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Air-sea gas exchange in Antarctic waters

PETER S. LISS*, ADELE L. CHUCK, SUZANNE M. TURNER and ANDREW J. WATSON

School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK
** Corresponding author: p.liss@uea.ac.uk*

Abstract: The flux of gases between the atmosphere and the oceans can be calculated from the product of the concentration difference across the sea surface and a kinetic term, often called a transfer velocity. The transfer velocity is frequently parameterized in terms of wind speed, although the actual exchange process is also affected by waves, bubbles, wind fetch, and less certainly by surfactants and chemical reactivity. There is currently an uncertainty of about a factor of two in using the wind speed parameterization. In view of the windiness of the Southern Ocean, transfer velocities will often be high, although there are few published *in situ* measurements of transfer rates made in the region. Data for gas concentration fields in the Southern Ocean are generally sparse compared to other better studied oceanic areas. In this paper we discuss what is known for the region for carbon dioxide, including the oceanic sink for man-made inputs to the atmosphere; dimethyl sulphide, where there appears to be a substantial source, which has the potential for a significant climatic effect due to the low particulate loading in the region; and organo-halogen and alkyl nitrate gases, where marine emissions may play an important role in controlling the oxidation capacity of the Antarctic atmosphere.

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Introduction

In this paper we deal with approaches which have been taken for the calculation of gas fluxes across the air-sea interface and illustrate the approach with examples of a variety of gases important for climate and air chemistry, with particular reference to the atmosphere and the seas around Antarctica. We start with the basic equation describing the transfer of gases across the sea surface, as follows:

$$F = K_{(T)} * \Delta C \qquad (1)$$

Where F = net air-sea gas flux, $K_{(T)}$ = overall or total transfer velocity, $\Delta C = (C_a * H^{-1}) - C_w$, C_a = concentration of gas in air, C_w = concentration of gas in water, H = Henry's law constant = (C_a/C_w) at equilibrium.

In the next section we discuss the transfer velocity term in Eq. (1), consider factors which control its value and review methods which have been used recently to measure it at sea. In subsequent sections the emphasis is more on the concentration difference term (ΔC) and its use, along with knowledge of $K_{(T)}$, to calculate net gas fluxes. Finally we draw some brief, general conclusions. Where sufficient data are available, we attempt to use information on uncertainties in both the $K_{(T)}$ and ΔC terms in Eq. (1) to estimate the overall uncertainty and variability in air-sea gas flux estimates in the Antarctic region.

Transfer velocity

The transfer velocity term in Eq. (1), which quantifies the kinetics of air-sea gas exchange, is controlled by a variety of factors. For the sparingly soluble gases studied here (CO_2, dimethyl sulphide (DMS), organo-halogens and alkyl nitrates) these factors include wave height and slope, wind fetch, sea state, bubble field and degree of white capping, all of which directly or indirectly affect the amount of mixing in the surface water. Because these factors are largely wind driven they are often amalgamated together in terms of wind speed (u), and data displayed as K vs u plots. Other properties which may be important for air-sea gas transfer rates include surfactants and the chemical reactivity of the gas in seawater. The importance of these latter two factors is less well established, with considerable controversy over the role of surfactants (contrast the results reported in Frew 1997 and Nightingale *et al*. 2000a), and with chemical reactivity only likely to be important for gases with very rapid aqueous phase chemistry. Useful references which deal with the basic theory behind Eq. (1), as well as the various controlling processes mentioned here, are to be found in the papers by Liss (1983), Liss & Merlivat (1986), Frost & Upstill-Goddard (1999), Nightingale & Liss (2004), as well as various chapters in the books edited by Liss & Duce (1997) and Donelan *et al*. (2002).

A useful starting point for a discussion of recent field studies to measure transfer velocities *in situ* is the paper by Liss & Merlivat (1986). From a combination of theory, results from wind tunnel experiments and a field study carried out on a lake using the purposeful tracer sulphur hexafluoride (SF_6) (Wanninkhof *et al*. 1985), they described the K vs u relationship in terms of three equations. Each equation corresponded to a particular wind speed range and the associated wave field. At low winds (≤ 3.6 m s^{-1}) the rate of increase of K with u was small and the water surface was essentially smooth. There followed an intermediate wind speed range (3.6 to about 13 m s^{-1}) where the water surface was progressively covered with first capillary and subsequently larger waves with concomitant increase in the slope of the K vs u relationship; and finally at wind speeds greater than approximately 13 m s^{-1} there was progressive wave breaking with the production of an increasing number of bubbles. The presence of bubbles, which can act as gas exchangers in their own right as well as leading to differential effects depending on gas solubility, led to a further enhancement in the K/u slope. The importance of waves and, at high wind speeds, bubbles in enhancing K is emphasized in this treatment. A further point is that at that time (the mid-1980s) there were few if any field results which could be used to determine the form of the K vs u relationship at sea and so test the appropriateness of the proposed parameterization. Some earlier field studies using natural and bomb carbon-14 (Broecker & Peng 1974) and natural Rn-222 (Peng *et al.* 1979) had yielded large-scale or global average values for K, but had failed to determine its variation with wind speed.

The first study to measure gas transfer velocities at sea which overcame the deficiencies of these earlier attempts was that of Watson *et al.* (1991). They used the SF_6 purposeful tracer technique pioneered by Wanninkhof *et al.* (1985) but modified it for use at sea by incorporation of a second tracer (^{3}He) to take account of the fact that the SF_6 would be lost from the water not only by exchange across the sea surface but also by dispersion within the dosed water body. The equation describing the technique as used by Watson *et al.* is as follows:

$$(1/R)^{*}\,dR/dt = -\left(K_{^{3}He} - K_{SF_6}\right)/D \tag{2}$$

where R = [^{3}He]/[SF_6] and the square brackets indicate concentration, D = water depth and t = time.

The technique involves several assumptions including homogeneity of the water down to a depth D and that R is invariant with wind and sea state. The right-hand side of Eq. (2) involves the difference in transfer velocity of the two gases deployed. Ideally one gas and a non-volatile tracer (to account for horizontal and vertical mixing) would have been used but at that time no suitable non-gaseous, conservative substance was available. Thus, the two gases ^{3}He and SF_6 were released together and the change in their concentration ratio (R), due to the faster diffusivity of ^{3}He compared with SF_6 across the sea surface, determined over a period of several days. The method was first used in the southern North Sea and four data points were obtained.

Subsequently, it was found that spores of the bacterium *Bacillus globigii* and two rhodamines, WT and Sulpho-G, could be used as non-volatile tracers (Upstill-Goddard *et al.* 2001). Using these together with the gases ^{3}He and SF_6 gave an over-determined system in which transfer velocities can potentially be calculated using five different combinations of the tracers taken in pairs (and treating the two rhodamines as one tracer), according to a generalized form of Eq. (2). The results of a study carried out using this approach, as part of the ASGAMAGE experiment in the southern North Sea, are shown in Fig. 1.

