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Exchange Dynamics Reveal Significant Accumulation of Dimethylated Sulfur by Mediterranean Benthic Communities

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One fifth of Mediterranean waters can be classified as shelf—much higher than the global average. Consequently, the shelf/coastal zone plays a proportionally greater biogeochemical role than in the major oceans, including the support of a wide range of endemic or culturally important species and ecosystems. However, despite their known importance in regulating ecosystem function and the marine sulfur cycle, our understanding of the dynamics of dimethylated sulfur compounds such as dimethylsulphide (DMS) and dimethylsulphoniopropionate (DMSP) in Mediterranean benthic habitats is limited. Here, a community-level approach was adopted to quantify DMS and DMSP dynamics in Mediterranean ecosystems including seagrass (*Posidonia oceanica*) meadows, coralligène (an algal carbonate reef found along the Mediterranean shelf) and macroalgal stands. It was found that *P. oceanica* and coralligène are likely to act as significant benthic stocks of DMSP in the coastal/shelf environment. “Hotspots” of water column DMS and DMSP processing were observed where net benthic production was high (e.g., *P. oceanica* meadows), demonstrating that benthic communities are able to modify DMS biogeochemistry in the overlying water column. High variability between, and within, habitat types illustrates the importance of ecosystem structure and light availability in determining benthic DMS and DMSP accumulation, and highlights a previously under-appreciated complexity in benthic dimethylated sulfur dynamics.

Keywords: dimethylsulphide (DMS), dimethylsulphoniopropionate (DMSP), community, ecosystem, seagrass, crustose coralline algae (CCA), macroalgae

INTRODUCTION

The Mediterranean Sea is the largest and deepest semi-enclosed sea in the world, providing coastline to 21 states and serving as a tourist destination for 200 million people every year (Aquarone et al., 2010). The Mediterranean's varied geological history, including full isolation from primary oceans and subsequent abrupt flooding (Garcia-Castellanos et al., 2009), has shaped its current characteristics: one fifth of Mediterranean waters can be classified as shelf—much higher than the 7% global average (Pinardi et al., 2006). This has resulted in high cultural and biological diversity (Coll et al., 2010). Whilst comprising only 0.32% of the global ocean volume, the Mediterranean Sea harbors 4–18% of all known marine macroscopic species (Bianchi and Morri, 2000; Coll et al., 2010), including a high percentage of endemic and charismatic species (Coll et al., 2010). Thus, shelf waters and their associated benthic habitats play a proportionally greater

biological and biogeochemical role in Mediterranean ecosystem function than elsewhere. However, rates of biogeochemical processing remains a grand challenge in marine science (Achterberg, 2014), and deficiencies in observational data and multidisciplinary research strategies in the Mediterranean limits our modeling capacity for the region (De Madron et al., 2011). Acute anthropogenic pressures that threaten the long-term survival of Mediterranean coastal and shelf benthic ecosystems (Coll et al., 2010, 2012) further call for a detailed understanding of coastal / shelf biogeochemistry (Doney, 2010). The impact of long-term projected climate change on these ecosystems is likely to be complex and interactive (Lejeune et al., 2010)—some species may be “winners” (e.g., seagrasses, fleshy macroalgae), whilst others may be “losers” (e.g., calcifying macro- and micro-organisms) (Kroeker et al., 2013). The subsequent impact on benthic-pelagic coupling will almost certainly affect ecosystem structure and function, but these processes are not yet adequately understood for the present day (Griffiths et al., 2017), limiting the accuracy of future projections.

