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# Field Assessment and determination of concentration levels of Dimethylsulphide in Tropical Seawater

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**Abstract.** Dimethylsulphide (DMS) is an important climatically reactive trace gas which is emitted from the seawater to the atmosphere. It undergoes various oxidative reactions to produce cloud condensation nuclei, which affect the earth radiation budget. DMS and its precursor dimethylsulphoniopropionate (DMSP) were measured using a modified vapour generation – chemiluminescence (VG-CL) detection system that was designed for this study. The chosen sampling locations used for the measurement were Nigeria Institute of oceanography and marine research (NIOMR) and ELEGUSHI. They are situated along the Gulf of Guinea. The modified VG-CL analyser was used for trace analysis of dimethylsulphide in the study area. The mean concentrations of DMS in the surface seawater at the two sampling locations ranged from 0 to 35.53±2.34 nM, 10.67±0.28 and 44.95±0.27 nM, respectively. The average minimum and maximum concentrations of DMS and DMSP across the two locations were between 0 and 44.95 nM, respectively. The concentrations of DMS and DMSP were compared across the sampling locations, and the observed pattern showed that DMS for ELEGUSHI has a higher concentration than NIOMR. The result further revealed that the concentration of the DMS is a function of the sea surface temperature (SST) of the aquatic ecosystem. The observed DMS concentration data of this study provides a baseline measurement for the tropical Atlantic Ocean (Lagos), thus a significant addition to the global DMS database.

**Keywords:** Dimethylsulphide, vapour generation chemiluminescence detection, Seawater, ocean observation

## 1. Introduction

The ocean surface layer significantly plays a vital role in the climatic change of many biogenic gases to global emissions and is increasingly seen as a significant component of the climate system [1,2]. Dimethylsulphide (DMS) is a known dominant volatile sulphur containing a compound that is emitted from the ocean to the atmosphere [3,4]. The potential sources of atmospheric DMS are largely promoted by biogenically productive regions of the ocean surface, which invariably fillip the sea surface production of dimethylsulphide and its metabolite, dimethylsulphoniopropionate [5,6]. DMSP and DMS play crucial roles in the global sulphur cycle, marine microbial food web, and the global climate justifying the growing studies in the last three decades on the measurements, assessment of sea-air flux variations, and understanding of their biochemical pathways [7-10]. Dimethylsulphide is a climatically reactive gas that has the ability to be released to the lower atmosphere from seawaters, but it has been observed that it has an antagonistic effect when released [11,12]. Its release into the clean or unpolluted marine environment leads to the formation of cloud condensation nuclei once it undergoes different oxidation reactions [13,14]. As a result of



DMS cloud condensation nuclei-albedo feedback, the climate might differ due to variations in dimethylsulphide production. [15]. This is of climatic importance in the environment as it can alter the earth's radiation budget. As part of the efforts to determine the concentrations of DMS in the tropical Atlantic seawater, this study was carried out to measure the concentrations of the DMS using the modified vapour generation chemiluminescence detection [16].

## 2. Materials and method

### 2.1 Standards preparation

The stock solutions of dimethylsulphide at different concentrations were prepared from an analytical grade of DMS standard. 37  $\mu\text{L}$  of DMS standard was added into the water using a micropipette, and the plunger was immediately put back and inverted a few times gently for proper mixing to give 10 mM. 50  $\mu\text{L}$  of the prepared 10 mM DMS stock solution was added into the syringe, and it was made up to the mark with de-ionised water to prepare 10  $\mu\text{M}$  DMS of the second stock solution. 25, 50, 100, 150, 200 and 250  $\mu\text{L}$  of 10  $\mu\text{M}$  DMS was taken by micropipette into each 50 mL new syringe containing de-ionised water of about 45 mL to prepare 5, 10, 20, 30, 40 and 50 nM of DMS working solutions. Working solutions were stored at 4°C and also in the dark.

### 2.2 Sample Preparation

Seawater samples were collected with a syringe with a cap to prevent the formation of headspace which could lead to the escape of the dissolved DMS. The samples were immediately covered with aluminium foil. The syringes used for the sampling were rinsed with the water from the site before the collection of samples for analysis. Water samples were collected in triplicate at each sampling point and labelled immediately for easy identification. The water samples were refrigerated at 4°C in the laboratory to prevent the dissolved DMS from escaping to the headspace. The samples collected were preserved in the dark before the analysis.

### 2.3 Optimum conditions for vapour generation chemiluminescence detection (VG-CL)

The chromatographs obtained from the standard and sample analysis for the determination of DMS concentrations using VG-CL were optimised using the following optimisation conditions as shown in Table 1, and also, Figure 1 shows the peaks of DMS at various concentrations.