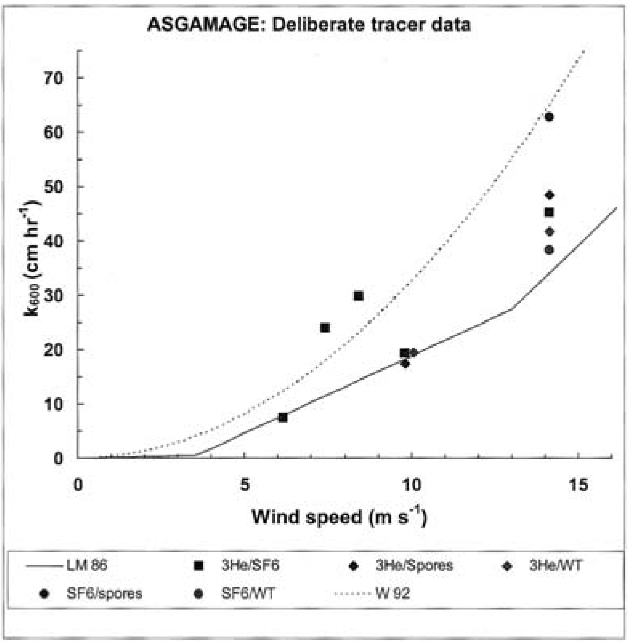

Fig. 1. Transfer velocity (K_{600}) derived from a variety of tracer pairs as a function of wind speed (Nightingale & Upstill-Goddard 1995). The predictions from the parameterizations of Liss & Merlivat 1986 (— LM86) and Wanninkhof 1992 (------ W92) are also shown.

The data points lie between the predictions of Liss-Merlivat (1986) and the alternative parameterization of Wanninkhof (1992). Where it is possible to get several simultaneous measurements of K from the different tracer pairs, the results are generally in rather good agreement. This is particularly useful at the wind speed of about 14 ms^{-1}, where four of the five data points are very similar, since in this relatively high wind regime it has proved very difficult to get experimental data from wind tunnels, let alone in the field. An assessment by Nightingale *et al.* (2000b) of multiple-tracer results for K has led to a parameterization based on this technique which lies between those of Liss-Merlivat (1986) and Wanninkhof (1992). Very recently, Wanninkhof *et al.* (2004) have published the first measurements of K in the Southern Oceans using the SF_6-^{3}He tracer pair.

Recently it has become possible to use the micrometeorological technique of eddy correlation to obtain values of K at sea. The eddy correlation method, which involves rapid measurement of gas concentrations in rising and descending parcels of air, has been widely used to

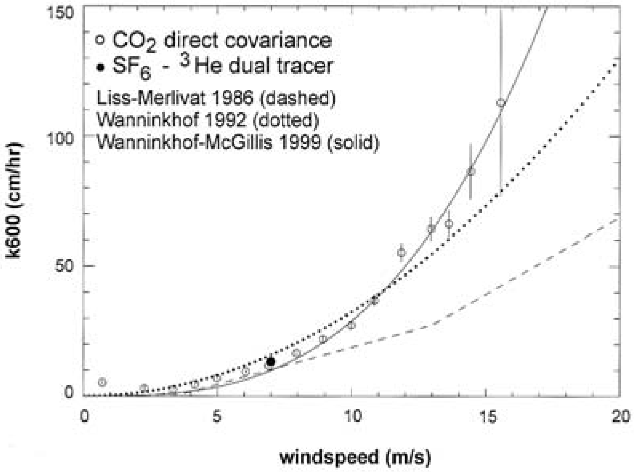

Fig. 2. Transfer velocity (K_{600}) determined by eddy correlation (direct covariance) in GasEx-98 and one K measurement obtained using the SF_6-^{3}He dual tracer pair, all plotted against wind speed. Also plotted are some widely used parameterizations of K vs wind speed.

measure CO_2 fluxes over land surfaces (Baldocchi *et al.* 2001). However, its application over the sea, where the CO_2 fluxes are generally significantly smaller than over land, has proved to be problematic. Despite a considerable amount of effort over many years, it is only very recently that reliable data have been produced. The technique was used to measure CO_2 fluxes over the north Atlantic in the GasEx cruise in 1998 (McGillis *et al.* 2001) and the results are shown in Fig. 2, which includes one data point obtained using the SF_6-^{3}He tracer pair.

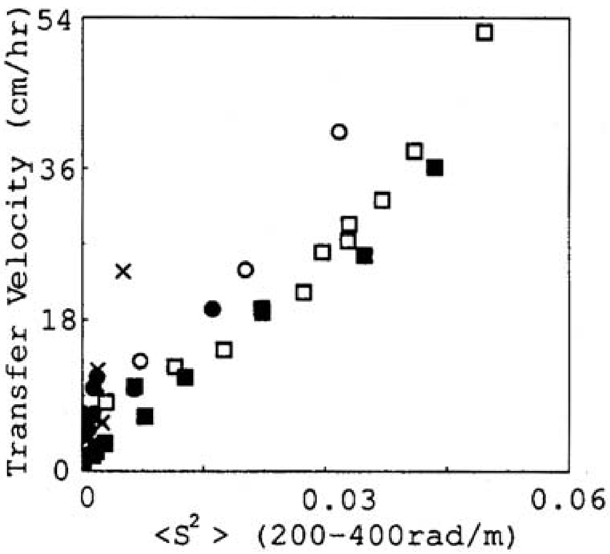

Fig. 3. Composite plot of gas transfer velocity inferred from laboratory and field measurements versus wavenumber-binned mean square slope between 200 and 400 radian/m. Laboratory gas transfer rates derived from mass balance methods, field results from the infrared technique. Circles = data from Heidelberg 4 m diameter channel. Squares = data from Woods Hole 0.5 m diameter channel. Crosses = North Atlantic field data. Filled symbols represent surfaces with films, open symbols represent clean surfaces. The Heidelberg tank used had a channel width of 0.3 m, the Woods Hole tank had a channel width of 0.1 m.

The data are believable, which is a substantial achievement given the difficulties encountered in previous attempts, and agree quite well with the predictions of the Liss & Merlivat (1986) and Wanninkhof (1992) relationships at low to moderate wind speeds. At wind speeds above about 12 ms^{-1}, K-values are higher than predicted by either of the above relationships. This led to a third predictive relationship (Wanninkhof & McGillis 1999), as shown in Fig. 2, which tracks the eddy correlation data. In view of the difficulty of measuring gas fluxes over the sea using micrometeorological techniques (as confirmed by the large error bars on some of the high wind speed points), it is to be expected that the results in Fig. 2 will not be the last word on this subject, but they still represent a huge advance. Possible reasons for the observed discrepancies in K as measured by eddy correlation and dual tracer approaches are discussed in Jacobs *et al*. (2002).

An altogether different approach to the estimation of air-sea gas transfer velocities has been described recently by Glover *et al*. (2002). In this they utilize the finding from wind tunnel and field studies that there is a close linear relationship between the mean square slope of surface waves and the transfer velocity, as illustrated in Fig. 3. Similar relationships are also presented in Bock *et al.* (1999).

Glover *et al*. (2002) then couple this finding with the ability of satellite mounted radar altimetry to determine sea surface roughness, in particular the mean square slope of surface waves as measured by their normalized microwave backscatter (Jackson *et al*. 1992). The procedure was applied to determine transfer velocities at nine oceanic locations over the period 1993–98. The results are shown in Fig. 4. Also plotted are transfer velocities estimated using the Liss & Merlivat (1986) and Wanninkhof (1992) relationships, using wind data from the NCEP reanalysis project (Kalnay *et al*. 1996).

