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Biological turnover of DMS, DMSP and DMSO in contrasting open-sea waters

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ABSTRACT: Speciation and turnover of the methylated sulfur compounds dimethyl sulfide (DMS), dimethylsulfoniopropionate (DMSP) and dimethyl sulfoxide (DMSO) were studied in waters of the open western Mediterranean, the near-coastal North Sea and the subpolar North Atlantic, with chlorophyll *a* concentrations spanning 2 orders of magnitude (0.12 to 13 µg l^{-1}). Particulate DMSP ($DMSP_p$: 5 to 340 nM) was the predominant pool in most waters. Dissolved and particulate dimethyl sulfoxide were also found at significant concentrations ($DMSO_d$: 2 to 25 nM, $DMSO_p$: 3 to 16 nM). Biological DMSP consumption rates were estimated from the time course of total (dissolved + particulate) DMSP concentration in dark incubations. Dimethyl sulfide production and consumption rates were determined by the 'inhibitor addition' method. High DMS production and consumption rates were found during a bloom of *Phaeocystis* sp. in North Sea waters. In all samples, turnover time constants for total DMSP and DMS were of the same order, ranging from 0.7 to 5.4 and from 0.3 to 2.1 d, respectively. DMS formation was the fate for 9 to 96% of the DMSP consumed. Use of chloroform as an inhibitor gave estimates of DMS production and consumption rates approximately 70% higher than those obtained with dimethyl disulfide and dimethyl selenide. In some incubation experiments, the time course of DMSO concentration has been followed along with DMS and DMSP for the first time. Evidence for active biological cycling (production and consumption) of DMSO in seawater is presented.

KEY WORDS: Dimethyl sulfide · Dimethylsulfoniopropionate · Dimethyl sulfoxide · DMS · DMSP · DMSO · Inhibitor technique · Bacteria · Phytoplankton

INTRODUCTION

In the last 2 decades, methylated sulfur compounds have attracted a great deal of attention from marine scientists for several reasons. Firstly, surface seawater concentrations of dimethyl sulfide (DMS) are sufficient that its emission accounts for ca 50% of the global biogenic source of sulfur to the atmosphere (Bates et al. 1992, Liss et al. 1997), thereby affecting atmospheric chemistry and the global radiative balance (Charlson et al. 1987, Andreae 1990, Malin et al. 1992). Secondly, the tertiary sulfonium compound dimethylsulfoniopropionate (DMSP) is a major form of reduced sulfur in marine particulate matter. DMSP is synthesized in algal cells, where it plays a number of important physiological roles related to its properties as a compatible solute (e.g. Kiene et al. 1996, Malin & Kirst 1997). DMSP may constitute as much as 10 to 20% and 50 to 90% of cellular organic carbon and sulfur, respectively, in phytoplankton known to produce large amounts of DMSP (Bates et al. 1994, Matrai & Keller 1994, Matrai & Vernet 1997). A third reason is that methylated sulfur compounds are potential C_1 substrates that can represent an important source of carbon, reduced sulfur and/or energy for bacterioplankton (Kiene 1993, Kiene et al. 2000, Simó et al. unpubl.). Indeed, a study indicated that DMSP-degrading bacteria can account for up to 10% of total bacteria at an open-ocean site (Visscher et al. 1992).

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Hence, because of its biogeochemical, ecological and biochemical implications, interest in methylated sulfur is currently increasing and diversifying (Kiene et al. 1996). In the epipelagic marine environment, methylated sulfur undergoes a maze of transformation processes involving a number of chemical species, including DMSP, DMS, dimethyl sulfoxide (DMSO) and methanethiol (CH_3SH). Increasing understanding of methylated sulfur cycling requires combining the study of individual production and turnover processes relative to the distribution of the particulate and dissolved pools of these different compounds.

DMSP release from phytoplankton and its degradation involves all levels of the food web, from viruses and bacteria to grazers (Dacey & Wakeham 1986, Belviso et al. 1990, Kiene & Bates 1990, Stefels & van Boekel 1993, Malin et al. 1998). Cleavage of DMSP by bacterial and algal DMSP-lyases is considered to be the main source of aqueous DMS, which in turn can be utilized by bacteria (e.g. Kiene & Bates 1990, Taylor 1993, Wolfe & Kiene 1993a). Alternative routes for microbial DMSP utilization exist, involving either uptake as osmotic solute (Wolfe 1996), double demethylation or demethylation and demethiolation to CH_3SH (Taylor & Gilchrist 1991, Visscher et al. 1992, Taylor 1993, Kiene 1996a,b). Furthermore, the latter compound can be used as a source of methionine to be incorporated into protein (Kiene et al. 1999). Recently, it has been recognized that DMSO is a ubiquitous pool of methylated sulfur in seawater and marine microorganisms (Simó et al. 1995, 1997, 1998a, Hatton et al. 1996, 1998, 1999, Lee & de Mora 1996, 1999), but very little is known about its origins and fate in the epipelagic zone.

This work reports on the biological cycling of DMS, DMSP and DMSO in a variety of marine waters: the oligotrophic, open, western Mediterranean Sea in summer, the shallow, near-coastal North Sea and the subpolar North Atlantic. The *inhibitor addition* and *net-loss curve* approaches have been used to determine microbial production and consumption rates. The methodological aspects of these approaches are discussed. A novel aspect of our work is that DMS and the particulate and dissolved pools of DMSP and DMSO have been monitored simultaneously in seawater incubation experiments for the first time. We present results that provide evidence for DMSO undergoing active biological cycling.

