two gaseous tracers it is the difference between their transfer velocities which is obtained. (If a non-volatile tracer (i.e. $k = 0$) of sufficient analytical sensitivity was available then R would give the transfer velocity of the volatile tracer directly.) With two gaseous tracers a second relationship is required to solve for the individual k values. This often takes the form of a power dependence of the Schmidt number (Sc, which is the ratio of the water viscosity to the diffusivity of the gas in water at a particular temperature). From both theory and laboratory experiments, for equation (2) k is found to be dependent on Sc raised to the -0.67 power, while for equation (3) the power dependence is -0.5. We have been able to check this latter exponent by deploying both tracers on a small freshwater lake (Upstill-Goddard *et al.* 1990). By budgeting the amount of both ^{3}He and SF_6 in the lake over a period of time, individual values of the two transfer velocities were obtained under identical conditions. The experiment was carried out on two occasions in November 1988 when the mean wind speeds were 3.8 and 5.8 m s^{-1}. The resulting values of the Sc exponent were -0.505 and -0.515, strongly supportive of the -0.5 dependence derived from theory and laboratory work for this wind speed range. At high wind speed (corresponding to equation (4) above) knowledge of the Sc exponent is essentially non-existent and we have had to assume the -0.5 value to remain applicable. It should be noted that all the data plotted on figure 5, as well as the L & M predictions, are normalized for a gas with $Sc = 600$ (which corresponds to CO_2 at 20 °C) by using the $Sc^{-0.5}$ relationship.

The double tracer technique was used on two North Sea CRP process cruises, in March and October 1989. Together they yielded four estimates of the transfer velocity and these are shown in figure 5. Three of the points are at wind speeds close to 12 m s^{-1} (range from 11.7 to 12.1 m s^{-1}) and cluster together just below the L & M line. The small range of transfer velocities between the three points (17.0 to 21.7 cm h^{-1}) can be taken as an *in situ* estimation of the reproducibility of the method (estimates of the 1σ error of the individual determinations are shown on the figure). The fourth point is at a significantly higher wind speed (17.5 m s^{-1}), and although the error bar is quite large, the mean value lies very close to the prediction from (4). However, one should not be overconfident of predictions which are supported by only one field measurement! Despite this cautionary note, we point out that this is the first time that an *in situ*, short term determination of the transfer velocity has been made under stormy conditions and the agreement with (4) must significantly increase the confidence we can place in the L & M predictions. The disagreement between the estimate of the global transfer velocity from bomb $^{14}CO_2$ and that predicted using (3) has important implications for estimating the flux of man-made carbon dioxide into the oceans, a discrepancy which has still to be resolved.

4. Air–sea fluxes

In this section we put together knowledge on North Sea trace gas concentration fields and air–sea transfer velocities discussed earlier in order to calculate fluxes across the sea surface in the study area. In view of the large volume of trace gas data generated in the project, most of the results of such flux estimates will be presented elsewhere, together with a full description of how the calculation is done. Here we illustrate the potential by giving examples of the DMS and methyl iodide fluxes and also show how such a detailed data base can be used to highlight uncertainties inherent in flux calculations which have to rely on more limited sets of results.

Table 1. *Fluxes of DMS from the North Sea in 1989 calculated by different methods*

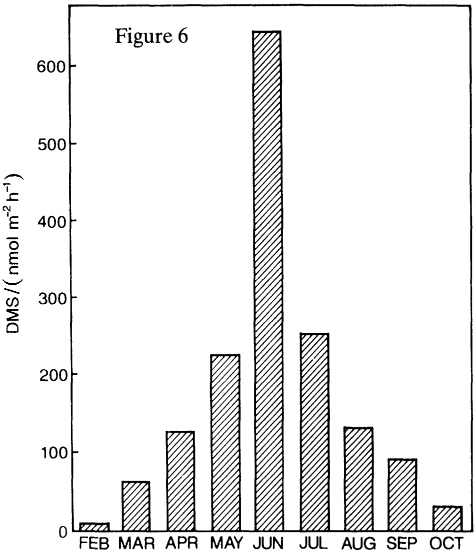
	DMS/(nmol m^{-2} h^{-1})			
month	climatic data[a]	product of means[b]	mean of products[c]	spatial means[d]
Feb	10	10	8	8
March	65	55	66	63
Apr	157	146	140	129
May	955	115	268	227
June	456	389	526	646
Jul	243	202	236	249
Aug	319	52	119	133
Sep	174	133	120	92
Oct	82	32	28	30

[a] Mean monthly climatic temperature, wind speeds (Meserve 1974) and DMS in 1989.
[b] As (a), but mean temperature and wind speed from Met. Office data for 1989.
[c] Met. Office data used to calculate fluxes at each station, which were then arithmetically averaged.
[d] As (c), but with spatial weighting.