The results are in reasonable agreement, with the satellite-derived values of K generally following the Liss & Merlivat relationship somewhat better than that of Wanninkhof. However, there are significant uncertainties associated with this approach, as with the others discussed earlier, so no firm conclusion should be drawn. However, the potential power of such remote sensing techniques for the estimation of gas transfer velocities is well illustrated by the results in Fig. 4. Satellite observing systems do not suffer from the obvious difficulties of making technically difficult measurements from a moving vessel at sea, a point particularly pertinent in the high wind situation where, as remarked earlier, there is currently a real paucity of field data. This is especially relevant in Antarctic waters in view of the prevailing high wind situation.

In this section we have presented the results of some new techniques for estimating gas transfer velocities at sea or remotely. All of them yield believable data, which is very positive, but all have built in assumptions which limit their reliability. In general, the differences between the various attempts at parameterizing K as a function of wind speed indicate a potential uncertainty of approximately a factor of 2 exists for the transfer velocity, and so for the flux calculated using Eq. 1. However, the discrepancy is sometimes not as great as this, (see for example the flux calculation in Table II of this paper), but can also be greater particularly at high wind speeds.

What is now needed is the further development of the approaches discussed above, as well as other potentially useful techniques, in addition to intercomparison studies to establish their accuracy and intercomparability. In the next section we consider air-sea gas fluxes in the Antarctic region, using CO_2, DMS, organo-halogens and alkyl nitrates as specific examples.

Carbon dioxide

In order to use Eq. (1) to calculate air-sea gas fluxes it is necessary to know not only the relevant transfer velocities but also the concentration field for the gas of interest and its variability in space and time. In the case of CO_2, defining the concentration field is particularly difficult since the concentration of the gas in near-surface ocean waters varies with change in water properties, such as temperature, as well as type (net photosynthesis or respiration) and degree of biological activity. Thus, although the atmospheric partial pressure of CO_2 may be reasonably constant for a particular region or time, the variability of the concentration in the water produced by the above processes often brings about a high degree of variability in the ΔC term in Eq. (1). Even the sign (which defines the net direction, in or out, of the CO_2 flux) varies spatially and temporally in response to seasonal changes in water temperature and biology. In this situation it is difficult to obtain the net flux of CO_2 into or out of the oceans since it is the outcome of a myriad of gross fluxes in both directions which are themselves varying in space and time. To deal with this problem a very large number of observations of surface water CO_2 concentrations are required. Ideally, these need to give good coverage of the whole oceans, as well as accounting for seasonal changes.

Over the last 30 years many measurements of surface water CO_2 concentrations have indeed been made in a wide variety of oceanic regions at different times and seasons, and these have been gathered together by Takahashi and co-workers (Takahashi *et al*. 2002). However, despite a data base containing well over a million measurements, Takahashi *et al*. have to interpolate and extrapolate extensively in order to calculate the net oceanic flux of CO_2. It is necessary to collapse (normalize) the available data (which has been collected patchily and intermittently over the past three decades) into one 'virtual' year (1995 is chosen) in order to produce the global map shown in Fig. 5. This task is made even more difficult because, over the period of the measurements, the atmospheric partial pressure of CO_2 has risen significantly due to fossil fuel combustion.

One of the major oceanic regions where CO_2 data coverage is particularly poor is the Antarctic, due to its inaccessibility and rough sea conditions. Thus, although Fig. 5 shows the whole area to be a net sink of about 29 x 10^{12} moles C yr^{-1} (from http://www.ldeo.columbia.edu/res/pi/CO2/), there is considerable uncertainty in the overall estimate and even more over its variability between different regions of the Antarctic oceans and with season therein. This last point is especially significant for Antarctic waters with their strong inherent seasonality in marine biological activity.

Since calculation of air-sea fluxes of CO_2 using the approach via Eq. (1) suffers from the problems outlined above, which are particularly severe in the Antarctic region, it is not surprising that other ways of estimating the flux of the gas have been attempted. One approach has been to examine the atmospheric partial pressure record at two long-term air sampling sites and by inversion to infer the sign of the source/sink from the Southern Ocean. The only suitable sites available are the South Pole and Cape Grim, Tasmania (40º41'S, 144º 41'E). Carbon dioxide partial pressures at the South Pole are found to be generally slightly higher than those at Cape Grim. Since there are essentially no terrestrial or anthropogenic sources (or sinks) in the latitude band between the two sites the conclusion has been drawn that the polar Southern Ocean is a small net source of CO_2 to the atmosphere, which is opposite to the situation shown in Fig. 5. The most recent analysis of the atmospheric data (Rodenbeck *et al*. 2003) continues to show this effect, and the discrepancy remains unresolved.

A third approach to this problem is through the use of numerical models. These have been used to estimate the net air-sea flux of CO_2, as well as the amount of anthropogenic carbon which has entered the oceans over a particular time period. A number of models have been constructed and run, and intercomparison of the model outputs has been organized through the OCMIP ('Ocean Carbon Model Intercomparison Project') activity of IGBP-GAIM (International Geosphere-Biosphere Programme-Global Analysis Interpretation and Modelling). The results from the model intercomparisons for the net air-sea flux of CO_2 by latitude band during the 1990s are shown in Fig. 6 and for the cumulative uptake of anthropogenic CO_2 since the Industrial Revolution in Fig. 7. In these models, it is generally the Wanninkhof (1992) parameterization which is used for the CO_2 transfer velocity.