MATERIALS AND METHODS

Sulfur analyses. DMS, DMSP and DMSO were analyzed following methods of reaction, purge, cryogenic trapping and sulfur-specific gas chromatography described elsewhere (Simó et al. 1996, 1998b). Analytical error was ≤10% (coefficient of variation) and detection limit was 3 pmol S. Compounds measured in 5 to 50 ml aliquots of seawater filtered through Whatman GF/F glass fiber filters (nominal pore size: 0.7 µm) were operationally considered as 'dissolved'. The filters were treated for determination of 'particulate' (GF/F-retained) DMSP and DMSO. Total DMSP ($DMSP_t$) and DMSO ($DMSO_t$) were calculated as the sum of the dissolved and the particulate pools, except in the North Atlantic incubations, where $DMSP_t$ was determined by subtracting DMS from hydrolyzed unfiltered samples.

Sampling. Samples used in this study were collected during oceanographic cruises in the open Mediterranean Sea (June 1995) and the North Atlantic Ocean (June/July 1998), and boat trips to the North Sea (June, July and August 1996). Sample dates, locations and description are given in Table 1. Ship track and sampling routines for the Mediterranean cruise onboard the RV 'Hespérides' are reported elsewhere (Simó et al. 1997). The North Atlantic samples were taken on board the RRS 'Discovery' during the UK Natural Environmental Research Council's Atmospheric Chemistry Studies of the Oceanic Environment—Marine Aerosol and Gas Exchange (ACSOE—MAGE) North Atlantic Experiment (Simó & Pedrós-Alió 1999a). Regarding the waters for the 6 North Atlantic experiments, they were all taken from the surface bottle of the CTD casts, except the last one which was collected from surface with a bucket. North Sea waters were collected at a station 10 km off Great Yarmouth (Norfolk, England). The water column depth was 29 m. Ten liter samples were taken in glass bottles (Simó et al. 1998a). In all cases, samples were stored cool in the dark and either analyzed or set up to incubate no more than 3 h (typically 1 h) after collection.

Incubation experiments. Unfiltered seawater was distributed into acid-rinsed glass bottles. In the Mediterranean and North Atlantic, 2 l amber bottles, capped with a ground glass stopper, were used. In the North Sea, we used clear 1 l bottles with Teflon septa and screw caps. In all cases, incubation bottles were completely filled at the start of the experiment, and the headspace created by withdrawing subsamples over time was always less than 25% of the total volume, so that cumulative losses of DMS by partitioning into the headspace were less than 3% of the original DMS. All waters were incubated in the dark within 1 to 3°C of the *in situ* temperature. Bottles were carefully inverted to mix contents following inhibitor or DMS additions, and just before subsampling. Subsamples were withdrawn through Teflon tubing attached to a glass syringe.

Inhibitor additions. Inhibitor compounds which were used include chloroform (Carlo-Erba, Milano,

Italy), dimethyl disulfide (DMDS, Aldrich, UK), dimethyl selenide (DMSe, kindly provided by D. Nedwell) and nitrapyrin (2-chloro-6-[trichloromethyl]-pyridine, Sigma, Spain). Microvolumes of pure chloroform were added to a final concentration of 500 µM (Kiene & Service 1991, Wolfe & Kiene 1993a). A microvolume of DMDS was used to prepare a stock solution of 4.5 mM in Milli-Q water. Of this solution 140 µl was added to 2400 ml of sample to make a final DMDS concentration of 260 nM. DMSe was added from a concentrated solution made by weighting cold pure compound into a crimp vial with distilled water. Volumes of this concentrated stock were withdrawn with a syringe through the Teflon-faced septum and added to the incubating waters. Nitrapyrin was dissolved in Milli-Q water to saturation (ca 30 mg l^{-1}), and volumes of this solution were added to seawater incubations to make up a final concentration of ca 1 µM. This concentration has been reported to inhibit ammonia oxidation in cultures of nitrifying bacteria (Belser & Schmidt 1981, Taylor 1983, Oremland & Capone 1988). In all cases, the time of additions was taken as the time 0 of the incubations.

Estimating production and consumption rates. DMS consumption rates were estimated from the difference between the slope of the initial linear part of the DMS time-course in the inhibitor-treated sample and that of the control sample (Kiene & Bates 1990). The slope in the inhibited sample was taken as the rate of DMS production, that is, DMSP consumption through cleavage (Bates et al. 1994). Assuming that no DMSP is synthesized *de novo* by organisms during the dark incubation period, the observed disappearance of total (particulate + dissolved) DMSP reflects the turnover of DMSP by consumption processes. Thus, the rates of DMSP consumption were calculated from the time-course of $DMSP_t$ concentration in unamended samples, which we call the *net-loss curve* approach. Since $DMSP_t$ disappeared quasi-exponentially (rather than linearly) at the time resolution of the analyses, a first order loss rate constant (d^{-1}) was determined as the slope of the plot of the natural log of $DMSP_t$ concentration versus time (Kiene 1996a). By multiplying this constant by the initial (*in situ*) $DMSP_t$ or $DMSP_d$ concentration, the $DMSP_t$ or $DMSP_d$ consumption rate was obtained. Turnover of any dimethyl sulfur species with respect to biological consumption is described by the time constant τ, which is equivalent to the 'partial turnover time' due to microbial processes (the 'total turnover time' should include other loss processes such as photolysis and ventilation). We acknowledge that there is a large uncertainty associated with the determination of turnover rates and times. The uncertainty originates mainly from 3 sources: (1) The error between replicate DMS analyses which can be reasonably confined to ≤10%. (2) The error associated with slope calculations from the DMS (or $DMSP_t$) versus time plots. Typical errors computed from regression analyses (including the differences between replicate datapoints and consumption rates calculated by difference) ranged from 7 to 50%, but were usually around 20%. In 1 case (MED2D: Mediterranean deep chlorophyll maximum, DCM) consumption rates calculated by difference were very low, and the corresponding error was very high (100%). (3) The chloroform effect, whereby leakage of DMSP from the particulate to the dissolved DMSP pool can occur. This may lead to possible overestimation of DMS production and consumption rates (Wolfe & Kiene 1993a).