This last point is dealt with first and table 1 refers. Here different ways of calculating the sea-to-air flux of DMS for each month are shown. The first two columns show the flux obtained from the mean concentration field for each month multiplied by the corresponding transfer velocity, calculated from either the mean monthly climatic temperature and wind speed or the mean of these values from Meteorological Office data for the relevant months in 1989. (Water temperatures are required for calculation of *Sc* values; wind data from the Meteorological Office had to be used since suitable instrumentation was not available on *Challenger* for direct measurements). In contrast, the final two columns give the fluxes calculated as the arithmetic mean of the products of the DMS concentration measured at each station multiplied by the transfer velocity calculated using the corresponding Meteorological Office temperature and wind speed data. In the final column spatial averages have been taken to avoid bias due to uneven sample distribution.

It is clear from table 1 that different ways of calculating the flux can lead to significant differences in the results. This arises mainly from the fact that, as shown in figure 5, the relationship between transfer velocity and wind speed is not a simple linear one. In some cases discrepancies between the different approaches are quite small (e.g. March), whereas in other cases, such as May, they are very large. May in 1989 was much less windy than indicated in the climatically averaged data in Meserve (1974), which leads to a several fold decrease in calculated flux between the first and last three columns. Even when actual winds are used the 'product of means' and 'mean of products' approaches lead to fluxes which differ by about a factor of two. In previous studies the measured concentration field and/or the meteorological data were generally not as detailed as those available here and in these cases the product of means approach is all that has been possible.

In our view the mean of products approach (together with spatial weighting, if necessary) is to be preferred wherever the data base is large enough to justify its use. Thus, we conclude that the best estimates of DMS fluxes from the North Sea are those given in the final column of table 1 and these are shown in figure 6. The clear



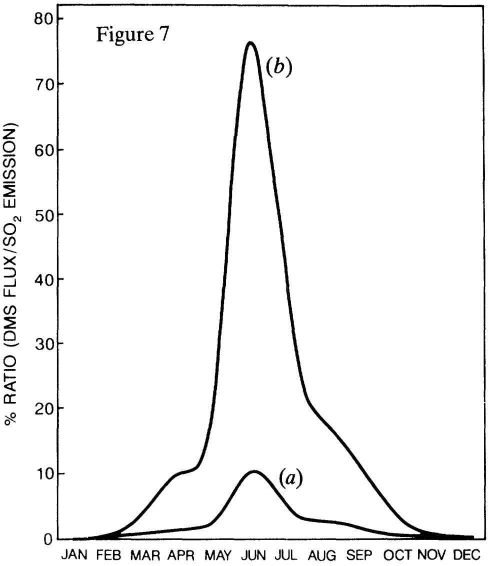


Figure 6. Monthly mean DMS fluxes from the southern North Sea for February to October 1989 (the method of calculation is discussed in the text).

Figure 7. Ratio (%) of DMS flux from the southern North Sea to input of SO_2 to the atmosphere from European anthropogenic emissions as a function of time of year. Both DMS and SO_2 emissions are per unit area and time. In curve (*a*) the man-made emission rate is for the whole of Europe (EMEP grid), whereas in curve (*b*) the emission rate is for Scandinavia only.

seasonality in the flux, expected from the concentration data (figure 1), is apparent. However, it should be noted that the maximum flux is in June whereas the maximum mean concentration is in May (figure 2). This mismatch arises from the winds in May being exceptionally light, as noted earlier.

In view of the potential importance of DMS fluxes for the acidity of rain and atmospheric aerosols, in figure 7 we compare the biogenic DMS flux from the North Sea with the man-made emission of sulphur from Europe to the atmosphere (Iversen *et al.* 1990). What is plotted for each month is the ratio (as a percentage) of the sulphur (as DMS) coming from the North Sea to the emission of man-made sulphur (mainly as SO_2) from Europe, both expressed per unit area and time. Curve (*a*) shows that for the European land area as a whole (EMEP grid) the North Sea emits sulphur in June at about 10% of the rate of anthropogenic inputs, with lower percentages for other months. Curve (*b*) represents the same calculation but for emissions from Scandinavia only. Here the North Sea flux in June is about 75% of the equivalent emission from this rather lightly industrialized/urbanized region. We conclude that for such areas the biogenic flux from the North Sea may be a significant source of atmospheric sulphur in spring and summer; a conclusion which receives support from the studies by Fletcher (1989) and Tarrason (1991).

Finally, in figure 8 the monthly, average, sea-to-air fluxes of methyl iodide are presented. The low fluxes in May and August relative to those in adjacent months are more due to the moderate mean wind speeds in those months than to any abrupt change in CH_3I concentrations in the water (see figure 3). The results in figure 8 have been calculated using the mean of products approach and for this reason, as well as because of the large number (*ca.* 100) of data points going to make up each monthly mean, they should be more reliable than anything attempted hitherto.