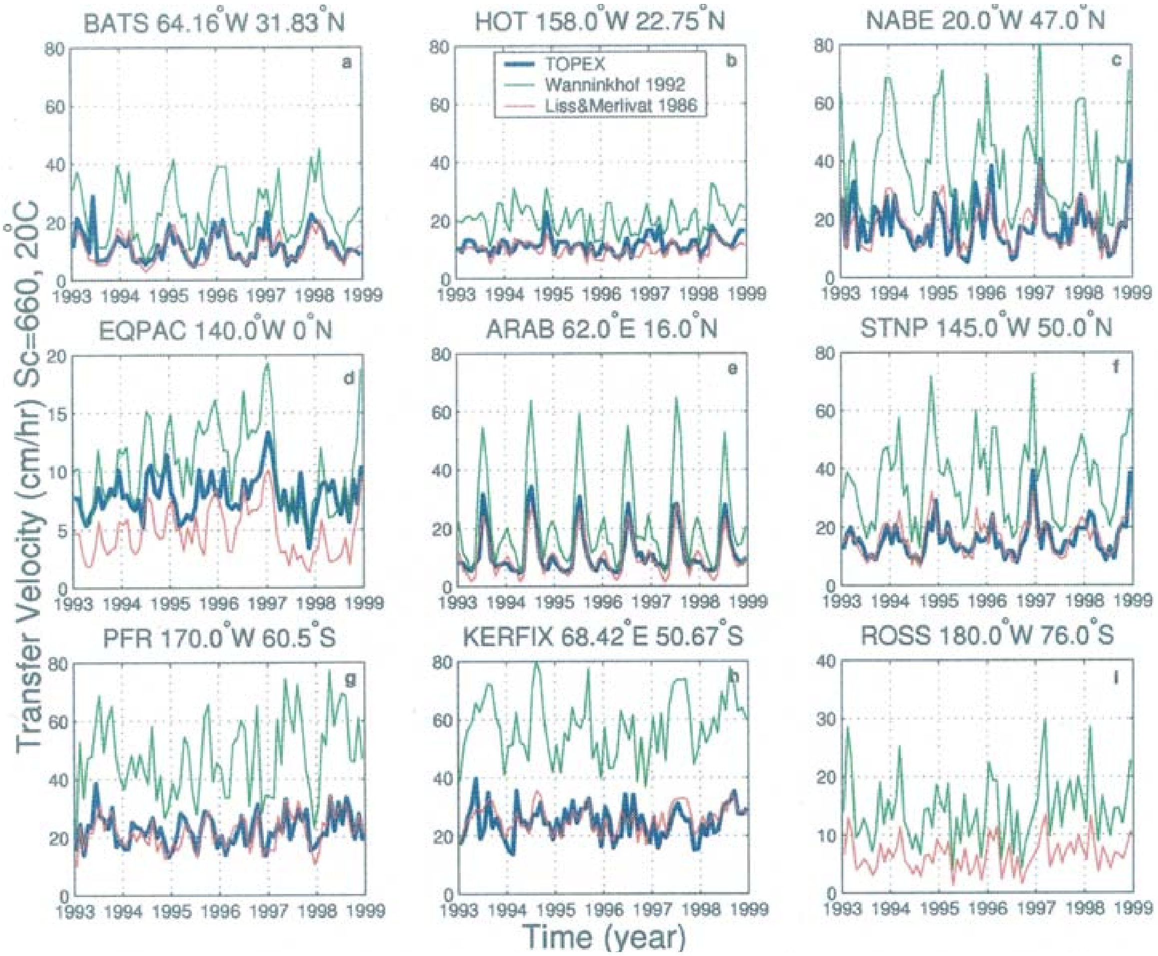

Fig. 4. Six year time-series of gas transfer velocity at 9 JGOFS sites around the globe. Gas transfer velocities derived from the TOPEX algorithm are shown in blue, from Wanninkhof (1992) in green, and from Liss & Merlivat (1986) in red (Glover *et al*. 2002).

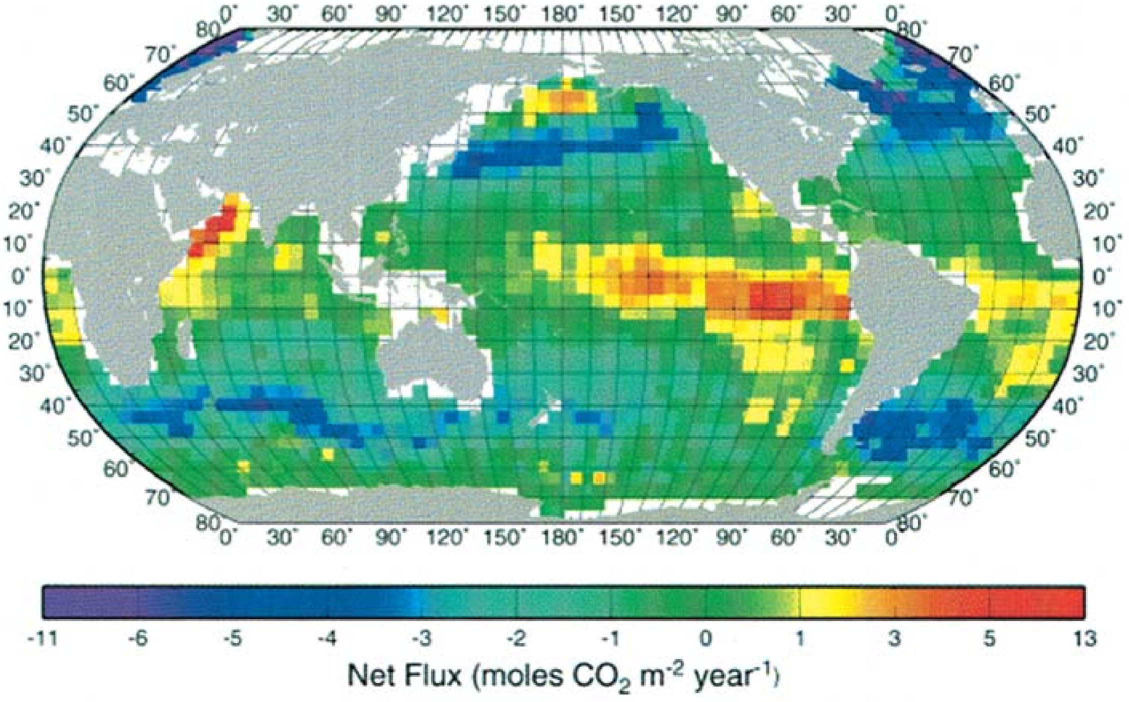

Fig. 5. Global climatology of the annual net air-sea CO_2 flux based on interpolation of air-sea pCO_2 differences referenced to the year 1995 (Takahashi *et al*. 2002).

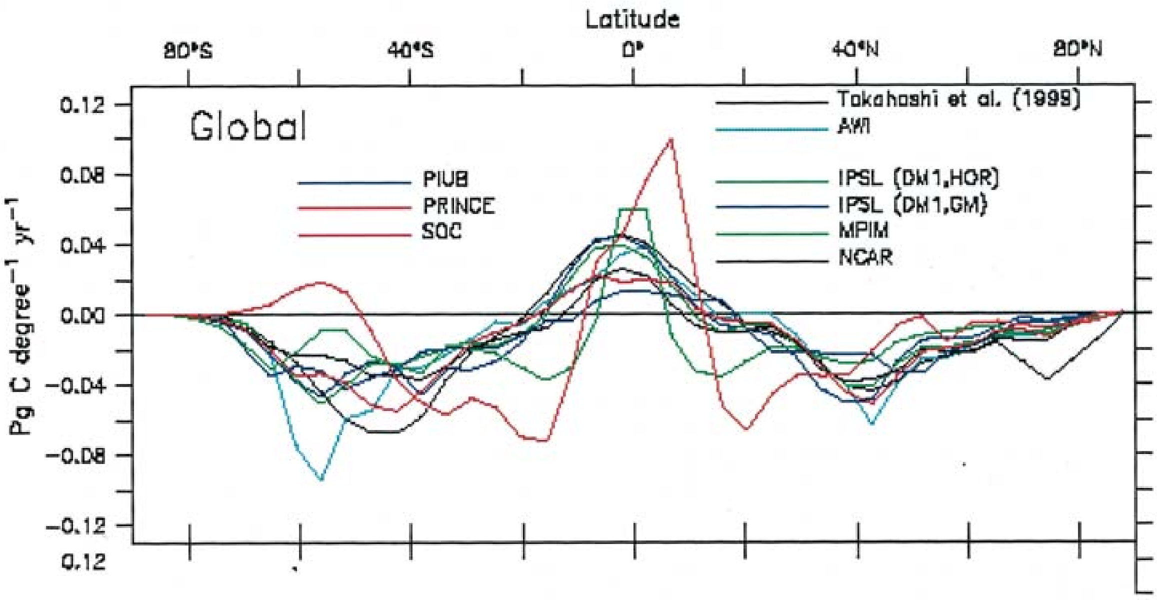

Fig. 6. Comparison of the output of various models for the net air-sea flux of CO_2 by latitude band during the 1990s (Ocean Carbon Model Intercomparison Project 2 (OCMIP-2 http://www.ipsl.jussieu.fr/OCMIP/)).

The results shown in Fig. 6 indicate that there is reasonable agreement over the gross features of the areal distribution of CO_2 oceanic sources and sinks, with the tropics being sources to the atmosphere and temperate and high latitude (non-ice covered) regions being sinks. There is general concordance between this overall pattern and that shown in Fig. 5 for the approach through Eq. (1). Notwithstanding the apparent agreement between the models, we note that this is rather better in the northern compared with the southern hemisphere. This divergence is particularly marked between 40ºS and 80ºS, where there is disagreement even over the sign of the net flux direction, with most models indicating a net sink but with one showing a net source. Since this zone covers Antarctic waters, this lack of agreement is particularly relevant to the present discussion.