Benthic production of dimethylated sulfur—particularly dimethylsulfide (DMS) and its precursor dimethylsulphoniopropionate (DMSP)—is known to be significant for a range of benthic ecosystems, including coral reefs (e.g., Van Alstyne et al., 2006; Fischer and Jones, 2012), saltmarshes (e.g., Steudler and Peterson, 1984) and macroalgal assemblages (e.g., Burdett et al., 2015). Dimethylated sulfur is a major component of the marine sulfur cycle, but has also been linked with key ecosystem functions including organismal tolerance to environmental variability (e.g., Burdett et al., 2013) and community-level trophic interactions via infochemical signaling (Wolfe et al., 1997; De Bose et al., 2008; Seymour et al., 2010; Savoca and Nevitt, 2014). However, the role of Mediterranean shelf and coastal ecosystems in dimethylated sulfur production is poorly researched, despite the prevalence of shelf waters and the known role as a source of atmospheric DMS (Simo et al., 1997; Besiktepe et al., 2004) and algal-derived sulfate aerosols (Ganor et al., 2000). *Posidonia oceanica*—a seagrass species endemic to the Mediterranean—and coralligenous frameworks (locally known as “coralligène”)—unique reef-like structures composed of encrusting red coralline algae—are widespread throughout the Mediterranean (Martin et al., 2014; Telesca et al., 2015) and support highly diverse ecosystems (Hemminga and Duarte, 2000; Ballesteros, 2006). Red coralline algae and *P. oceanica* are also known to be significant producers of dimethylsulphoniopropionate (DMSP) (Borges and Champenois, 2015; Burdett et al., 2015). The Mediterranean has been noted to be an important source of atmospheric (DMS, a breakdown product of DMSP), but we have little information on the role of Mediterranean benthic communities (as fully integrated systems) in the production of dimethylated sulfur compounds.

Community-level investigations of biogeochemical dynamics provide a more accurate representation of natural ecosystem responses (Riebesell and Gattuso, 2015), but this approach remains poorly adopted, in part due to greater logistical complexities (Riebesell and Gattuso, 2015). The aim of this study was to investigate the Mediterranean benthos in terms of

DMSP stock and community-level benthic-pelagic exchange of DMS and DMSP. This will provide new insight into the role of Mediterranean benthic communities in the cycling of these ecologically and biogeochemically important compounds.

MATERIALS AND METHODS

Study Site and Sample Collection

Sampling took place at Banyuls-sur-Mer, south-west France along a depth gradient in August 2014; benthic DMSP concentrations (Borges and Champenois, 2015; Burdett et al., 2015) and DMS production rates (Vila-Costa et al., 2008) are known to be highest in the summer months. There were four main sampling depths, at which dominant substrate types were sampled:

- 2 m: *Padina* sp. gardens, dead seagrass mats, sand patches (top 1 cm sampled); collected via snorkeling
- 3 m: *Posidonia oceanica* meadow (leaves sampled); collected via snorkeling
- 15 m: coralligène (*Mesophyllum alternans*) and sand patches (top 1 cm of sand sampled); collected via SCUBA
- 20 m: coralligène (*Mesophyllum alternans*) and sand patches (top 1 cm of sand sampled); collected via SCUBA

At each depth, the dominant substrate types were sampled for intracellular DMSP concentrations ($n = 10$ samples per substrate type). Immediately on collection, intracellular DMSP samples were returned to the laboratory, where they were patted dry and their mass recorded and stored in 10 M NaOH in 5 ml crimp-top vials fitted with Pharma-Fix septa (Fisher Scientific).

Net community benthic flux of dissolved DMSP (DMSP_d) and DMS were determined for each substrate type ($n = 5$ per substrate type) using unstirred *in situ* benthic chambers that were fixed to the seabed (270 ml volume, 95 cm² surface area, transparent to incoming photosynthetically active radiation). Larger chambers (3,650 ml volume, 180 cm² surface area) were used on the seagrass bed because of the height of the plants. Initial water samples (T_0) were taken with glass syringes fitted with a one-way valve and transported back to the laboratory for processing (<20 min travel time). Chambers were then closed and the incubation started. Incubations lasted for ~4 h (exact time noted for each incubation), following which a second water sample (T_1) was taken from each chamber using a glass syringe and transported back to the laboratory. On return to the laboratory, water samples were immediately processed following the small volume gravity filtration method (Kiene and Slezak, 2006), allowing for the determination of DMSP_d, particulate DMSP (DMSP_p) and DMS. Storage in NaOH converts all DMSP in samples to DMS for quantification via gas chromatography (GC, instrumental details below).

Water samples were also taken at 3–5 depths through the water column depending on the overall depth ($n = 5$ per depth), including one depth close to the seabed. As with the benthic samples, one batch of water samples were immediately processed on return to the laboratory (T_0), whilst a second batch of water samples were taken from gas-tight chambers maintained at ambient conditions for the same duration as the benthic chamber

incubations (T_1), allowing for complementary determination of net changes in water column concentrations at the same time as the benthic flux measurements ($T_1 - T_0$, i.e., positive change = net increase in concentration). Net water column concentration changes near the sea bed were subtracted from the associated benthic incubation measurements to differentiate between net concentration changes as a result of water column or benthic drivers (i.e., acting as a control).