Table 1: Optimisation conditions for VG-CL operations

Items	Conditions
Ozone flow rate	300 mL/min
Ozone level	80
Pressurising air	30 mL
Shaking time	1 minute
Sample volume	10 mL
Sample rate	50-200 ms
PMT voltage	670 Volts
Data logger	-10 to +10 volts

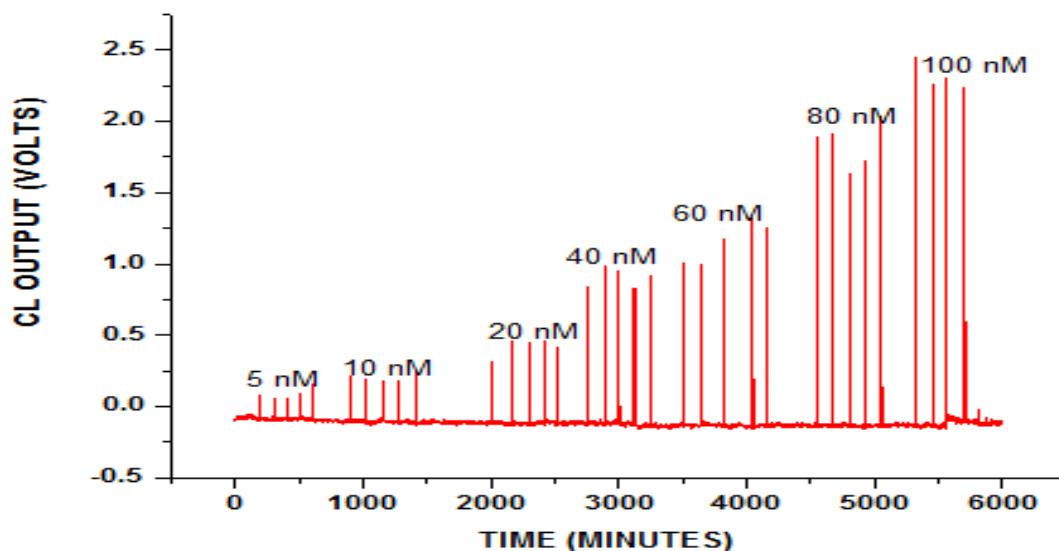


Figure 1: DMS standards at various concentrations analysed by VG-CL

### 3. Results and discussion

Table 2 shows the concentrations of DMS in nanomolar at different times for the samples collected at NIOMR. At 1:15 pm, the concentration of DMS was 2.41 nM. Furthermore, at 2:30 pm there was a tremendous increase in the concentration of DMS to about 16.73 nM and at a much higher time of 2:45 pm, the nanomolar of 35.53 nM was obtained. This variation observed within this time may be as a result of the intensity of the sunlight within the time frame as DMS is known to be highly volatile. However, at 2:30 pm, a rapid increase in the concentration of DMS was observed for both samples; the highest value was recorded in sample A having a value of 17.75 nM. At 3:45 pm, a sharp reduction in the nanomolar concentration was observed in the selected samples. Sample A has concentrations that ranged 2.36 and 33.87 nM. The highest and lowest values of the nanomolar concentration were observed at 2:45 pm and 1:15 pm respectively. However, between 1:45 and 2:45 pm, there was no detection in sample A. For sample B, the concentrations ranged from 2.46 to 37.18 nM with the highest value of 37.18 nM observed at 2:45 pm. The mean value, standard deviation and standard error mean of samples A and B were given as 7.58 nM and 7.91 nM, 9.08 nM and 9.38 nM, 2.34 nM and 2.42 nM, respectively. Also, the DMS concentrations of the water samples collected at Elegushi Beach at different times were shown in Table 3.

**Table 2:** Time concentrations (nM) of DMS from NIOMR location

Time (am/pm)	Sample A	Sample B	Average (nM)
10:00	8.52	8.48	8.5±0.02
10:30	6.72	5.48	6.1±0.88
11:00	6.52	5.39	6.0±0.80
11:30	3.88	4.07	3.98±0.13
12:00	4.82	4.54	4.68±0.20
12:30	5.01	4.07	4.54±0.66
1:00	3.59	3.49	3.54±0.07
1:15	2.36	2.46	2.41±0.01
1:30	3.33	3.32	3.33±0.00
1:45	ND	ND	ND
2:00	ND	8.40	8.14±5.94
2:15	ND	ND	ND
2:30	17.75	15.71	16.73±1.44
2:45	33.87	37.18	35.53±2.34
3:00	17.32	16.09	16.71±0.88