Turning to Fig. 7, we note that from 80ºN to about 30ºS the agreement between the different models for the

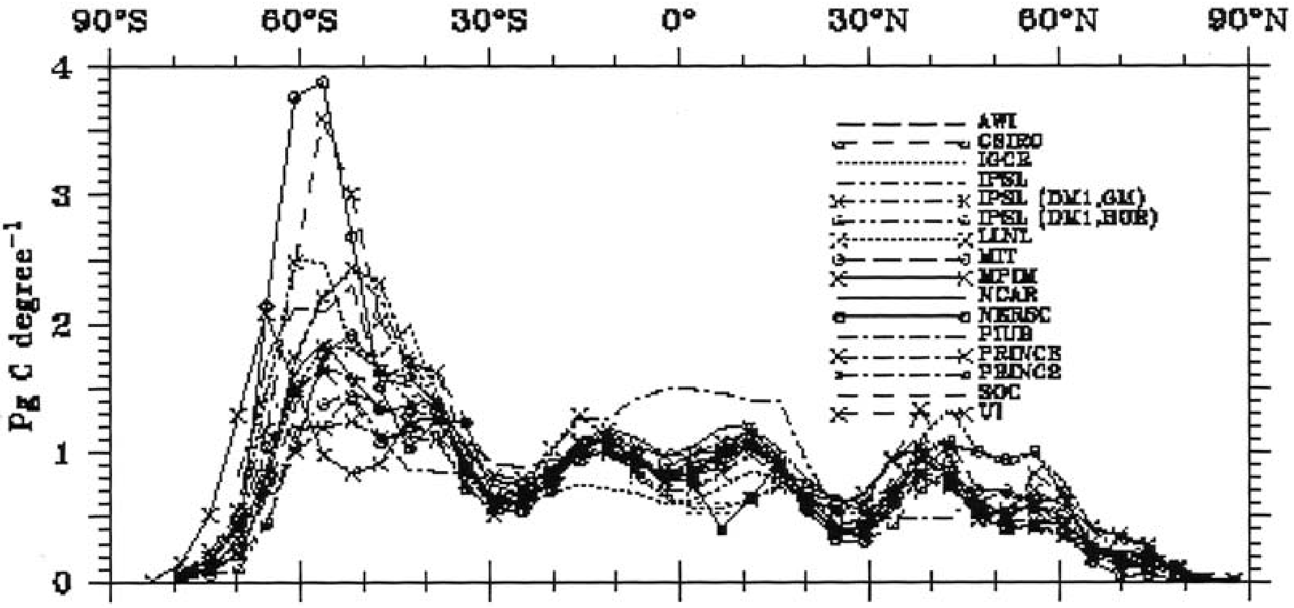

Fig. 7. Comparison of the output of various models for the cumulative uptake of anthropogenic CO_2 since the Industrial Revolution (Ocean Carbon Model Intercomparison Project 2 (OCMIP http://www.ipsl.jussieu.fr/OCMIP/)).

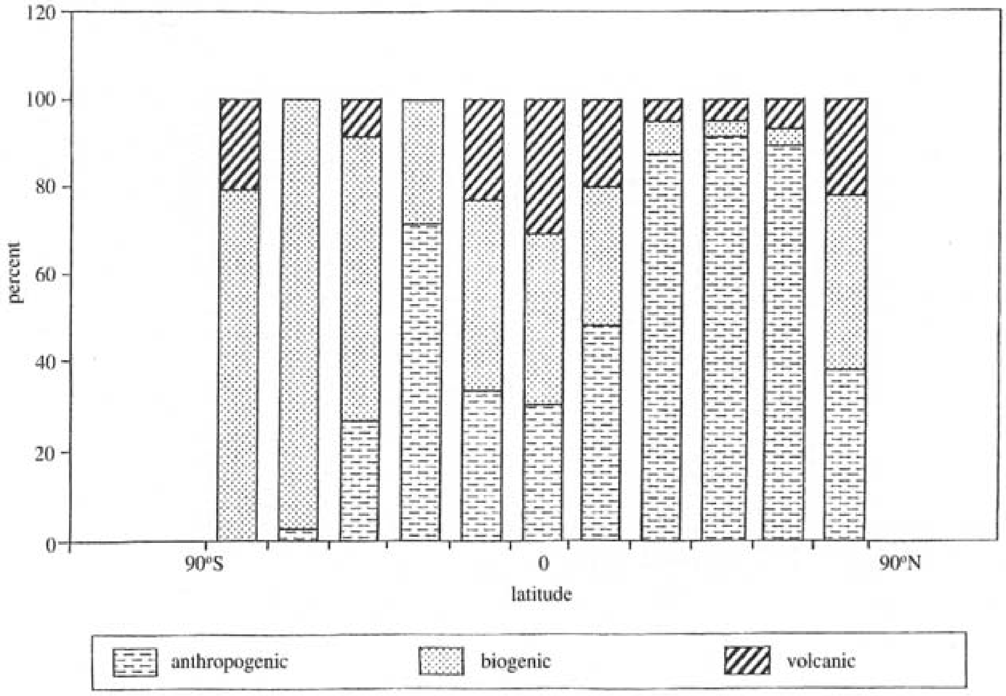

Fig. 8. Latitudinal dependence of percentage contribution of sulphur emissions from anthropogenic, biogenic, and volcanic sources (after Bates *et al.* 1992).

cumulative uptake of man-made CO_2 is generally rather good. However from 30ºS southwards the models show widely differing results, although this region is where the highest uptake rates are predicted by almost all the models. Again this indicates the large uncertainties which exist over the size of the southern hemisphere oceanic, including Antarctic waters, sink for anthropogenic CO_2, although stressing its quantitative importance in the global carbon budget.

The reasons for the discrepancies between the various models for both CO_2 exchange and uptake of anthropogenic carbon are not well understood. Particular uncertainties include lack of knowledge on how deep waters mix and the structure of convection and overturning, as well as how these processes should be incorporated into numerical models. The situation is exacerbated by the paucity of data from field measurements with which to 'tune' the models.

Recently results of ocean inversion models for the global air-sea fluxes of CO_2 have been published (Gloor *et al.* 2003). These calculations also rely on knowing the ocean circulation, which is taken from an ocean General Circulation Model. They estimate what air-sea flux, integrated over decades, would be needed to reproduce the observed distributions of "excess CO_2". Like the forward based model estimates, this technique indicates that the Antarctic region is a substantial sink, with much of the uptake being carried northward in newly formed Antarctic Intermediate water.

Dimethyl sulphide

The gas dimethyl sulphide (DMS) is produced by various algal species in the surface oceans (Liss *et al.* 1997) and is a major component of the natural sulphur cycle (along with emissions of sulphur volatiles from volcanoes). On emission from the sea to the atmosphere DMS is oxidized to form a number of products (including methane sulphonic acid, SO_2 and sulphate) which are important for the acid/base chemistry of atmospheric aerosols and precipitation, as well as in the formation and growth of particles which can act as cloud condensation nuclei (CCN) and so affect cloud albedo and hence climate (Charlson & Rodhe 1982, Charlson *et al.* 1987). In industrialized and heavily populated areas of the globe, particularly in the Northern Hemisphere, this natural cycle is strongly overlain by man-made emissions of SO_2 and its sulphate oxidation product. Bates *et al.* (1992) have estimated the relative contribution to sulphur emissions to the atmosphere from anthropogenic, marine biogenic (DMS) and volcanic sources; the results are shown in Fig. 8.