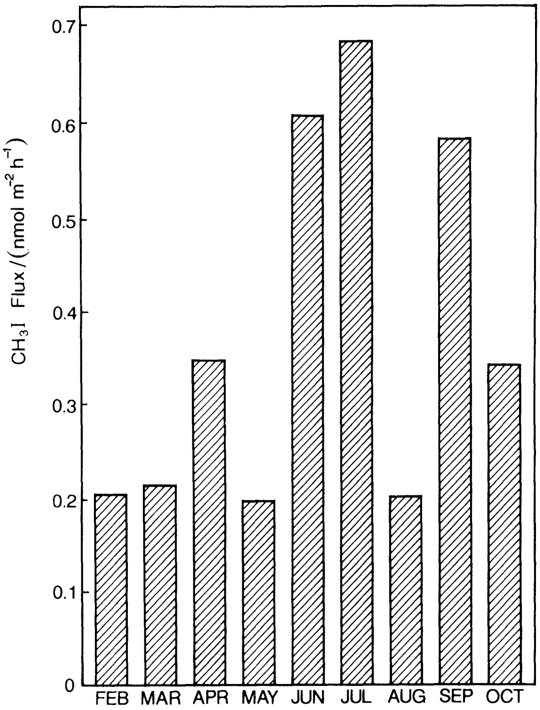


Figure 8. Monthly mean methyl iodide fluxes from the southern North Sea for February to October 1989.

For help with work at sea we thank Simon Allerton, Elisabet Fogelqvist, Luke Jackson, Jane Stevenson and Rik Wanninkhof, as well as the officers and crew of RRS *Challenger*. Financial support from the Natural Environment Research Council, the Department of the Environment and the Commission of the European Communities is gratefully acknowledged.

References

Andreae, M. O. 1986 The ocean as a source of atmospheric sulfur compounds. In *The role of air–sea exchange in geochemical cycling* (ed. P. Buat-Ménard), pp. 331–362. Dordrecht: D. Reidel.

Barrie, L. A., Bottenheim, J. W., Schell, P. J. & Rasmussen, R. A. 1988 Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere. *Nature, Lond.* **334**, 138–141.

Charlson, R. J., Lovelock, J. E., Andreae, M. O. & Warren, S. G. 1987 Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature, Lond.* **326**, 655–661.

Fletcher, I. 1989 North Sea dimethyl sulfide emissions as source of background sulfate over Scandinavia. In *Biogenic sulfur in the environment* (ed. E. S. Saltzman & W. J. Cooper), pp. 489–501. Washington, D.C.: American Chemical Society.

Iversen, T., Halvorsen, N. E., Saltbones, J. & Sandnes, H. 1990 Calculated budgets for airborne sulphur and nitrogen in Europe. EMEP/MSC-W Report 2/90.

Liss, P. S. 1983 Gas transfer: experiments and geochemical implications. In *Air–sea exchange of gases and particles* (ed. P. S. Liss & W. G. N. Slinn), pp. 241–298. Dordrecht: D. Reidel.

Liss, P. S. 1991 The sulphur cycle. In *Climate and global change* (ed. J. C. Duplessy, A. Pons & R. Fantechi), pp. 75–89. Brussels: CEC.

Liss, P. S. & Merlivat, L. 1986 Air–sea gas exchange rates: introduction and synthesis. In *The role of air–sea exchange in geochemical cycling* (ed. P. Buat-Menard), pp. 113–127. Dordrecht: D. Reidel.

Liss, P. S., Malin, G., Turner, S. M. & Holligan, P. M. 1992 Dimethyl sulphide and *Phaeocystis*: a review. *J. mar. Systems*. (In the press.)

Meserve, J. M. 1974 *US Navy marine climatic atlas of the world*, vol. 1: *North Atlantic Ocean*. (371 pages.) Washington, D.C.: US Government Printing Office.

Nightingale, P. D. 1991 Low molecular weight halocarbons in seawater. (313 pages.) Ph.D. thesis, University of East Anglia.

Plane, J. M. C. 1989 Gas–phase atmospheric oxidation of biogenic sulfur compounds: a review. In *Biogenic sulfur in the environment* (ed. E. S. Saltzman & W. J. Cooper), pp. 404–423. Washington, D.C.: American Chemical Society.

Scranton, M. I. & McShane, K. 1991 Methane fluxes in the southern North Sea: the role of European rivers. *Cont. Shelf Res*. **11**, 37–52.

Shaw, G. E. 1987 Aerosols as climate regulators: a climate–biosphere linkage? *Atmos. Environ*. **21**, 985–986.