Table 1. Characteristics of the water samples used for this study

Sample code	Latitude	Longitude	Date (mo/d/yr)	Time	Temp. (°C)	Water column depth (m)	Depth sampled (m)
Mediterranean							
MED2S	40° 41′ N	02° 51′ E	6/7/95	09:00	19.6	2100	5
MED2D	40° 41′ N	02° 51′ E	6/3/95	11:00	13.5	2100	50
North Sea							
NS1	52° 31′ N	01° 51′ E	6/19/96	07:30	14.3	29	0
NS2	52° 31′ N	01° 51′ E	7/18/96	07:30	15.5	29	0
NS3	52° 31′ N	01° 51′ E	8/2/96	07:30	18.0	29	0
North Atlantic							
NA1	59° 20′ N	19° 00′ W	6/8/98	14:00	10.8	2750	1
NA2	59° 34′ N	21° 07′ W	6/16/98	04:10	11.7	2850	4
NA3	59° 54′ N	20° 44′ W	6/23/98	03:45	11.5	2800	0
NA4	60° 26′ N	20° 39′ W	6/27/98	02:30	11.2	2600	0
NA5	59° 48′ N	20° 57′ W	6/28/98	02:30	11.0	2800	0
NA6	59° 46′ N	20° 39′ W	7/3/98	03:10	11.8	2800	0

Disregarding the 'chloroform effect', we estimate the typical error of turnover rates and times to be <50%, usually around 20%.

Chlorophyll *a* and phytoplankton. A fluorometric method was used to measure chlorophyll *a* (chl *a*) in 90% acetone extracts (Parsons et al. 1984). Phytoplankton speciation and abundance were obtained by inverted microscopy observations of samples preserved in acid Lugol's solution or formalin (Utermöhl 1931).

RESULTS AND DISCUSSION

Methylated sulfur speciation

The concentrations of methylated sulfur compounds and chl *a* in the different seawater samples are shown in Table 2. In all but 1 case, the speciation was dominated by $DMSP_p$. $DMSP_d$ and DMS occurred at very variable levels. $DMSO_d$ and $DMSO_p$ exhibited similar concentrations, of the same order of magnitude as those of DMS and $DMSP_d$. The highest concentrations of most compounds were found in the North Sea sample NS1, collected during a bloom of the colonial haptophyte *Phaeocystis* sp. It is well known that this phytoplankton species is one of the major producers of DMSP. The $DMSP_t$:chl *a* ratio obtained in this case (NS1) was 37 nmol μg^{-1}, which falls within the range observed for similar *Phaeocystis* blooms (38 to 48 nmol μg^{-1}, Liss et al. 1994). The $DMSP_t$:chl *a* ratios found in the North Atlantic ranged from 27 to 107 nmol μg^{-1}, only slightly lower than those previously reported for the same area (Malin et al. 1993).

Incubation experiments

The concentrations of methylated sulfur compounds in several untreated incubations are shown in Fig. 1. Patterns for DMS concentration over incubation periods up to 12–24 h included slow but significant, nearly linear increases in Mediterranean samples and NA2, and slight changes in North Sea and the other North Atlantic waters. $DMSP_p$ (or $DMSP_t$) decreased from the beginning in all but 1 case (NS2), where it increased a little in the first 4 h before declining. $DMSP_d$ always exhibited temporary production followed by removal, which supports its role as an intermediate pool in the release and metabolism of planktonic DMSP. The $DMSO_d$ data, where available, presented the most variable patterns: net increase followed by steady state or removal, and steady time-course. $DMSO_p$ was only monitored in NS2, and its concentration trend was very similar to that of $DMSO_d$. To our knowledge, this is the first time that all dimethylated sulfur species (including DMSO) have been monitored in this type of incubation experiments. The behavior of DMSO is worth stressing, since the biological transformations of this compound in aerobic seawater are virtually unknown. In 3 out of 4 dark incubations, the observed significant changes in DMSO concentration with time were suggestive of biota-related processes of production, release and consumption.

Table 2. Ambient concentrations of dissolved and particulate dimethylated sulfur species (nM), chlorophyll *a* ($\mu g\ 1^{-1}$), and dominant nano- and micro-phytoplankton in the water samples used for turnover experiments. All values are means of duplicate measurements. Sample codes and characteristics are shown in Table 1