Additional water samples (concentrations only, no flux calculations) over deeper coralligène substrate were taken at four additional sites, in water depths of 25, 35 m (3, 19, and 34.8 m), 45 m (3, 24, and 44.8 m) and 65 m (3, 34, and 64.8 m) water depths by deploying Niskin bottles to the specified depths ($n = 5$ per depth per sample site, DMS and DMSPd concentrations only).

All sampling took place during the day (incubations conducted ~10 a.m.–2 p.m.; intracellular DMSP samples taken ~midday). A subset of the full sample collection was also taken during the night (~10 p.m.–2 a.m.) to provide complementary night-time measurements.

Dimethylated Sulfur Analysis

All water samples were quantified for DMS via GC-FPD using the purge-cryotrap method previously described (Turner et al., 1990; Kiene and Slezak, 2006). Intracellular DMSP samples were analyzed by direct injection of the vial headspace into the GC injector port. A SRI 8610C chromatograph was used for all analyses, fitted with a 15 m capillary column set at 45°C and a nitrogen carrier gas (8 psi). The FPD detector was at 150°C for all analyses (air @ 2 psi, H₂ @ 27 psi). A DMSP standard was used to calibrate the analyses, obtained from Research Plus Inc. The limit of detection for intracellular samples was 1 µg S (headspace injection method) and 0.18 ng S for water samples (cryotrap method); standard and sample precision was within 1%.

Statistical Analyses

ANOVAs were used to compare intracellular DMSP concentrations and dimethylated sulfur production between benthic types. Correlation analyses were used to investigate the relationship between water column dimethylated sulfur concentrations and depth. Statistical analyses were conducted in R v3.2.0 and Minitab v14.1. For all parametric tests, the data met assumptions for normality and homogeneity of variance. Cross-sectional plots of water column concentrations and change in concentrations over time were plotted using Ocean Data View V4.7.8 using weighted average gridding interpolation.

RESULTS

Intracellular/Associated DMSP Concentrations

There was a significant difference in intracellular/associated DMSP concentrations between the different benthos types sampled, spanning three orders of magnitude [$F_{(12, 130)} = 13.03$, $p < 0.001$; Table 1]. The highest observed intracellular concentrations were for the dead *P. oceanica* mat during the day, followed by the sand at 15 m (associated DMSP) and *M. alternans* that make up the coralligène framework (Table 1).

TABLE 1 | Intracellular and associated DMSP concentrations of key Mediterranean benthos.

Benthos type	Depth (m)	Time of day	Intracellular/associated DMSP µmol g ⁻¹
<i>Padina</i> sp.	2	Day	793 ± 84
		Night	341 ± 53
<i>Posidonia oceanica</i>	3	Day	1,013 ± 204
<i>P. oceanica</i> mat	2	Day	4,783 ± 1,166
		Night	297 ± 113
Coralligène	15	Day	1,900 ± 538
		Day	73 ± 23
	Night	34 ± 4	
Sand (associated DMSP)	2	Day	1,436 ± 461
		Day	2,437 ± 569
	15	Night	13 ± 4
		20	Day
Night	2 ± 0		

Stocks of intracellular/associated DMSP by mass (µmol g⁻¹) from *Padina* sp. (brown macroalgae), *Posidonia oceanica* leaves and dead mats (seagrass), coralligenous framework (red coralline algae), and neighboring sand flats. Bold text indicates there was a significant difference between day and night values of the same benthos type at $p < 0.05$. Data presented as mean ± SE.

DMSP concentrations were consistently higher during the day, but this was only significant for the dead *P. oceanica* mats and the sand at 15 m (associated DMSP) (Table 1).

Community Level Production of Dimethylated Sulfur

There was a significant difference in the benthic production of DMS [$F_{(8, 27)} = 90.86$, $p < 0.001$] and DMSPd [$F_{(8, 34)} = 23.51$, $p < 0.001$] across the macrophytic benthic types (Figure 1; coralligène from different depths considered separately). No significant correlation was observed between the rates of change in dimethylated sulfur and intracellular DMSP of the primary benthic component. During the night, DMS and DMSPd production by the *P. oceanica* meadow community was significantly higher than the other benthic communities. During the day, DMSPd, but not DMS, production were significantly higher in the *P. oceanica* meadow compared to other benthic types. High DMS production was also recorded from the dead *P. oceanica* mat. During the night, significant DMS uptake by the 15 m depth coralligène community was observed. Production / uptake rates by other benthic communities were lower and statistically similar. In contrast to intracellular DMSP, no consistent trend between day/night comparisons was observed. Measured concentrations for T0 and T1 incubation timepoints are provided in Figure S1 in the Supplementary Information.