It is clear from Fig. 8 that oceanic biogenic sources are dominant at many latitudes in the Southern Hemisphere, particularly so south of about 45º, whereas man-made sources dominate for much of the Northern Hemisphere. Thus, by far the best place to study the natural sulphur cycle is in the southernmost half of the Southern Hemisphere, including Antarctic waters, where the natural cycle operates without major confusion arising from the effect of man-made emissions. A further reason for making such studies in these relatively pristine areas of the globe is because the number density of cloud condensation nuclei (CCN) tends to be low due to the small percentage of ice-free land area and the relatively small role of anthropogenic combustion processes, both of which are sources of CCN to the

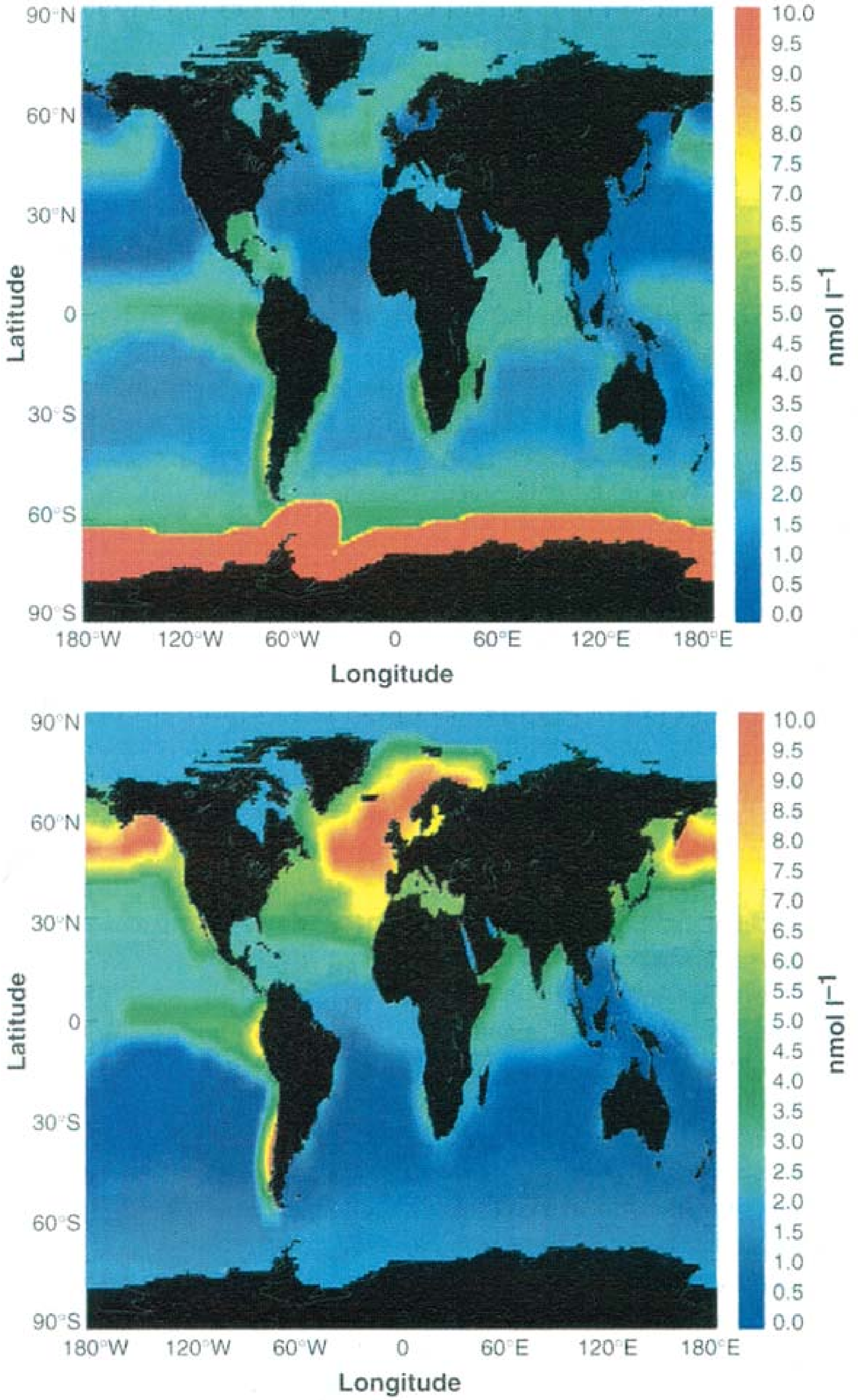

Fig. 9. Global distribution of sea surface dimethyl sulphide (DMS) concentrations for January (upper panel) and July (lower panel) (from Kettle *et al*. 1999).

atmosphere. As Twomey (1991) has shown, the relationship between CCN number density and cloud albedo is highly non-linear, with cloud albedo being most susceptible to change in CCN at low particle numbers, e.g. in the Antarctic marine atmosphere, which is far from ice-free land and pollution sources of particles.

Although such environments are scientifically the obvious places for studying the DMS system, due to their remoteness and often poor weather conditions rather little data exists for these areas. Kettle *et al*. (1999) assembled the