ND - Not detected

**Table 3:** Time concentrations (nM) of DMS from Elegushi Beach 1 location

Time (am/pm)	Sample A	Sample B	Average (nM)
10:00	10.47	10.87	10.67±0.28
10:30	16.56	17.03	16.80±0.33
11:00	14.00	14.08	14.04±0.06
11:30	21.01	21.00	21.01±0.01
12:00	13.67	13.91	13.79±0.17
12:30	12.58	13.26	12.92±0.48
1:00	13.81	14.19	14.00±0.27
1:15	12.05	11.54	11.79±0.36
1:30	12.78	13.06	12.92±0.20
1:45	12.54	13.05	12.80±0.36
2:00	45.14	44.76	44.95±0.27
2:15	12.94	12.87	12.91±0.05
2:30	11.20	11.98	11.59±0.55
2:45	9.46	9.94	9.70±0.34
3:00	11.50	11.30	11.40±0.41

The DMS was detected in both samples A and B with the lowest and highest mean values of 9.7 nM and 44.95 nM, respectively. It was equally observed that the highest value of DMS was attained at 2:00 pm. Tables 4 and 5 presented the relationship between sample A and B as obtained in Tables 3 and 4. Thus; it can be explained that there is no significant difference in both samples analysed. This was justified by the result obtained in Tables 4 and 5. The results suggest that enhanced biogenic productivity is a function of the sea surface temperature [17]. According to [18], the rate of DMS efflux from Amsterdam Island in the southern Indian Ocean was increased by over 50% following 1°C increase in SST. The report by [18] agreed with the results of this present study. Indicatively, there was a relative increase in the concentration of DMS at 2:45 pm and 2:00 pm at NIOMR and Elegushi Beach locations, respectively, with increased in SST by 2 to 3°C. According to [19], the seasonal variations of gaseous DMS and its oxidation products at a remote coastal location in the Eastern Mediterranean Sea as well as the diurnal variation of DMS during two intensive measurement campaigns. It was observed that DMS concentrations tracked at sea surface temperature (SST)

ranged from  $0.87 \text{ nmol m}^{-3}$  in the winter to a high concentration of  $3.74 \text{ nmol m}^{-3}$  in the summer. Similarly, it was also observed that in the diurnal studies, the DMS concentrations were lowest when it was coldest (just before sunrise) but rose rapidly as it warmed thereafter, after which they dipped slightly and then experienced a further rise as the temperature increases, whereupon a decline in both temperature and DMS concentration set in, continuing until before sunrise.

**Table 4:** Paired sample test (n=15)

	Paired Differences		SEM	95% CI		t	df	Sig (2-tailed)
	Mean	SD		Lower	Upper			

SPL-sample, SD-standard deviation, SEM-standard error mean, CI- confidence interval

**Table 5:** Paired sample test (n=15)

	Paired differences		SEM	95% CI		t	df	Sig (2-tailed)
	Mean	SD		Lower	Upper			

SPL-sample, SD-standard deviation, SEM-standard error mean, CI- confidence interval

Although the value of DMS reported by [19], was low compared to the values reported in this present work, it should be noted that other environmental factors could be responsible for the massive production of DMS observed. It is worthy of note that in marine environments, it is difficult to establish the dominant factor(s) affecting DMS production owing to the involvement of multiple physical processes such as salinity, temperature, light intensity and biological processes such as organism interactions at various trophic levels [20]. Although, the consumption by bacterial might lead to the removal of DMS [21]. As a result of this, about 1% of DMSP produced in the ocean surface layers is being released into the atmosphere [22-24]. These levels are in agreement with the concentrations obtained from other studies earlier carried out on dimethylsulphide and dimethylsulphoniopropionate in the Eastern part of China Sea and Yellow Sea [25].

#### 4. Conclusion

The research showed that the concentration of DMS was successfully measured using the VG-CL. The two (2) sampling locations were used for this study. The mean concentrations of DMS in the surface seawater at the sampling locations along the tropical Atlantic Ocean ranged from 0 to  $35.53 \pm 2.34 \text{ nM}$  and  $10.67 \pm 0.28$  to  $44.95 \pm 0.27 \text{ nM}$ , respectively. The average minimum and maximum concentrations of DMS and DMSP across the two locations were 0 and  $44.95 \text{ nM}$ ,  $2.05$  and  $40.91 \text{ nM}$ , respectively. **Acknowledgement**

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**Conflicts of Interest:** The authors declare no conflict of interest.

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