Water Column Concentrations and Net Change over Time

A trend toward lower DMSPp (9.93 ± 1.92 nM, mean ± SD) concentrations compared to DMS (12.37 ± 1.37 nM) and DMSPd

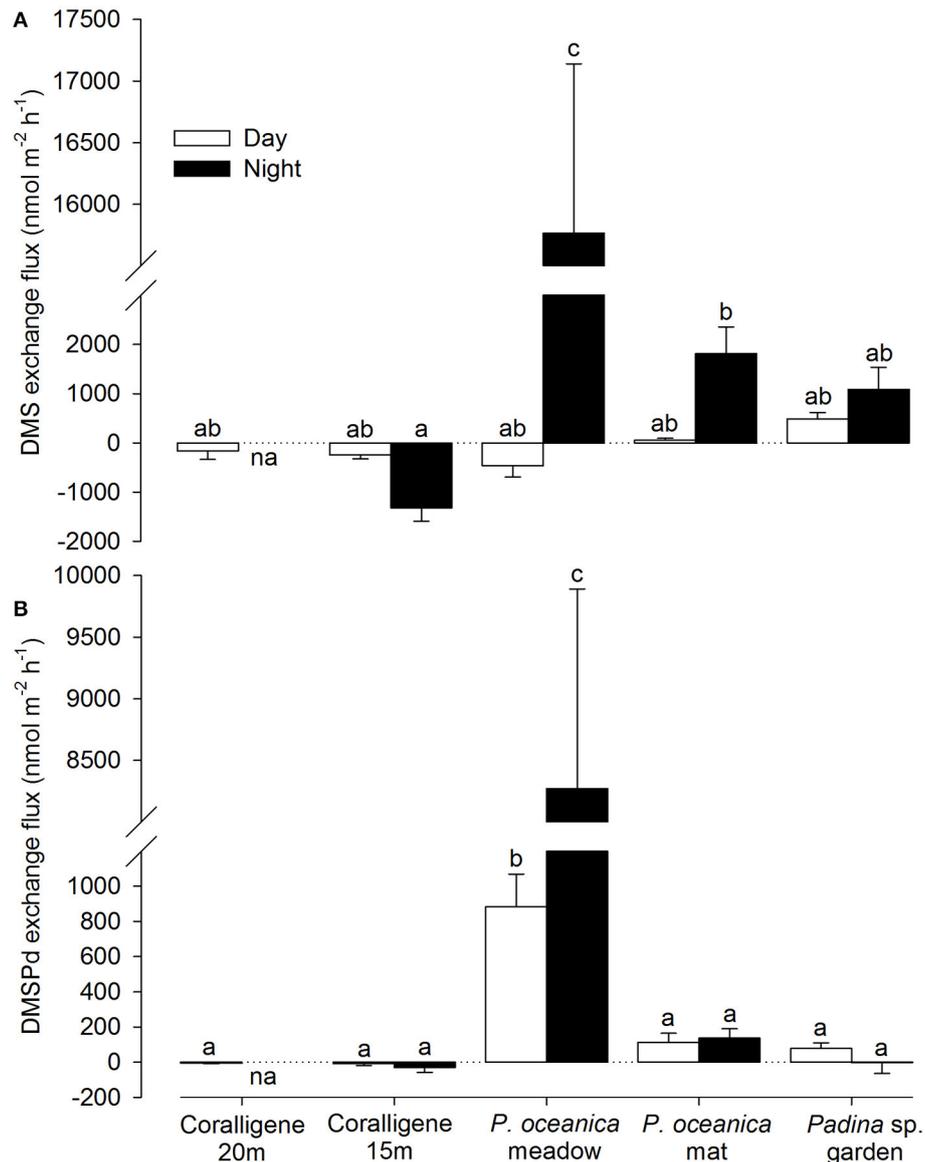


FIGURE 1 | Community-level exchange flux of dimethylated sulfur from key Mediterranean benthos. Net exchange flux in **(A)** DMS and **(B)** dissolved DMSPd (DMSPd) from coralligene, *Posidonia oceanica* meadows and dead mats and *Padina* sp. garden communities during the day (white bars) and night (black bars). Data presented as mean \pm SE. Bars with different letters a-c are statistically different in net concentration change at $p < 0.05$. na = data not available. Positive flux indicates a net release from the benthos.