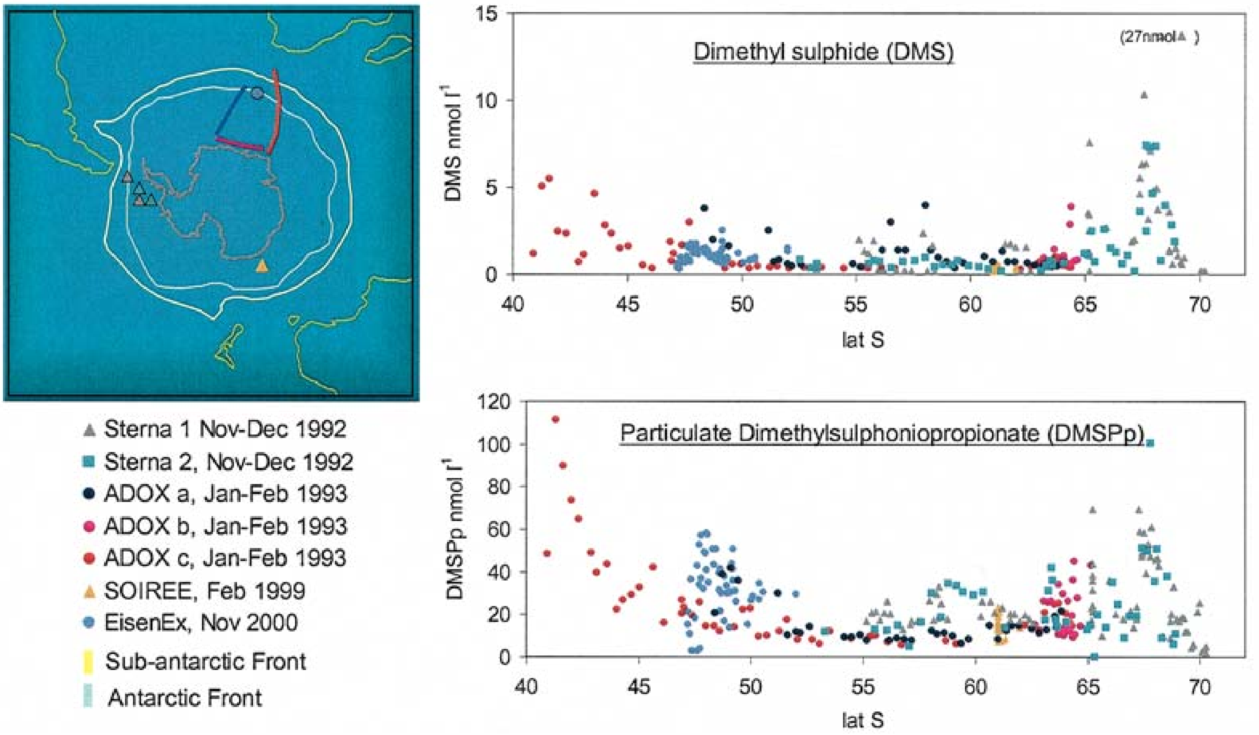

Fig. 10. Dimethyl sulphide (DMS) and particulate dimethylsulphoniopropionate (DMSPp) concentrations measured on several cruises in the Southern Ocean.

global data set of DMS measurements in seawater, comprising almost 16 000 individual data points. This has now been supplemented by T. Bates and J. Johnson with an additional 6000 measurements and the entire data set is accessible online (http://saga.pmel.noaa.gov/dms/). Although this may seem like a large number of observations, it is rather small compared with the more than a million observations which make up the equivalent CO_2 dataset (Takahashi *et al*. 2002), discussed earlier. However, the comparison is over simplified since the DMS flux is a one-way flow out of the oceans, whereas the net CO_2 exchange is the result of the difference between two large in and out fluxes, which require a large number of observations for their accurate definition. As with the situation for CO_2, the DMS water concentrations show considerable spatial and temporal (particularly seasonal) variability. At a global level this strong seasonality is well illustrated by the Kettle *et al*. data compilation, as shown in Fig. 9, which gives the oceanwide distributions of DMS in seawater for January and July.

Table I. Summary of data in Fig. 10 by latitude band (all concentrations are in nmol l^{-1}).

lat band, °S	avg. DMS	min. DMS	max. DMS	avg. DMSPq	DMS sample no.
40 to 45	2.71	0.72	5.50	54.71	11
45 to 50	1.22	0.32	3.78	30.73	65
50 to 55	0.72	0.31	2.53	15.79	26
55 to 60	0.88	0.20	3.97	16.44	42
60 to 65	0.69	0.16	3.94	17.84	85
65+	3.35	0.20	27.03	27.85	58

Table II. DMS fluxes for Antarctic summer (October–March) calculated using different parameterizations of the transfer velocity, K. Data are given as means and ranges, in parentheses, for two regions of the Antarctic Ocean. Seasonal, mean sea surface temperatures and wind speeds are from the Climate Diagnostics Center, NOAA-CIRES: 2°C, 9 m sec^{-1} for 55°S–65°S and -1°C, 6.5 m sec^{-1} for 65°S–75°S.

		Flux µmol m^{-2} summer^{-1}		
Region	DMS nmol l^{-1}	L&M 1986[c]	Night 2000[d]	W&M 1999[e]
55°S–65°S[a]				
This work	0.79 (0.18–4.0)	276 (63–1389)	362 (83–1821)	352 (81–1772)
Kettle *et al*. 1999	3.0 (3.5–5.0)	1054 (1229–1756)	1381 (1612–2302)	1344 (1568–2240)
65°S–75°S[b]				
This work	3.35 (0.2–27.0)	599 (36–4833)	779 (46–6287)	519 (31–4188)
Kettle *et al*. 1999	11.0 (13–25)	1967 (2325–4470)	2558 (3024–5815)	1704 (2014–3873)

[a,b] approximate to Longhurst provinces, Antarctic (ANTA) and Austral Polar (APLR), respectively.
[c] Liss & Merlivat 1986.
[d] Nightingale *et al*. 2000b.
[e] Wanninkhof & McGillis 1999.

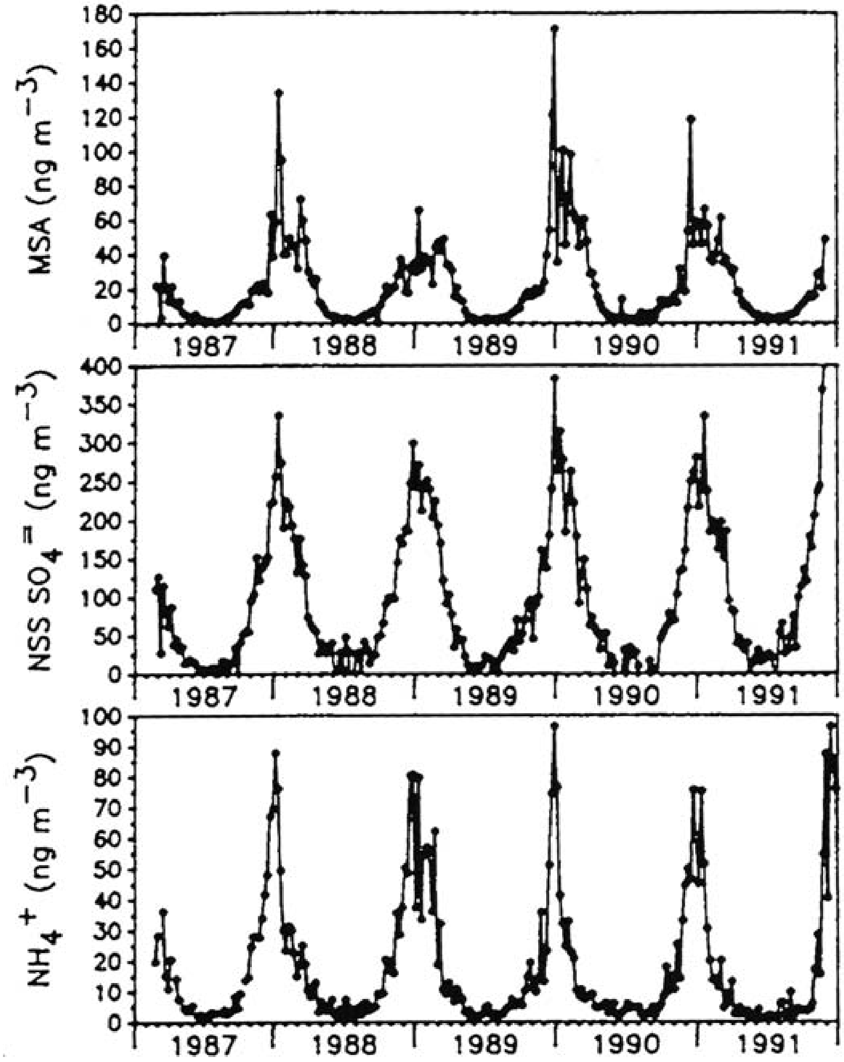

Fig. 11. Time series of weekly-average atmospheric aerosol concentrations of methane sulphonic acid (MSA), non-sea salt sulphate (NSS SO^{2-}_4) and ammonium (NH_4^+) at Mawson, Antarctica (from Savoie *et al.* 1993).

