

# UNCERTAINTIES IN FLUX ESTIMATIONS OF BIOGENIC GREENHOUSE GASES FROM THE WORLD'S OCEANS

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We determine the concentrations of  $N_2O$ ,  $CH_4$ ,  $OCS$  and  $(CH_3)_2S$  (DMS) in surface waters of estuaries, shelf, shelf edge, open oceans using continuous equilibration techniques and automated gas chromatography (RAPSOMANIKIS *et al.*, 1994). Atmospheric concentrations of these gases are also determined in tandem. Horizontal profiles during cruise tracks have time resolution of up to one hour (in the worst case of  $OCS$ ). Super- or under-saturation of surface sea waters for these gases is established, after computing equilibrium air-sea values using our high precision atmospheric concentration measurements and Henry law constants. The following basic equation for flux density calculations of the *i*th gas is used :

$$F_i = K_i \cdot \Delta C_i \quad (1)$$

where  $F_i$  = flux density, in units of concentration (mass/volume)/unit area/unit time

$K_i$  = mass transfer coefficient in units of length/unit time

$\Delta C_i$  = concentration difference between the atmosphere and surface waters in units of concentration i.e. mass/ volume.

The concentration difference,  $\Delta C_i$ , can be measured relatively accurately and precisely with modern instrumental, automated methods and the equilibrium calculations described above. In the case of DMS concentration of ocean surface waters exceed atmospheric concentrations by orders of magnitude, so that in flux density measurements one can ignore the later in calculating DCDMS. Large uncertainties persist on the parameterisation of the mass transfer coefficient  $K_i$ .

The simple case of DMS fluxes is treated here, using results from two cruises. The first cruise took place near the Antarctic peninsula between 10 December 1991 and 2 January 1992 (PFS Polarstern; Cruise ANT X/1b). The second cruise took place in the Eastern Mediterranean (Aegean, Levantine and Ionian Seas) between 2-18 July 1993 (RV Aegaio; Cruise "EGAMES"). Sea surface water samples were collected, filtered on line and analysed using a literature method (ANDREAE and BARNARD, 1983). In brief, a measured volume of water was purged with helium, the volatile DMS was trapped in a U tube filled with chromatographic packing and cooled to liquid nitrogen temperatures. Upon heating, DMS was separated from other volatile sulphur compounds, and detected in a sulphur selective FPD (flame photometric detector). Quantification was carried out using a series of liquid DMS standards in glycol, added to, DMS free, sea water. Surface sea water temperature, salinity, absolute wind speed and other meteorological parameters were continuously recorded from the ship's sensors. The DCDMS values obtained from the above cruises are treated using the  $K_i$  values obtained from equations obtained from experiments using: (a)  $SF_6$  as a tracer in lakes (UPSTILL-GODDARD *et al.* 1990), (b)  $SF_6$  and  $^3He$  as dual tracers in stormy seas (Watson *et al.* 1991), which is based on the Liss and Merlivat model, (c)  $SF_6$  and  $N_2O$  in a large wave generating wind tunnel (WANNINKHOF and BLIVEN 1991) and (d) an empirical approach for air-water gas exchange (GOSINK 1992). The two cruises present two contrasting environments for the calculation of flux densities of DMS. On one hand the productive and cold Antarctic waters with moderate to high wind velocities prevailing at the time of the cruise and on the other hand the Eastern Mediterranean marginal seas with high sea surface temperatures, low DMS concentrations and low wind velocities, are considered. Transfer coefficients calculated for the prevailing conditions at the time of sampling and using calculation methods (a) to (d) were used in equation (1) to determine flux densities for each cruise. Because of the uncertainties involved in each calculation method of these coefficients, the uncertainty of the flux densities calculations may also be within a factor of two. The values of the coefficients calculated by methods (a) to (d) fall within the uncertainty of each other. In a simple error propagation exercise, the overall uncertainty never exceeds 50%. At very high DMS concentrations and moderate wind velocities the flux densities are concentration dominated. At medium to high wind velocities and low DMS concentrations, there is no dominant factor for at least three of the models (Mediterranean cruise). It is hence obvious that there exists not a simple and single way of establishing the accuracy of these estimates across the wind velocity and concentration spectrum. It is also obvious that simple parameterisation of  $K_i$  against wind velocity, sea water temperature and diffusion coefficients, is not always possible. A number of other parameters like breaking waves and bubble formation may need determination and consideration in the calculation of  $K_i$  (WALLACE and WIRICK, 1992; FARMER *et al.*, 1993). An alternative, but not simple way, is to directly measure flux densities i.e. the  $F$  parameter in equation (1), using the "eddy correlation" technique. A stable platform, or corrections for the movement of the sampling platform (ship, buoy or floating platform) are necessary in this case. Also, corrections for flow distortions due to the shape of the sampling platform or the inflow of air to the sampling lines, are necessary. A fast response, sensitive, detector is also required for the gas(es) that are going to be measured so that fluctuation in vertical flux densities can be resolved. If  $\Delta C_i$  can be calculated by determining the concentration of the *i*th gas in the surface sea waters, then  $K_i$  can be determined using again equation (1). Parameterisation of the  $K_i$  in these measurements will depend on the number of parameters measured at the time. The uncertainties in measuring flux densities and hence fluxes of greenhouse gases from the world's oceans have been assessed by treating data for DMS flux densities from two contrasting oceanic areas. The possibility to measure transfer coefficients by the "eddy correlation" method is appealing but not simple.

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