(13.32 ± 1.02 nM) was observed when all water column samples were treated as one dataset (i.e., regardless of depth/location), although this difference was not significant [$F_{(2, 63)} = 1.41$, $p = 0.253$, **Figure 2**]. Similarly, neither water column DMS, DMSPd nor DMSPp were significantly correlated with the depth at which the sample was taken (**Figure 2**).

Net change in DMS and DMSPd concentration was highest in the water column overlying the seagrass beds (**Figure 3**), where a net DMS accumulation rate of >10 nM h⁻¹ contrasted with a net DMSPd utilization rate of >10 nM h⁻¹. Shallower and deeper than this, net change in DMSPd was <1 nM h⁻¹. DMS water

column production rates in deeper waters was generally higher than DMSPd rates, up to 5 nM h⁻¹. Measured concentrations for T0 and T1 incubation timepoints are provided in Figure S1 in the Supplementary Information.

DISCUSSION

This work has provided new information on the role of Mediterranean benthic macrophytic communities in the production and exchange dynamics of ecologically important dimethylated sulfur compounds. Coral reefs are the most widely

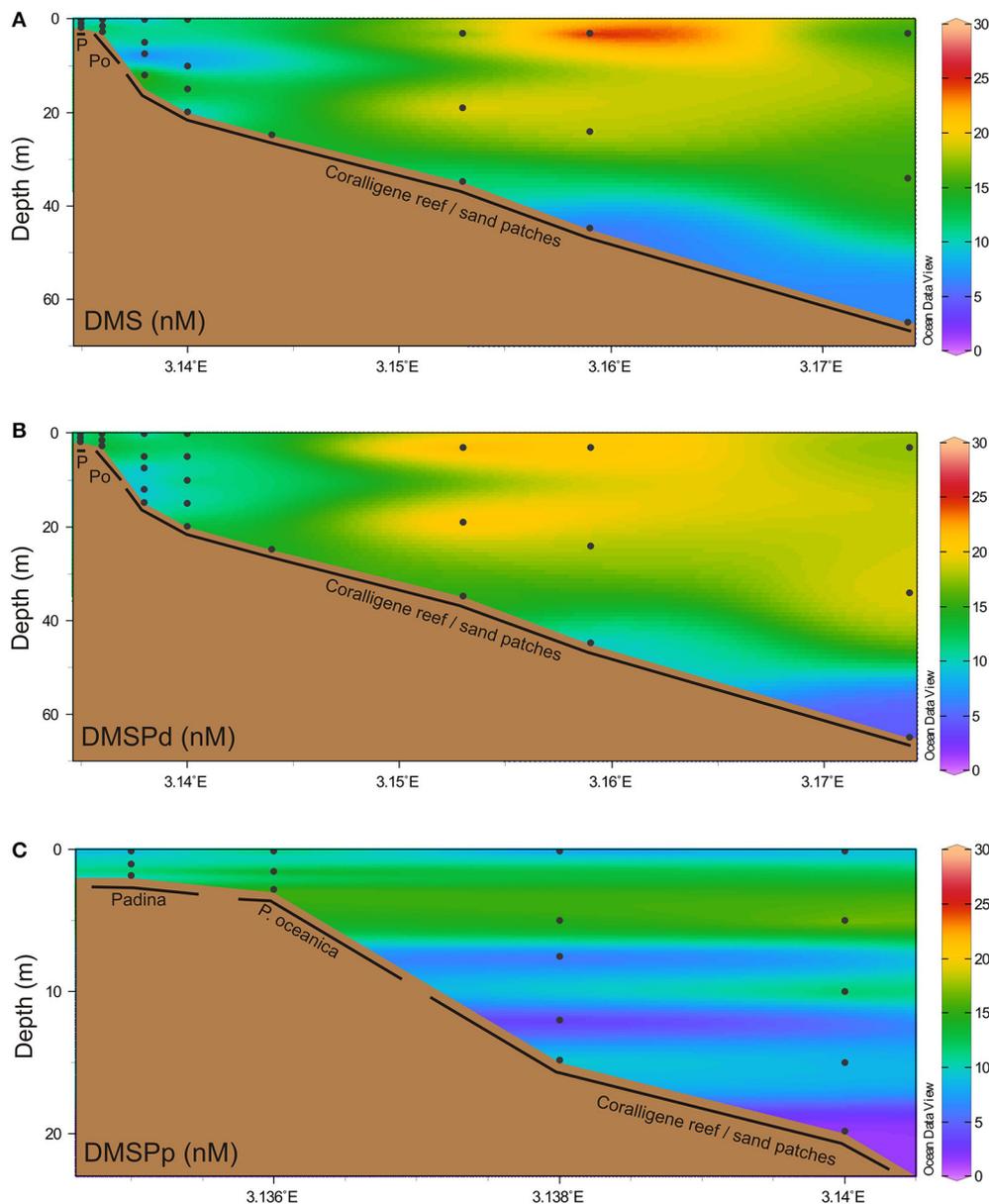
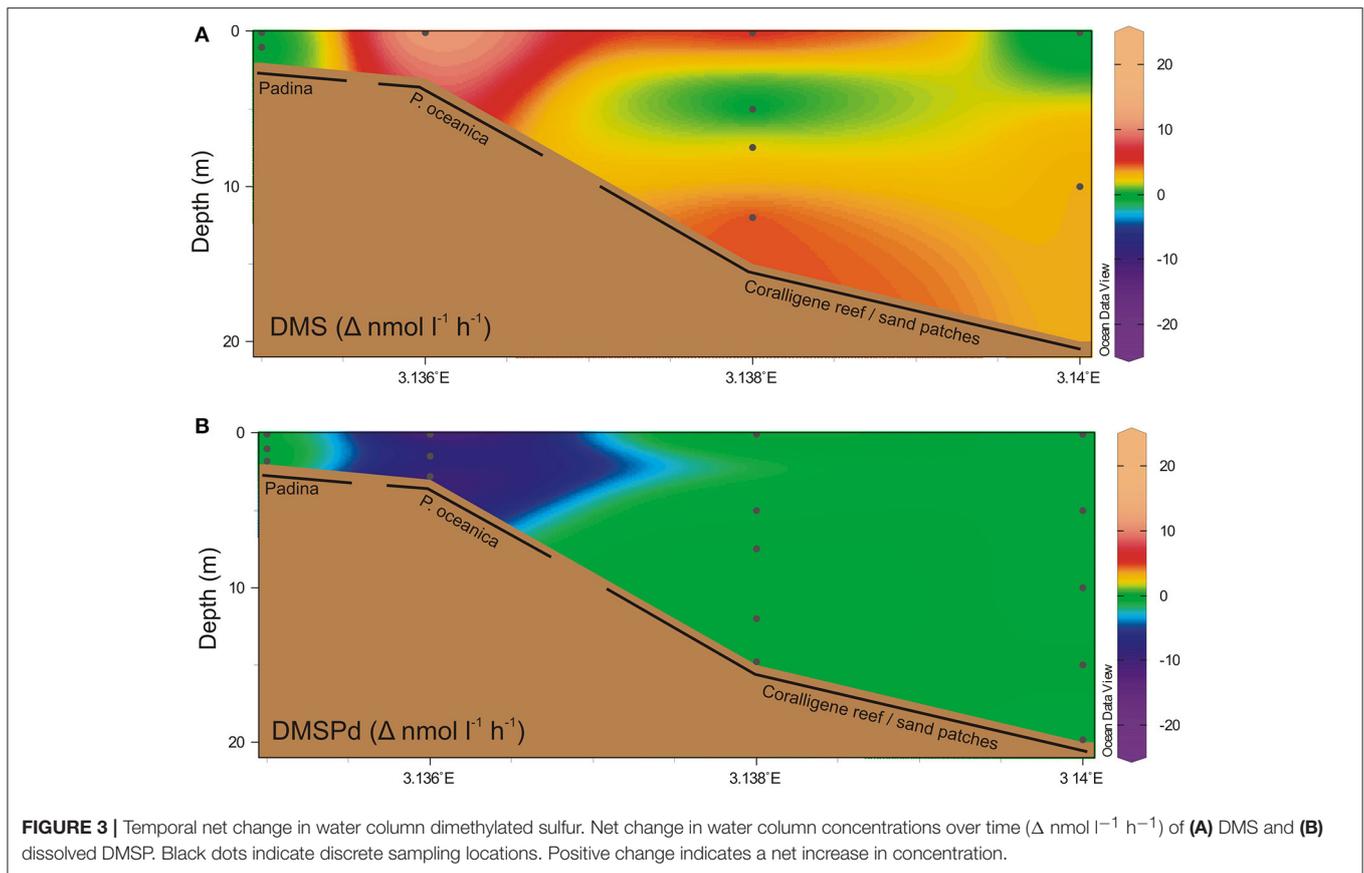