The results shown in Fig. 9 show particularly high DMS levels in Antarctic waters in Southern Hemisphere summer. However, closer examination of the Kettle *et al.* dataset indicates a severe paucity of measurements in this region, and with a significant bias towards inshore and coastal water compared with open ocean areas. Thus, the high DMS concentrations in Fig. 9 should be treated with caution. More detailed information on the situation in Antarctic waters, particularly for the data-poor offshore oceanic waters, is shown in Fig. 10 and summarized in Table I. Also included are measurements of dimethylsulphoniopropionate (DMSP), the algal precursor of DMS.

In order to assess how the flux of DMS from Antarctic waters is controlled by concentration fields and transfer velocities, we have constructed Table II. This is only for the summer season since there are no published data for the winter period. Calculation of fluxes for winter would be further complicated by the presence of sea ice. We have used three parameterizations for the transfer velocity since there is currently no consensus on a best method, as discussed earlier. The fluxes are calculated using seasonal averages for DMS, temperature and wind speed because there are insufficient data for a month by month analysis. The results show that there is little variation in the fluxes calculated from the different transfer velocities and that the major difference is caused by the variation in DMS, with the Kettle *et al.* data producing much higher fluxes. The reason that the different transfer velocity formulations produce rather similar fluxes is due to the mean summer wind speeds in the region, which lie in the range where the three parameterizations all predict similar values of K. At higher or lower wind speeds significantly greater differences in flux would be obtained. Since the major uncertainty in the sea-to-air emission of DMS in Antarctic waters lies with the concentration field, it should be relatively straightforward to improve our knowledge by increasing the number of measurements, at least for the summer period.

Notwithstanding the above discussion on DMS concentrations and fluxes in Antarctic waters, the seasonality shown by the data is clearly established (Turner *et al*. 1995, Kettle *et al*. 1999), as is expected for a biologically formed gas such as DMS. This strong seasonal pattern is confirmed by atmospheric measurements of the main oxidation products of DMS in air (methanesulphonate (MSA) and non-sea salt sulphate (NSS SO^{2-}_4) in the Antarctic region. The data set from Savoie *et al*. (1993) of MSA and NSS SO^{2-}_4 in atmospheric aerosols collected over a five year period at Mawson (67º36'S, 62º30'E), a coastal site on Antarctica, is shown in Fig. 11.

The marked and consistent seasonal pattern for these DMS oxidation products in clear from the figure. In addition a similar seasonality is also shown by ammonium (NH_4^+), for which an analogous cycle of seawater ammonia production and emission to the atmosphere has been proposed (Liss & Galloway 1993). Although significantly north of Antarctic waters, confirmation of these seasonal effects is provided by the large data set of atmospheric measurements collected over many years at Cape Grim (40º41'S, 144º41'E) and summarized in Ayers *et al*. (1997) and Ayers & Gillet (2000). These data also provide evidence for the role of marine DMS emissions in the formation of CCN and in affecting cloud albedo (Boers *et al*. 1994).

We can conclude that Antarctic waters are quantitatively a very important component of the natural sulphur cycle, without knowledge of which there is great difficulty in assessing any anthropogenic perturbation produced by current and potential future emissions of sulphur to the atmosphere. These inputs are currently largely in the heavily industrialized northern regions of the globe but in future may show large increases in the Southern Hemisphere, where the naturally low levels of aerosol particles will make the impact on cloud albedo even more profound (Twomey 1991). Despite their importance, Antarctic waters and atmosphere are severely understudied with respect to the sulphur cycle due to their remoteness and poor weather conditions. In order to calculate air-sea fluxes of DMS, we lack coverage of concentration measurements both spatially and with season, and because of the generally higher wind regime the uncertainty in transfer velocity values is greatest, as discussed earlier.

Organo-halogens and alkyl nitrates

Organo-halogen gases (in this context, single carbon compounds containing up to four individual or mixed halogen atoms) and alkyl nitrates (here particularly methyl and ethyl nitrates) are trace volatiles formed in the near-surface oceans by either microbiological and/or photochemical processes. In general they are supersaturated in seawater relative to their atmospheric concentrations so that there is a net flux from oceans to atmosphere (Moore & Groszko 1999, Chuck 2002, Chuck *et al*. 2002, Quack & Wallace 2003). Once in the lower atmosphere they are subject to breakdown, the products of which can have important implications for the level of oxidants, particularly ozone and OH radicals, which are major controls on the atmosphere's capacity to cleanse itself of natural and man-made compounds. Organo-halogens with longer lifetimes can also play a role in the breakdown of stratospheric ozone (WMO 1999).

Studies of organo-halogen gases in the Antarctic region are few but those which have been carried out suggest that these waters may be strong producers of brominated compounds (Fogelqvist & Tanhua 1995, Schall *et al*. 1997), particularly in sea ice communities (Sturges *et al*. 1993). In contrast, concentrations of iodinated compounds are reported to be significantly lower in Antarctic waters than in other ocean areas (Chuck *et al*. unpublished), which may provide some useful clues as to the production mechanisms for halogenated gases.

Although there are currently no direct measurements of alkyl nitrates in Antarctic waters, there is indirect evidence of an important marine source in this area. For example, high atmospheric levels of methyl nitrate have been measured at Neumayer Station on Antarctica (70º37'S, 8º22'W) (Jones *et al.* 1999, McIntyre 2001), as well as between 45º and 70ºS (Talbot *et al*. 2000), which leads these authors to invoke a significant marine source. A study by Jones *et al*. (1999) of the budget of oxidized nitrogen in the coastal Antarctic troposphere has shown that alkyl nitrates, and in particular methyl nitrate, dominate the budget. Jones *et al*. suggest that, if their data are representative of the wider Antarctic troposphere, the nitrate observed in ice cores is likely to arise predominantly from organic, as opposed to inorganic, sources, as has been generally assumed. Thus, it is important to study the alkyl nitrate budget not only because of its importance for understanding the chemistry of the Antarctic atmosphere currently but also to aid in interpretation of the nitrate record in Antarctic ice cores. Given the very small data base of concentration measurements for organo-halogens and alkyl nitrates in the Antarctic region, an assessment of the variability and uncertainty in air-sea fluxes is unwarranted at present.

Summary

The above discussion on air-sea gas exchange in Antarctic waters leads to the following straightforward conclusions:

1) The Antarctic region is poorly studied and sampled due to its remoteness and rough weather conditions.

2) Despite the difficulties posed by 1), it is clear that the region is an important player in the natural carbon cycle and a major sink for anthropogenic CO_2. The Southern Ocean is an area where the mathematical models of CO_2 uptake and exchange show the greatest discrepancies.

3) Because of the weakness of other sources of particles, the role of DMS as a precursor of new particle

formation and growth is particularly important in the region.

4) Despite having been little studied, the role of organo-halogen and alkyl nitrate gases appears to be significant for atmospheric redox chemistry in the Antarctic atmosphere.

5) Due to the high wind regime, estimation of air-sea transfer velocities for Antarctic waters are subject to significantly greater uncertainties than for other ocean areas.

6) Research priorities identified in this paper include: i) Field intercomparison studies of the various approaches now available for estimating air-sea gas transfer velocities, and the processes that control them, ii) Enhancement of the existing data bases for CO_2 and DMS in Antarctic waters, particularly for the former in winter and for both in terms of spatial coverage, iii) Establishment of a data base of concentration measurements for calculating air-sea fluxes of trace gases important for atmospheric composition and climate, to include organo-halogens, non-methane hydrocarbons, alkyl nitrates, NH_3, N_2O *inter alia*.

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