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Modified VG-CL Detection System for Baseline Assessment of Dimethylsulphide and Dimethylsulphoniopropionate in Tropical Atlantic Seawater

E. A. Adedapo^{1*}, N. U. Benson^{1*}, A. B. Williams¹ and K. Toda²

¹Department of Chemistry, Covenant University, Km 10 Idiroko Road, Ota, Ogun State, Nigeria.

²Department of Chemistry, Kumamoto University, Kumamoto, Japan.

*Corresponding authors email: nsikak.benson@cu.edu.ng;

adebusayo.adedapo@covenantuniversity.edu.ng

Abstract.

Several studies have been carried out to measure the concentrations of dimethylsulphide (DMS) and dimethylsulphoniopropionate (DMSP) in coastal and open marine ecosystems. The present study attempted the fabrication of a cost-effective, highly sensitive and portable detection system based on vapour generation and chemiluminescence for a pilot assessment and determination of DMS and DMSP concentrations in tropical Atlantic seawater samples. The Sultan Beach and Badagry parts of the Atlantic Ocean were chosen as designated locations for this study. Vapour generation chemiluminescence (VG-CL) detection system is a device that can measure the concentration (nM) of DMS and DMSP by allowing DMS vapour which in turn reacts with ozone to produce chemiluminescence which can be detected by a photomultiplier (PMT). The mean concentrations of DMS and DMSP in the surface seawater at the sampling location were 5.80 ± 0.71 to 19.40 ± 0.57 nM and 11.00 ± 0.42 to 34.70 ± 1.13 nM, respectively. The average minimum and maximum concentrations of DMS and DMSP across the location were between 0 and 40.91 nM, respectively. This study serves as a baseline measurement of DMS concentrations in the tropical Atlantic Ocean (Lagos).

Keywords: Dimethylsulphide, VG-CL detection, Seawater, Photomultiplier

1. Introduction

Dimethylsulphide is known as the main biogenic source of volatile sulphur compound in the marine environment [1], [2]. The production of dimethylsulphide (DMS) and its release into the atmosphere is known to be one of the essential biogenic sources of atmospheric sulphur [3]. Dimethylsulphoniopropionate (DMSP) is an organic sulfur compound that is ubiquitous in the euphotic zone. It is produced from a variety of halophytic plants to function as osmotic regulation [4]. It is categorically well-known among the oceanic phytoplankton [4]. The primary precursor of DMS is the dimethylsulphoniopropionate (DMSP) which is the microalgal metabolite that leads to the production of DMS via intracellular DMSP breakdown by phytoplankton [5]. Some biological activity has been known to be responsible for the production of DMS within the water column, which in turn can be removed by some abiotic loss mechanisms and also through biological consumption [6]. However, there are still limitations to the understanding of these processes. The production of DMS and acrylate with the generation of a proton was achieved through enzymatic cleavages of DMSP by lyase pathway [7]. Most marine bacteria contained DMSP lyase enzymes, and it was also found in phytoplankton, namely *Phaeocystis sp* and *E. huxleyi* [8], [9], [10]. The DMSP functions as a cryoprotectant, grazing defender, osmolyte, chemoattractant or anti-oxidant [11], [12], [13]. Some microalgae are also capable of releasing



untransformed DMSP produced as a result of mortality and exudation. Extracellular and bacterial enzymes help to convert part of the dissolved DMSP to DMS [14], [15], [16]. It has been reported that photochemical reactions and heterotrophic bacteria could influence the oxidation of DMS and its metabolism, respectively [17]. Additionally, it has been reported that only a small portion of the DMS produced was emitted into the atmosphere [18]. The oxidation of DMS in the atmosphere occur to produce sulphonic methane acid and non-sea salt sulphates which are known to be responsible for the formation of cloud condensation nuclei (CCN). These processes might influence the backscattering of solar radiation and cloud formation therefore, an influence on climate system has been documented [19], [20], [21], [22], [23]. A number of studies carried out recently have shown that DMS gives a minor product (about 50%; frequently only 5–10% of the sulfur) of DMSP_d metabolism under most circumstances in the marine water column [24], [25], [26]. Many pieces of evidence favoured demethiolation/demethylation pathway as being the major fate of DMSP produced in the seawater [25]. Recently, a lot of efforts has been made to study the biogeochemical processes which control the concentration of seawater DMS and its emission to the atmosphere coupled with the global DMS distribution in the seawater microlayer surface. Nevertheless, in comparison to other regions, the tropical Atlantic seawater has received little or no attention as regards the measurements, emission and distribution of biogenic sulphur in the seawater [27], [28]. In view of this, vapour generation chemiluminescence detection system was fabricated and re-modified from the previous design [29] for better selectivity and sensitivity. The focus of this study was, therefore, the determination of DMS and DMSP concentrations in seawater samples collected from the tropical Atlantic Ocean around the Lagos State (Sultan Beach Badagry), using this modified vapour generation chemiluminescence detection [29].