FIGURE 2 | Water column concentrations of dimethylated sulfur. Water column concentrations (nM) of **(A)** DMS, **(B)** dissolved DMSP (DMSPd), and **(C)** particulate DMSP (DMSPp). Black dots indicate discrete sampling locations. P, *Padina*; Po, *Posidonia oceanica*.

studied ecosystem with regards to the benthic production of dimethylated sulfur compounds. Algal intracellular DMSP concentrations measured here are comparable, if not somewhat higher, than scleractinian corals, but remain less than the extremely high DMSP concentrations found in mucus ropes (Van Alstyne et al., 2006). Intracellular DMSP concentrations of *Spartina alterniflora*, one of the few DMSP-producing higher plants, are typically lower than those measured here (McFarlin and Alber, 2013), as are previous estimates for seagrasses (e.g., *Zostera marina*: 139 nmol g^{-1} wet weight, *P. oceanica*: $5 \text{ } \mu\text{mol g}^{-1}$ dry weight) (Jonkers et al., 2000; Borges and

Champenois, 2015). However, in these studies, leaves were cleaned of epiphytes prior to analysis. Here, the intracellular DMSP concentrations reflect the seagrass “holobiont” (i.e., including all associated epiphytes and microorganisms). Whilst this likely contributed to the observed high variability between samples due to heterogeneity in epiphyte composition, it means the concentrations presented here are more representative of the natural community found *in situ*, and are more comparable to other higher plants (e.g., *Spartina alterniflora*), where extracellular accumulation of DMSP is known to occur (Dean and Kiene, 1992).



The combined high intracellular DMSP concentrations and widespread distribution in the Mediterranean (Martin et al., 2014; Telesca et al., 2015) means that both *P. oceanica* meadows and coralligène reefs act as significant benthic stocks of DMSP. Since coralligène can be found at greater depths than other macrophytic ecosystems (up to at least 120 m; Ballesteros, 2006), this increases the potential depth range of benthic DMSP stocks into the mesophotic zone—an area of the ocean whose biogeochemical importance is only now being realized (Giering et al., 2014). Further investigations are required to determine the relationship between coralligène intracellular DMSP and depth, to establish the importance of mesophotic coralligène communities as a benthic DMSP stock. Rapid declines in intracellular DMSP concentrations with depth have been previously observed in corals, attributed to a combination of factors including thermal boundaries and declines in irradiance and holobiont community interactions (Yost et al., 2012). It is proposed that similar factors play a role in the observed attenuation of coralligène intracellular DMSP concentrations with depth. While *Padina* sp. intracellular DMSP concentrations were also high, its spatially limited distribution means that this macrophyte (and associated community) is unlikely to represent a major, regional-scale, stock of DMSP.

Due to varying methodologies adopted by different studies to quantify the flux of dimethylated sulfur from benthic

habitats, it is difficult to make robust comparisons with other systems, particularly since this study focused on community-level responses rather than isolated individuals. Average net production of DMS and DMSPd from the *P. oceanica* community was high during the night, perhaps reflecting an overflow mechanism for removing DMSP from cells during a daytime accumulation (Stefels, 2000), or an increase in night-time grazing activity that can facilitate intracellular DMSP release (Van Alstyne, 2009). Dimethylated sulfur release from re-processing of this organic matter by faunal and microbiological activity at the sediment surface may explain why DMS exchange rates were higher than previous individual organism studies (which cannot integrate processes happening at the sediment surface). DMS production is also known to be higher in anoxic seagrass-based sediments (Jonkers et al., 2000). The coralligène communities, which have an intermediate level of structural complexity, were characterized by only small net exchanges in DMS and DMSPd. In contrast to all other habitat types, a significant net uptake of DMS by the coralligène community during the night at 15 m depth was observed. This may reflect a unique microbial community that favors DMS utilization rather than production, which could be significantly impacting dimethylated sulfur cycling in deeper coastal/shelf waters of the Mediterranean (where coralligène formations are found). Microbial activity is a critical for the processing of dimethylated sulfur compounds (Moran et al.,