Sample code	DMS	$DMSP_d$	$DMSO_d$	$DMSP_p$	$DMSO_p$	Chl *a*	Predominant phytoplankton (>50% biomass)
Mediterranean							
MED2S	7.3	1.6	4.9	10	16	0.12	Flagellates[b], coccolithophorids, dinoflagellates
MED2D	1.3	1.0	3.0	5.3		1.29	Flagellates + small haptophytes, dinoflagellates
North Sea[a]							
NS1	65	150	25	340	16	13.26	*Phaeocystis* sp. (>95%)
NS2	1.6	4.3	4.9	5.2	3.9	1.33	Heterotrophic dinoflagellates
NS3	0.8	4.0	2.3	7.1	2.7	2.74	Heterotrophic dinoflagellates, diatoms
North Atlantic							
NA1	2.7	1.1	3.8	28	2.8	1.09	Dinoflagellates, diatoms, coccolithophorids
NA2	4.9	9.1	6.4	30	6.6	0.70	*Emiliania huxleyi*
NA3	9.8	24	8.0	174	33	1.86	Dinoflagellates, flagellates
NA4	5.5	15	15	91	19	1.57	Flagellates, dinoflagellates
NA5	5.0	17	8.3	53	7.3	1.26	Dinoflagellates, flagellates
NA6	5.3	24	26	117	24	1.51	Dinoflagellates, flagellates, diatoms, coccoliths

[a] After Simó et al. (1998a)
[b] Including *Phaeocystis* sp.

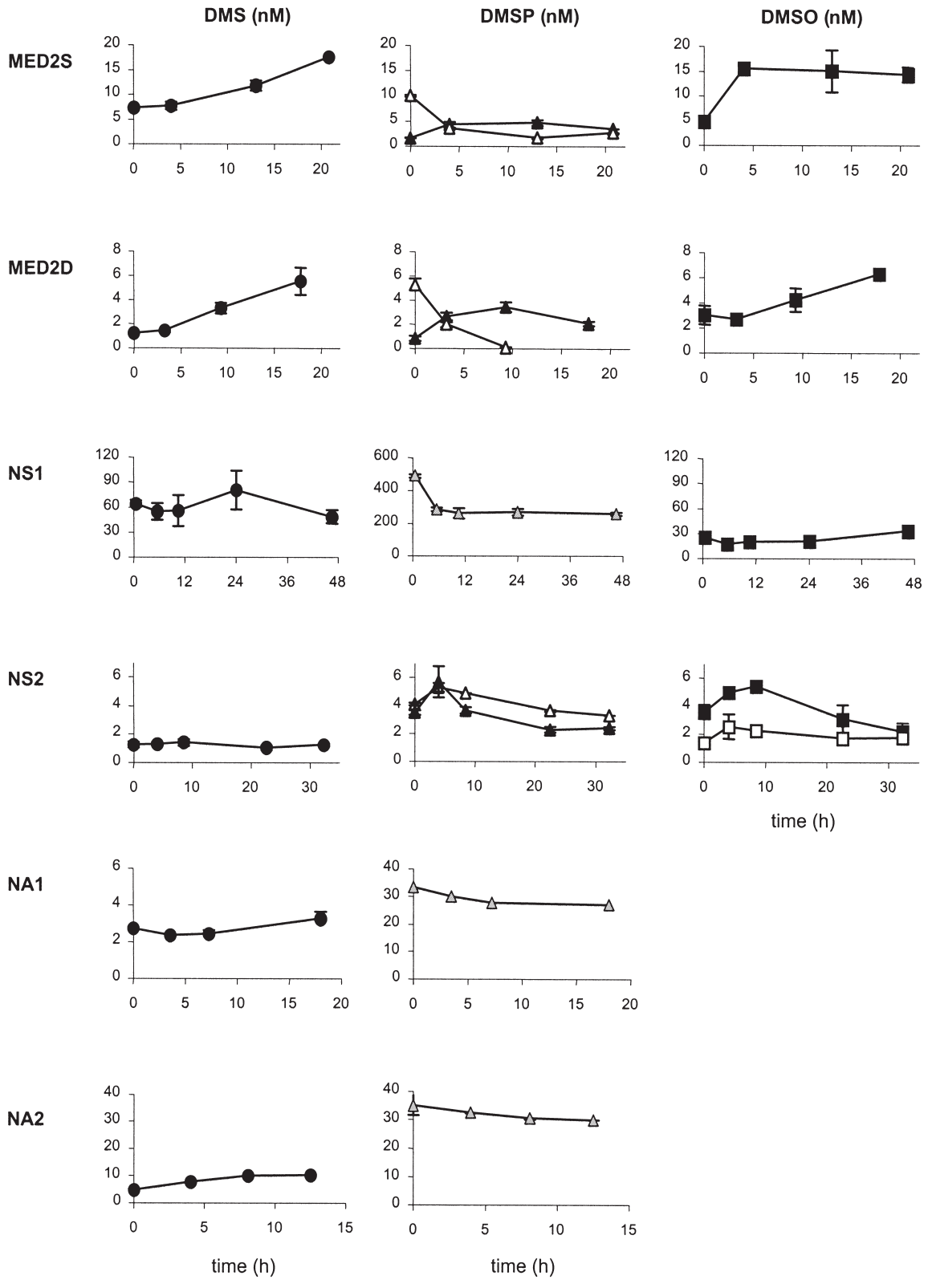

Fig. 1. Dark incubations of unamended seawater from the northwestern Mediterranean (MED2S, MED2D), the North Sea (NS1, NS2) and the North Atlantic (NA1, NA2). Time-course plots of the endogenous pools of DMS, DMSP and DMSO (filled symbols: dissolved pools; open symbols: particulate pools; grey symbols: total [dissolved + particulate]). Error bars represent the scatter of duplicate measurements. Characteristics of the water sampled can be found in Table 1