2. Methodology

2.1 Standards preparation

The stock solutions of dimethylsulphide at different concentrations were prepared from DMS standard (Analytical grade) purchased from Alfa Aesar, ThermoFisher (Kandel) Germany. 37 μL of DMS standard was measured using a micropipette and diluted with de-ionised water, and the plunger was immediately put back and inverted a few times gently for proper mixing to give 10 mM. A volume of 50 μL 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 μM DMS of the second stock solution. 25, 50, 100, 150, 200 and 250 μL of 10 μM 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. For the preparation of DMSP standards, 10 mM of the standard was prepared by dissolving 0.134 g in 100 mL volumetric flask with distilled water. 50 μL of 10 mM DMSP stock solution was added into the 50 mL volumetric flask and was makeup to the mark to prepare 10 μM as the second stock solution. The preparation of working solutions of DMSP for the calibration was done by taking 25, 50, 100, 150, 200 and 250 μL of 10 μM DMSP by micropipette into 50 mL to produce 5, 10, 20, 30, 40 and 50 nM of DMSP. Working solutions prepared were stored at 4°C in the dark.

2.2 Sample Preparation

The seawater samples for the determination of DMS and DMSP were collected using enclosed syringes with caps to prevent the formation of headspace, which could affect the measurement of DMS and stored using 250 mL amber bottles. The samples for DMS were immediately covered with aluminium foil. Seawater samples were collected in duplicates at designated locations and labelled immediately for easy identification. Samples were placed in a refrigerator at 4°C within two hours after collection. The samples collected were preserved in the dark prior to the analysis.

2.3 Optimum conditions for VG-CL

The optimisation conditions for the operation of the modified vapour generation chemiluminescence detection are indicated in Table 1. These conditions help to produce good chromatographs for both the standards and sample measured for DMS and DMSP concentration.

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

3. Results and discussion

Table 2 shows the DMS concentrations of the water samples collected at Suntan Beach at different times. The DMS concentration was detected in both samples A and B with the lowest and highest average values of 5.80 nM and 19.40 nM, respectively. It was observed that very high concentrations of DMS were recorded within 2:30 - 3.00 pm time frame. Also, there was an increase in the concentration of DMS measured between 10:00 to 11:00 am from 5.80 ± 0.71 to 9.39 ± 0.27 nM. Low concentrations were observed at about 11:30 am but increased at 12:00 to 9.50 ± 1.41 nM. However, there was a slight drop in the DMS concentrations (9.20 ± 0.85 nM) measured at 12:30 pm. More so, there was a drop in the DMS concentration between 1:15 to 1:30 pm, which may be due to the temperature difference or the direction of wind speed when the samples were taken. There was a sharp increase in the concentration of DMS between 1:45 and 2:00 pm at 12.00 ± 0.14 and 12.39 ± 0.26 nM respectively. Even though there was a decrease in the mean concentration (10.80 ± 1.06 nM) at 2:15 pm, a spike in concentration (19.40 ± 0.57 nM) at recorded 2:45 pm.

Table 3 shows the DMSP concentrations of the water samples collected at Suntan Beach at different times. The DMSP concentration was detected in both samples A and B with the lowest and highest mean value being 11.00 nM and 34.70 nM respectively. There was an increase in the concentration of DMS measured from 10:00 to 11:00 am which was from 11.00 ± 0.42 to 21.00 ± 0.71 nM. A slight decrease was noticed at 11:30, 12:00 and 12:30 am with the values of 19.35 ± 0.7 , 20.50 ± 0.42 and 20.90 ± 0.71 nM. It was increased to 1:00 pm to 24.15 ± 1.91 nM. Although there was a slight drop in the concentration of DMSP at 1:15 pm, it does not affect the continuous increase that was observed between 1:30 and 1:45 pm until the highest concentration was noticed at 2:45 pm with the value of 34.70 ± 1.13 nM. It should be noted that the highest value of DMSP that was recorded at 2:45 pm corresponded with the same time at which a high concentration of DMS was measured. Also, the same pattern of increase in the concentration of DMS and DMSP was observed which increased in the afternoon.