2012; Curson et al., 2017), and the microbial community of crustose coralline algae is known to be highly specific (Sneed et al., 2015). Further investigation into the specific microbial communities associated with each benthic type (and their functionality) is thus required. Additionally, invertebrate accumulation of dimethylated sulfur (Van Alstyne and Puglisi, 2007) may be elevated during the night due to increased grazing activity.

A consistent daytime increase in intracellular DMSP across all benthos types was observed, supporting the proposed antioxidative role for DMSP (and its breakdown products) in marine macrophytes (Rix et al., 2012; Burdett et al., 2014). However, day/night trends of dimethylated sulfur benthic flux across habitat types were less consistent, reflecting the increase in community complexity as one moves through ecological scales—intracellular DMSP concentrations were determined from the holobiont of individual organisms, whilst benthic exchange fluxes were determined at the ecosystem community level, i.e., integrating the interactive effect of multiple organisms and holobionts across multiple trophic levels. This underlines the importance of *in situ* measurements conducted at the community level, rather than on isolated individuals in controlled laboratory environments, for appreciating the true biological and biogeochemical complexity of natural marine systems (Gattuso et al., 2014).

Despite the apparently large benthic release of DMS from *P. oceanica* meadows, sea-air flux of DMS in the Mediterranean is relatively modest (Simo et al., 1997; Simó and Grimalt, 1998; Besiktepe et al., 2004). Borges and Champenois (2015) previously suggested that DMSP released by seagrass plants might accumulate within the seagrass canopy. This study supports that hypothesis and extends it to also include DMS, but also demonstrates that seagrass community dynamics can influence water column dynamics meters above the canopy, creating a biogeochemical “hotspot” of DMS production and DMSPd utilization. Interestingly, another DMS “hotspot” was also observed around the 15 m coralligène community, despite small net uptake of DMS/DMSP, suggesting that the presence of high-DMSP containing organisms (such as coralline algae) can influence overlying water column concentrations without significant benthic-pelagic exchange. It is therefore suggested that high-DMSP producing benthic communities influence microbial/phytoplankton communities and biogeochemical functionality overlying the habitat, perhaps through the provision of other nutrients not measured here (e.g., organic matter substrate, nitrogen, phosphorus, etc.). Benthic influences of water column concentrations of dimethylated sulfur also helps to explain the lack of correlation between water column DMS/DMSPd/DMSPp concentrations and sample depth.

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CONCLUSIONS

This work highlights the role of the Mediterranean coastal/shelf ecosystems as a significant stock of DMSP, but also that their role as sources or sinks of dimethylated sulfur is system-specific and related to structural complexity, highlighting the complex nature of dimethylated sulfur cycling in the shelf and coastal zone. Biogeochemical processing was especially evident for *P. oceanica* meadows—a DMSP stock which has faced rapid decline since the late 1800s (Waycott et al., 2009), but one which was able to modify dimethylated sulfur dynamics in the overlying water column and drive localized biogeochemical “hotspots.” Although smaller in their intracellular concentrations, this study suggests that coralligène communities may affect dimethylated sulfur dynamics at the regional scale because of this ecosystem’s widespread distribution throughout the Mediterranean. However, the sensitivity of coralline algae to projected environmental change (Burdett et al., 2012, 2015) threatens the long-term survival of the coralligène ecosystem. Distinct diel patterns provide further evidence for a link between dimethylated sulfur and photosynthetic processes. Importantly, this study took a community-level approach, thus providing a relevant baseline from which to move forward when monitoring future changes to marine communities from an ecological and biogeochemical perspective.

AUTHOR CONTRIBUTIONS

HB designed the study, collected and analyzed the samples, analyzed the data and wrote the paper.

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SUPPLEMENTARY MATERIAL

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Conflict of Interest Statement: The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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