Turnover rates

Among the different approaches that have been reported to estimate turnover rates for DMS (Kiene & Bates 1990, Wolfe & Kiene 1993a,b, Ledyard & Dacey 1996, Kiene 1996a,b), we used the *inhibitor addition method* (see 'Materials and methods'). For DMSP turnover rate estimation we employed the *net-loss curve* approach (see 'Materials and methods'), since no sound and selective inhibitor of all processes of DMSP consumption has been identified to date. Addition of glycine betaine (GBT) to incubated seawater appears to block $DMSP_d$ utilization for short incubations (<6 h, Kiene & Gerard 1995), but not at the longer incubation times used in our study. It is most likely that GBT competitively blocks $DMSP_d$ uptake by bacteria, but it is not clear whether GBT would affect non-bacterial processes of $DMSP_d$ degradation, such as the action of algal DMSP-lyases (Stefels & van Boekel 1993) and zooplankton incorporation during digestion of grazed phytoplankton (Wolfe et al. 1994, Tang et al. 1999). We chose endogenous total (dissolved + particulate) DMSP as the variable to calculate turnover rates because its variation with time should be accounted for by actual DMSP consumption, whereas each one of the $DMSP_d$ and $DMSP_p$ pools results from the combined effects of consumption (metabolism, cleavage) and partitioning (release, uptake). To our knowledge, only van Duyl et al. (1998) have estimated the DMSP consumption rate from the loss of total DMSP. All other previous studies used either the endogenous or low-level added $DMSP_d$ (Kiene 1996a, Kwint et al. 1996, Ledyard & Dacey 1996). We notice that the *net-loss curve* method may be slightly underestimating DMSP consumption if some DMSP is produced by phytoplankton in the dark. There is some evidence that DMSP biosynthesis is a light-dependent process (Simó et al. unpubl., but the possibility that algae keep producing DMSP at the very beginning of the dark incubations cannot be totally excluded.

At the oligotrophic, open Mediterranean station, the DMS consumption rate estimated using the chloroform inhibition technique was 10 times higher at the surface (MED2S, 7 nM d^{-1}) than that observed for water from the DCM 4 d earlier (MED2D, 0.7 nM d^{-1}, Table 3). On the basis of the obtained rates and the observed initial *in situ* concentrations, we estimate that the DMS turnover time was 1 d at the surface and 1.9 d within the DCM. Similar time constants have been reported for other oligotrophic and/or open-sea areas, such as the equatorial Pacific (0.6 to 4.6 d, Kiene & Bates 1990), the Northeast Pacific (0.7 d, Bates et al. 1994), the Sargasso Sea (1.6 to 2.1 d, Kiene 1992; <1 d, Ledyard & Dacey 1996) and the Labrador Sea (0.5 to 6.2 d, Wolfe et al. 1999). DMS production (DMSP cleavage) rates were quite similar at the 2 depths (10 nM d^{-1} at the surface, 7 nM d^{-1} at 50 m, Table 3), so that production and consumption appeared to be tightly coupled at the surface but decoupled in the DCM. $DMSP_t$ consumption rates were 12 nM d^{-1} at the surface and 8 nM d^{-1} in the DCM (Table 3), resulting in turnover time constants of 1 and 0.8 d, respectively. If we assume that all DMSP was being consumed from the $DMSP_d$ pool (which

Table 3. Rates of microbial DMS consumption, DMS production through DMSP cleavage, and $DMSP_t$ consumption (nM d^{-1}). Biological turnover times for DMS (τ_{DMS}: d) and total and dissolved DMSP (τ_{DMSP_t} and τ_{DMSP_d}: d). Sample codes and characteristics shown in Table 1

Sample Code	DMS consumption[a]	DMSP cleavage[a] (DMS production)	$DMSP_t$ consumption	τ_{DMS}	τ_{DMSP_t}	τ_{DMSP_d}[b]	% DMSP cleaved
Mediterranean							
MED2S	7.2	9.5	12	1.0	1.0	0.1	78
MED2D	0.7	7.4	7.7	1.9	0.8	0.1	96
North Sea							
NS1	122	157	730	0.5	0.7	0.2	22
NS2	2.3	1.9	7.2	0.7	1.3	0.6	26
North Atlantic							
NA1	8.1	6.8	20	0.3	1.5	0.1	34
NA2	3.3	14	14	1.5	2.7	0.6	95
NA3	4.6	19	37	2.1	5.4	0.7	52
NA4	6.1	9.7	65	0.9	1.6	0.2	15
NA5	6.7	6.7	76	0.8	0.9	0.2	9
NA6	2.1	9.8	43	0.6	3.3	0.6	23

[a]Chloroform was used for the determination of DMS production and consumption rates in Mediterranean and North Sea sample incubations, whereas DMDS was used in the North Atlantic

[b]Lower limit, as it assumes that all DMSP turns over through the dissolved pool

does not necessarily hold true), these turnover rates would result in $DMSP_d$ time constants of 0.1 d for both depths. These are lower than the lowest $DMSP_d$ turnover times reported for the Sargasso Sea (0.4 to 2.8 d, Ledyard & Dacey 1996). However, our turnover time constants are to be taken as lower-limit estimates, since it is likely that part of the DMS is produced directly from $DMSP_p$ without going through the bulk $DMSP_d$ pool.