Table 2. Time concentrations (nM) of DMS from Sultan location

Time (am/pm)	Sample A	Sample B	Average (nM)
10:00	6.30	5.30	5.80 ± 0.71
10:30	7.50	8.55	8.03 ± 0.74
11:00	9.58	9.20	9.39 ± 0.27
11:30	7.02	7.85	7.44 ± 0.59
12:00	8.50	10.50	9.50 ± 1.41

12:30	8.60	9.80	9.20±0.85
1:00	11.30	10.50	10.9±0.57
1:15	8.50	8.89	8.70±0.27
1:30	7.54	7.20	7.37±0.24
1:45	12.10	11.90	12.00±0.14
2:00	12.20	12.58	12.39±0.26
2:15	10.05	11.55	10.80±1.06
2:30	18.10	19.10	18.60±0.71
2:45	19.80	19.00	19.40±0.57
3:00	18.20	18.55	18.38±0.25

Table 3. Time concentrations (nM) of DMSP from Sultan location

Time (am/pm)	Sample A	Sample B	Average (nM)
10:00	11.30	10.70	11.00±0.42
10:30	19.50	19.00	19.25±0.35
11:00	21.50	20.50	21.00±0.71
11:30	18.85	19.85	19.35±0.71
12:00	20.20	20.80	20.50±0.42
12:30	21.40	20.40	20.90±0.71
1:00	25.50	22.80	24.15±1.91
1:15	18.55	18.85	18.70±0.21
1:30	25.50	24.50	25.00±0.71
1:45	28.80	28.20	28.50±0.42
2:00	26.85	26.25	26.55±0.42
2:15	30.50	29.80	30.15±0.50
2:30	31.55	33.55	32.55±1.41
2:45	33.90	35.50	34.70±1.13
3:00	32.50	31.55	32.03±0.67

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.

Table 4. Paired sample test (n=15)

	Mean	SD	Paired Differences		T	df	Sig (2-tailed)	
			SEM	95% CI				
				Lower				Upper
SPL A-SPL B	0.34	0.91	0.24	-0.85	0.16	-1.47	14.00	0.165

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

Table 5. Paired sample test (n=15)

	Mean	SD	Paired Differences		T	df	Sig (2-tailed)	
			SEM	95% CI				
				Lower				Upper
SPL A-SPL B	0.27	1.19	0.31	-0.38	0.94	0.89	14.00	0.384

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

At Sultan location, the anthropogenic activities around this area are less but the influence of the neighbouring activities around the highly populated area might contribute to the pollution of the seawater. The release of human wastes can enhance the production of more marine algae which are the main sources of DMSP and subsequently lead to the production of more DMS. Also, human waste has been known to increase, the nutrients of the water bodies which in turn can increase the chlorophyll level [30], [31], [32]. This may lead to phytoplankton bloom and thus encourage the production of more of the DMSP metabolite which has been produced from the enzymatic activities on the marine algae and which is the main precursor of DMS produced to the surface of the seawaters.

The concentrations of DMS are generally lower when compared with those of DMSP and usually fall in the range of 1 to 30 nM [33]. Higher concentrations of DMS was reported which was up to 290 nM. This might be found in blooms of certain DMSP producing phytoplankton such as *Phaeocystis pouchetii* as bacteria which utilise DMSP for the production of DMS have been isolated from seawater [34], [35]. The report has it that DMSP is released upon cell lysis, either as a result of the death of the cell or mechanical disruption which is caused by zooplankton grazing [36]. Also, digestion within the zooplankton and enzyme activities from the algal cells coupled with bacterial action increase the breakdown to DMSP [37], [38], [39]. This might be the reason why there is high DMSP in the afternoon due to the increase in temperature which in turn lead to cell lysis or death of zooplankton.

It should be noted that the high concentration of DMSP noticed in this research can be because some marine phytoplankton and microalgae functions as an osmotic and also, the activeness of phytoplankton species contributed to the production of DMSP [40], [41].

Conclusion

The results from the samples collected showed that the concentration of DMS in the sea could be highly variable in time and under identical circumstances. The observed DMS concentration in seawater samples could be dependent on the time of day when the samples were collected for the analysis. The use of VG-CL has proven to be useful and cost-effective in the present study for the quantification of DMS and DMSP levels in the tropical Atlantic seawaters when compared to the other expensive analytical methods. Also, the modified VG-CL is very sensitive and selective as it can measure low concentrations of less than 5 nM.

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

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