CHAPTER 5

Experimental Results on DMSP and DMS
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5.1 Influence of salinity shock on DMSP production by plankton

As detailed in section 2.1.3 a diatom species (*Skeletonema Costatum*) was subjected to salinity shock by adjusting the salinity of the ambient medium through the addition of deionised water. In order to follow the effect of state of growth on DMSP production plankton cultures of two days (young and in active growing phase) and eleven days (almost near stationary growth phase) old plankters were used in this experiment. The cultures were grown at a salinity of about 35 and temperature of 28°C. Shock experiments were conducted over a salinity range of 20 to 35. In addition to DMSP (total, includes dissolved and particulate), phytoplankton cell numbers and chlorophyll a were also measured. Samples were subjected for DMS and DMSP analyses within 5 minutes of giving the salinity shock. Fig. 5.1 depicts the variations in these parameters in response to the amount of deionised water added. In spite of the overall decreasing trends in both DMSP observed (DMSP_{obs}) and DMSP expected (DMSP_{exp}, based on dilution) with increasing dilution the former is higher than the latter; with more or less equal difference particularly when added water was more than 10 ml (Fig. 5.1). This implies that salinity shock (or sudden gradient in salinity) is more important, than the extent of dilution, for the production of DMSP_t by the diatom. More significantly, the trend in increased DMSP production does not seem t
Fig. 5.1. Behaviours of DMSP expected (dashed line) and actual (continuous line) concentrations, and phytoplankton cell counts and chlorophyll during a salinity shock experiment on diatom in the laboratory. Blue symbols are for diatom cell numbers and green are for chlorophyll.
depend on the age of the diatom. However, aged (eleven day old) diatoms seem to be more sensitive and produce 3-5 times DMSP compared to that by younger ones (two day old). Even if we correct the total DMSP production to plankton cell basis, the aged plankton is evaluated to produce about twice than the young culture (Fig. 5.1). The hike in DMSP production occurs despite decreased phytoplankton cell numbers with dilution in both the cases. While chlorophyll in the two-day-old culture did not show no clear trend it decreased in the aged culture. The DMSP is known to function as an osmolyte in plankton cells [Dickson et al., 1980, 1982; Vairavamurthy et al., 1985]. Thus in order to maintain the osmotic pressure inside the body the phytoplankton produces DMSP to circumvent sudden changes in salinity, positive or negative. The above experiment reveals that changes in salinity are more important in the production of DMSP by plankton than the simple salinity of the ambient medium in which they grow. For instance, Stefels and Dijkhuizen [1996] reported negligible increase in the total DMSP content in the first 6 hours in cultures grown under different salinities ranging from 0 to 50 ppt. Thus we propose that it is the stress that leads to enhanced DMSP production. In the present case that stress was manifested in the form of sudden changes in salinity.

5.2 DMSP degradation

5.2.1 Decomposition in marine air

In the first experiment several membrane filter papers loaded with DMSP of 0.34 nmol were exposed to marine air at a height of 6m above the
Fig. 5.2. Loss of DMSP with time from a) loaded membrane filters in air and b) in seawater.
sea level. These filters were periodically removed and analysed for DMSP. Fig. 5.2a shows the degradation of DMSP in air. Results revealed a decreasing trend in DMSP with time; drastic fall occurred in the first 5 minutes of exposure (the minimum time we could allow between loading and analysis). A loss of over 90% in 5 minutes suggests that significant portion of ejected aerosol DMSP could be rapidly lost to atmosphere. The loss rate might have been underestimated because the allowed 5 minutes may have been longer for 90% decomposition of DMSP. The DMSP loss thereafter was relatively slow as 30% of 0.035 nmol, present after 5 minutes of exposure, was found on filters at 7 hours.

5.2.2 Decomposition in seawater

In the second experiment 0.081 nM of DMSP was introduced in a litre of seawater in a beaker. Before the experiment, the seawater sample (collected from surface) was exposed to ultraviolet radiation to deactivate microbial populations. Blank runs were made on the seawater sample prior to the addition of DMSP. The spiked seawater sample was exposed to sunlight, adjacent to the laboratory, on the main deck of the ship. The sample was periodically subjected to purging with air using syringe, in order to simulate the introduction of atmosphere species (chemical species, eg. Nox, hydroxyl radicals etc.) and possibly including bacteria. Aliquots of the seawater sample were periodically sampled and analysed for DMSP after alkali hydrolysis. Even here, as in filter experiments briefed above, a rapid fall in DMSP was found (Fig. 5.2b). The DMSP analysis here would represent the sum of DMS
and DMSP present in the seawater sample. Our results suggest that a compound (probably methanethiol) with a retention time of 1.5 min, was formed in significant concentrations during the hydrolysis. As the alkali hydrolysis of DMSP is expected to lead only to the formation of DMS and acrylic acid, the appearance of peaks with 1.5 min retention time indicates that the DMSP decomposition in seawater is possibly resulting in an intermediate compound, which upon hydrolysis yields methanethiol. Formation of such compound may also be possible during DMSP decomposition in air. The unknown intermediate compound should be studied in detail and characterized in order to understand the dynamics of dimethylsulphur compounds in the marine environment.

During a declining phase of *Emiliana huxleyi*, Levasseur et al. [1996] found decrease in DMSP concentrations coinciding with a sharp increase in bacterial abundance and growth. The rapid loss of DMSP, as in our experiments, indicated the involvement of bacteria. Bacteria have been found to utilize DMSP and convert it to methanethiol. The methanethiol is later converted to methionine and taken up in the amino acid pathway [Simo and Pedros-Alio, 1999]. The above fall in the levels of DMSP on the filter paper and in seawater can thus be attributed to the rapid removal by photolytic and chemical reactions or possibly bacterial degradation.
The salient features from laboratory experiments are:

1. Salinity shock enhances DMSP production in phytoplankton.

2. DMSP production during the shock experiments does not depend on exposure time and salinity of medium.

3. DMSP is unstable in marine air and seawater and can be decomposed by chemical species, photolysis or bacteria.

4. During the DMSP decomposition to DMS there appears to be an intermediate product, which upon alkali hydrolysis possibly yields methanethiol.