Similar DMS production and consumption rates were found in the mesotrophic waters of the North Atlantic using DMDS as inhibitor (consumption: 2 to 8 nM d^{-1}, production: 7 to 19 nM d^{-1}, Table 3), which gave DMS turnover times of 0.3 to 2 d. $DMSP_t$ was consumed at 14 to 76 nM d^{-1}. That is, $DMSP_t$ turned over in 1 to 5 d and $DMSP_d$ turned over in 0.1 to 0.7 d (lower limit). In North Sea waters, chloroform-amended incubations gave an extremely high DMS consumption rate in the presence of a high *Phaeocystis* cell number (NS1, 122 nM d^{-1}) and a much lower rate when there was no *Phaeocystis* bloom (NS2, 2 nM d^{-1}, Table 3). However, the resulting time constants were comparable (0.5 and 0.7 d). Biological turnover times for DMS of 0.2 to 5.6 d have been reported for coastal and shelf seawaters (Kwint et al. 1996, Ledyard & Dacey 1996, Wolfe et al. 1999). DMS production rate levels paralleled those for consumption (157 and 1.9 nM d^{-1}, Table 3), which might again indicate coupling between production and consumption. $DMSP_t$ was consumed at 730 nM d^{-1} in the bloom and at 7.2 nM d^{-1} in the non-bloom waters, i.e. $DMSP_t$ turned over in 0.7 and 1.3 d, respectively. Hence, $DMSP_d$ turned over in (minimum) 0.2 and 0.6 d. Similar $DMSP_d$ turnover times of 0.3 to 0.7 d (Ledyard & Dacey 1996), 0.04 to 0.9 d (Kiene 1996a) and 0 to 0.8 d (Kwint et al. 1996) have been reported for eutrophic coastal waters.

If the rates of DMSP consumption through cleavage, estimated as DMS production with the *inhibitor method*, are compared with the rates of $DMSP_t$ turnover, estimated from first order loss curves, the fraction of DMSP cleaved to produce DMS can be calculated (Table 3). A large portion of DMSP (78 to 100%) was cleaved in surface and subsurface open Mediterranean waters, as well as in the North Atlantic sample NA2, whereas a lower fraction (9 to 52%) was found to cleave in most North Atlantic waters as well as in the near-coastal North Sea waters, even during the *Phaeocystis* bloom. Note that the DMSP cleavage (DMS production) rates for the Mediterranean and North Sea samples might have been overestimated by the use of chloroform (see next subsection). Comparison of these values with others from previous studies is difficult because very few data exist, and they appear to be quite variable. Ledyard & Dacey (1996) reported proportions from 11 to 100% in oligotrophic waters and 25 to 30% in coastal waters. Bates et al. (1994) estimated that 33% of the DMSP was cleaved at an open oceanic site, Kiene (1996b) reported proportions from 12 to 66% in coastal waters with salinities >30‰, and Kwint et al. (1996) and van Duyl et al. (1998) found them to be 0 to 100% and 0 to 49%, respectively, in North Sea coastal blooms of *Phaeocystis*. Our results are consistent with the idea that cleavage to DMS is the fate for only part of the DMSP pool, and that the other biological sinks, such as microbial demethylation and incorporation into protein, can be as significant as (generally larger than) DMS production (Belviso et al. 1990, Kiene & Service 1991, Taylor & Gilchrist 1991, Kiene 1992, 1996a,b, Visscher et al. 1992, Kiene et al. 1999, Simó & Pedrós-Alió 1999a,b). Recent studies suggest that the fraction of DMSP consumption which yields DMS production may depend on the combination of bacterial sulfur demand and DMSP availability (Kiene et al. 2000), and, in the open ocean, may be controlled by the vertical mixing of surface waters (Simó & Pedrós-Alió 1999b).

In 6 out of the 10 samples incubated, DMS production and consumption processes had comparable rates, which might suggest tight coupling (Table 3). This was not so in MED2D, NA2, NA3 and NA6. Coupling of DMS production and consumption means that the microorganisms responsible for DMS cycling adapt to rates of substrate availability (Kiene & Service 1991). This was especially striking in the *Phaeocystis* bloom, where high rates of $DMSP_d$ cleavage were found together with high rates of DMS consumption. Similar results have been reported recently by van Duyl et al. (1998). It has commonly been speculated that, in view of the apparent low saturation kinetics of DMS consumers, large releases of this compound during late stages of DMSP-producing phytoplankton blooms might result in accumulation of high concentrations of DMS in seawater (e.g. Kiene & Service 1991, Wolfe et al. 1999). Our results show that high production rates can be accompanied by high consumption rates. Hence, factors other than high production rates must be responsible for a build-up of DMS concentration. According to our estimates only 22% of $DMSP_t$ was cleaved to DMS in the *Phaeocystis*-dominated sample NS1 (Table 3). This fraction should be accounted for by both bacterial and algal DMSP-lyase activities, while most of the remaining DMSP should be metabolized through other bacterial processes, such as demethylation. Thus, overall bacterial processes dominated DMSP consumption in comparison to the enzymatic cleavage linked to algae at that phase of the bloom. Similar observations were made by Kwint et al. (1996) and van Duyl et al. (1998) in mesocosm-enclosed and free-living *Phaeocystis* blooms, respectively, in coastal North Sea waters.

Effects of chloroform and use of other inhibitors

Chloroform has been used many times to determine DMS cycling rates in seawater (e.g. Kiene & Bates 1990, Kiene & Service 1991, Kiene 1992, Wolfe & Kiene 1993b, Bates et al. 1994, Simó et al. 1995, Kieber et al. 1996, Kwint et al. 1996). However, it has been observed that its use may lead to overestimation of DMS production and consumption rates by causing release of DMSP from cells, especially at doses higher than 500 µM (Wolfe & Kiene 1993b).