Solomon, S. 1990 Progress towards a quantitative understanding of Antarctic ozone depletion. *Nature, Lond*. **347**, 347–350.

Tarrason, L. 1991 Biogenic Sulphur Emissions from the North Atlantic Ocean. EMEP/MSC-W Note 3/91. Blindern, Oslo: The Norwegian Meteorological Institute.

Upstill-Goddard, R. C., Watson, A. J., Liss, P. S. & Liddicoat, M. I. 1990 Gas transfer velocities in lakes measured with SF_6. *Tellus* B **42**, 364–377.

Watson, A. J., Upstill-Goddard, R. C. & Liss, P. S. 1991 Air–sea gas exchange in rough and stormy seas measured by a dual-tracer technique. *Nature, Lond*. **349**, 145–147.

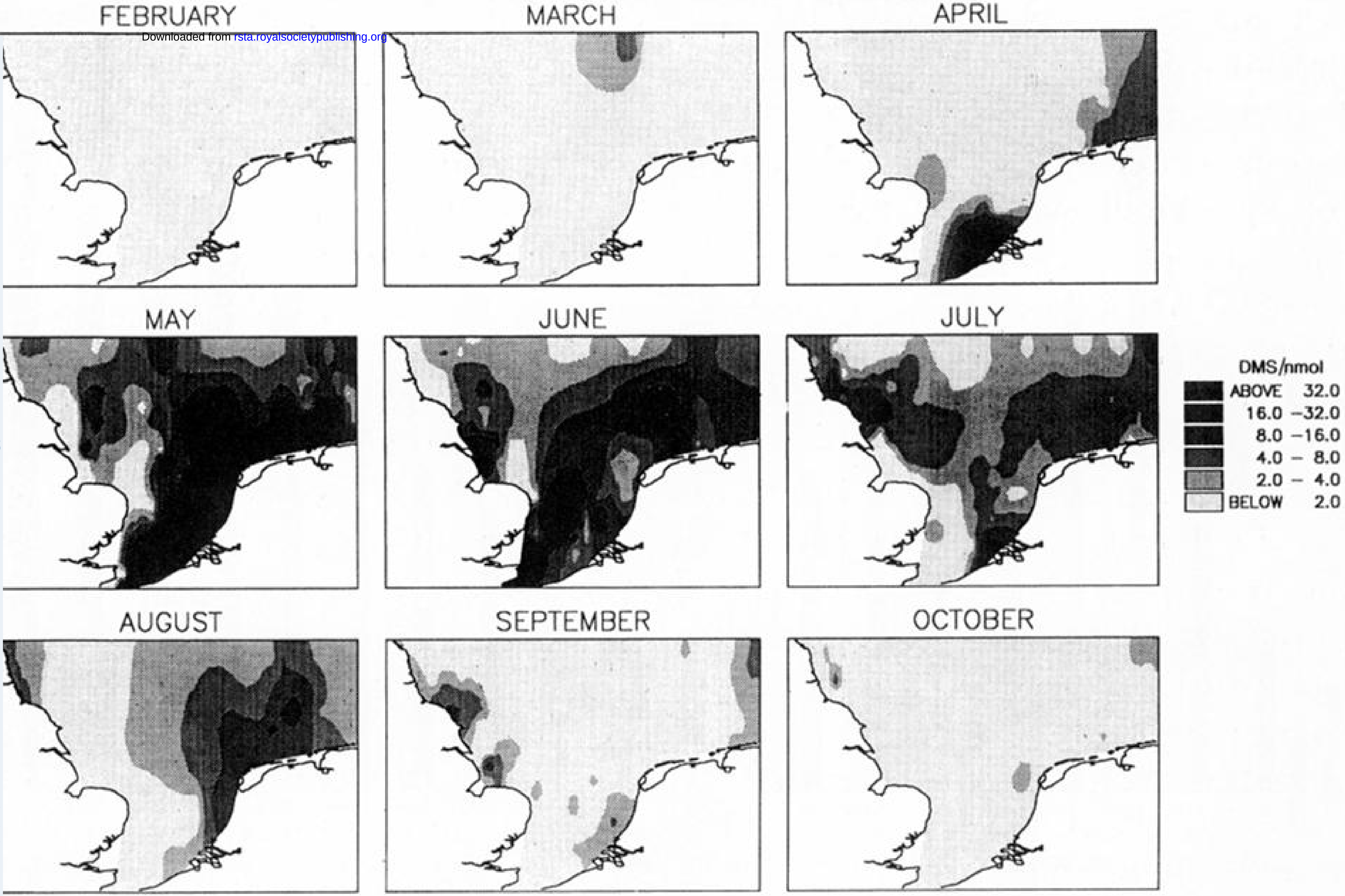


Figure 1. Spatial distribution of DMS in surface waters in the southern North Sea for months of February to October 1989.