To examine the extent to which 500 µM chloroform might cause overestimates of DMS consumption in our samples, we ran North Sea and North Atlantic water incubations with addition of dimethyl selenide (DMSe) and dimethyl disulfide (DMDS), respectively, in parallel to chloroform additions. It has been reported that many dimethylated substrates are effective inhibitors of DMS metabolism, with DMDS being amongst the most effective (Wolfe & Kiene 1993a). It was expected that DMSe, because of its similarity to DMS, would have a competitive effect on the enzymes involved in DMS metabolism, hence inhibiting DMS consumption at low concentrations (D. Nedwell pers. comm.). Indeed, concentrations of 17, 55 and 88 nM of DMSe, approximately 10 to 70 times the endogenous DMS concentration in NS2, caused accumulation of DMS above the control from 8 h on (Fig. 2a). The DMS consumption rate calculated from DMSe inhibition was 1.3 nM d^{-1}, whereas that calculated from chloroform inhibition was 2.3 nM d^{-1}. That is, the 'chloroform rate' exceeded the 'DMSe rate' by 75%. Likewise, in North Atlantic waters the 'chloroform rate' (13.9 nM d^{-1}) also exceeded the 'DMDS rate' (8.1 nM d^{-1}) by 70% (Fig. 2b). Our data support previous evidence that chloroform addition may lead to overestimation of DMS production and consumption, notably by promoting DMSP release from phytoplankton cells. It is also feasible that, because of its nature as inhibitor of demethylating reactions (Oremland & Capone 1988), chloroform also may block bacterial $DMSP_d$ consumption by demethylation reactions, thus favoring the cleavage pathway to DMS. However, the pioneering studies on the use of this inhibitor for DMS metabolism showed no evidence of chloroform blocking or slowing DMSP consumption by non-DMS-producing degradation pathways (Kiene & Service 1991).

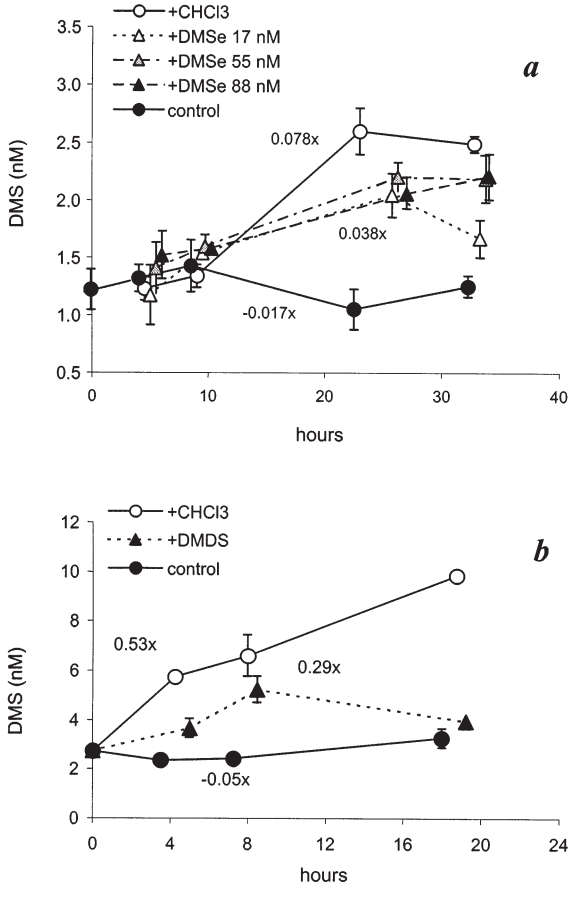

Fig. 2. Dark incubations of seawater from the North Sea, sample NS2 (a) and the North Atlantic, sample NA1 (b). Comparison of the time-course of DMS concentration with and without addition of 500 µM chloroform, and varying amounts (17 to 88 nM) of dimethyl selenide (a) and 260 nM dimethyl disulfide (b) as inhibitors of microbial DMS turnover. Superimposed numbers represent the slopes of linear regression fitted to the first 3 time-points. Error bars represent the scatter of duplicate measurements. Characteristics of the water sampled can be found in Table 1

It is clear that we need to know much better how the different inhibitors of DMS consumption work before assuming that chloroform-obtained rates of DMS consumption and DMSP cleavage presented in Table 3 are overestimates. As explained above, one would expect that DMSe and DMDS gave more reliable results. Indeed, Simó & Pedrós-Alió (1999a) showed that the use of DMDS with North Atlantic waters gave good predictions of DMS short term (<5 h) concentration changes. However, the fact that DMS went down after 8 h in the presence of DMDS in sample NA1 (Fig. 2b) leaves some concern on the efficiency of this inhibitor in the mid and longer run.

The case of DMSO

DMSO is found in a wide variety of marine environments and constitutes a substantial pool of methylated sulfur in seawater, with concentrations higher than those of DMS and in some cases even greater than those of dissolved and particulate DMSP (e.g. Hatton et al. 1996, Lee & de Mora 1996, Simó et al. 1997; compilation in Simó 1998). At present the role, origins and fate of this com-

pound in seawater are unclear. Laboratory (Brimblecombe & Shooter 1986) and field (Kieber et al. 1996) studies have shown that DMSO is the photo-oxidation product of at least part of the dissolved DMS. Another potential source for DMSO is bacterial oxidation of DMS. Bacteria have been cultured that are capable of DMS-to-DMSO transformation, either anaerobically by photoautotrophy, or aerobically by heterotrophic co-metabolism or monooxygenase activity (see reviews in Taylor & Kiene 1989, Taylor 1993, Hatton et al. 1996). Also, a number of anaerobes and aerobes are capable of growing on DMSO as an electron acceptor or as a carbon and energy source (Zinder & Brock 1978, De Bont et al. 1981; reviews in Taylor & Kiene 1989, Kiene 1993, Taylor 1993). However, in spite of all these potential metabolic pathways, little is known of the importance, and even the occurrence, of biological DMSO cycling in the epipelagic marine environment.

Recently, Simó et al. (1998a) found that particulate matter, and particularly phytoplankton cells, plays a key role in the occurrence of DMSO in seawater. These authors and Lee & de Mora (1999) suggested that a biosynthetic pathway in eukaryotic organisms must exist, and that leakage or release from microbiota may represent a major source of dissolved DMSO. In the present study we measured a pool of particulate DMSO (Table 2), and results from the several incubation experiments (Fig. 1) indicate that biological cycling of DMSO does take place. The observed changes in $DMSO_d$ concentration in the dark cannot be explained by photochemical processes. Further, there is no apparent concurrence of these increases with decreases in DMS concentration or reduced DMS accumulation rates, and hence no direct evidence for the production of $DMSO_d$ via dark oxidation of dissolved DMS. In addition, in sample NS2, $DMSO_p$ increased in the first 4 h, suggesting intracellular production in organisms. Therefore, it is likely that the concentration increases of $DMSO_d$ in all incubations are accounted for by release from intracellular reservoirs.

Among the potential processes for aerobic bacterial conversion of DMS into DMSO is oxidation by ammonia monooxygenase (AMO) and methane monooxygenase (MMO), as seen in cultured marine strains of nitrifiers (e.g. Juliette et al. 1993) and methanotrophs (Fuse et al. 1998). We tested the occurrence of monooxegenase oxidation of DMS in several of our water samples using nitrapyrin (2-chloro-6-[trichloromethyl]pyridine) at a concentration of ca 1 µM, which has been reported to inhibit the action of AMO in cultures of chemoautotrophic nitrifiers (Taylor 1983, Oremland & Capone 1988, Bédard & Knowles 1989). Addition of nitrapyrin in 4 incubation experiments stimulated no apparent response in the DMS pool (data not shown). Some extra release of $DMSO_d$ was observed in 1 of the experiments, probably due to toxic effects of nitrapyrin on algae. Hence, no indication of DMS-to-DMSO oxidation by nitrifying bacteria was obtained. This result is not surprising, since nitrification activity in surface waters is generally negligible.

On the other hand, $DMSO_d$ consumption in 1 of the incubation experiments (NS2, Fig. 1) provides circumstantial evidence for the occurrence of bacterial metabolism of DMSO, as observed previously by Kiene & Gerard (1994) in a longer term incubation. Determining the rate of DMSO turnover relative to those of DMS and DMSP would require further experiments with the use of inhibitors of DMSO metabolism or with $DMSO_d$ additions. However, a rough estimation can be made from the incubation experiment NS2, in which $DMSO_p$ was monitored along with $DMSO_d$ (Fig. 1). After initial production, total (particulate + dissolved) DMSO exhibited a net consumption rate of 4 nM d^{-1}, that is, a turnover time of 2 d. This is longer than the turnover times for $DMSP_t$ (1.3 d) and DMS (0.6 d) in the same sample.

Under the aerobic conditions of our incubations, DMSO is a potential substrate for methylotrophic bacteria with the known metabolic pathways involving initial reduction to DMS (reviewed in Taylor 1993). In the incubation where total DMSO disappearance was observed, it was not accompanied by apparent DMS production (NS2, Fig. 1). However, in that sample DMS production and consumption were tightly coupled, which might preclude seeing any effect of DMSO reduction, if any, on DMS accumulation. Alternatively, it can well be that DMS is not released when produced intermediately in the bacterial intracellular DMSO reduction chain to sulfide.

CONCLUSIONS

Our results agree with previous work in that DMS and DMSP turnover processes in seawater are very dynamic, with biological turnover times between a few hours and a few days for both compounds. Especially for DMS, it appears that both tight couplings and decouplings of production and consumption can occur even at very high rates of DMS production, which were previously seen as 'saturating' for DMS consumers. Bacteria play a key role in DMSP consumption and DMS production by switching between cleavage and the other DMSP utilization pathways. What controls such switching dynamics is not yet clear, but we have shown that the DMS yield of DMSP turnover may vary between 5 and ~100%. Very recently, vertical mixing of surface waters (Simó & Pedrós-Alió 1999b) and DMSP availability in relation to bacterial sulfur demand (Kiene et al. 2000) were suggested as factors controlling the DMS yield of DMSP transformations.

Both hypotheses deserve further investigation. The introduction of inhibitors of DMS metabolism other than chloroform should refine our estimation of turnover rates, since our results agree with some previous work in that they point to chloroform leading to overestimation of DMS cycling rates. In this respect, DMSe showed inhibitory action at low concentrations and holds promise as an inhibitor of DMS consumption in fieldwork. Further, we propose the *net-loss curve* approach with total DMSP as a method to estimate the rate of biological DMSP consumption through all transformation pathways, with the assumption that no DMSP is produced *de novo* by phytoplankton in the dark. Finally, this work reports for the first time the short-term, dark accumulation of $DMSO_d$ in seawater samples. This production is consistent with the recent finding that some phytoplankton produce and release DMSO. Our results also show that active biological turnover may follow $DMSO_d$ release. Further research into production and turnover of DMSO and the role of this compound in the marine biogeochemical DMS cycle is clearly warranted.

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